THE CHEMISTRY

OF THE

MATERIALS OF ENGINEERING.

A HANDBOOK FOR ENGINEERING STUDENTS.

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PREFACE.

FOR several years the Author has given a course of lectures to engineering students on the Materials of Engineering, and he has felt the need of a suitable text book for the class. To meet this need this little book has been prepared, and it has been published in the hope that other teachers and students may find it useful. It covers ground which was unoccupied, except by larger treatises which are beyond the reach of ordinary students. One of the great difficulties has been to give each subject a space somewhat proportionate to its importance to the engineer, and though great care has been taken, it is unlikely that the arrangement will please all.

It is impossible to enumerate the authorities that have been consulted, and very few references have been given, as the students, at the stage when they will use this book, are hardly likely to be in a position to read the Transactions of Societies, &c. It is hoped that this little book may be useful as introduction to the larger books on the subject.

Glasgow,
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THE CHEMISTRY

OF

MATERIALS OF ENGINEERING.

INTRODUCTION.

In this volume it is intended to discuss the chemistry of the various materials used in engineering, as far as this is of importance to the engineer. This is a branch of the subject which is much neglected by practical men, and to which most text-books devote little space, though it is one the importance of which can hardly be over-estimated. The physical properties of the materials are to such a large extent dependent on their chemical composition, that experiments on the former without due attention being given to the latter must always be unsatisfactory and incomplete, and the results obtained, if not incorrect, are very frequently misleading.

Many investigations which have been made into the properties of metals, and on which great industry and skill have been expended, are quite valueless because sufficient note has not been taken of the chemical properties of the specimens used.

In order to understand chemical facts of any kind, some knowledge of the principles of chemistry is, of course, essential. The necessary amount, which is small, may be obtained from any of the many elementary text-books which are on the market,* and every engineer who desires to know

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* Such as the author's "Elementary Chemistry." Blackie and Son. 2s. 6d.

something of the materials he is using should devote a little time to mastering the elements of the science.

The chemical questions which are likely to be of interest to the engineer, or which may arise in his practice, are various.

1. The chemical composition of the materials, with special reference to the influence of the various constituents on the physical properties on which their usefulness depends, as, for instance, the effect of silicon on the tensile strength of steel, or the influence of varying quantities of silica on the setting power of a cement.

2. The changes which may be brought about in the chemical composition of materials by the treatment to which they may be subjected in the processes of manufacture, such as forging, casting, &c.

3. The action on the materials of the various substances with which they may be brought in contact in use, as, for example, the influence of air and moisture on iron, or the disintegrating action of air, &c., on building stones.

4. The changes which take place in the processes of manufacture by which various constituents are taken up or eliminated, and the materials assume the form in which they are used. A full consideration of this part of the subject belongs to technical chemistry or metallurgy.

Chemical Composition.—The chemical composition of a substance includes not only the nature and amount of the constituents present, but also the way in which they are combined together, for two substances may contain the same elements in the same proportions, and yet have very different properties.

Chemical analysis has now reached such a high degree of perfection, that it is in most cases easy to determine with accuracy the quantities of the various elements and acid radicals that are present in any substance, and for most purposes this is all that is required. An ordinary chemical analysis, however, even if made with perfect accuracy, gives no information as to the way in which the constituents are arranged, and in some cases this is of even more importance than the ultimate composition.

It must be remembered that, as a rule, the materials of engineering are not definite compounds in which the elements are necessarily united in fixed proportions, but they are mixtures of various elements and compounds, and before we can be certain of the composition of such a substance we must determine the proportion in which each of these constituents is present.

The object of proximate analysis is to split up the substance, not into its ultimate elements, but into the various units; themselves possibly compounds; of which it is built up. In a few cases only have the methods of proximate analysis been brought to anything like the perfection which has been reached by the methods of ultimate analysis, so that very frequently chemical analysis has to be supplemented by various physical tests in order to obtain the required information. No doubt in the near future the methods of proximate analysis will be much improved, and it will become possible to determine the actual composition of complex bodies. At present it is in most cases only possible to determine elements and certain radicals, and the state of combination in which these exist can only be guessed at.

Within the last few years the microscope has been brought into use as an aid to proximate analysis, and very much valuable information has been obtained by its use; indeed, some prevalent ideas as to the structure of materials have been revolutionised. It need hardly be remarked that the ultimate molecules can never be observed by any microscope, so that its use can tell us nothing of ultimate chemical composition; but in many cases substances apparently homogeneous are really mechanical mixtures of two or more substances, the separate portions of which are large enough to be recognised under the microscope.

Two methods of microscopic examination are used, both very simple in theory, but attended with considerabe difficulty in practice. Materials which are transparent in thin sections are ground down as thin as possible, and are then examined in the usual way by transmitted light. Opaque bodies are polished till the surfaces are absolutely smooth and free from marks; the sample is then treated with acid, or etched, and examined by means of reflected light.

Changes Produced by Treatment.—The materials used by the engineer are subjected to various operations in the shops, such as melting, forging, annealing, and these may induce considerable chemical changes. In some cases elements are taken up from the fuel or other substances with which the material is in contact; in others elimination may take place by oxidation or by liquation. Very frequently, however, the changes produced do not alter the ultimate but only the proximate composition, none of the elements being removed and no fresh ones added, but the elements re-arranging themselves so as to take up new forms and build up new compounds. Changes of this kind are of very great importance, and recent work with the microscope has done much to reveal their true character. Among the most important of such changes may be mentioned those which take place in the hardening, tempering, and annealing of steel.

Action of Various Agents.—The materials of engineering are intended for use under very various circumstances, and they have to be placed in conditions where they will be acted on by various agents, such as water, air, acids, &c., and on their power of resisting these influences their durability depends. Iron exposed to moist air rusts, and most metals are corroded more or less. Most stones resist the action of the air to a considerable extent, but all are more or less attacked in course of time, and some will stand well in the country, but yield quickly to the influence of the air of towns. A study of the corrosive action of the various substances with which the materials may be brought in contact is of the utmost importance, because without it the engineer cannot select the material which will be most suitable under any given conditions, or decide what are the best precautions to take to prevent or retard decay.

Chemistry of Manufacture.—The chemical changes which take place during the various operations by which the metals or other materials are produced are only of secondary interest to the general engineer, yet he should have some knowledge of them, so that he may know the possible limits of the composition of the materials he uses, as far as these depend on the processes of manufacture. It is not very uncommon for an engineer to specify a material to be made by a particular process with properties which are incompatible with the process by which it is to be made. In some cases, too, materials are classified according to the method of production, and it is important that the engineer should know the peculiarities of composition which the processes necessitate.

Classification of Materials.—In discussing the various materials it is essential to adopt some form of classification, and the following will be most convenient for the purpose :

I. Metallic materials.
  1. The metals.
  2. Alloys.
II. Non-metallic materials.
  1. Structural materials. Wood, stone, &c.; clay ware, bricks, tiles, &c.; cements and mortars.
  2. Fuel.
  3. Water.
  4. Miscellaneous materials, lubricants, paints, &c.

PART I.—METALLIC MATERIALS.

CHAPTER I.

CHEMISTRY OF IRON.

Pure Iron.—Though iron is so abundant and so widely distributed, the pure metal is very difficult to prepare, so much so indeed that it can only be obtained in small quantities by laboratory methods, and may be considered as a chemical curiosity. Various methods of preparation have been suggested. The most successful consist in the preparation of a pure iron compound such as the oxide or chloride, and the decomposition of this by hydrogen at a moderately high temperature, under such conditions that the reduced metal cannot take up foreign constituents.

The purest iron obtainable on the large scale is very mild steel made in the basic open-hearth furnace, and this for many purposes may be considered as being pure.

Magnetism.—One of the most striking properties of iron is that of becoming magnetic when it is brought into a magnetic field. The amount of magnetism which the iron will take up depends on its character : the softer and purer the iron, the more readily is it magnetised, and the more quickly it reaches its point of maximum magnetisation (or saturation), and the higher is said to be its magnetic permeability. When the iron is removed from the magnetic field it will retain more or less of this induced magnetism. Pure iron retains hardly any, whilst steel, which is iron containing about 1 per cent of carbon, though very difficult to magnetise, retains a large proportion of the magnetism, and thus becomes a permanent magnet. The magnetic retentivity of iron is low, whilst that of steel is high.*

The presence of foreign constituents very much modifies the magnetic properties of iron, the general tendency of impurities being to reduce the magnetic permeability, whilst the retentivity may be considerably increased, or may be diminished or destroyed.

Some other metals have decidedly magnetic properties, but none to anything like the same extent as iron. Nickel and cobalt are next in order.

Action of Oxygen.—Dry oxygen or air has no action on iron at ordinary temperatures. At below a red heat oxidation begins, and a black scale—iron scale—forms on the surface of the metal. This scale is usually said to be the black oxide, Fe_3O_4. It is, however, of indefinite composition, varying between FeO and Fe_3O_4, and may be regarded as being a mixture or compound of the two oxides. In the case of scale formed in flakes or sheets, the inner side approaches nearest to the composition FeO, and the outer side is nearly Fe_3O_4. At a white heat the scale fuses, and is then Fe_3O_4. Under ordinary circumstances the scale is non-adherent, and in rolling plates, &c., it is brushed off, so as to leave a clean surface of the metal. It is soluble in acids, and in some operations it is removed by dipping the article in dilute acid, or "pickling." At high temperatures the scale is dissolved by borax, and silica combines with it, forming a fusible ferrous silicate, in which any excess of ferric oxide dissolves. Hence borax and sand are used as fluxes in welding.

When iron is exposed to moist air, in presence of carbon-dioxide at ordinary temperatures, it rusts rapidly, a brown hydrate of ferric oxide being formed. The action by which the rust is produced is somewhat complex; it depends on the joint action of air, moisture, and carbon-dioxide, and in the absence of any one of these the action ceases. The

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* The term "coercive force," which was at one time general, is no longer used.

series of actions seem to be something as follows: The water containing carbon-dioxide is a weak acid (carbonic acid), which attacks the iron, forming ferrous carbonate (or bicarbonate), and liberating hydrogen, $H_2O + CO_2 + Fe = FeCO_3 + 2H$. On exposure to the air the ferrous carbonate is rapidly oxidised to the brown hydrate, carbon-dioxide being liberated, ready to dissolve in water, and attack fresh iron, $4FeCO_3 + 2O + 3H_2O = 2Fe_2O_33H_2O + 4CO_2$. It will be seen that the action takes place in a cycle, starting with iron and carbon-dioxide and ending with ferric hydrate and carbon-dioxide. Therefore a very small quantity of carbon-dioxide is able to rust a large quantity of iron, and there is no necessary quantitative relation between the quantity of carbon-dioxide, and the amount of rust formed. Once rusting has started, it will go on rapidly, for the rust is hygroscopic, and thus brings fresh water in contact with the metal, and the action evolves heat, which facilitates the oxidation.

The reactions described above are the principal, but not the only ones, which take place, for all iron rust contains a small quantity of black oxide, F_3O_4, in addition to the ferric hydrate.

The corrosive action of air, moisture, and carbon-dioxide is much modified by the presence of impurities, some facilitating and some retarding it. The whole question of the corrosion of various forms of iron and the methods of preventing it will be discussed later.

Action of Acids.—Iron is readily attacked by most acids, with the formation of ferrous salts and the liberation of hydrogen. Thus, with hydrochloric acid, $Fe + 2HCl = FeCl_2 + 2H$, and with sulphuric acid, $Fe + H_2SO_4 = FeSO_4 + 2H$, and the action of carbonic acid has been given above. Moderately strong nitric acid dissolves iron, forming ferric nitrate, and aqua regia dissolves it, forming ferric chloride. Very strong sulphuric acid has but little action, a layer of anhydrous ferrous sulphate being formed, which, being insoluble in the acid, protects the metal from further action

Very strong nitric acid apparently does not attack the metal, but throws it into a passive condition, in which it will not dissolve in dilute nitric acid, and will not precipitate copper from its solutions. Various explanations have been given of this action, but the usually accepted view is that the passivity is due to the formation of a superficial layer of black oxide, Fe_3O_4, which is adherent and protects the metal from further action.

The presence of various foreign constituents in iron may greatly reduce its solubility, so that pans made of the alloys may be used for operations in which acids are present, but, as a rule, all varieties of iron are corroded even by dilute acids.

Iron Salts and Solutions.—Iron forms two series of salts, the ferrous, of which ordinary green vitriol, ferrous sulphate, $FeSO_4 7H_2O$, may be taken as the type, and ferric, of which ferric chloride, $Fe_2 Cl_6$, is the best known example. Most of the iron salts are soluble in water, the ferrous salts giving solutions which are almost colourless or pale green, whilst the ferric salts give yellow solutions. The ferric salts in aqueous solution have a great tendency to form basic salts, which, being insoluble, are precipitated, this action taking place much more readily on heating; and in the laboratory iron is frequently separated from its solutions by boiling a nearly neutral solution of a ferric salt. The ferrous salts are oxidised on exposure to the air, both in the solid condition if moisture be present, and in solution, with the formation of brown basic ferric salts. As is well known, the crystals of green vitriol soon become brown on exposure to the air, as also do various iron ores which contain the iron in the form of sulphide or carbonate, and neutral solutions soon become turbid from the deposition of brown basic salts. In presence of iron or iron salts water soon becomes charged with almost insoluble basic salts, by the action of the carbon-dioxide and oxygen which it contains, as already explained; but if the water be kept boiling, so that the carbon-dioxide and oxygen are expelled, oxidation cannot take place.

The action of water containing carbon-dioxide on iron carbonate is of interest, as by it iron is dissolved from the minerals in which it occurs, carried away in solution, and subsequently re-deposited. The carbonate is insoluble in water, but dissolves in water containing carbon-dioxide, a bicarbonate, which is soluble, being formed thus : $FeCO_3 + CO_2 + H_2O = Fe_2H_2(CO_3)_2$. On exposure to the air the bicarbonate is decomposed, as already explained. It is by these reactions that the brown deposit so common in the streams in iron districts has been produced, and no doubt the same action has largely assisted in the formation of some iron ores.

Ferrous salts in solution are readily oxidised to the ferric condition by oxidising agents, such as strong nitric acid, chlorine, bromine, &c., and ferric salts are reduced by reducing agents such as zinc, sulphurous acid, and hydrogen sulphide.

Reduction of Iron Compounds.—All iron salts with volatile acids are converted into ferric oxide, Fe_2O_3, by heat : thus, in case of the carbonate, $2FeCO_3 = Fe_2O_3 + CO + CO_2$; and the sulphate, $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$. The red oxide is left in a very fine state of division, and is used as a polishing material and as a pigment under the name of rouge. If a very high temperature be used, the red oxide loses oxygen, and forms black oxide, $3Fe_2O_3 = 2Fe_3O_4 + O$.

The oxides of iron are very readily reduced by all reducing agents at moderate or high temperatures. With carbon or carbon-monoxide the action begins below redness, and at higher temperatures the liberated iron takes up carbon. Hydrogen reduces the oxides below a red heat, the metal being left in a spongy form, which, on exposure to the air, oxidises the more readily the lower the temperature at which reduction has been effected.

Iron and Carbon.—When iron is heated in contact with carbon, or any substance containing carbon, such as carbon-monoxide, coal gas, &c., combination rapidly takes place, and under suitable conditions may go on till about 4½ per cent of carbon has been taken up.

In ordinary solid irons the carbon may exist in two forms : (1) As carbon mechanically mixed with the mass of the iron, and (2) in chemical combination either with the whole of the iron or in solution in it, or as a definite carbide mixed through the iron. These two forms of carbon may be called uncombined or free, and combined, and they may be distinguished by their behaviour when the sample of iron is treated with acids. When a sample of iron containing carbon is dissolved in fairly strong acid, the combined carbon escapes with the hydrogen which is evolved, whilst the uncombined or free carbon, not being acted on by the acid, is left in the insoluble residue.

The free and combined carbon may each apparently be present in two forms.

1.—Free Carbon.

a. Graphitic Carbon.—When a sample of ordinary grey pig iron is dissolved in acid, a bulky residue is left, which contains silica and carbon. The former can be dissolved away by caustic soda, and a black residue of carbon in the form of shining flakes remains. This graphite is slowly oxidised by boiling with strong nitric acid, and on drying may be burnt in oxygen. Graphite is rarely present in irons containing less than 1·5 per cent of carbon.

β. Graphitic Temper Carbon is a black amorphous powder, left on solution of certain varieties of iron in acid. Chemically it seems to be identical with graphite, and it is uncertain whether it is not simply a modification of that substance.

2.—Combined Carbon.

a. Carbide Carbon.—This is a definite carbide, having the formula Fe_3C, and containing, therefore, 93·3 per cent of iron, which was first isolated by Abel. When iron containing this carbide is dissolved in acid in the ordinary way, the carbon is evolved in the form of hydrocarbons with the gas ; but if very dilute cold acids, or a mixture of sulphuric acid and potassium dichromate, be used, the iron dissolves, and the carbide is left in the form of a brownish mass. This carbide oxidises very readily on exposure to the air, and dissolves on boiling in nitric acid.

β. *Hardening Carbon.*—This form of carbon—so called because it is the form in which the element mainly exists in hard steel—is evolved with the gas when the iron is dissolved in acids. When the metal is dissolved in cold nitric acid (sp. gr. 1·2), the carbon separates as a black mass, which dissolves on shaking.

The properties of the metal depend not only on the quantity of carbon, but on the form in which it is present. The influence of the various forms of carbon will be discussed in connection with the different varieties of iron.

Iron and Silicon.—Iron and silicon combine very readily when the two elements are heated together, and when iron is strongly heated with carbon and silica, the silica is partially reduced and passes into the iron. The amount of silicon which iron can take up seems to be unlimited, and irons are made commercially containing 10 to 15 per cent. Silicon is so like carbon in its chemical character, that it was long thought that what was true of the one should be true of the other, and, therefore, that as carbon exists in iron in the two forms, free and combined, silicon should do the same, and in the older books accounts are given of the occurrence of a graphitic form of silicon in iron. The existence of this is, however, more than doubtful, as all attempts to isolate it have failed, and it is almost certain that silicon exists in iron only in combination. The amount of silicon which iron can take up under suitable conditions seems to depend almost entirely on the temperature, assuming that there be plenty both of silica and carbon present.

The influence of silicon on the physical properties of the metal will be considered later, but it exerts a chemical action which is of great importance—that is, it tends to prevent the iron, as it solidifies, retaining the carbon in the combined form, and causes it to be thrown out in the form of graphite, thus tending to make the pig iron grey.

Irons containing a large quantity of silicon are hard and brittle, silver white, with a bright metallic lustre, and they resist the corrosive action of air and acids better than most other forms of iron.

Iron Silicates.—As remarked above, ferrous oxide combines readily with silica to form a fusible ferrous silicate, and advantage is taken of this in welding, where silica is used as a flux. These silicates are produced as slags in a considerable number of metallurgical operations. They are usually black in colour, and very fusible; indeed, iron silicates are among the most fusible of the silicates. Silica can combine with very varying amounts of oxide of iron, the silicates ranging from very basic to very acid; the basic silicates are the most fusible. The most common silicates are the mono-silicate, $2FeO, SiO_2$, with about 30 per cent of silica, and the bi-silicate, FeO, SiO_2, with about 45 per cent.

The silicates are very readily formed when ferric oxide is heated with silica and reducing agents, and once formed, they are difficult to reduce, unless some basic material such as lime be present to combine with the silica. No ferric silicates are known, as Fe_2O_3 does not combine with silica, but ferrous silicate can dissolve and carry away a considerable quantity of ferric oxide; hence this is very frequently present in slags.

Iron and Sulphur.—When iron and sulphur are heated together, they combine readily, forming a very fusible sulphide (FeS), and as this will dissolve to some extent in molten iron, most irons contain small quantities of sulphur. The amount of sulphur present in iron is never large, and its influence seems to be opposite to that of silicon, as it tends to keep the carbon in the combined condition, and prevents the separation of graphite.

Iron and Phosphorus.—Iron and phosphorus combine very readily when they are heated together, forming very fusible phosphides. The same phosphides are formed when iron phosphate is heated strongly with carbon or other reducing agent, the reaction being $Fe_2(PO_4)_3 + 12C = Fe_2P_3 + 12CO$.

Apparently phosphorus may be present either combined with the whole of the iron, or as definite phosphide, and its presence affects the physical properties of the metal to a very considerable extent.

Alloys.—Iron forms alloys readily with almost all the metals, and some, such as those with manganese, aluminium, chromium, and nickel are in constant use. The influence of the alloying metal varies according to the other impurities which are present.

CHAPTER II.

SOURCES OF IRON.

Iron Ores.—Minerals containing iron are very widely distributed, and very abundant in nature, but unless they contain a large percentage of iron, and are free from deleterious impurities, it will not pay to work them, and only such as can be economically worked are called *ores.* The ores as raised consist of two portions, the mineral which contains the iron, and the gangue or vein stuff which is always mixed with the mineral, and which to some extent must always be raised with it. It is quite easy, in most districts, to obtain hand specimens of the minerals nearly pure, but when the ore is raised on the large scale, a considerable quantity of gangue must be raised with it; and therefore, however pure the iron mineral may be, the ore as supplied to the smelter may be far from pure.

The influence of the gangue is twofold. It diminishes the percentage of iron in the ore, and it may introduce impurities which may make smelting difficult or lessen the value of the metal obtained; hence, for practical purposes, a mere consideration of the mineral which is the essential constituent of the ore is of little value without taking into account also the nature of the gangue.

Iron ores may be classified in several ways, the most convenient classification being that based on the nature of the mineral present.

1. Black or magnetic ores.
2. Red ores or hæmatites.
3. Brown ores or brown hæmatites.
4. Spathic ores.
5. Clay-band ores.
6. Black-band ores.

Magnetic Ores.—These ores contain magnetite or magnetic iron ore, Fe_3O_4, and as this, when pure, contains over 72 per cent of iron, they may be very rich. They are black in colour, magnetic, and very dense. Black ores are not very widely distributed in nature, and they occur always in rocks that have undergone metamorphic change. The only important European localities are Sweden and Norway, whence large quantities have been exported. The ores sent from these countries are usually very free from sulphur and phosphorus, and are therefore very valuable for making pig iron for the various steel processes, and Swedish pig made from them has attained a very high reputation ; but all black ores are not so pure. Many of the deposits in those countries contain considerable quantities of sulphur and phosphorus, and it is by no means uncommon to find black ores with iron pyrites disseminated through them, though such are not usually exported.

Red Ores.—These ores are essentially hæmatite, Fe_2O_3, which contains, when pure, 70 per cent of iron. They are usually red, though some varieties, as for instance the specular ores of Elba, are black. They may be so hard that a knife will not scratch them, or they may be soft and earthy. The red ores are more widely distributed than the black ores, but the only British locality in which they occur in any quantity is North Lancashire and Cumberland, where they are largely worked. The ores of this district are very free from sulphur and phosphorus, and are therefore of great value for the steel processes, where those elements are specially objectionable. Pig iron made from them is often called hæmatite pig.

With the growth of the Bessemer and Siemens steel industries the demand for good hæmatites became much larger than the English districts could supply, and very large quantities are now imported from elsewhere. The principal source of the hæmatites now used in this country is Bilbao, in Spain. The ores from this district are red and brown. The principal red ore is known as campanil; it is free from sulphur and phosphorus, and the gangue is chiefly carbonate of lime, which acts as a flux in smelting. Hæmatites are also imported from Elba (specular ore, nearly black in colour, with a metallic lustre and very dense), Algeria, and other localities. Red ores are very abundant in the United States. The red ores imported to this country are, as a rule, nearly free from sulphur and phosphorus, because this is the only class of ore for which there is a demand, but purity is by no means a universal character of hæmatites. Some of the hæmatites from the south of Spain, and many that occur in America, contain considerable quantities of phosphorus.

Brown Ores.—The brown ores consist essentially of one of the hydrates of ferric oxide. Three of these are known as minerals—limonite, $2Fe_2O_33H_2O$; göthite, $Fe_2O_3H_2O$; and turgite, $2Fe_2O_3H_2O$; but most brown ores consist mainly of limonite, which, when pure, contains about 60 per cent of iron. They are usually brown, but sometimes nearly black in colour, the powder, however, being always brown, and they may be hard, dense, and compact, or soft and earthy. The brown ores are very widely distributed, occurring in England in Northamptonshire, Lincolnshire, and the Forest of Dean, in all of which localities they contain phosphorus. Considerable quantities of brown ore are imported from Bilbao (rubio ore), and from the south of Spain, and as these varieties are as free from sulphur and phosphorus as the red ores from the same districts, they are of considerable value. The brown ores are usually of later geological age than the red or black ores, and in many cases they have been produced by the action of air and moisture on carbonates.

Spathic Ores.—These consist essentially of siderite or chalybite, and ferrous carbonate, $FeCO_3$. Pure spathic ore is not common, the only locality in England where it occurs being the Brendon Hills, in Somersetshire. This ore is highly manganiferous, and is not now worked. Spathic ores are yellowish in colour, often inclining to pink if much manganese be present; they are soft enough to be readily scratched with a knife, and have a characteristic pearly lustre. On exposure to moist air they rapidly oxidise, and are converted superficially into hydrate, $2FeCO_3 + O + xH_2O = Fe_2O_3xH_2O + 2CO_2$; at the same time a portion of the carbonate is often dissolved by the water, containing carbon-dioxide, and carried away. The brown ores of Northamptonshire and Bilbao are formed by the oxidation of carbonates, and traces of the original mineral are frequently found.

An impure spathic ore is largely worked in the Cleveland district, in the north of Yorkshire. The ore is greenish in colour, oolitic in structure, and abounds in fossils, the two principal beds being known as the avicula and pecten beds, from the shells which they contain in abundance. They contain about 30 per cent of iron, a considerable quantity of carbonate of lime, and, as is always the case where fossils are abundant, a considerable quantity of phosphorus. These ores are smelted in the Middlesbrough district, for the manufacture of Cleveland pig iron.

Clay-band Ores.—These ores are carbonate of iron, $FeCO_3$, mixed with a considerable quantity of clayey matter; indeed, they may be regarded as being clays or shales which have become impregnated with the iron carbonate. They are very abundant in the coal fields of Staffordshire, South Wales, and Lanarkshire, in all of which districts they are largely worked; indeed, until quite recently they were the staple ores of the British iron industry. They are of all colours, from black to white, and occur either in beds or in nodular concretions in beds of shale. As a rule they exactly resemble shales, and have nothing in their appearance to indicate the quantity of iron which they contain. They usually contain much phosphorus, and are only suitable for making the common varieties of pig iron.

Black-band Ironstones.—These ores were discovered by Mushet, in Lanarkshire, in 1801, and since 1830 have been very largely worked in that district, and they occur in smaller quantities in some other of the coal fields. They are essentially ferrous carbonate, mingled with a considerable quantity of coaly matter, generally so much that when once ignited they will continue to burn. They may be regarded as being beds of coal which have become saturated with the iron carbonate. They contain about 30 per cent of iron, but as the coaly matter burns away they are much richer after calcination; they always contain a considerable quantity of sulphur and phosphorus. They are usually black or brown in colour, very frequently show distinct lines of stratification, and much resemble a coal or coal shale in appearance. Before Mushet discovered their real value they were called "wild coal," and were thrown away.

Other Materials Used as Sources of Iron.—A few materials, not strictly speaking ores, are used occasionally in iron smelting. Iron pyrites, FeS_2, is a very abundant mineral, but cannot be used directly for the production of iron. It is, however, largely used as a sulphur ore for the manufacture of sulphuric acid, as it contains, when pure, over 53 per cent of sulphur. When the sulphur has been burnt out—$2FeS_2 + 11O = Fe_2O_3 + 4SO_2$—the residual ferric oxide, known as burnt ore or "blue billy," is sometimes used for smelting; it is, however, not suitable for the purpose, as the removal of the sulphur is never complete. Many samples of pyrites contain copper, which remains in the burnt ore, and when this has been ground, and the copper extracted, the residual ferric oxide, then known as purple ore, is free from sulphur; it is, however, in too fine a state of division to be suitable for smelting, and is therefore only mixed in small quantities with other materials, and it is used for sealing the bells of the blast furnaces and other similar purposes.

The tap cinder and mill cinder from the malleable ironworks are mainly ferrous silicates, and therefore contain a large quantity of iron. They are smelted either by themselves or in admixture with ores, and as they contain a large quantity of phosphorus, they yield a very phosphoric pig.

Other Classifications of Ores.—Ores may be classified in various other ways, any one of which may be found convenient for special purposes.

1. According to the nature of the gangue.
    - (1) Siliceous ores: Those in which the gangue is mainly silica, such as the hæmatites of Cumberland, &c.
    - (2) Calcareous ores: Those in which the gangue is mainly carbonate of lime, such as campanil, &c.
    - (3) Argillaceous ores: Those in which the gangue is clay, as the clay-band ironstones.
    - (4) Aluminous ores: Those in which the gangue is mainly alumina, as the Antrim aluminous ores.
    - (5) Bituminous ores: Those in which there is a considerable quantity of coaly matter.

This classification is convenient for the smelter, who has to decide how best to mix his ores so as to need the least possible quantity of flux.

2. According to the impurities present.
    - (1) Pure ores: Such as the Cumberland or Bilbao hæmatites, containing little phosphorus or sulphur.
    - (2) Phosphoric ores: Those which contain a considerable quantity of phosphorus, such as the Cleveland ores and the black-band ores.
    - (3) Sulphurous ores: Those which contain much sulphur, as some of the clay-band ores.
    - (4) Manganiferous ores: Those containing manganese, such as the Somersetshire spathic ores.

(5) **Titaniferous ores**: Those containing titanium; as, for example, many of the iron sands.

This is convenient for smelters making different varieties of iron. It is clear that the classes are not mutually exclusive, but that an ore might belong to more than one of them.

3. According to physical character.

(1) **Hard ores**: Those which are hard, compact, and dense, such as Elba specular ore, some hæmatites, &c.

(2) **Soft ores**: Those which are soft, and crumble easily, such as many brown ores, Cleveland ores, &c.

TABLE I.—EXAMPLES OF IRON ORES.

	Gellivara magnetite.	Hodbarrow, Cumberland.	Rubio, Bilbao.	Cleveland.	Black-band. Scotch.	Clay-band. Staffordshire.
Iron	69·51	63·0	54·90	31·71	38·57	35·74
Manganese	·07	Trace.	·55	·40	·25	·5
Lime	·20	·90	Trace	....	1·06	2·60
Magnesia	·68	·30	·15	5·36	3·116	1·26
Phosphorus	·01	·01	·01	·9	·41	·20
Sulphur	·04	·03	·01	·1	·25	·10
Titanic acid	·63	....	....	....	....	....
Carbonic acid ..	....	·75	....	31·80	33·68	30·21
Silica	1·90	7·5	8·30	8·80	1·58	10·63
Alumina	·25	·45	1·10	1·32	1·10	5·70
Water	·14	....	10·30	2·70	·59	1·64
Coaly matter....	....	....	....	....	7·69	1·59

CHAPTER III.

PIG IRON.

Pig Iron.—This is the most impure form of iron, which comes into the market usually containing only from 92 to 93 per cent of iron, and at least 1·5 per cent of carbon. It derives its name from the fact that it is cast, from the furnace in which it is made, into large ingots or pigs, each of which weighs about 1 cwt. When it has been re-melted and cast into any required form, it is usually called cast iron. Cast or pig iron is not by any means a definite substance; and its properties and composition may vary between very wide limits.

Pig iron is commercially classified into six classes or grades, the classification depending entirely on the appearance of the fracture. The grades are usually known as Nos. 1, 2, 3, 4, mottled, and white.

No. 1 Pig.—This is the greyest of all the irons. The fracture is dark grey or nearly black in colour, and is largely crystalline, flakes of graphite being easily distinguishable. This iron melts to a very thin liquid, and can be readily cast, the fluid metal flowing into even the minutest cavities of the mould; hence it makes very fine castings, but owing to its crystalline structure, and the presence of the large quantity of graphite crystals, the castings are weak and brittle.

No. 2 Pig.—This is very similar to No. 1, but the crystalline flakes are smaller. The metal flows less freely, but the castings are stronger than with No. 1.

No. 3 Pig.—In this the grain is still smaller. The melted metal does not flow so freely, but the castings are stronger than those made with the lower numbers. This, with or without the admixture of smaller quantities of other numbers, is the iron used for all heavy castings and for general work.

No. 4 Pig is still closer in grain, the crystalline structure being so fine that the fracture appears almost granular. The colour is still dark grey, but paler than in the lower numbers. The metal does not flow very freely, and can only be used for very rough and heavy castings. No. 4 pig is often divided into two sub-classes, No. 4 foundry and No. 4 forge.

White Iron.—This stands at the other extreme of the series from No. 1. The colour of the fracture is silver white, the metal close grained, with no trace of distinct flakes of graphite. It is hard—sometimes so hard that a file will not touch it—and brittle, and when melted it flows very sluggishly, so that it cannot well be used for making castings.

Mottled Iron.—This stands between No. 4 and white iron, and consists of a mass or matrix of white iron, scattered through which are a large number of specks of grey iron, about No. 4.

Nos. 1 to 4 (foundry) are usually called grey or foundry pigs; No. 4 (forge), mottled and white, are called white or forge pigs.

Chemical Composition.—As will be judged from the varieties of pig iron mentioned above, the chemical composition must vary very much. Of the various foreign elements which are present in pig iron, two, carbon and silicon, may be considered as being essential, as without them the metal would not be pig iron; whilst the others may be regarded as being non-essential or accidental constituents, since, though they are always present in larger or smaller quantity, and have great influence on the quality of the iron, their absence would not prevent the metal being called pig iron.

Carbon.—Carbon is usually regarded as being the one essential constituent in pig iron, and it is always present in quantities varying between 1½ and 4½ per cent, usually about 2½ to 3½ per cent, the quantity being frequently, though not by any means invariably, larger in grey irons than in white. It is always present in the two forms, graphitic and combined.

The graphitic carbon is present in large quantity in No. 1 iron, and the separate crystalline flakes can usually be detected on the fractured surface, and often can be picked off with a knife; whilst in white iron, at the other end of the series, no graphite can be seen. The graphitic carbon is present in some form of combination or in solution in the molten iron, but separates out during solidification, so that with the lower number irons, as they solidify, some of the separated graphite rises to the top, and forms the well-known scum or kish; the quantity, of course, being largest with No. 1, whilst white iron throws up none. The graphitic carbon does not seem to have any very great influence on the quality of the iron, except that the crystals of graphite scattered through the metal must break its continuity, and thus render it weaker.

The combined carbon is of very much more importance—indeed it is the most important of all the constituents—and on it to a large extent the nature of the iron depends. It is in chemical combination with the iron, so cannot be detected by the eye, and when the metal is dissolved in acid it passes completely away with the hydrogen, imparting to the gas a most unpleasant odour. Turner* gives the following as being the percentage of combined carbon which should be present in pig irons of various qualities:—

	Combined carbon.
Extra soft siliceous grey iron	0·08
Soft cast iron	0·15
Maximum tensile strength	0·47
Maximum transverse strength	0·70
Maximum crushing strength	over 1·00

The first two would be about No. 1, the third No. 3, the fourth about No. 4, and the last white.

The grading, as usually conducted, by mere judgment of the fracture, is most uncertain, and is quite valueless as a means of determining the nature of the iron.

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* *Iron*, page 191.

Many suggestions for a better system of grading have been made; the most satisfactory, no doubt, would be one based on the percentage of combined carbon present.

The amount of combined carbon present in a sample depends on various conditions, very largely on chemical composition, some constituents, such as silicon, having a great power of throwing the carbon into the graphitic form, whilst others, such as manganese, tend to keep it combined, so that highly siliceous pigs are always grey, and manganiferous pigs are always white. But it also depends on physical treatment, especially on the rate of solidification. Slow solidification and cooling tends to allow of the separation of graphite, while rapid solidification tends to prevent this, and to keep the carbon in combination, thus whitening the iron. Advantage is taken of this in "chill casting," where the metal is cast in a mould, part of which is of metal. In contact with the metal, or "chill," the liquid iron is quickly solidified, and, thus retaining its carbon in combination, has the hardness of white iron, whilst the other portions of the casting, in which cooling is so slow that the graphite can separate, have the toughness of grey iron.

The change from white to grey iron may be brought about without actual fusion. If the metal be kept at a high temperature for some time, the carbon gradually passes into the graphitic condition.

Silicon.—Another very important constituent in ordinary pig iron is silicon. It is present in all cast iron, and its presence may be considered as essential. There seems to be no limit to the amount of silicon with which iron can combine, but when there is more than about 4 per cent present the metal is hard and brittle, and is of little use for engineering purposes. Not long ago it was believed that silicon was always objectionable in iron, and therefore that the freer an ordinary pig was from it the better. This is now known not to be the case, a certain quantity of silicon being almost always very advantageous. The influence of silicon on the strength of cast iron has been investigated by Turner,* and the results he obtained for tensile strength, crushing strength, and transverse strength are shown in the diagram, fig. 1, copied from his paper.

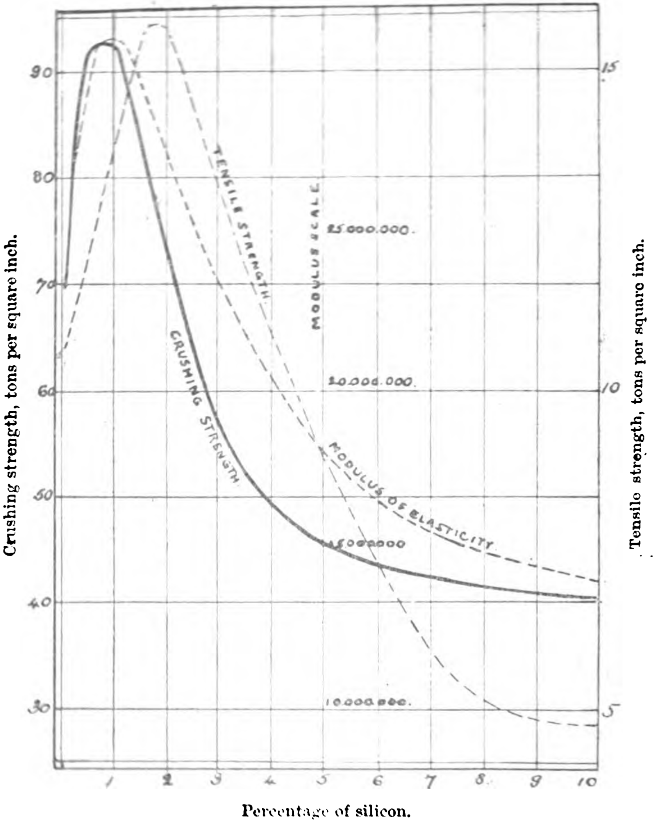

FIG. 1.

Looking at the curve of tensile strength, for instance, it will be seen that with no silicon the iron used for the experiments

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* J. C. S., 1885.

had a strength of about 12 tons; as the silicon increased to about 1·8 per cent, the tensile strength increased to about 16 tons, and then as the silicon was further increased, the strength decreased, till with 4 per cent of silicon the metal was about as strong as with none, and with 10 per cent the strength had fallen to under 5 tons. For the other properties the results are very similar, cach property rising to a maximum with increase of silicon up to a certain point, and then decreasing as the quantity is further increased.

Turner gives the following figures as to the best proportion of silicon for various properties, as deduced from his experiments :—*

Maximum hardness	under	·8
Crushing strength	about	·8
Modulus of elasticity	about	1·0
Density in mass	about	1·0
Tensile strength	about	1·8
Softness and working qualities	about	2·5
Lowest combined carbon	under	5·0
Combined crushing and tensile strength, transverse strength	about	1·4

Turner himself pointed out that these figures were only exactly true under the conditions of his experiments—that is, with metal containing about the same percentage of carbon and other elements as that with which he worked. The principle, however, holds true in all cases, but with varying amounts of other elements the exact position of the maximum points of the curves might vary somewhat.

The action of silicon on iron is to harden it, alloys of iron and silicon being hard and weak. In this, therefore, it exactly resembles carbon in its action; and though the hardening is very marked in extreme cases, when a large quantity of silicon is present; the action of silicon, when present in small quantities, is much less noticeable

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* *Iron*, page 195.

than that of carbon. Silicon also has an indirect action in pig iron, which in many cases more than neutralises its direct hardening action—that is, it has a great tendency to throw the carbon out of the combined and into the graphitic condition, and thus to soften the metal. These two actions go on side by side, so that the actual result will always be the algebraic sum of the two.

Referring once more to the curve of tensile strength, it will be seen that the silicon, up to nearly 4 per cent, increases the strength of the iron, probably because the strength due to the reduced quantity of combined carbon is greater than the weakening due to the presence of the silicon, but beyond that the latter action predominates, and the iron is weakened. So with the hardness, in spite of the hardening effect of silicon ; the addition of that element up to about ·8 per cent actually softens the metal.

This action of silicon is of enormous importance in the working of cast iron. When iron is exposed to oxidising agencies, as when it is melted in the cupola, the silicon oxidises out before the carbon, each re-melting reducing the silicon very considerably, but making very little change in the carbon. As a result, if the silicon be very high, re-melting will improve the metal up to a certain point, but beyond that it will deteriorate it, tending to make it white, by the removal of the silicon, allowing the carbon to pass into the combined condition. In some foundries, highly siliceous irons, such as those now made by the use of a very hot blast, are kept melted, and exposed to the air in a reverberatory furnace, so as to oxidise out the excess of silicon, and bring the metal to the best composition for foundry work. Silicon is also now largely used in the foundry—in the form of a highly siliceous iron—for adding to cast iron that has gone "white" by re-melting, so as to bring it back to the grey condition. Since the presence of silicon tends to keep the metal grey, a large quantity is very objectionable in metal intended for chill casting.

The presence of a considerable quantity of silicon seems to very much increase the power of the metal to resist the corrosive action of the air moisture and dilute acids.

Sulphur.—Sulphur is almost always present in iron, but usually only in small quantity. As a rule, white irons contain more sulphur than the greyer forms, and to such an extent is this the case that sulphur has been sometimes put down as being the cause of whiteness. There is little doubt but that sulphur does tend to throw the carbon into the combined condition, and thus whiten the iron, but it can only have this influence under conditions which are otherwise favourable to the formation of white iron. The presence of a considerable quantity of silicon seems to be incompatible with the presence of much sulphur, and when grey irons, very rich in sulphur, have been prepared, most of the sulphur seems to be exuded on solidification in the form of sulphides, or of a very sulphury iron. Hence, when pig iron is melted in a cupola in contact with coke containing sulphur, but little sulphur will be taken up until the silicon is considerably reduced in quantity, but then the sulphur which may be absorbed will very materially help to whiten the iron. Good foundry iron should not contain more than ·15 per cent of sulphur, and Turner states* that "in irons which contain but little silicon, and where the equilibrium of the carbon is more easily affected, 0·05 per cent of sulphur may quite spoil the metal for special purposes, on account of the increased combined carbon, and consequently greater hardness and brittleness." The sulphur is frequently very irregularly distributed in the mass of iron.

Phosphorus.—All cast iron contains phosphorus in larger or smaller quantity. In pig to be used for making mild steel by the acid processes it should not exceed ·05 per cent; but in foundry pig it may be as high as ·75, or even 1 per cent.

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* *Iron*, page 201.

The effect of phosphorus is two-fold. It increases the fluidity of the metal, and makes it run well, so that it will make good castings, and all the best grades of foundry pig contain a very considerable quantity of phosphorus, ordinary Scotch pig containing about ·75 per cent.

Owing to this action, phosphoric iron sets more slowly than non-phosphoric, and thus allows ample time during solidification for the separation of the carbon in the form of graphite. Phosphorus therefore tends to make the iron grey, and is very objectionable in iron intended for making chill castings.

The presence of phosphorus tends to make the iron hard and brittle, and therefore a large quantity is objectionable where great strength is required. For strong castings about ·5 per cent is the best quantity, but where fluidity is the principal quality required a much higher percentage is allowable.

Manganese.—This element is almost invariably present in small quantities, and if the quantity does not exceed 1 per cent it is not objectionable. Like silicon, it has a double action—a direct hardening action, and an indirect softening action; the latter being due to the strong tendency to eliminate sulphur in the form of manganese sulphide. Manganiferous irons, therefore, are less likely to take up sulphur than those which are free from that element. Manganese also seems to facilitate the rusting of iron containing it.

Action of Aluminium.—Aluminium does not occur in cast iron, but it has been suggested to add it for various purposes. Its action is much the same as that of silicon, but very much more energetic, so that only a small quantity need be added to convert a white iron into grey. It also diminishes the shrinkage and increases the strength of the casting, especially as regards resistance to impact. The soundness and the density of castings are also improved.*

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* Turner, *Iron*, page 179.

Many other elements are occasionally present in pig iron, but their influence is not of sufficient importance to be considered here.

Influence of Composition on the Quality of Pig Iron.—As will be seen from what has been already said, the quality of a pig iron depends entirely on its chemical composition, and though there are a few points in the proximate composition which are not quite settled, enough is known to enable us to judge what will be the properties of the iron from its analysis. It is impossible, however, to form any satisfactory judgment, or at anyrate more than a partial one, from the determination of only one or two of the constituents. Pig iron is a very complex body; the various constituents not only have each their own action, but they modify the influence of the others in such a way that it is only by the consideration of the whole that a sound judgment can be formed, and most of the so-called failures of the chemists have been due to the neglect of some data which should have been taken into account.

It must be borne in mind, also, that a mass of cast iron is not by any means necessarily homogeneous. The changes which take place during solidification may, and indeed do, lead to the segregation of certain impurities in one portion, and sometimes the extrusion of others at another, and this is unavoidable, since a mass of iron cannot be all cooled at once, or at the same rate.

The heterogeneity of pig iron is well shown by the separation of graphite during the solidification of grey iron, and by the peculiar mottled structure of mottled iron. These are extreme cases, but the same phenomena are always present to a greater or less extent, as is shown by microscopic examination.

CLASSIFICATION OF PIG IRONS.

Pig irons go by various names, a few of which are worth noting.

Hæmatite or Bessemer Pig.—This is pig iron made from hæmatite or other ores, free from phosphorus, and is suitable for use in the Bessemer or Siemens steel processes. It must not contain more than ·05 of phosphorus and ·01 of sulphur. It is usually high in silicon (about 3 to 3·5 per cent), and often contains a good deal of manganese.

Scotch Foundry Pig.—Pig made for foundry purposes from Scotch clay-band or black-band ores. It usually contains from ·7 to 1 per cent of phosphorus, and about 2·5 per cent of silicon. It is excellent for foundry purposes.

Staffordshire All Mine Pig.—Pig iron made in Staffordshire from ore, without the addition of cinder, contains about ·5 to ·75 per cent of phosphorus.

Cinder Pig.—Pig made from tap cinder and other forms of slag. It is very impure, and is usually very high in phosphorus.

Cleveland Pig.—Pig made in the Middlesbrough district from Cleveland ores. It contains about 1 per cent of phosphorus, and 2·5 per cent of silicon.

Basic Pig.—Pig made for use in the basic Bessemer process. It contains very little silicon, not more than 1 to 1·5 per cent, and is very frequently white. It also contains from 1 to 3 per cent of phosphorus.

Silicon-eisen, or Silicon Pig, is pig iron containing 5 to 15 per cent of silicon.

Spiegel-eisen and Ferro-manganese are alloys of iron and manganese, containing from 20 to 85 per cent of manganese. The presence of manganese allows 5 or 6 per cent of carbon to be taken up.

Cold-blast Pig is pig iron made in furnaces worked with the cold blast. It is usually low in silicon.

CHAPTER IV.

PRELIMINARY TREATMENT OF THE ORES.

IT is frequently necessary or advisable to subject the ores to some preliminary treatment before smelting, so as to remove as much as possible of the gangue, and thus reduce the amount of material charged to the furnace for each ton of iron, and diminish the expense of working.

Hand Picking.—This is frequently resorted to at the mine. The large lumps are broken up with hand hammers, and pieces of gangue which obviously contain no ore are thrown on one side. This process is expensive and inefficient.

Dressing.—The methods of dressing used with most metallic ores are not applicable to iron ores. They necessitate the ore being in the condition of a coarse powder, which is quite unsuitable for blast-furnace smelting, and, at the same time, the process is too expensive for general use on iron ores.

Magnetic Separation.—This method of dressing has recently been introduced with some success in certain cases, but is only directly applicable to magnetic ores. The ore is powdered, and is brought in contact with revolving magnets which, acting on it, pick out the magnetic particles and carry them away, leaving the non-magnetic gangue behind. This process not only concentrates the ore, but as the sulphur, in sulphurous magnetites, is in the non-magnetic portion, it is left behind, and the ore is purified ; the concentrated ore, being in powder, is moulded into briquettes for smelting. The process is, however, costly, and therefore, though efficient, it can only be used where the dressed ores will be very valuable.

Magnetic concentration is only directly applicable to magnetic ores, but since hæmatites and carbonates become magnetic on roasting at a high temperature, the ferric oxide being converted into magnetic oxide $3Fe_2O_3 = 2F_3O_4 + O$

they may be roasted and then concentrated. This, however, adds seriously to the cost of treatment, and can only be applied in cases where the ore and gangue are not very intimately mixed. In the case of clay-band and black-band ores the mixture is so intimate that separation of ore from gangue is impossible.

Calcination.—Iron ores which contain matter that can be expelled by heat are almost always subjected to calcination before they are sent to the furnace. The calcination, by driving out the volatile matter, reduces the weight of the ore, sometimes by 20 to 30 per cent, removes sulphur, and makes the ore more porous.

The changes produced by calcination are simple. The water is expelled from hydrates, $Fe_2O_3xH_2O = Fe_2O_3 + xH_2O$, carbonates are decomposed, oxides being left, lime in the case of calcium carbonate, ferric oxide in the case of ferrous carbonate $CaCO_3 = CaO + CO_2$, $2FeCO_3 = Fe_2O_3 + CO + CO_2$.

Any iron pyrites present is decomposed—$2FeS_2 + 11O = Fe_2O_3 + 4SO_2$, the sulphur being evolved as sulphur dioxide, provided it be not present in large quantity, and the air supply be sufficient, and any bituminous matter is burnt out. Care must be taken in calcination that the temperature does not rise too high, or, especially in presence of bituminous matter, ferrous silicates may be formed, which, being fusible, will cause the whole mass to frit together. The calcined ore should, as a rule, be red or brown in colour; if it be black, it shows either that ferrous silicate has been formed, or that the ferric oxide has been converted into magnetic oxide.

Magnetites and hæmatites are never, and brown ores only rarely, calcined, but with all others calcination is the rule.

The ores are either calcined in heaps or in kilns. The former method is very simple. A layer of wood or coal is spread on the ground, and on this is piled the ore to be calcined in layers, alternately with layers of fuel. The heap is then lighted, and the combustion is regulated to some extent by shading off the wind with wooden screens. In the case of bituminous ores no fuel is required except a little to start combustion, but with clay-band ores half a cwt. may be required for each ton of ore. The calcination in heaps is very irregular and uncertain, as it is almost impossible to regulate the combustion properly, and one portion of the heap is often over-burnt, whilst another is hardly calcined at all.

Calcination in kilns differs from that in heaps only in the fact that the mixture of ore and fuel is contained in a kiln. The kilns are of various forms and sizes, but the most common now is a stack, 20 ft. or more in height, and 8 ft. or 9 ft. in diameter, circular in section, the upper portion being carried on columns between which the charge is drawn, a cone often being fixed in the centre to throw the descending charge outwards. Owing to there being less loss of heat, less fuel is required for kiln than for heap calcination, and at the same time the action is much more regular and complete.

THE MANUFACTURE OF PIG IRON.

Smelting the Ore.—The process of the manufacture of pig iron is very simple in principle.

The furnace used is commonly called a blast furnace. It is a nearly vertical stack of masonry, the upper portion being usually cased with iron, and carried on a series of iron columns. The interior, which is lined with refractory fire brick, is shaped as shown in fig. 2, though the exact form varies. At the bottom of the furnace is a cylindrical portion, or hearth. Above this the diameter increases to the bosh, which is the widest part; above this, again, the "shaft" decreases in diameter to the stock line, which is the level at which the top of the charge should be when the furnace is at work, and above this it may or may not be contracted to the "throat."

In the throat is fixed the charging apparatus, so arranged that the furnace top can be kept closed when the charge is not being actually introduced, the gases being drawn off by a pipe, and either passed direct to the boilers where they are to be burnt, or—when coal is the fuel used—first through condensers, for the recovery of the tar and ammonia. Various forms of charging apparatus are used, but that shown in the sketch, and known as the "bell and cone," is the most general. A wrought-iron inverted cone is fixed in the throat of the furnace, and in this is another cone or bell, carried on an arm, with suitable gearing, so that it can be raised or lowered as required. When the bell is up, it is in contact with the lower edge of the cone, and thus a tight joint is made; when it is lowered, there is an annular space by which the charge can drop into the furnace.

Near the bottom of the furnace is a ring of openings, T O, through which the tuyeres for the supply of air are passed. The tuyeres are conical iron pipes, and as the air is now almost always heated, these are surrounded by water tuyeres, which are usually coils of pipe through which water can be made to circulate, so as to keep the tuyere pipes cool, and prevent their rapid destruction, which would otherwise take place, owing to the great heat of the furnace and of the hot air. The air is forced in under pressure by means of a blowing engine, and is heated up to from 800 deg. Fah. to 1,400 deg. Fah., by being passed through heating stoves.

In the hearth itself there are two openings, or tap holes, a lower one near the bottom, and an upper one near the top. The lower opening is for the escape of the fused iron. When the furnace is at work, it is closed by a plug of clay, but when sufficient iron has accumulated to necessitate "tapping," this is forced out with an iron bar, and the liquid metal is run into the sand or pig moulds. The upper opening, or cinder tap, is for the escape of the slag or cinder. This is closed with clay also, but is opened more frequently than the metal tap, and the slag or cinder is run into moulds, or, more usually, into wagons, and is thrown away.

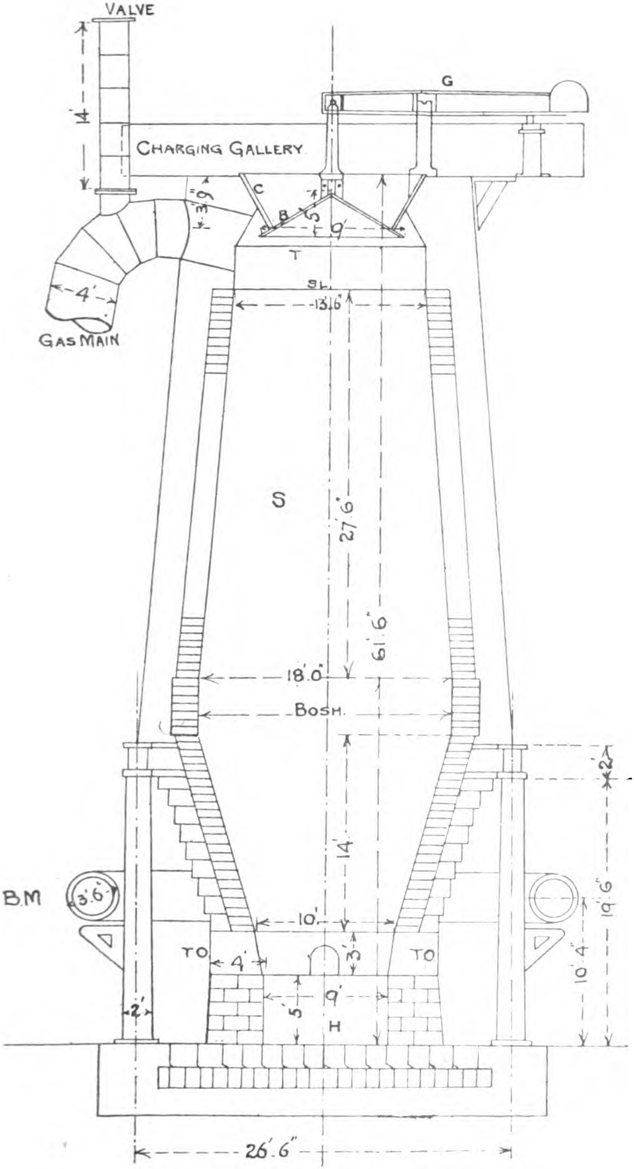

FIG. 2.—A modern blast furnace. B M—Blast main. S—Shaft. H—Hearth. T O—Tuyere openings. B—Bell. C—Cone. G—Gear for raising and lowering cone.

Outside the furnace are the various necessary appliances—the pig bed in which are made the moulds to receive the iron, the blowing engines, the heating stoves, &c., &c.*

THE INCOME OF THE FURNACE.

The charge is introduced into the furnace at the top, and the furnace, whilst working, is kept filled up to the stock line. The charge consists of three portions—the ore, the flux, and the fuel, and this, with the addition of the air which is blown in, is the income of the furnace.

1. *The Ore.*—This always contains the iron in the form of oxide, since, as already explained, if it were present in any other form in the original ore, it would be converted into oxide by the calcination. Mixed with the oxide of iron there is always a certain amount of earthy material.

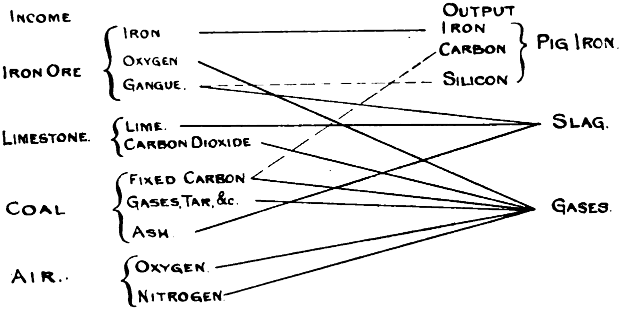

FIG. 3.

2. *The Fuel.*—The combustion of this produces the heat necessary to bring about the various chemical changes, and to melt the iron and the slag; at the same time, either directly or by means of the carbon-monoxide produced by its partial combustion, it acts as a reducing agent, and separates the oxygen from the iron.

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* For further particulars, see the author's "Elementary Metallurgy."

In most districts the fuel used is coke, but in Scotland splint coal is the general fuel. Coke is the best fuel, but the conversion of the coal into coke is an expensive, and, as usually conducted, very wasteful operation, and only certain varieties of coal will make good coke. The coal suitable for use in the blast furnace raw—*i.e.*, uncoked—is of a kind which will not make good coke. So, whether coke or raw coal will be used will depend largely on the nature of the coal available in any particular district. When raw coal is used the furnace gases contain tar and ammonia, which may be recovered, and when the coal is first coked the same products may be obtained from the coke ovens. As a rule, much larger furnaces can be used when coke is the fuel than when raw coal is used, because the residue left on heating splint coals is more or less friable, and is incapable of supporting the great weight of a very high column of materials.

3. *The Flux.*—As the materials charged into the furnace can only leave it in the liquid or gaseous condition, everything that goes in must either be melted or gasified. The gangue of the ore and the ash of the fuel are, as a rule, infusible; and therefore something must be added to combine with them, and form a fusible slag. In most cases limestone is the material added. The carbon-dioxide is expelled, and the lime combines with the silica and alumina present to form silicate of alumina and lime, which, if the constituents are present in suitable proportions, is fusible at the temperature of the furnace.

4. *Air.*—This is an essential part of the income of the furnace. The nitrogen passes through unchanged. The oxygen combines with the carbon, and as the temperature is very high, and carbon is in excess, carbon-monoxide is formed, $C + O = CO$, with very little, if any, carbon-dioxide.

THE OUTPUT OF THE FURNACE.

1. *Pig Iron.*—This is the material for the preparation of which the furnace is worked. It consists of all the iron

which was in the ore, with about 5 to 8 per cent of other materials taken up from the charge.

2. *Slag.*—This consists of all the earthy material of the ore, the ash of the coke, and the lime of the limestone. It is essentially a silicate of lime and alumina, but the proportions of the various constituents vary very much according to the nature of the gangue of the ore, the temperature of the furnace and other conditions. The nature of the slag is very closely connected with that of the iron produced, and the furnace-man can judge to a large extent how the furnace is working by the slag which is tapped out. The slag is usually nearly white, and may be either stony or glassy, according to its composition and the rate at which it is cooled. Sometimes, especially when the furnace is working cold, a black slag containing iron, called scouring cinder, is produced. When this is the case the iron made is usually white. When maganese and other metallic oxides are present the slag may be variously coloured.

3. *Gases.*—The gases consist essentially of nitrogen and carbon-monoxide, with a certain amount of carbon-dioxide, produced by the action of the carbon-monoxide on the oxide of iron, a small quantity of hydrogen from water carried in by the air, and, when coal is used, tarry matters and hydrocarbon gases. The amount of carbon-monoxide is so large that the gases are always combustible, and are now always used for firing boilers and heating the air for the furnace. When raw coal is used, the tar, which amounts to about 70 gallons per ton of coal consumed, is recovered, and by distillation converted into pitch and oils. Coal contains from ½ to 1½ per cent of nitrogen, and when it is distilled, either in a retort or blast furnace, about 16 per cent of this passes away in the form of ammonia. It is therefore possible to recover from the gases of blast furnaces fed with raw coal—as that suitable for the purpose contains a large quantity of nitrogen—about 22 lb. to 25 lb. of sulphate of ammonia for each ton of coal consumed.

The relation of income to output is shown diagrammatically in fig. 3. The quantities will, of course, vary very much according to circumstances. The amounts for an ordinary Scotch furnace will be about—

Income.				Output.		
Iron ore		2·5	tons.	Pig iron	1	ton.
Iron	1		,,			
Oxygen	·43		,,			
Earthy matters.	1·07		,,			
Limestone		·50	,,	Slag	1·51	,,
Lime	·28		,,			
Carbon-dioxide.	·22		,,			
Coal		1·52	,,	Gases	8·13	,,
Carbon	·97		,,			
Ash	·16		,,			
Gases	·49		,,			
Air		6·12				
Total		10·64		Total	10·64	

Chemical Changes in the Blast Furnace.

The changes by which the income of the furnace is converted into the output are, on the whole, fairly simple. It must be remembered, however, that the interior of the blast furnace is inaccessible, and that the materials in it are exposed to conditions which it is impossible to reproduce in the laboratory, so that necessarily many changes take place, the nature of which can only be guessed, and those which are known to take place may be accompanied by others of which nothing is known, and, therefore, it is not surprising that changes take place which it is not easy, sometimes even not possible, to explain.

The air is blown into the furnace at a high temperature, and at once combines with the carbon, forming carbon-monoxide, thus further increasing the temperature. The zone where the air comes in contact with the fuel is, therefore, the hottest part of the furnace. As the hot gases ascend they meet the descending cold charge, and impart their heat to it so completely that they should leave the furnace at a temperature of about 600 deg. Fah. Obviously, when the furnace is working continuously, the temperature at any point must remain fairly constant, the hot gases ascending being cooled, and the charge descending being heated. The temperatures at the various parts of the furnace have a very great influence in determining the chemical changes which take place.

Immediately the charge is let into the furnace it comes in contact with the ascending gases. The heat of these at once acts on the coal, which is distilled, gases and tar being distilled out, and the residue or coke descending with the charge. Though the furnace itself is very hot lower down, the coal is thus distilled at a low temperature, and the tar which is produced is quite different from that obtained from gas retorts, where the distillation takes place at a very high temperature.

Reduction of the Iron.—The gases, as they ascend from the zone of fusion, contain about 34·5 per cent of carbon-monoxide, and 65·5 per cent of nitrogen, with small quantities of hydrogen and hydrocarbon gases. When the iron ore is charged into the furnace it comes in contact with these gases; they penetrate into it, and reduction at once begins, $Fe_2O_3 + 3CO = 2Fe + 3CO_2$, the iron being reduced and the carbon-monoxide converted into carbon-dioxide. Thus the gas as it leaves the furnace contains carbon-dioxide. If all the iron in the ore were reduced by carbon-monoxide, under ordinary conditions about one-third of the carbon-monoxide would be used up, and the escaping gases would contain about twice as much carbon-monoxide as carbon-dioxide, and these proportions are held in practice to indicate good working of the furnace. The action of carbon-monoxide on iron-oxide begins considerably below a red heat, though it is much hindered if a large proportion of carbon-dioxide be present, and as the temperature rises it becomes more rapid. The more porous the ore—that is, the more readily the gas can permeate it—the more rapidly will reduction take place. The reduction should be practically complete before the descending charge reaches the zone where the temperature is high enough for the hot carbon to attack the carbon-dioxide formed, $CO_2 + C = 2CO$, because, as will be evident from the equation, each 44 parts of carbon-dioxide formed under such conditions would take up and carry away twelve parts of carbon, which, if it had not been thus removed, would ultimately have been burnt at the tuyeres, and would have helped to keep up the temperature of the furnace. One of the advantages of a tall furnace and slow driving is that it allows longer time for the reduction by carbon-monoxide before the temperature is high enough for the carbon to act on the carbon-dioxide, and this is no doubt one reason why tall furnaces are more economical than short ones. The iron separated still retains the form of the mass of ore, and is in the condition of spongy, nearly pure, iron.

Decomposition of the Limestone.—As the charge descends and becomes hotter the limestone is decomposed, $CaCO_3 = CaO + CO_2$. This change, however, does not take place to any great extent, till the temperature is high enough for the carbon present to attack the carbon-dioxide and reduce it to carbon-monoxide.

Carburisation of the Iron and Formation of Slag.—The descending charge, by the time it reaches the very hot part of the furnace, will, therefore, consist of iron in a spongy form, lime, the earthy materials of the ore and coke.

The iron soon begins to combine with the carbon either from the solid coke or from the carbon-monoxide, or perhaps from both, and the cast iron thus formed melts, whilst the lime combines with the silica and alumina present, and forms the slag.

Reduction of Silicon.—If no other changes took place, the cast iron would contain only iron and carbon, but reactions always go on, by which other constituents are reduced and taken up by the iron.

Silica, SiO_2, which is an oxide of the element silicon, is always present in the gangue of the ore and the ash of the coke. The silica is not reduced by carbon alone, except at the temperature of the electric furnace, but in presence of iron the reduction takes place more readily, the iron combining with the liberated silicon. A high temperature and the very presence of a large proportion of free silica are essential to the reduction of silicon. Irons high in silicon are produced, therefore, when the furnace is working very hot, and as one of the principal effects of the use of the hot blast is to increase the temperature of the zone of fusion, hot-blast irons are usually richer in silicon than those made with the cold blast. At the same time, the more lime there is present in the charge, the less siliceous will be the slag, and the less silicon will be reduced. When a very high temperature is used, and very acid slags—*i.e.*, slags rich in silica and poor in lime—are produced, the iron is likely to be very siliceous; whilst under opposite conditions, with a low temperature and slags rich in lime, the iron will be low in silicon.

It is not always easy to regulate the quantity of silicon in an iron, and when a new furnace is blown in the first charges of iron are often highly siliceous, silica being taken up from the new lining, and making the slag too acid. It is impossible to make iron quite free from silicon, as the reduction takes place to some extent at the temperature necessary for the fusion of the pig iron; and less than 1 per cent is very exceptional.

Reduction of Phosphorus.—Phosphorus is always present, in larger or smaller quantity, in the ore or limestone, either as calcium phosphate, $Ca_3(PO_4)_2$, or as iron phosphate, $Fe_3(PO_4)_2$. As already remarked, iron phosphate is reduced to phosphide when strongly heated with carbon, so that any phosphorus present in that form will pass into the iron. Calcium phosphate would only be reduced by carbon alone to calcium phosphide, which would pass into the slag; but in presence of silica phosphorus is liberated, and at once combines with the iron, thus—$Ca_3(PO_4)_2 + 3SiO_2 + 5C = 3CaSiO_3 + 5CO + 2P$. By these or similar reactions the whole of the phosphorus in the charge is transferred to the iron, and therefore, when an iron free from phosphorus is required, it must be made from phosphorus-free materials. Hence the demand for hæmatite and other ores containing but little phosphorus, and the care which is taken to estimate the phosphorus in all the materials which enter the furnace when Bessemer pig is being made. On the other hand, for the basic steel processes, irons high in phosphorus are required, and materials are used containing a large quantity of that element.

Reduction of Sulphur.—Sulphur is always present, in larger or smaller quantity, in the materials charged into the furnace. Only a small portion of this finds its way into the iron, but as even in small quantities it is very objectionable, great care is taken to prevent more sulphur finding its way into the furnace than can be helped. The sulphur may be in the coal as pyrites (FeS_2) or calcium sulphate ($CaSO_4$), or in the iron ore, or in the limestone. The conditions under which sulphur passes into the iron are not very well known. White irons made at a low temperature are usually high in sulphur, whilst grey irons, made at a high temperature, contain much less. It is usually stated that a high temperature is favourable to the formation of calcium sulphide, which passes into the slag, whilst a lower temperature favours the formation of iron sulphide, which passes into the iron; and whilst this is no doubt the case, it does not explain the whole matter. A very basic slag—*i.e.*, one rich in lime—is also favourable to the removal of sulphur, whilst an acid slag has the reverse action. Mr. E. L. Rhead has recently investigated this subject,* and he comes to the conclusion that silicon is the active agent in removing sulphur from iron; that at high temperatures, in presence of excess of lime, silicon decomposes lime, forming silica,

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* West of Scotland Iron and Steel Institute Journal, vol. iv., page 102.

and liberating calcium, and this then combines with the sulphur to form calcium sulphide, which passes into the slag. It is certain that highly siliceous irons rarely, if ever, contain much sulphur, and calcium has occasionally been found in iron.

Many methods have been suggested for the removal of sulphur from iron, but the only one which seems to have been successful up to the present is that of Mr. Saniter, which consists in mixing the molten iron with a mixture of calcium chloride and lime. If the materials be dry, only a small quantity of silicon is removed; but if moisture be present, then a much larger quantity may be oxidised out.

The action of the calcium chloride, or fluoride, seems to be, chiefly at anyrate, to dissolve the lime, which is the active agent, and thus bring it into more intimate contact with the metal. There is always some reduction in the quantity of silicon, and Rhead contends that this is quite enough to account for the removal of the sulphur by the decomposition of the lime, and formation of calcium sulphide. The use of alkalies, as cyanide, or in some other form, has been suggested, and may in some cases effect the partial removal of the sulphur by the formation of sulphides. Manganese also, under some conditions, has the same effect, manganese sulphide being formed.

Reduction of other Substances.—Many other substances may pass into the iron; indeed, it may be said that any substance in the charge which is capable of being reduced by carbon will, to a greater or less extent, pass into the iron. Hence manganese, which is an almost universal constituent of iron ores, is always present, and copper, arsenic, and other elements are frequently found. Iron ores are, however, so abundant, that those containing deleterious reducible impurities would not be smelted.

Lead and zinc are frequently present in iron ores, but the metals, when reduced, do not enter the iron. Zinc is very volatile, and passes away with the gases. Lead is partially volatilised, and the remainder sinks to the bottom of the hearth, and, as it does not alloy with the iron, runs out with it when the metal is tapped.

Various other reactions take place which are not of much practical moment. Cyanides are always formed. The alkaline salts present are decomposed by the hot carbon, the metal being liberated, and, combining with the hot carbon and nitrogen, form cyanide; *e.g.*, $Na_2CO_3 + 4C + 2N = 2NaCN + 3CO$. The cyanide is volatile at the temperature of the zone of fusion, and therefore passes upwards with the gas; but it condenses before the top of the furnace is reached, and is therefore brought down by the descending charge, to be re-volatilised when it reaches the boshes. In this way a large quantity of cyanide may collect in the furnace, and many metallurgists hold that it plays an important part in completing the reduction of the oxides of iron, it being a very powerful reducing agent.

CHAPTER V.

MALLEABLE IRON.

THIS is undoubtedly the form of iron with which man was first acquainted. It can be readily prepared in small hearths or forges, and it does not require any elaborate machinery for working it. With a hammer and anvil the smith can forge any of the ordinary articles required by men for their daily work, and it was only when large and heavy articles, or smaller articles in large numbers, were required, that the work of the smith was to a large extent superseded by machinery driven by power.

The characters which mark wrought iron off from the other forms are—First, it is infusible at ordinary furnace temperatures, and therefore cannot be cast; second, when strongly heated it becomes plastic, so that it can be hammered into any required form; and third, that portions can be united by welding—that is, by heating till the metal is soft, and then bringing the surfaces to be united into close contact under pressure or impact. It is called malleable iron on account of this malleability; wrought iron, because it can be wrought with a hammer; and sometimes weld iron, because it is made up of portions which have been welded together.

Wrought iron is, chemically, nearly pure iron, though the composition of different samples varies very considerably, and scattered through it are always particles of slag or oxide, which are merely mechanically mixed. Whilst the chemical composition, no doubt, has a very important influence on the quality of the iron, this is also much affected by the mechanically intermixed impurities, and by the physical structure.

Owing to its infusibility at the temperature at which it is prepared, the metal is not fused, but is aggregated into mass from a pasty condition, and to this it largely owes its peculiar characters.

If it were necessary to define malleable iron, we should say, "It is nearly pure iron, which has been aggregated into mass from a pasty condition, and which contains intermixed solid matter."

Malleable iron should be malleable and ductile both hot and cold, and should weld well. When it cannot be worked at a red heat without cracking, it is said to be red-short; whilst when it cannot be worked at ordinary temperature, it is said to be cold-short. An iron may be red-short, and yet be capable of being worked in the cold; whilst an iron may work well at a red heat, and yet be cold-short; or it may work under neither conditions, and be both hot and cold short.

In studying the chemistry of malleable iron, it is necessary to consider both the combined and intermixed impurities.

Carbon.—Carbon is always present, though the quantity should be very small, and in good malleable irons, where softness is the principal character required, it should not exceed ·1 per cent. The carbon is all in the combined form, and the effect of combined carbon, as already remarked, is to increase the hardness and the tensile strength of the metal; therefore, of course, decreasing its toughness and working qualities. A good malleable iron should have a tensile strength of about 22 to 23 tons on the square inch, with an elongation of 25 to 30 per cent on an 8 in. test piece. Engineers sometimes specify a higher tensile strength, and no doubt this can be readily attained by leaving a larger quantity of carbon in the metal, and thus necessarily at the cost of softness, and therefore of elongation, of the test piece. High tensile strength, therefore, apart from the quantity of carbon present, is no criterion as to the quality of the iron. Where hardness is required, as in armour plates, the carbon is sometimes as high as ·25, but the metal is then becoming steely.

Silicon.—The action of silicon is in some respects much the same as that of carbon—that is, it increases the hardness of the metal, and also tends to make it brittle at low temperature—that is, cold-short. About ·1 per cent of silicon seems to have no injurious effect, but when it reaches ·25 its presence becomes very injurious. There is, however, a good deal of uncertainty as to the exact influence of silicon in malleable iron, and various experimenters have obtained very discordant results. It is not at all certain that all the silicon obtained by analysis exists in the iron as such; some may be present as intermixed silica, or as a silicate of iron decomposable by acids; and whilst there is no doubt that silicon in actual combination would harden the metal very seriously, probably silica or a silicate merely intermixed would have very little effect. When an iron is well made from a suitable pig iron, the silicon is usually not present in large enough quantity to have any ill effect.

Phosphorus.—This element is always, and rightly, regarded as being most injurious in malleable iron, as it hardens the metal, and produces well-marked cold-shortness; but observers are not at all agreed as to the amount of phosphorus required to make the iron distinctly cold-short. Eggertz says that with ·25 per cent the metal will be cold-short; Karsten gives ·5 per cent, and others have given both higher and lower figures.

The cause of these differences is, no doubt, that the phosphorus may exist in the iron in two distinct forms. It is well known that during the shingling of the puddled bloom a considerable quantity of a very liquid phosphide of iron is squeezed out, and some of this must always be left, mixed with the iron, so that there may be in the metal phosphorus in the form of globules of phosphide of iron, $Fe_3 P$, or of manganese, Mn_3P_2, as well as phosphorus in combination with the mass of the iron. This question has recently been investigated by Baron Jüptner,* and he finds that when iron is dissolved in acids, part of the phosphorus—that which is in combination with the whole of the iron—is evolved as hydrogen-phosphide, PH_3, whilst the remainder is left as globules of phosphide, insoluble in the acid, and that whilst the former has a very great hardening power and renders the iron cold-short, the latter has but little effect. In one example which he cites two irons, A and B, gave on analysis, respectively, ·4423 and ·4557 per cent of phosphorus, the other constituents being about the same, and whilst both were cold-short, the former was far the worst. On examination he found that the first, when treated with acids, evolved 80·33 per cent of its phosphorus as hydrogen-phosphide, whilst the latter evolved only 63·35 per cent. If we assume that this represents the phosphorus present in such form of combination as to be injurious, the percentages of such phosphorus would be in A ·3552, and in B ·2886.

Baron Jüptner suggests that the phosphorus which is evolved as hydrogen-phosphide should be called dangerous or hardening phosphorus, whilst that present as phosphide

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* Journal of Iron and Steel Institute, 1897, vol. i., page 22, *et seq.*

should be called phosphide-phosphorus, the difference being exactly analogous to that between hardening carbon and carbide carbon.

When a sample of phosphoric iron is suddenly cooled, a larger quantity of phosphorus passes into the hardening condition, whilst when it is annealed the quantity in this form is reduced. It also seems that carbon tends to cause the separation of phosphide; and the larger the quantity of carbon, the larger will be the proportion of phosphide and the smaller that of hardening phosphorus; and therefore the less carbon the metal contains, the more injurious will the phosphorus be likely to be. Phosphorus may also be present as phosphate in the intermixed slag.

Sulphur.—This constituent is rarely present in more than very minute quantities in finished iron, as it makes the metal red-short, and therefore interferes with its working. The exact point at which the red-shortness begins is uncertain, various amounts, from ·03 to ·07 per cent, being given. Any quantity of sulphur which can be present in iron that has been rolled or forged is not likely to have any serious direct effect on the quality of the metal; but since the red-shortness may lead to the production of internal cracks, an iron high in sulphur should always be viewed with suspicion. When the iron is dissolved in acids, the whole of the sulphur is rarely evolved, as hydrogen-sulphide, an insoluble sulphide, may be left; or sulphur may be left in the form of an oily compound. The sulphur does not seem to exist in two different forms in iron.

Copper has much the same effect as sulphur, but it is not often present in malleable iron. *Manganese* has little effect, unless it be present in considerable quantity, which is rarely, if ever, the case.

Intermixed Impurities.—These are mainly oxide of iron and slag, though, as remarked above, phosphides, and perhaps sulphides, may also be present. As the iron comes from the puddling furnace as the puddled bloom, it is a spongy mass, into which the air can to some extent penetrate, thus producing oxide. The globules of iron, as they form, are surrounded by a thin layer of slag, and though a good deal of this is squeezed out when the iron is hammered, some always remains, and solidifies in the iron.

The amount of intermixed slag varies from about ·5 to 2·5 per cent, with an average of about 1 per cent. The physical structure of the metal, after working, is largely due to the presence of this slag.

Micro-structure of Malleable Iron.—Under the microscope, wrought iron is seen to consist of a mass of separate grains of ferrite, or pure iron. These grains are probably crystals of the cubic system, the granular form being produced by the interference of one crystal with another, and through this are scattered very irregular masses of slag, and sometimes of other impurities. The arrangement of the slag masses is very much modified by the treatment to which the iron has been subjected. In a hammered bloom they are irregular masses, but in iron which has been rolled they are drawn out into long fibres or threads.

Structure of Wrought Iron.—The physical structure of wrought iron is very much modified by the work which is put upon it. As the bloom leaves the hammer, it is far from homogeneous or uniform in structure, and the intermixed slag is in large, irregular masses. The bloom is rolled out into a bar, which is cut up. The fragments are piled, and the pile is heated to welding temperature. When the pile becomes hot the slag melts, and to a certain extent sweats out, so that at each re-heating the quantity of slag is reduced, but perhaps the quantity of oxide is increased. The pile is again rolled down, cut up, piled, heated, and again rolled, and so on, according to the quality of iron being made.

The bloom simply rolled out is known as puddled bar; when it has been cut, piled, and again rolled, it is Merchant Bar; after another treatment, it is Best; after another, Best Best; and still another makes it Treble Best. It will be seen that, except for the small amount of slag which is removed by liquation and some slight oxidation, the only changes which this treatment can produce are those of structure. As the mechanical treatment goes on, the fibre which is characteristic of wrought iron develops. The cause of this fibre is very simple: the rolling forces the slag into strings or fibres, and these prevent the adjacent portions of iron welding together, and thus give the appearance of fibre. When a piece of rolled iron is examined under the microscope, the slag fragments are seen to have been extended into long fibres, whilst the mass of the iron has undergone no change; the granular structure already mentioned remaining unchanged, the separate particles not having become elongated. The reason for this, no doubt, is that at the welding temperature the crystals have sufficient molecular freedom to re-arrange themselves. Thus the fibre is due to the presence of a weak body in the strong iron, and must be a source of weakness rather than of strength. Fibrous iron is no doubt stronger than non-fibrous, because the weakening effect of the intermixed slag is least when it is in the condition of fibres running in the direction in which the stress is applied, but such iron is weaker than metal of the same quality in which there is no intermixed slag.

Burnt Iron.—When iron is heated to a high temperature or for a long time it undergoes a peculiar change. It becomes brittle, cold and hot short, and can only be worked with the very greatest care, and it breaks with a coarsely crystalline, shining fracture. It is then said to be burnt.

The explanation of burning has been much discussed, and the cause cannot be said to be certainly known. Two views are held:

1. That the burning is due to oxidation, oxide of iron being formed in the iron, and thus making it brittle. In some cases the carbon is somewhat reduced; in others, oxide of iron has been found, without any serious reduction in the carbon; but it seems to be possible to produce burnt iron under conditions where oxidation is not likely to occur.

2. The other view is that the burning is due to a molecular change in structure, the iron being heated strongly

enough to allow crystallisation to take place, with, to some extent, the re-arrangement of the impurities present, and that this structure remains permanent as the metal cools, It is stated that a burnt iron can be made good again by very careful forging, and this would agree better with the physical than with the chemical theory.

The presence of phosphorus and carbon increases, whilst the presence of manganese diminishes, the tendency of an iron to burn.

CHAPTER VI.

THE MANUFACTURE OF MALLEABLE IRON.

MALLEABLE iron may be prepared directly from the ore, and this no doubt is the way in which it was first obtained. It is now, however, almost invariably prepared from pig iron, by the process of puddling.

Puddling.—This process was invented by Cort, in 1784, and has been considerably modified since his time. It is apparently a very simple process, but the reactions which take place in it are somewhat complex.

The furnace used is a very small reverberatory furnace, the principal characteristics of which are its small size, the large size of the fireplace in proportion to that of the hearth itself, and the nature of the working bottoms, or fettling.

An ordinary puddling furnace is shown in section in fig. 4. The hearth is about 6 ft. long and 3 ft. wide, and is provided with a working door on one side only. The fireplace has an area of from one-third to one-half that of the hearth, and is also provided with one door.

A charge of 4 cwt. to 6 cwt. of suitable pig iron is melted on the hearth of the furnace, oxide of iron being also frequently added. The melted mass soon becomes covered with a layer of slag, and the whole is in a state of tranquil fusion. Soon the surface of the liquid mass becomes agitated, and appears to boil—whence the process is sometimes called pig boiling—this being due to the escape of carbon-monoxide liberated by the reactions. A considerable quantity of slag has formed by this time, and is sometimes tapped off. Granules of iron now begin to separate in the molten metal, and these soon become so numerous that the whole mass becomes pasty, or the iron "comes to nature." The temperature is now raised to the highest possible point; the pasty metal is pressed together into a mass, and then broken up into balls, about 80 lb. in weight, which are lifted out of the furnace, taken to the hammer, and hammered or shingled into a solid mass. The process occupies two or three hours, sometimes less, often more, and the amount of malleable iron yielded is almost always less than that of the pig charged, the loss varying from 5 to 20 per cent, according to the composition of the pig iron used and the way in which the process is worked. Each ton of puddled bar produced will need about 25 cwt. of coal, and a considerable quantity of fettling for the furnace, as this needs repair after each charge. Two men work each furnace, and the labour, especially towards the end of the process, is very heavy.

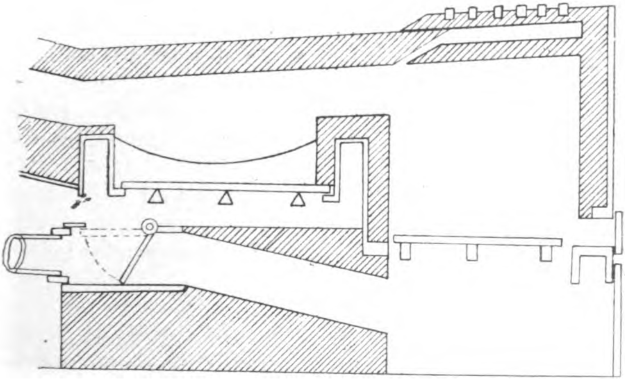

FIG. 4.—Puddling Furnace.

Chemistry of the Process.—The nature of the changes which have to be brought about will be readily seen by comparing typical analyses of the pig iron used and the bar iron produced.

	Pig iron.	Malleable iron.
Carbon	3·5	·10
Silicon	2·0	·05
Sulphur	·03	·02
Phosphorus	·75	·10
Manganese	1·00	·10

It will be seen that the process is essentially one of purification, and that practically the whole of the impurities have to be got rid of, and these being all more or less oxidisable, they are oxidised out, and removed mainly as oxides, a considerable quantity of iron being oxidised at the same time, and passing into the slag, though the loss of iron thus produced may be made up by iron reduced from the fettling.

The process may be divided into four stages :—

1. The melting-down stage ;
2. The stage of quiet fusion, or the clearing stage ;
3. The boiling stage ;
4. The balling-up stage ;

during each of which chemical changes take place.

The Melting-down Stage.—During this stage, the iron exposed to the products of combustion, and the air which finds access, is partially oxidised, the oxide at once uniting with the sand adhering to the pigs, to form a fusible silicate. Thus, $2Fe + 4O + Si = 2FeO, SiO_2$, though other silicates may be formed, and also some black oxide, Fe_3O_4, which dissolves in the liquid slag. The molten iron is thus covered with a layer of slag.

The Clearing Stage.—The first foreign constituent to oxidise is probably the manganese ; though, no doubt, the oxidation of the other constituents also commences at once. The oxidation is not brought about directly by the action of the air, but indirectly by the action of the oxide of iron in the slag. It must be remembered that the molten iron is covered with the slag containing silicate and oxide of iron, and also that it rests on a bed or fettling of oxide of iron. The workman stirs the slag vigorously into the iron, and scrapes the bottom of the furnace with his rabble, so as to bring the molten iron as closely as possible into contact with the oxide. The reactions at this stage are not very complex. The oxide of iron, acting on the manganese, forms oxide of manganese, which combines with silica and enters the slag, $Fe_3O_4 + 4Mn = 3Fe + 4MnO$. The oxide of iron also attacks the silicon, forming silica, which in presence of oxide of iron at once forms silicate. For example, $Fe_3O_4 + Si = 2FeO, SiO_2 + Fe$, though the exact composition of the silicate formed may vary very much, the slag being more or less basic, according to circumstances. It will be seen that each 28 parts of silicon will combine with 112 parts of iron, and thus, if the oxide of iron by which the silicon is oxidised were obtained entirely by oxidation of the iron, the loss would be very heavy. A portion only of the oxygen is, however, so supplied, a considerable portion being obtained from the fettling. If all the oxygen were supplied by the fettling, each 28 parts of silicon oxidised would add 112 parts of iron to the charge.

The oxide of iron formed by oxidation of the iron, and in the fettling also, attacks the carbon, $Fe_3O_4 + 4C = 3Fe + 4CO$, but during this stage very little carbon-monoxide is given off.

The Boiling Stage.—During this stage the same reactions go on, but the carbon is now more rapidly attacked, and a vigorous boiling begins. It will be remembered that it is mainly the carbon which imparts the fluidity to the cast iron, and therefore—the temperature not being high enough to fuse the wrought iron—the mass becomes pasty as the carbon is removed. The cast iron may be considered as being a homogeneous liquid, but as the constituents are oxidised out, malleable iron is formed. At first this seems to remain in solution in the more impure iron, but as this is gradually reduced in amount, the malleable iron separates in granules, which coalesce to form the mass of malleable iron or the bloom.

The Balling-up Stage.—During this stage but little further chemical action takes place; air may find its way into the porous bloom, and thus continue the oxidation to some extent, and may also form oxide of iron, which remains with the iron.

Removal of other Impurities.—So far it is only the removal of the essential constituents that has been described. The removal of the accidental constituents, such as sulphur and phosphorus, is also very important. These elements are so easily oxidised when by themselves, that they might be expected to be very easily removed from the iron. This, however, is not the case, since the sulphide and phosphide which they form with iron are very stable bodies, and are very difficult to remove.

The phosphorus is always oxidised to some extent during the process, passing into the slag as iron phosphate, and this the more readily the more basic the slag—*i.e.*, the less silica it contains; but a considerable quantity always remains in the iron, probably as phosphide. The sulphur is slowly oxidised, but only a small portion is removed by the time the carbon is all gone and the iron comes to nature. If the process could be continued longer, it is probable that almost the whole of the sulphur might be removed.

Influence of the Fettling.—The fettling of the furnace has a very considerable effect in assisting the purification of the iron. Cort used sand for fettling, and it will be seen at once that this is a very unsuitable material. It has no oxidising power, and therefore, when it is used, all the oxidation must depend on the oxide produced by the oxidation of the iron itself, unless ferric oxide be added to the charge. Silica, also, readily combines with oxide of iron, forming silicate, and this tends to largely increase the amount of slag produced. A material called "bull-dog," a mixture of ferric oxide and silica, made by roasting the slag from the puddling furnace, is often used. The only objection to it is that it tends to increase the quantity of slag, because, when acted on by silicon or carbon, ferrous silicate is formed, thus—$Fe_2O_3SiO_2 + C = 2FeO, SiO_2 + CO$. The quantity of ferric oxide in the bull-dog is usually much larger than that represented by the formula, $Fe_2O_3SiO_2$. The best fettling materials, and those now most largely used, consist essentially of oxide of iron, with but little silica, such as some of the hæmatites. When hæmatite fettling is used, it sometimes happens that the weight of bar obtained is larger than that of the pig iron used, the iron reduced from the fettling more than balancing the impurities oxidised out, and the iron oxidised.

Influence of the Constituents of the Iron on the Process.—Since pig iron varies very much in composition, the process may be more or less influenced by the proportion of impurities that may be present. At first sight it would seem that, as the object of the puddling is to remove the impurities, the smaller the quantity of these to be removed the better it would be ; but this is not by any means necessarily the case. If the percentage of silicon, for instance, be very low, the iron will probably be white. In that case it will not melt to a very fluid liquid, and the puddling has to be conducted "dry"—that is, the metal is only pasty, and is never properly liquefied. Dry puddling is the form invented by Cort, and he therefore used a white pig iron. Ordinary white pig iron usually contains sulphur, which is very objectionable, and therefore, when it is required for puddling, it is usually prepared from grey iron by refining.

When the silicon is too high, say above 3 per cent, a very large quantity of slag is necessarily produced, and this may lead to a large loss of iron ; at the same time, as very siliceous slags are not very fusible, the slag will tend to be thick, or will work cold, and the temperature of the furnace must be increased. If the quantity of silicon be too low, the oxidation of the iron may go on too rapidly, and oxide of iron may be formed largely in excess of that which the silica produced by the oxidation of the silicon can take up. This excess of oxide, mixing with the slag, makes it infusible, or dry. If the silicon be high and the carbon low, then the iron may come to nature, owing to the removal of the carbon, whilst there is enough silicon left to spoil the bar produced. The best amount of silicon is probably from 1·5 to 2 per cent. Nearly all irons now used for puddling contain considerably more than this, and therefore the loss is usually high.

The amount of carbon present is of little moment, provided it be at least half per cent more than the silicon. About 80 per cent of the phosphorus is removed during puddling, so that that element must not be present in such quantity that the 20 per cent left will have an injurious effect on the bar, Sulphur is only partially removed, and therefore the pig iron for puddling should be as free as possible from it.

Influence of Method of Working.—It will be seen that the object of the process is to remove the oxidisable impurities. and that this is brought about not directly by the action of the air, but indirectly through the oxide and silicate of iron in the slag with which the metal is covered. The oxidation goes on perfectly well under a silicate of iron slag, but not under one which is mainly silicate of manganese, since manganese oxides are not decomposed by carbon or silicon at the temperature of the puddling furnace. As the slag has to act on the iron, the puddler mixes it in with his tools, and therefore it must not be too liquid. Oxidation must not be too rapid, or a large quantity of black oxide or ferric oxide will be formed, and these being fusible with difficulty, the slag will be too thick; on the other hand, if the oxidation be not rapid enough, the process will be unduly prolonged. Very frequently iron scale or hæmatite is added to supply oxide, in addition to that produced by the oxidation of the iron.

Further Treatment of the Bloom.—The bloom, as taken from the puddling furnace, consists of a soft mass of granules of iron, each surrounded by a thin skin of slag or very fusible iron compounds, partially, no doubt, iron phosphide.

As the particles become agglomerated the surface diminishes, and the liquid sweats out. Under the hammer this takes place to a much larger extent, each stroke forcing out a shower of red-hot liquid material. The bloom rapidly cools, so that a considerable quantity of this matter still remains entangled in it. As the liquid drains out of the bloom on its way to the hammer, air finds its way in, and thus some oxide of iron is formed, which, being infusible at the temperature of the bloom, remains in it. The hammered bloom therefore consists of iron containing slag, oxide, phosphate, and other materials mechanically intermixed. The subsequent mechanical treatment—rolling, shearing, piling, re-heating, and re-rolling—has the effect of breaking up these impurities, and distributing them more evenly through the mass, and at each heating a small quantity of the more fusible constituents liquates, or is squeezed out. Hence, whilst these processes have very little effect on the chemical composition of the metal, they materially alter its physical structure, ultimately developing the fibre, which has been already mentioned.

THE FINERY.

Before the invention of puddling, malleable iron was made in the "finery," or "refinery," and this process lingered on in South Wales for the manufacture of iron for tin plates long after it had been abandoned elsewhere. At the present time the finery is only used in Yorkshire as a preliminary to puddling. The finery is a shallow hearth, about 5 ft. by 3 ft., and 12 in. deep. A coke fire is lighted on this, and when it has burnt up the pig iron is put on the top, and air is blown in from a series of two to five tuyeres. The iron speedily melts, and sinks through the coke. The layer of coke being thin, air finds its way through to the iron, and oxidation takes place, and the silicon, a very small proportion of the carbon, and some of the iron are oxidised. When it is judged that sufficient silicon has been removed, the iron is tapped into suitable moulds.

In South Wales the iron from the coke finery was tapped into similar but smaller hearths fed with charcoal—the charcoal fineries—where the process was continued until the carbon was all out, and malleable iron was obtained.

Direct Production of Malleable Iron from the Ore.—As already remarked, iron is easily separated from its oxides by carbon or carbon-monoxide at a dull red heat, and this reduction takes place at a temperature far below that at which the iron can take up carbon, and thus pass into the condition of cast iron. If, therefore, the iron be reduced at a low enough temperature, and then be removed from the furnace, malleable iron will be obtained.

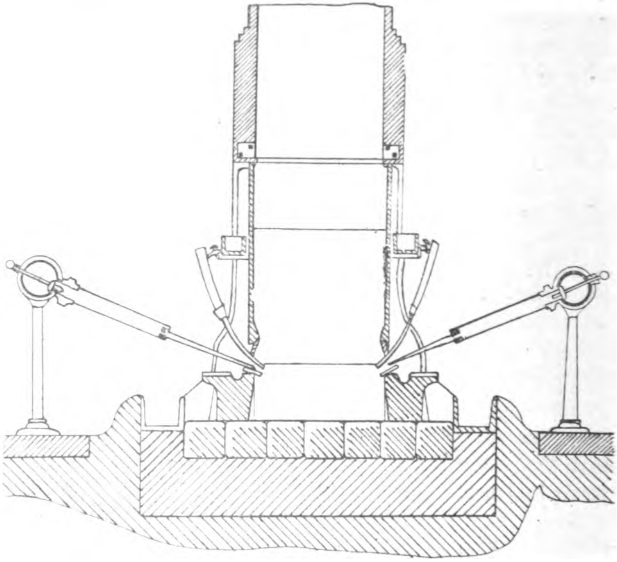

FIG. 5.—Finery.

In the older methods of preparing malleable iron from the ore, of which the Catalan process may be taken as the type, small hearths were used. In the Catalan forge the hearth is a small rectangular cavity, set in a low platform of masonry, so that a tap hole can be provided for running off the slag. There is a single tuyere placed in a sloping position above the hearth. The mixture of ore and charcoal is charged into the hearth in portions so as to keep it full, and combustion is maintained by the blast from the tuyere playing upon the top. The iron is reduced, and sinks to the bottom of the hearth in pasty masses, whence the workman, after pressing into a solid bloom with an iron tool, lifts it out by means of tongs, and takes it to the hammer.

Only very pure oxide ores can be used for these processes, and the yield is always low, often not 50 per cent of the iron in the ore, because silicates of iron are formed by the action of the silica in the ore on the ferric oxide in presence of carbon, and these are not reduced by carbon at the temperature of the hearth. Iron made in hearths is of very uncertain composition, and is very frequently steely, owing to some carbon having entered into combination. Iron is now only made direct from the ore in small hearths in a few localities far removed from centres of iron production. Other methods for the direct production of malleable iron, depending, however, on exactly the same principles, have been recently suggested. Siemens suggested a rotating furnace, fired with gas, the finely-divided ore being partially reduced with charcoal, and partially by the reducing atmosphere of the furnace. The reducing agents not being in excess, though the temperature was high, carbon was not likely to be taken up.

Iron sponge is sometimes prepared by reducing pure hæmatites in closed, externally-heated retorts, by means of carbon or by carbon-monoxide, the metal being allowed to cool before coming into the air, and afterwards being heated in a separate furnace for shingling, or pressed cold in a powerful hydraulic press. These processes are, however, only used to a very small extent, and are of little importance.

CHAPTER VII.

STEEL.

UNDER the name steel are included metals which differ very much in character and properties, but as these pass into one another by insensible gradations, it is impossible to separate them, they must therefore be included in one class and under the one name.

Irrespective of the methods of manufacture, the only division that can be made is into high carbon steel and mild steel; though even here it is impossible to say exactly where the one ends and the other begins. High carbon steel contains from ·5 to 1·5 per cent of carbon, and is hardened when heated to redness and cooled in water, whilst mild steel is not sensibly hardened under the same conditions, and contains from a trace to ·5 per cent of carbon. The very mild varieties of steel do not differ in chemical composition from wrought iron except that, having been melted, they contain no intermixed slag or oxide. The high carbon steels contain a larger percentage of carbon, but not of the other constituents. In carbon content, but in this only, steel (except the very mildest forms) is intermediate between cast iron and wrought iron, for the steel must be as free as wrought iron from other impurities. The statement which is so frequently made that steel occupies a position intermediate between cast iron and wrought iron is incorrect, and very misleading, and has led to the introduction of many impracticable methods for preparing steel.

Carbon in Steel.—As mentioned above, the amount of carbon in steel may vary very much, and with it the properties of the metal; and not only does the quantity vary, but also the form in which it may be present.

Graphite never occurs except occasionally in very high carbon steels. Graphitic temper carbon occurs more frequently, but also only in high carbon steels, and then in small quantity. Both the forms of combined carbon occur.

In steels which have been suddenly cooled by being heated and plunged into water, the carbon is mainly present as hardening carbon; whilst in steels which have been slowly cooled, it is mostly present as carbide carbon. The form in which the carbon is present has a profound influence on the character of the steel.

The carbon is the most important constituent of the steel, and on it its character mainly depends; indeed, for most purposes, the nearer the steel approaches to pure iron and pure carbon the better. The influence of carbon is to harden the metal, and at the same time increase its tensile strength, and diminish the extension which takes place before fracture, each addition to the percentage of carbon increasing the tensile strength, and at the same time making the metal harder, more brittle, and more likely to crack when suddenly heated or cooled, and diminishing the extension and contraction of area which take place before fracture. Hardness and strength are, of course, more or less incompatible with ductility, and therefore any element which increases the one must decrease the other; but it by no means follows that the increase and decrease will be by the same amount, or even in any fixed proportion, and when hardness and strength are required they are better obtained by means of carbon than by any other of the hardening elements, because the ill effects are least with it. "Strength must be bought at a certain cost, and this cost is less in the case of carbon than with any other element."* It will be quite obvious, therefore, that the amount of carbon in a steel which is best will depend entirely on the purpose for which the metal is to be used, and the property which is considered to be of most importance. For making a lancet great hardness is required and a high carbon steel must be used; whilst for structural purposes, especially in conditions where the metal is subject to shocks, a very mild steel is required. For a rail which must be strong, but at the same time must be hard enough

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* Campbell, "Structural Steel," page 256.

to wear well, an intermediate amount of carbon will be required, and so on. Hence in ordering steel for any purpose, the engineer usually specifies the amount of carbon which it is to contain, and in cases where softness is important he also specifies the maximum tensile strength it is to have.

The amount of carbon usually contained in steels for various purposes is about

For razors	1·5	per cent.
,, hard files	1·375 ($1\frac{3}{8}$)	,,
,, turning tools, drills, &c.	1·25	,,
,, large turning tools, dies, &c.	1·125 ($1\frac{1}{8}$)	,,
,, cold chisels, &c.	1	,,
,, setts, wood chisels, &c.	·875 ($\frac{7}{8}$)	,,
,, dies, &c.	·75	,,
,, springs, &c.	·5	,,
,, rails	·4 to ·45	,,
,, boiler plate	·25 to ·3	,,
,, bridge work, &c.	·2	,,
,, wire, thin sheets, &c.	·1 to ·15	,,

These figures can, of course, only be taken as examples. Each engineer will specify the percentage of carbon which he thinks will give the best results for the purpose which he has in view.

Relation of Carbon Contents to Tensile Strength.—As already remarked, the larger the percentage of carbon which is present, the stronger will be the metal, but the less it will extend before fracture. It is impossible to give a definite relationship between carbon and tensile strength, as the other elements which may be present exert a very considerable influence. The purest iron—*i.e*, the mildest steel which it is possible to obtain—has a tensile strength of about 17 tons to the square inch. With about ·18 of carbon the tensile strength will be 30·5 tons, with an elongation of 22 per cent on 8 in.; with ·22 of carbon the tensile strength will be about 32·5 tons, with an elongation of 23 per cent; and with ·25 per cent of carbon the tensile strength will be about 35 tons, and the elongation about 20 per cent. With ·5 per cent of carbon the tensile strength will be 45 tons or thereabouts, and with the very hardest steels the tensile strength may be as high as 100 tons, and the elongation nil.

Silicon.—Silicon is always present in steel, and sometimes is intentionally added. The effect of this element has been very much discussed; many experiments have been made, and the most discrepant results have been obtained. Some metallurgists consider it to be highly objectionable, even in very small quantities; others think that it has little or no influence; whilst others again, say that in moderate quantities it may even be an advantage. The great difficulty in this, as in many other cases, is the elimination of the influence of other constituents which may increase or mask the influence of the silicon itself. Silicon, as has been already stated, has a hardening influence on iron, which is very much less than that of carbon. It might, therefore, be expected that silicon would harden and strengthen the metal much in the same manner as carbon does, but to a less extent; and this is found to be the case. According to some experiments made by Turner, the increased tensile strength due to the addition of ·2 per cent of silicon was only about 4,000 lb. (1·8 tons). In many works rails are made containing over ·5 per cent of silicon, which pass all the tests and wear well, and a well-known authority has recently stated that "silicon up to ·3 per cent, with carbon ·30 or ·40 per cent, does not harden steel or make it brittle, and diminishes its strength in such small degree as not to imperil the safety of the rail."*

Hard steel suitable for tools not unfrequently contains a considerable quantity of silicon, without being injuriously affected. Campbell states that "silicon cannot be classed among the highly injurious elements," and that it is "only reasonable to suppose that small quantities cannot exert a very deleterious influence"; and Howe concludes that there

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* Sandberg, Proceedings Institute Mechanical Engineers, 1890, page 301.

is no evidence that silicon, in moderate quantities, is injurious to a steel. When the amount of silicon is very high, reaching 5 per cent or so, its influence becomes well marked: the metal becomes hard, strong, and brittle. In one case given by Hadfield, a bar containing 5·08 per cent of silicon gave a tensile strength of about 46 tons, with an elongation of only ·3 per cent in 2 in.

Phosphorus.—This element is rightly regarded as being the greatest enemy of the steelmaker, and its evil influence is recognised both by the engineer and the metallurgist.

A very large number of experiments have been made with phosphoric steel, and the results obtained have often been extremely erratic; sometimes of two pieces of almost identical composition, and tested under the same conditions, the one would have a high tensile strength and give a good elongation and contraction, whilst the other would be very brittle. What is the cause of this difference is at present uncertain. In small quantities, up to say ·1 per cent, phosphorus increases the tensile strength of the metal, very frequently with but slight decrease in extension or reduction of area before fracture, so that the testing machine may fail to detect the influence of the element at all. When, however, the metal is subjected to a shock—that is, a stress suddenly applied—or to a vibratory stress, it will break very readily, and with a very small load. This brittleness under shock is the most marked character of phosphoric steel, and is one which unfits it for almost all uses in the arts. The effect of phosphorus seems to be greater in steels which are high than in those which are low in carbon, so that it is very highly objectionable in tool steels. One effect of phosphorus is the production of a coarsely crystalline structure, and no doubt to this, in some measure at least, its brittleness is due. This also lowers the temperature to which it is safe to heat the metal in working.

Sulphur.—It has been already pointed out that sulphur produces red-shortness in malleable iron, and its influence is much the same in steel. Steel containing sulphur has a coarsely crystalline structure, tends to crack in rolling, and welds badly. The amount of sulphur which is allowable varies with the amount of other elements that may be present. In the presence of manganese a larger quantity is allowable than if that element is absent, whilst with copper the reverse is the case; ·08 per cent of sulphur is sufficient to interfere with the rolling qualities of the metal, and the less there is present the better.

The quantity of sulphur present in steel does not seem to have any effect on the tensile strength or elongation of the metal in the cold, though it is stated that small quantities increase the tensile strength.

Manganese.—In the manufacture of mild steel manganese is always added, and has important effects on the quality of the steel. It counteracts the influence of sulphur, and causes the metal to aggregate in finer crystals than it would otherwise do. Manganese increases the tensile strength of the metal, but greatly increases its tendency to crack when suddenly cooled. Up to 1 per cent in a mild steel has little injurious effect, but a larger quantity tends to make the metal brittle under shock. In high carbon steels a very much smaller quantity only is allowable.

Copper.—This is rarely present in British steels, but is often to be found in those made from ores which contain copper. Campbell states that 1 per cent may be present without injuring the steel, provided there be but little sulphur; but that if the sulphur be up to ·08 or ·10, the metal will be red-short. Copper also reduces the welding power of the metal, especially if sulphur be present; but, he adds, "in all cases the cold properties seem to be entirely unaffected."

Aluminium.—This metal is often added during casting, but a trace only remains in the metal. It seems to have little or no effect on the qualities of the metal until it reaches about ·2 per cent. With ·5 per cent the tensile strength is increased, and elongation and reduction of area are diminished. Some observers state that even a very small quantity of aluminium is injurious.

Arsenic.—This element is not frequently present in any but the minutest quantity. With ·10 to ·15 per cent there is no noticeable change, but with larger quantities the metal is hardened, and its ductility is reduced.

Oxide of Iron.—This is said to be present in steels, especially if an insufficient quantity of recarburiser has been added. There is, however, too little evidence at present to enable a definite opinion to be formed, but Campbell thinks that it raises the ultimate strength.

Cumulative Influence of the Impurities.—It will be seen that almost all the impurities that can be present in a steel influence it in the same direction, tending to increase its hardness and strength, and diminish the ductility. It is therefore quite impossible to draw conclusions as to the quality of a sample of metal from a consideration of one constituent only, and it is manifestly difficult to sum the action of so many separate factors, and as all have their influence, it is still more difficult to isolate and determine the influence exerted by any particular one.

H. H. Campbell has recently worked out the problem more completely than has been done before by any worker, and his results are of the very utmost importance. All interested should refer to his "Structural Steel" for particulars as to his methods. His chief conclusions are :—

1. "The strength of pure iron, as far as it can be determined from the strength of steel, is about 38,000 lb. or 39,000 lb. per square inch (17 to 17½ tons).

2. "An increase of ·01 per cent of carbon raises the tensile strength of acid steel about 1,210 lb. per square inch, and of basic steel about 950 lb.

3. "An increase of ·01 per cent of manganese has very little effect on acid steel, unless the content exceeds ·60 per cent, but it raises the strength of basic steel about 85 lb. per square inch.

4. "An increase of ·01 per cent of phosphorus raises the

tensile strength of acid steel about 890 lb. per square inch, and basic steel about 1,050 lb.

5. "The following formulæ will give the ultimate strength of ordinary open-hearth steel in pounds per square inch, the carbon, manganese, and phosphorus being expressed in units of ·001 per cent, and a value being assigned to R according to the conditions of rolling and the thickness of the piece :—

"*Formula for Acid Steel.*

"Ultimate strength = 38,600 + 121 carbon + 89 phosphorus + R.

"*Formula for Basic Steel.*

"Ultimate strength = 37,430 + 95 carbon + 105 phosphorus + 8·5 manganese + R.

6. "The metals from which these data were derived were ordinary structural steels, ranging from ·02 to ·35 per cent of carbon, and it is not expected that the formulæ are applicable to higher steels or to special alloys.

7. "A considerable difference may be found between steels which apparently are of the same composition, and which, as far as known, have been made under the same conditions.

8. "In the case of acid steel, an increase in manganese above ·60 per cent will raise the tensile strength above the amount indicated by the formula, the increase being quite marked when a content of ·80 per cent is exceeded.

9. "In steels containing ·30 to ·50 per cent of carbon, the value of the metalloids is fully as great as with lower steels, while the presence of silicon in such metal in proportions greater than ·15 per cent seems to enhance the strengthening effect of carbon."

Since all the foreign elements act much in the same way as carbon in hardening the metal, when they are present in larger quantities the less carbon will be required to produce a given amount of hardness, but in all cases where possible carbon alone should be the hardening agent, and the nearer the steel approaches to pure iron and pure carbon the better.

CHAPTER VIII.

HARDENING AND TEMPERING STEEL.

ONE of the most important properties of steel is that of becoming hard when heated to redness and suddenly cooled, by dipping in water or otherwise ; indeed, this may almost be taken as the characteristic of steel, though much of the mild steel made to-day does not sensibly harden under these circumstances. The property of hardening commences with a comparatively small quantity of carbon, becomes marked when this reaches about ·5 per cent, and with higher percentages becomes very decided. It is on this that the value of steel for many purposes depends ; a cutting tool, for instance, is forged into shape whilst the metal is soft, and then by hardening it is made capable of taking a sharp cutting edge. Obviously, the harder the steel is to be made the more carbon it should contain, and therefore steels are made to contain varying amounts of this element, as required, the temper of the steel depending upon the quantity present.

The following is about the usual carbon content of steels for various purposes :—

Razor temper, 1·5 per cent carbon. Steels of this composition will become very hard and take a very keen edge, but the metal is very difficult to work.

Saw-file temper, 1⅜ per cent carbon. These steels also harden well, take a keen edge, and are somewhat difficult to weld.

Tool temper, 1¼ per cent carbon. This steel does not become so hard as those above, but is hard enough to take a very keen edge. It is easier to work, and with great care can be welded

Spindle temper, 1⅛ per cent carbon. This does not harden sufficiently for ordinary cutting tools, but is very useful for large tools ; it also requires very great care in welding.

Chisel temper, 1 per cent carbon. This is a very useful steel; it hardens well, though to a less extent than those containing more carbon, and when not hardened is very tough. It is useful for cold chisels and other tools which are to have a sharp cutting edge, whilst the unhardened parts must be strong and tough, such as cold chisels, &c.

Set temper, ⅞ per cent carbon. This is a very tough steel, but does not harden well; it is used for cold sets and other tools which have to stand heavy blows.

Die temper, ¾ per cent carbon. This metal is specially useful where capacity to stand great pressure is required, as in dies, &c.

Steels containing less carbon than this do not harden enough to be used for tool making, and gradually pass into the condition of mild steels, as the carbon, and with it the power of hardening, diminish, and the latter ultimately disappears. Steels containing less than ⅞ per cent of carbon weld easily.

The hardness which a steel will take depends upon its composition, and also on the rate of cooling: the more rapid the cooling, within limits, the greater will be the hardness. Water is the general hardening liquid, as it is always at hand, and owing to its great mobility, high specific heat, and the high latent heat of steam, it is very efficient. Usually the article to be hardened is dipped into water, but sometimes (especially in the case of very large articles) the water is thrown on to it in the form of a spray. When greater hardness is required, mercury is sometimes used, its high conducting power compensating for its low specific heat, whilst where less hardening is required, oil is sometimes used.

Tempering.—When an article has been hardened it is usually too hard for use, as the hardness is necessarily accompanied by brittleness. In order to remedy this, the hardness is partially removed, or the article is tempered. Tempering consists in gently heating the metal to a moderate temperature, and then cooling it. The higher the temperature to which it is heated, the more of the hardness is lost, till, if it were heated to a red heat and slowly cooled, it would be annealed and restored to its soft condition. For tempering—*i.e.*, when the temperature used is considerably below a red heat—it is immaterial whether the cooling be rapid or slow.

When the metal is heated it oxidises on the surface, and whilst the film of oxide is very thin, it shows iridescent colours, the exact colour varying with the temperature to which it is heated, and the temperature is very frequently judged from the colour of the oxide film. Other methods of judging are to smear the metal with tallow, and note the effect of the heat on that; to heat the metal in an oil bath, or in a bath of molten alloy, which melts at about the temperature required.

The following table, which is mainly that given by Mr. Howe in his "Metallurgy of Steel," will illustrate the tempering temperatures:—

TEMPERATURES FOR TEMPERING STEEL.

Oxide tint.	Temperature. Cen.	Fah.	Appearance of oil bath.	Alloy.
1. Pale yellow	220	428	—	7 lead 4 tin.
2. Straw	230	446	—	8 lead 4 tin.
3. Golden yellow	243	469	Just smoke	8½ lead 4 tin.
4. Brown	255	491	—	14 lead 4 tin.
	260	500	Strong dark smoke	
5. Brown, dappled with purple	265	509		
	276	530	Abundant black smoke	
6. Purple	277	531	—	19 lead 4 tin.
7. Violet				
8. Bright blue	288	550	—	48 lead 4 tin.
9. Full blue	293	559		
	304	580	Can be lighted, but does not continue to burn.	
10. Dark blue	316	600	Lights spontaneously.	50 lead 2 tin.
11. Just visibly red	—	—	Burns rapidly.	All lead.

This table must only be taken as an example, since no two workers are agreed as to the exact temperatures corresponding to the different tints.

No. 1 is the temperature for lancets, which require the very keenest cutting edge, with but little toughness; and No. 2 is that for razors, general surgical instruments, engraving taps, dies, cutters, &c., where hardness and good cutting edge are the principal requisites. No. 3 is the temper for penknives, hammers, taps, reamers, and dies, for wrought and cast iron, copper, brass, &c., and cold chisels for cutting steel. No. 4 is for cold chisels, shears, scissors, hatchets, &c., where cutting edges are required, but where considerable strength is also necessary. No. 5 is suitable for axes, planes, lathe tools for copper, &c.; No. 6 for table knives, large shears, wood turning and cutting tools, cold chisels for soft cast iron, and other articles where great hardness is not required, but where elasticity and strength are important. No. 7 is for cold chisels for brass; No. 8 for swords, watch springs, &c., and articles where elasticity is one of the principal properties required; No. 9 for fine saws, augers, &c.; No. 10 for hand and pit saws, and cold chisels for wrought iron and copper; and No. 11 for some spiral springs, and for metal for clock makers' use, this being the softest metal used.

It must be borne in mind that steel of suitable quality must always be used. It would, for instance, be impossible to make razor steel of metal containing only ·75 per cent of carbon, however well all the operations were conducted, so that the colour on the temper scale is only a guide when the proper quality of metal is used. It must also be noted that long heating at a lower temperature may ultimately produce the whole range of colour, and to some extent the same effect as shorter heating at the higher temperature.

Cause of Hardening and Tempering.—The hardening is evidently due to a chemical change in the metal, but as nothing is either added or taken away, the change can only be of the nature of a rearrangement of the constituents already present in the metal. Two views are held. The one which is that now generally accepted is that the hardening is due to an alteration in the condition in which the carbon exists in the iron; the other, which is now advocated by some distinguished metallurgists, is that the hardening is due to an allotropic modification of the iron itself.

The Carbon Theory.—It has already been pointed out that carbon can exist in steel in two forms of combination: first, as a definite carbide, Fe_3C, disseminated through the metal, carbon so existing being called carbide carbon; and second, in combination with or in solution in the whole of the iron, this form being called hardening carbon. When a sample of ordinary soft or annealed steel is examined, it is found that most of the carbon is in the carbide condition; and when a sample of hardened steel is tested, most of the carbon is found to be in the condition of hardening carbon, whilst tempered steel contains both varieties, in quantities varying with the temperature of tempering. It was natural, therefore, to assume that the change in the condition of the carbon accounted for the change in the metal.

As a piece of steel is heated the carbide seems to break up gradually, the carbon passing into solution in the whole of the iron—that is, into the hardening condition. The change takes place at about 860 deg. Cen. = 1,576 deg. Fah., which has therefore been called the critical temperature of the iron. If the metal be allowed to cool slowly, the carbon passes back into the carbide condition, and when cold the metal is soft. If, however, the metal be cooled very quickly over the critical point, there will be no time for the change to take place before the temperature at which the particles have sufficient mobility to re-arrange themselves is passed, the carbon remains in the hardening condition, and the metal is hardened.

When the steel has been hardened by sudden cooling, it is usually too brittle and too devoid of elasticity for use, whence it is necessary to temper it. The carbon in the hardening condition is in an unnatural condition under stress, and is ready to return to the carbide condition as soon as it can. Even at a moderate temperature the particles acquire sufficient mobility for the change to begin, and when the metal is heated, therefore some of the carbon returns to the carbide condition—the amount depending on the temperature—and the metal is thus partially softened or tempered. As the temperature is not above the critical point, it is a matter of no moment whether the subsequent cooling be rapid or slow.

Allotropism Theory.—The other view of hardening of steel attributes it to the existence of two allotropic modifications of iron, which have been called respectively α, or soft iron, and β, or hard iron. Pure iron is in the soft or α condition at ordinary temperatures, but when it is heated to about 700 deg. Cen. it passes into the β, or hard form ; but on cooling over the critical point it returns to its original condition, however quickly it may be cooled. If, however, the iron be not pure, but contains certain impurities, especially carbon, the change on heating takes place exactly as before ; but on cooling quickly the carbon, or other impurity, retards the change to α iron, so that the metal is not able to pass completely into the soft condition, and it remains hard. This theory has been ably advocated by Prof. Roberts-Austen, and to this it largely owes the prominence which it now has.

It does not follow that the change of the carbon from the hardening to the carbide condition will take place at the same temperature as that at which the iron passes from the β to the α condition. Indeed, usually this does not seem to be the case, the change in the iron taking place at a higher temperature than that of the carbon. Prof. Roberts-Austen says : "It follows that if a steel be quickly cooled after the change from β to α has taken place, but before the carbon has altered its state . . . then the iron should be soft, but the carbon hardening carbon, and as such the action of a solvent, should show that it cannot be released from the iron in the black carbide form. This proves to be the case, and affords strong incidental proof of the correctness of the view that two modifications of iron exist. . . . It will be seen, therefore, that although the presence of carbon is essential to the hardening of steel, the change in the mode of existence of the carbon is less important than has hitherto been supposed. The α modification of iron may be converted into the β form by stress applied to the metal at temperatures below a red heat, provided the stress produces permanent deformation of the iron."*

Allotropism.—When an element exists in two or more forms, which have different properties, these are said to be allotropic. There are many examples of allotropic modifications, mostly, however, among the non-metals. Carbon exists in at least two forms, which differ in almost all their properties—the diamond, and graphite or blacklead. Sulphur exists in three or four forms, each of which differs from the others in some respects, though the difference is not so well marked as in the case of carbon. Phosphorus oxygen and other elements also exist in allotropic modifications. Allotropism among the metals is not so well marked, perhaps, because the one form is in most cases so much more stable than the others; but one or two cases have been made out with certainty. The most marked case is perhaps that of gold, which exists in two forms—a black, non-lustrous form, and the ordinary yellow form, with a bright metallic lustre, the former being converted into the latter by being heated to redness.

The differences between hard and soft steel are very considerable, and if no other explanation could be given of them, it would be quite sufficient to entitle the two forms to be regarded as allotropic modifications of the metal. In the case of ordinary high carbon steels the differences are well marked: the hardened steel is very much harder; its tenacity is from two to four times as great as when in the unhardened condition, whilst the elongation and contraction of area are very much diminished. The hardening effect of sudden cooling is,

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* "Introduction to the Study of Metallurgy," page 126, third edition.

of course, best seen in the case of high carbon steels, as with very mild steels the hardening is hardly, if at all, noticeable; but even with these the quenching increases the tenacity very considerably. In some cases quoted by Howe,* very soft steels, containing ·09 and ·06 per cent of carbon, had their tenacity increased from 48,574 lb. and 47,040 lb. respectively to 91,750 lb. and 135,000 lb. by sudden cooling. These differences seem greater than could be accounted for by any change in the condition of the carbon. The density of hardened steel is also somewhat less than that of the soft metal.

When iron is heated to redness it loses its magnetic properties completely, which might well be due to an allotropic change; and though it recovers these on cooling, whether slowly or quickly, the magnetic properties of the soft and hard steel are very different.

Cooling of Steel.—In 1869 Gore noticed a very peculiar behaviour on the part of steel as it slowly cools. This phenomenon, which was called recalescence, has been very fully investigated, and has thrown considerable light on the changes which may take place during heating and cooling, the investigations having been rendered possible by the introduction of the Le Chatelier pyrometer.

When iron as pure as it can be obtained—that is, that produced by electrolysis—is heated to redness, and allowed to cool slowly, the temperatures being taken by the Le Chatelier pyrometer, the temperature is observed to fall steadily, at a nearly uniform rate, till a temperature of about 870 deg. Cen. is reached; then the fall of temperature suddenly is arrested. As the loss of heat from the radiating metal must be constant, this means that some change is taking place in the metal itself by which heat is evolved. As there is no carbon, this cannot be due to a change in the form in which the carbon is present; but it may be due to the passage of the iron from the β to the α condition, as allo-

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* Journal of the Iron and Steel Institute, 1895, vol. ii., page 275.

tropic changes are always attended with the evolution or absorption of heat.

With mild steel the cooling changes are more complex. The metal cools uniformly till a temperature of about 750 deg. is reached; then the rate of cooling is temporarily diminished, and a little below 700 deg. there is a second retardation of cooling. If the second of these be due to the change of the carbon from the hardening to the carbide condition, the first may be due to a change from β to α iron. As the quantity of carbon is increased the two points come nearer together, so that with high carbon steel there is only one period of recalescence, but that is far more marked than in either of the other cases. In this case, therefore, if the two changes take place, they must occur at almost exactly the same time, and at a temperature of about 670 deg. Cen. (steel with 1·25 per cent carbon), though the large amount of heat evolved is no doubt chiefly due to the change in the condition of the carbon. This is so marked that the steel actually becomes visibly hotter, and glows, and therefore the name recalescence has been given to the phenomenon.

To retain the iron in the β condition as it cools, when quenched, the presence of some foreign element is necessary, though it is not likely that in any case the whole of the iron can be so retained, and the effects of quenching nearly pure iron seems to show that even in the absence of foreign elements a small portion of the metal may remain in that form. Carbon is the most efficacious element for hardening iron, but other elements have a somewhat similar effect. As, however, these have in most cases only been tested in the presence of carbon, it is not easy to judge what their effect would be by themselves.

The effect of manganese is somewhat peculiar. When manganese steel (20 per cent of Mn) is cooled, it shows but little trace of any retardation of cooling—that is, manganese may retain the iron completely in the β form. Manganese steels are very hard, and they are non-magnetic.

Among the elements which are thought to favour the retention of the iron in the β condition are carbon, nickel, and manganese, whilst chromium, tungsten, silicon, arsenic, phosphorus, and sulphur are thought to facilitate the passage of the iron into the α form. In the case of the former group, the atomic volume—that is, atomic weight divided by the specific gravity—is less than that of iron (7·2), and in the latter group it is larger.

It will be seen that according to both theories the presence of carbon is essential to the retention of the steel in its hard condition; according to the carbon theory, the carbon is the direct cause of the hardness; according to the allotropic theory, the carbon is only the indirect cause, it preventing the change in the iron from the β to the α form. Both theories have able advocates, and both have much evidence to support them. It is impossible at present to speak with absolute certainty on the matter. It may be that both changes are important.

Effect of Work.—It may be convenient here to call attention to the effect of cold work on steel, since this is in many respects very similar to the effect of heating and sudden cooling, and it has been suggested that this, too, may produce an allotropic modification of iron. Howe suggests that the iron present in such steels should be called provisionally δ iron, as it is not at all certain, even if it be an allotropic modification, that it is identical with β iron.

Cold working, or even pressure, when it is accompanied by permanent distortion, undoubtedly produces marked effects on steel; whilst, however great the pressure, if there be no permanent distortion, no change is produced. Work hardens the metal, increases its tenacity, and decreases its extension before fracture, and it is stated that iron which has been subjected to work evolves more heat when dissolved in acids than iron which has not been so worked does. When ordinary iron is subjected to stress in the testing machine, the elongation increases regularly with the stress; then at a certain point the metal breaks down—Mr.

Howe calls this the jog—and the extension increases greatly without any increase of stress, after which stress and extension increase together. If, however, the metal has been subjected to work so as to produce permanent distortion, then the stress and extension increase together without any definite breaking-down point. M. Charpy points out that the magnetic retentivity also increases at the moment the jog takes place, but increases very little afterwards with continued strain. The density of the metal is also diminished by work just as by quenching, but by annealing these effects are destroyed.

Whilst the effects of cold working are in many respects similar to those of sudden cooling, they are not sufficiently marked to justify the assumption that the iron has passed into an allotropic modification, and the existence of δ iron must be held to be at present "not proven."

CHAPTER IX.

PREPARATION OF STEEL.

STEEL may be prepared in four ways.

1. Direct from the ore.
2. From malleable iron.
3. From pig iron by partial decarburisation.
4. From pig iron by complete decarburisation, and subsequent addition of carbon.

Of these only the second and third methods are in extensive use.

1. DIRECT PRODUCTION OF STEEL.

This process is now never used, as the results obtainable by it are very uncertain, and it is impossible to ensure the production of a metal of even approximate uniformity of composition. The method of working was exactly the same as that for the production of malleable iron direct from the ore, but by keeping the iron heated for some time in contact with the carbon, steel, or at anyrate a steely iron, was produced. This necessarily lacked homogeneity, and contained intermixed slag and oxide, as it had not been fused, but only separated in the pasty condition. When cold, it was therefore broken up and melted in crucibles.

2. Manufacture of Steel from Malleable Iron.

This method has been in use for a very long time, and until quite recently was the only one carried on. It is generally called the "cementation process," and is based on the fact that when iron is heated in contact with carbon, the carbon travels into the metal and combines with it, thus converting it into steel.

The Cementation Process.—This process was introduced into Sheffield by Huntsman in 1770, and it is still almost entirely confined to that town, which has therefore become the centre of the steel trade of Great Britain.

The furnace consists of an arched chamber, along the centre of which runs the fireplace. On each side of the fireplace is placed a large box or chest, or pot, made of stone slabs resting on bricks, so arranged that the flame from the fire can circulate under it. The chest may be 15 ft. long, 4 ft. deep, and about 3 ft. wide. At the end of the chamber is the fireplace door, and a manhole opening which is bricked up when the furnace is in operation. The whole chamber is covered with a stack to carry off the products of combustion.

A layer of charcoal in small lumps, sifted from dust, is spread on the bottom of the chest, and on this is put a layer of malleable iron bars 3 in. to 6 in. wide, and about ½ in. thick. This is covered with charcoal; then another layer of bars is put, then more charcoal, and so on, till the chest is full, and the whole is then covered with a layer of some material which, when heated, will make an air-tight cover. A material often used is the powder which comes from the grindstones, known as wheel-swarf. This is a mixture of sandstone powder from the grindstones and fine steel dust from the tools ground. It is mixed with water, and spread over the chests. As the temperature rises the iron oxidises, and enough silicate of iron is formed to bind or frit the whole together. When the chests are filled and covered, the manhole is bricked up, and the fires are lighted. In about 48 hours the temperature is up to cementation point, and it is maintained at this for a period of from six to nine days, according to the amount of carbon it is desired to impart to the iron. The fire is drawn, the chests allowed to cool for a few days, and then the charge is withdrawn.

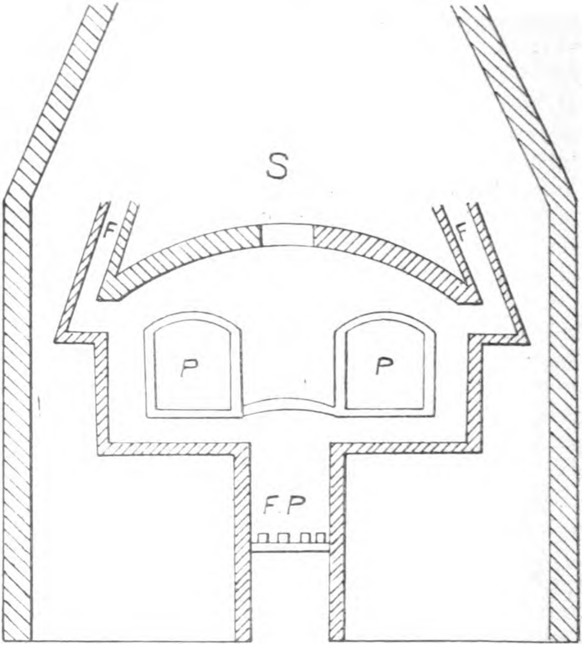

FIG. 6.—Cementation furnace.
P—Pots or chests. F P—Flue place. F—Flues. S—Shaft.

Blister Steel.—The bars withdrawn from the chests are in the condition of blister steel. They will have gained about 1 per cent in weight, and the surfaces are covered with a larger or smaller number of blisters of varying sizes, whence the name. When the bar is broken it is found to be quite different in appearance to the malleable iron which was put into the chests. There is usually a centre core or sap of unaltered malleable iron surrounded by a crystalline layer of steel, but in the case of very high carbon steels the sap may have disappeared, and the whole bar become crystalline. There is no sharp line of demarcation between the sap and the outer layer of steel, the one passing gradually into the other; nor is all the steely portion of the same composition, the outer layers containing more carbon than those beneath.

Theory of the Process.—The carbon is transferred from the charcoal outside to the iron, though both have remained through the whole time in the solid condition. There is now no doubt but that, under certain conditions, solid carbon can diffuse into iron; but under the conditions of cementation it is not likely that this takes place to any extent; it is far more likely that the transference is brought about by the medium of gases.

Though the iron is surrounded by carbon, air is present in large quantities in the spaces between the fragments of charcoal, and even in the pores of the charcoal itself, for charcoal is very porous. When the chest is heated this air in contact with the carbon combines with it, and carbon-monoxide is produced, so that the bar, in addition to being in contact with carbon, is surrounded by an atmosphere of carbon-monoxide. At high temperatures iron is permeable to carbon-monoxide, so that the gas readily diffuses into the bars; but when carbon-monoxide comes in contact with very hot iron, it is dissociated, with the formation of carbon-dioxide and the separation of carbon; thus $2CO = CO_2 + C$. The carbon being deposited in contact with the iron, and then combining with it, the carbon-dioxide will at once diffuse out, and, coming in contact with the hot carbon, will be re-converted into carbon-monoxide, and will be ready to begin its action again, and so on. There will therefore be, at any point in the mass of iron, a double stream of gas—carbon-monoxide, diffusing inwards, and carbon-dioxide, diffusing outwards. But carbon-dioxide may act on the carbon already deposited, oxidising it to carbon-monoxide, so that there will always be the double action, and thus the carbon is transferred further and further into the heart of the bar, instead of being all deposited near the outer surface. When, however, the centre of the bar contains so much carbon that any carbon-dioxide formed would be decomposed, then the action must cease; the outflowing stream of carbon-dioxide would cease also, and carbon would be rapidly taken up by the outer layers of the bar, which would ultimately pass into the condition of cast iron, and melt; and this actually happens if the action be allowed to go on too long.

The blisters on the bars seem also to be due to the action of the carbon-monoxide. It is obvious that the action above described will not be capable of producing blisters, because the volumes in the gases are not changed by the reactions. As already pointed out, malleable iron is never homogeneous, but always contains scattered through it particles of oxide of iron and slag, these being the more regularly distributed the more frequently the metal has been sheared, piled, re-heated, and rolled. If a particle of carbon be deposited in contact with a particle of oxide of iron, reduction will at once take place, and carbon-monoxide will be formed. This will exert considerable pressure, and will be unable to get away, except by the very slow process of diffusion. If it be liberated near the centre of the mass, the resistance of the metal will be sufficient to keep the gas confined till it can diffuse away. If, however, it be near the surface, the thin layer of soft iron at the welding temperature will not be able to resist the pressure, and will therefore be thrown up into a blister. When the iron has been well worked, so that the impurities are very evenly distributed, the blisters are numerous and small; but when it has been only imperfectly worked, then the blisters are more scattered, but are much larger. Numerous small blisters, evenly distributed, are therefore held to indicate a good metal. When the metal converted into steel is free from intermixed impurities, as when very mild steel is used in place of malleable iron, the blisters are absent.

Shear Steel.—The blister steel is too lacking in homogeneity to be of use, and unless it is to be melted, it must be made more homogeneous by methods exactly similar to those used for malleable iron—that is, the bars are sheared, piled, re-heated, and rolled down into bars. When this is done once the steel is called single-shear steel; when it is repeated, it is double-shear steel. It is obvious that whilst these operations may improve the physical character of the steel, by making it more homogeneous, they can have little, if any, effect on its chemical characters. The shear steel is worked into the required form by rolling or hammering, exactly in the same way as malleable iron.

Crucible Cast Steel.—Even when the steel has been sheared and rolled several times it is far from homogeneous, and if greater uniformity be required it has to be melted, and as the melting is always carried out in crucibles, the resulting metal is called "crucible cast steel."

The steel is broken up into pieces of a convenient size, placed in crucibles—each holding about 80 lb.—and melted. The melting requires the very greatest skill and care, as the metal is very easily spoilt at this stage. "Should a piece of coke accidentally find its way into the pot, the ingot will show a bright, sparkling fracture. Technically speaking, it will be said to 'stare,' and under the hammer it will prove hot-short, and crumble to pieces. If the steel be not long enough in the fire, it will teem fiery, and produce a honeycombed ingot; and the same result will follow if it be too hot when poured. If it remain too long in the fire, it will teem dead, and the fracture of the ingot will look scorched; and though exceptionally sound, it will be brittle if hard, and wanting in tensile strength if mild. If the molten steel be chilled before it is poured into the mould, which may be detected by the stream skimming over it as it is teemed, the fracture of the ingot will appear dull in colour, and full of small holes or honeycombs."*

The changes produced in the melting are chiefly physical. Intermixed impurities are separated, and the metal becomes homogeneous and crystalline, and at the same time carbon and silicon are taken up and the gases occluded in the steel are partially expelled. The steel is usually cast into ingots, which are then worked by rolling and forging.

Case Hardening.—This process, which is very largely used, is identical in principle with the cementation of malleable iron. Articles of malleable iron are frequently required to have hard surfaces, and this condition can be readily produced by case hardening. The malleable iron article is embedded in some carbonaceous material, in an iron box or chest, and this is heated to redness for a day or more. Carbon is taken up, the outer layers of the metal are converted into steel, and thus the surface is hardened, the hardness being much increased by sudden cooling. For case hardening, organic matter containing nitrogen, such as leather cuttings, &c., is almost always used in place of carbon; but whether the nitrogen has any action is uncertain; probably it has not. When articles made of mild steel are case hardened, they are said to be made of mild centered steel.

Harveyising.—This is simply case hardening, or surface steeling, of armour plates of large size, and does not differ in principle from the case hardening of smaller articles. In the case of armour plates, two plates are often carburised at the same time, the faces to be hardened being towards one another, with a layer of charcoal between them. The plates are then built up with brickwork, so as to prevent access of air, and are heated in a regenerative furnace for a

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* H. Seebohm. "On the Manufacture of Crucible Cast Steel," page 13.

week or more, after which they are allowed to cool. Sometimes a block of pressed charcoal is used instead of a layer of charcoal, but this does not seem to have any advantage. The plate is bent to the required form after carburising, and is then hardened by being heated to redness, and quenched with water.

Malleable Castings.—Similar in principle, though with an opposite purpose, is the method of making malleable castings. Cast iron is always more or less brittle ; but if the casting be embedded in some oxidising material, such as hæmatite, and heated for some time to redness, the carbon will be oxidised from the outer portions, which will thereby be converted into malleable iron—as far as chemical composition is concerned. Malleable castings are always lacking in strength, the metal being left porous by the removal of the carbon, and the articles are rarely malleable, as it is usually not possible to convert the whole of the metal. Obviously, castings made of iron containing much graphite are not suitable for rendering malleable.

3. PREPARATION OF STEEL BY THE PARTIAL DECARBURISATION OF PIG IRON.

Two methods have been used.

(1) *Puddled Steel.*—Since steel is intermediate in carbon content between pig iron and malleable iron, it might, if there were no other injurious impurity to remove, be possible to stop the puddling process at such a point as to leave any required amount of carbon in the resulting metal. It is obvious, however, that as silicon and phosphorus would also be only partially removed, only pig irons nearly free from these would be available for the production of puddled steel. The furnace which was used for puddling steel was similar to that used for puddling iron, but smaller. As all the carbon was not to be burnt out, the metal did not come to nature, but had to be made sufficiently pasty to allow of balling up by reducing the temperature. As there was no change to indicate when sufficient carbon had been

removed, the point at which to stop was uncertain, and therefore it was almost impossible to make metal of uniform quality, and this alone proved to be a fatal objection to the process.

Puddled steel is no longer made, but every now and then we hear of malleable iron of abnormal strength being produced in the puddling furnace. This is quite simple if a little carbon be left in the metal, but it then ceases to be malleable iron and becomes steel, or perhaps a steely iron, and the increase in strength is attended with loss of ductility, and thus the metal loses the most essential character of good malleable iron.

(2) *The Original Bessemer Process.*—Though the Bessemer process as now invariably worked belongs to the next group of steel-making processes, as at first used it was a decarburising process, the object being to make steel by partial decarburisation. In this the process was quite successful, and by using Swedish iron low in silicon, and free from sulphur and phosphorus, excellent tool steel was prepared. For about two years Messrs. Bessemer and Co., of Sheffield, made steel by this process, and it was only when the demand for mild steel became very great, and it was found that the process was better suited for the production of this than of higher carbon steels, that this method of working was abandoned in favour of the one now always used. The one difficulty with the process was the determination of the end, but this could be judged by the time taken if the composition of the pig iron were known. The chemistry of the Bessemer process will be fully discussed in the next article, so a very brief outline will be sufficient here.

Pig iron is melted in a cupola, and is then run into a converter, a vessel so arranged that it can be turned over to receive or discharge the metal, and that when upright a stream of air can be blown through the molten metal. As the air passes through the metal oxidation takes place very rapidly, and the temperature becomes very high. At the beginning of the process the silicon is oxidised more

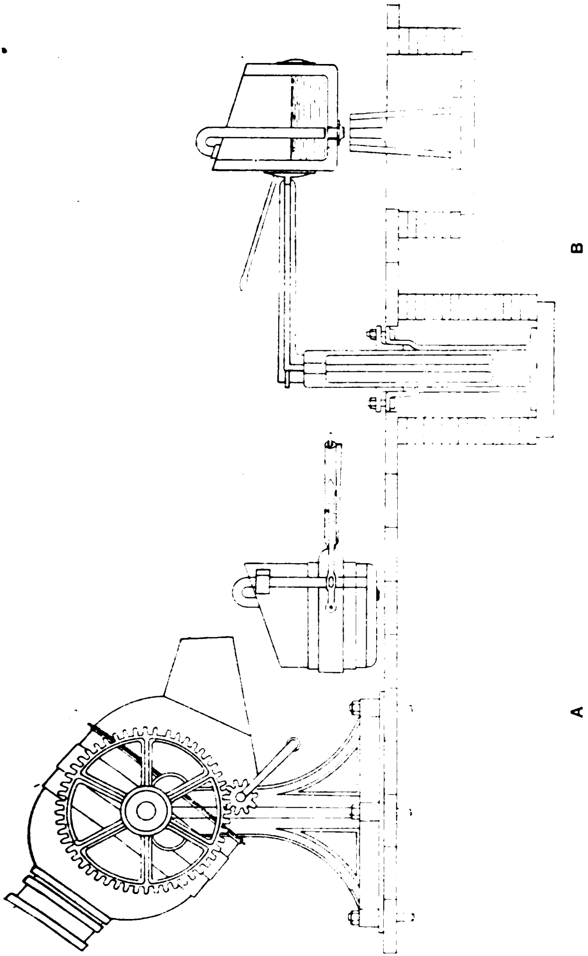

Fig. 7.—Early form of Bessemer plant. A—Converter and ladle. B—Ladle and crane in section

rapidly than the carbon, so that the proportion of silicon removed will be greater than that of carbon, and therefore, if the silicon be low, the amount left, when the carbon has been reduced to, say, 1 per cent, may be small enough

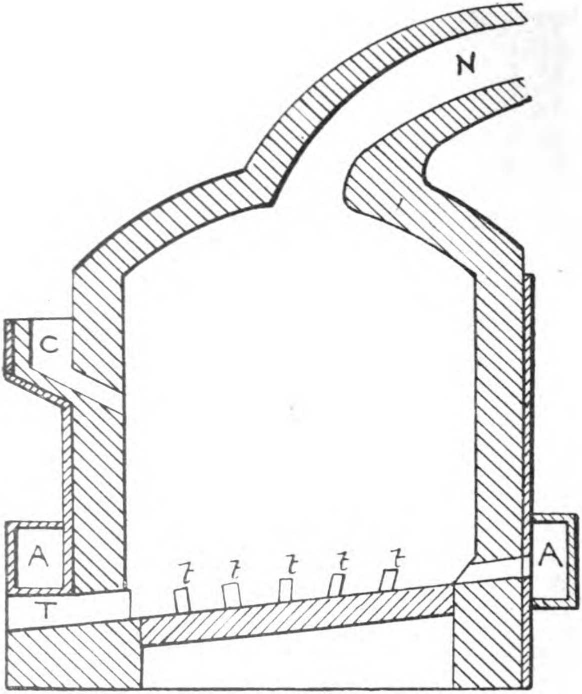

FIG. 8.—Swedish fixed converter (Avesta).
C—Charging opening. A—Air chest. *t*—Tuyeres. N—Throat

not to be objectionable. When it is judged that the charge has been sufficiently blown, the converter is turned over and the metal is poured into a ladle, from whence it is transferred to the moulds.

This process is still carried on in Sweden, and perhaps in other localities. The converters used in Sweden are not of the present tilting type, but are fixed, the tuyeres being arranged in a row near the bottom, and being so placed that the air gives the metal in the converter a rotary motion, and the area of the tuyere openings is much larger per ton of metal than in other forms of converter. The charge of two or three tons of pig iron is melted in a cupola and run into the converter; the blast having been previously started, the blow lasts about ten minutes or more, and when finished the metal is tapped out into a ladle and transferred to the moulds. The iron used is always good Swedish pig, low in silicon. Excellent steel is made by this process.

4. Preparation of Steel by Complete Decarburisation and Subsequent Addition of Carbon.

THE BESSEMER PROCESS.

The principle on which the Bessemer process is based is—as has been already indicated—that of removing the impurities of the pig iron by blowing air through it whilst it is in a molten condition. In the earliest forms of the process the blow was stopped whilst enough carbon remained to constitute the metal steel, but in the more recent forms the blow is continued till all the carbon and silicon are completely oxidised and removed, and the necessary amount of carbon is subsequently added in the form of ferro-manganese or spiegeleisen. By the original process high carbon steels were made, but by the modern forms mild steels only.

The Converter.—The vessel in which the blow takes place is called in this country the converter; in America, the vessel, and the usual form used, is that designed by Bessemer, though many variations have been made in detail in different plants. It consists of a shell of boiler plate thickly lined with ganister, or some other very refractory material.

At the bottom of the converter is an air chest, from which perforated clay cylinders—the tuyeres—pass through the lining into the interior. The vessel is carried on trunnions, and is so arranged that it can be turned completely over by means of suitable turning gear attached to one side. The air from the blowing engines passes up through one standard, through the trunnion, which is made hollow for the purpose, down by a blast pipe to the air box, and thence by the tuyeres to the interior of the vessel. The air pipe is so arranged that the blast can continue to enter the vessel whilst it turns through 90 deg. from the vertical to the horizontal position.

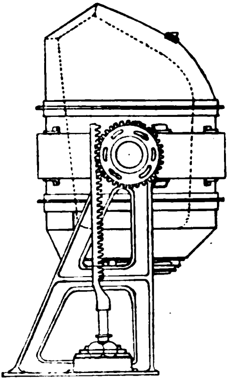

Fig. 8.—Modern Bessemer converter, showing turning gear.

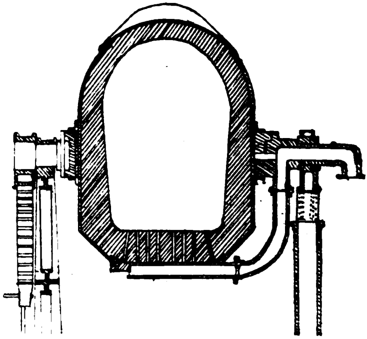

Fig. 9.—Cross-section of Bessemer converter, showing air pipe and tuyeres.

Arrangement of Plant.—Two converters are usually so arranged as to work alternately, and they are placed on opposite sides of the same casting pit. In the centre of the pit is fixed a rotating casting crane, carrying at one end a ladle large enough to contain the whole charge. The crane is provided with rotating and lifting mechanism, so that it can be brought under the mouth of the converter to receive the metal, or over the moulds, which are arranged round the pit, so as to run the metal into them. The ladle is lined with ganister, and is provided at the bottom with a tap hole, by which the metal is run into the moulds. The air supply and the motions of the converter are controlled by the foreman from a platform which commands a good view of the whole plant.

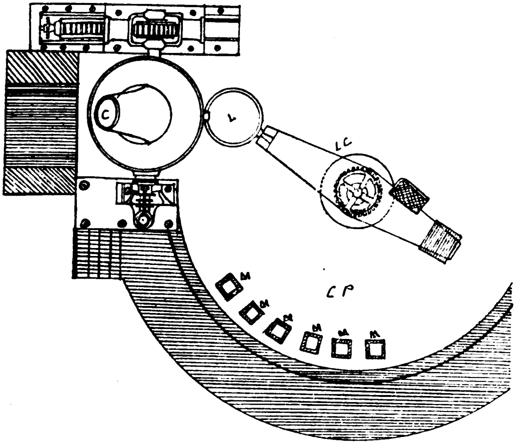

FIG. 10.—Plan of Bessemer casting pit.
M—moulds. C—converter. CP—casting pit.
L—ladle. LC—ladle crane.

Cupolas for melting the metal, cranes for lifting away the moulds and ingots, and other necessary appliances are provided.

The Blow.—The converter having been cleared of slag, and being still hot from the previous charge, is turned into a horizontal position, and the charge of pig iron—say 10 tons—is brought in a ladle from the cupolas, or, more rarely, direct from the blast furnace, and is run into the converter through a movable trough or spout, the converter being so shaped that the metal does not reach the openings in the tuyeres, or it would run down and stop them.

The blast is now turned on, and the converter is slowly turned up. As the metal comes over the tuyeres there is a vigorous ejection of sparks. As soon as the converter is up the shower of sparks diminishes, and a flame, not very luminous, is seen at the mouth of the converter, whilst there are frequent ejections of sparks of burning iron and slag. As the operation goes on the temperature rises, the flame increases in luminosity and size, and ultimately becomes very bright and dense. After a short time it begins to grow less bright, and at a certain moment, usually about twenty minutes from the time the blow was started, it grows suddenly much smaller, or drops. The blow is now over.

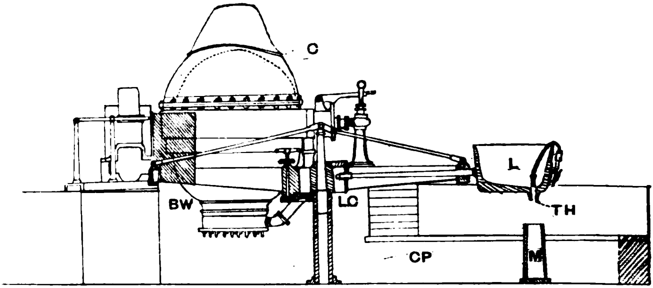

FIG. 11.—Section of casting pit, showing ladle and mould.

M—moulds. LC—ladle crane. BW—balance weight.
CP—casting pit. L—ladle. TH—tap hole.
C—converter.

The converter is turned down into the horizontal position again, as quickly as possible, the blast is turned off, the necessary quantity of spiegeleisen or ferro-manganese is thrown in, and the metal is poured at once into the ladle, to be distributed thence to the moulds. The converter is turned upside down, so as to remove a small quantity of pasty slag which has been formed, the interior is examined, repaired if necessary, and the converter is turned up ready for the next charge. The blow will have taken about twenty minutes, the preparation of the converter, say, another ten minutes; so that one 10-ton converter will be able to convert 20 tons of pig iron into steel each hour.

Chemistry of the Process.—The chemistry of the process is simple, and is almost identical with that of puddling, but the changes are brought about at very much higher temperatures, and under quite different conditions. As the air enters the hot metal, oxidation at once begins; the passage of the air keeps the mass in a constant state of violent agitation, so that any oxides formed at first are thoroughly mixed up with the mass, and the affinities have full play. Silicate of manganese is formed at the outset from the manganese and some of the silicon, $Mn + Si + 3O = MnSiO_3$. Silicate of iron is also formed, $Fe + Si + 3O = FeSiO_3$, and no doubt also oxide of iron, which much facilitates the bringing about of the reactions. When the silicon is considerably reduced the oxidation of the carbon goes on rapidly, probably mainly by the action of the dissolved oxide of iron, and the boil commences, carbon-monoxide being formed and evolved, and burning at the mouth of the converter, thus increasing the temperature and luminosity of the flame.

During these reactions the converter must not be allowed to become too hot. At very high temperatures the affinity of carbon for oxygen becomes greater than that of silicon for oxygen, and therefore, if the temperature be too high, the carbon might all be removed before the silicon was gone, and thus a bad steel must result. To avoid this the converter is sometimes turned down, and scrap is added in the middle of the blow, the cold scrap reducing the temperature very considerably. As the carbon is removed, the iron reaches the point when in puddling it would come to nature, but the temperature is now high enough to keep it melted. When the last of the carbon is removed the flame drops, the blow is over, and the converter is turned over as quickly as possible. If the blow were continued longer, the metal would be completely spoilt in a very short time ; for the more easily oxidisable substances being removed, the iron itself would be attacked, and the oxide thus formed would make the metal "rotten" and useless. Even when the blow is only just finished, some oxygen will have been taken up, quite enough, indeed, to make the metal unworkable, but not so much but that it can be removed easily.

It is necessary to add some material that will remove the oxygen which has been taken up, and at the same time add the requisite amount of carbon. The substance used is spiegeleisen or ferro-manganese. These are alloys of iron and manganese containing carbon, the former containing about 30 per cent, and the latter 80 per cent or more of manganese. The alloys dissolve in the hot metal, the manganese combines with the oxygen, forming oxide of manganese, which passes into the slag, whilst the iron and carbon pass into the metal. As enough manganese must be added to remove all the oxygen, and as this necessarily also adds carbon to the iron, the richer the manganese-iron alloy is in manganese, the less carbon will be added with the necessary amount of manganese, and therefore the milder will it be possible to make the steel.

The following analysis will indicate the nature of the changes which take place during the process, and will show how the composition of the finished steel is related to that of the iron used, and of the metal before addition of ferro-manganese.

	Pig iron.	End of first stage of blow.	After nine minutes' blow.	End of blow.	Steel ingot.
Carbon	3·270	2·170	1 550	·097	·566
Silicon	1·952	·790	·635	·020	·030
Sulphur..........	·014	trace	trace	trace	trace
Phosphorus	·048	·051	·064	·067	·055
Manganese	·086	trace	trace	trace	·309

It will be seen from these figures that the silicon is removed much more rapidly than the carbon during the early stages of the blow, and that the manganese is almost completely removed at the very outset, a further quantity being, however, added by the spiegeleisen at the end, and that the phosphorus is not removed at all, but rather seems to increase, this apparent increase being due to a decrease in the quantity of metal through which it is distributed.

The way in which the impurities are removed is very clearly shown by the curve given by Sir Lowthian Bell, and shown in fig. 12. The figures on the horizontal line represent times, those on the vertical lines the percentages of the various impurities removed. Since the phosphorus is not removed during the process, it is quite obvious that a pig iron free from phosphorus must be selected for use.

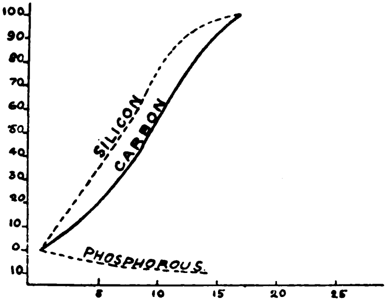

FIG. 12.

Sources of Heat in the Blow.—It may seem curious that blowing air through molten pig iron should not only not cool it, but should produce a temperature high enough to keep the carbon-free iron in a state of fusion. It must be remembered that the elements which have to be removed from the iron are burnt out, and that the combustion necessarily evolves heat.

Assume that the pig iron being used contains 2 per cent of silicon and 3·5 per cent of carbon. Then for each 100 lb.

of iron, 2 lb. of silicon will be burnt; and as the calorific power of silicon may be taken as 14,000 B.T.U., the heat evolved will be 28,000 units for each 100 lb. of iron converted.

If the carbon were burned to carbon-dioxide, its calorific power would be 14,500 B.T.U. It will, however, mostly be burned only to carbon-monoxide, the temperature being too high for the production of carbon-dioxide; so that its calorific power can only be taken as 4,350 B.T.U., and the heat evolved for each 100 lb. of iron will be 15,225 B.T.U. A portion of the iron will also be oxidised, the amount being about 2 per cent. Assuming the calorific power of the iron to be 4,300 B.T.U., the oxidation of the iron will give 8,600 B.T.U.; so that we have for each 100 lb. of iron—

2 lb. of silicon oxidised to SiO_2	28,000	B.T.U.
3·5 lb. of carbon oxidised to CO.........	15,225	"
2 lb. of iron oxidised to FeO	8,600	"
	51,825	"

Or, as there are, say, 10 tons or 22,400 lb. of iron, the total heat evolved in the converter will be 11,608,800 B.T.U. Assuming a good coal to have a calorific power of 15,000 B.T.U., this amount of heat will be equal to that which would be evolved by the combustion of 774 lb., or very nearly 7 cwt. of coal; and if it be remembered that this heat is evolved in the small converter, and in about twenty minutes, it will be seen at once that a very high temperature must be produced. This estimate of the heat evolution will be somewhat below the mark, because no account is taken of the oxidation of manganese and other minor impurities.

Bessemer Steel.—The steel made in the Bessemer converter is known as Bessemer steel, and it has now come very largely into use for many purposes, as it is quite equal to the steel made by any other process. It can be made of any carbon content between about ·2 and ·6. It is not advisable to make steels much higher than this by the Bessemer process, because, all the carbon being removed from the iron, the required amount must be added in the form of ferro-manganese, and therefore, when it is required to add a large quantity of carbon, a large quantity of ferro-manganese will be needed, and this may add too much manganese, and also may introduce other impurities.

The pig iron for use in the Bessemer process must be carefully selected. It must be nearly free from sulphur and phosphorus, and for the method of working used in this country should contain at least 2 per cent of silicon, as it is by the combustion of this that the principal part of the heat is produced.

THE BASIC BESSEMER PROCESS.

In the Bessemer process, as already pointed out, phosphorus is not removed, and therefore phosphorus-free iron must be used. The reason for this is that the silica in the lining of the converter and in the slags decomposes any phosphate of lime or iron which may be formed by oxidisation of the phosphorus, and as the phosphorus can only pass into the slag in the form of phosphates, that element cannot be removed; and even if phosphate were introduced, this would be decomposed, and the phosphorus would pass into the metal. If the silica or acid lining could be replaced by one of lime or other basic material, any phosphate of lime formed by the oxidation of the phosphorus would pass into the slag, and therefore it would be possible to manufacture steel from phosphoric pig irons, such as those of the Middlesbrough district.

A practicable method of doing this was first introduced by Messrs. Thomas and Gilchrist, and the process is therefore sometimes called by their name. As, however, it only differs from the Bessemer process by the substitution of a basic material for the ganister lining of the converter, it is best to call it the basic Bessemer process.

The Converter.—The converter used does not differ in any essential particular from that used for the acid process, except that it is lined with a different material. There is no basic material which is plastic enough to be made into bricks or furnace linings without the addition of a binding material, and the greatest difficulty the inventors of the process had to encounter was that of finding a suitable material for the lining. The material ultimately decided on was magnesium limestone, a mixture of the carbonates of lime and magnesium, containing a small quantity of silica. This is burnt at a high temperature to expel the carbon-dioxide, ground to a coarse powder, mixed with anhydrous tar, and moulded into the required form, either of bricks or furnace linings, at a temperature high enough for the tar to become soft, and so yield a more or less plastic mass. As it would be impracticable to use fireclay tuyeres in contact with the basic lining, either tuyeres of magnesite or of magnesium limestone are used, or, more usually, the bottom of the converter is made by ramming the mixture round a series of pins, which are subsequently removed, leaving air holes through the bottom itself.

The arrangement of the plant does not necessarily differ from that for the acid process, but as the quantity of slag produced is much larger, either larger converters are used, or, more usually, a smaller charge is worked. As a rule the converter is made with the mouth opening vertically upward, instead of the neck being curved backwards, as in most acid converters.

The Blow.—The converter is brought into a horizontal position. A quantity of lime—say 1 ton, but varying with the composition of the pig—is put into the converter, then the iron is run in, and the converter is turned up. The blow proceeds very much as in the acid process, except that the ejection of sparks is very much more vigorous, and the flame is much darker in colour, so that the changes are not so easy to notice. At the end of about 15 or 20 minutes the flame will drop, this indicating, as in the acid blow, the removal of the carbon. At this stage, however, but little phosphorus will have been removed, so the blow must be continued for a few minutes longer, this continuation being called the after-blow. During the after-blow a good deal of iron is oxidised, and a dense red smoke of oxide of iron escapes from the converter. The appearance of the flame gives no indication as to when the blow is over, so that when the foreman judges that the after-blow has been continued long enough, the converter is turned down, the blast stopped, and a sample of the metal is taken from the converter. This is cast into a small ingot, cooled, and broken, and from the fracture the foreman judges whether the blow is complete, and, if not, how much longer to blow it. If necessary, the converter is turned up, and after the necessary blow is again turned down and a sample taken, and so on until a satisfactory sample is obtained; then the slag is poured off the ferro-manganese added, and the metal is teemed into the ladle and distributed to the moulds exactly as in the acid process, whilst the converter is turned up again ready for another charge. Mr. Campbell states that there is a decided change in the flame when the phosphorus is reduced to ·05, which may be taken as an indication of the end.

Chemistry of the Blow.—It will be seen that the conditions of the blow are very different to those which hold in the acid process. There the metal was in contact with a siliceous converter lining; here it is in contact with a basic lining and with the large quantity of lime which was added. This somewhat re-arranges the conditions of chemical equilibrium. The silicon which may be present oxidises very rapidly, far more so than in the case of the acid blow, no doubt because of the large quantity of lime present, ready to take up the silica the moment it is formed; on the other hand, the manganese goes more slowly, because the silica does not demand its oxide so vigorously to form silicate. The carbon goes much as before, the nature of the lining having very little effect on it. When the flame drops the carbon is reduced to about ·1, but as the after-blow follows, the carbon is still further oxidised, and the last trace of it and of silicon may be eliminated. The phosphorus is very little acted on in the early stages, but as soon as all the carbon is removed the whole oxidising power of the oxygen of the air is concentrated on the phosphorus, and it is speedily oxidised, passing into the slag as calcium phosphate, not as the ordinary calcium phosphate, $3CaO$, P_2O_5 ($Ca_3P_2O_8$), but to a large extent as a tetrabasic phosphate, $4CaO$, P_2O_5 ($Ca_3P_2O_8CaO$, or $Ca_4P_2O_9$). Any sulphur that may be present is partially removed. The following analyses will give an idea of the nature of the changes which take place during the blow :—

	Pig iron.	After 2 min. 40 sec.	After 5 min. 21 sec.	After 10 min. 45 sec.	After 15 min. 13 sec.	After 19 min. 49 sec.	Rail steel.
Carbon	3·21	3·30	3·12	1·49	·05	..	·26
Silicon	1·22	·72	·15	·012	·008	·004	·01
Phosphorus ..	2·18	2·15	2·22	2·096	1·91	·087	·145
Sulphur......	·08	·047	·051	·051	·055	·056	·045
Manganese ...	1·03	·71	·50	·16	·01	..	·48

The nature of the changes is shown graphically in fig. 13, from Sir T. Lowthian Bell's "Manufacture of Iron and Steel."

As will be seen by comparing the last column with the one before, there is a slight re-reduction of phosphorus from the slag. This invariably takes place, and it is to avoid it reaching a serious amount that the slag is poured off before the ferro-manganese is added.

The amount of iron oxidised is greater in the basic than in the acid process, about 4 per cent passing into the slag, whilst undoubtedly some escapes in the gases, a heavy loss being always indicated by the escape of red fumes from the converter.

Sources of Heat.—The sources of the heat are much the same as in the acid process, but at the outset the silicon oxidises, then the carbon, and during the after-blow the heat is kept up by the combustion of the phosphorus.

Assuming the iron to contain 1 per cent of silicon, 3·5 per cent of carbon, 3 per cent of phosphorus, 4 per cent of iron being oxidised and passed into the slag, for each 100 lb. the heat evolution would be—

1 lb. of silicon	oxidised to	SiO_2	14,000	B.T.U.
3·5 lb. of carbon	„	CO	15,225	„
3 lb. of phosphorus	„	P_2O_5	31,110	„
4 lb. of iron	„	FeO	17,200	„
100 lb. of iron			77,535	„

or 1 ton equal 1,836,784 B.T.U., this being equivalent to the combustion of about 10 cwt. of coal of the same value as that previously mentioned. The greater amount of heat is required to melt the much larger amount of slag which is produced, owing to the lime which is added to the charge.

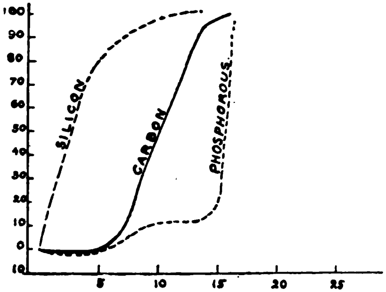

FIG. 13.

Basic Bessemer Steel.—The basic Bessemer process has been very largely used, especially on the Continent, but in this country, at anyrate, the steel made by it has not been so readily received as that made by the acid process, many engineers not feeling confidence in it.

It is possible by this process to make a steel milder than any that can be made by the acid process, because the carbon and silicon are more completely removed by the blow. Much of the steel made has been equal to any made by the acid process; but still there is reason for the lack of perfect confidence, as will be seen from a consideration of the method of manufacture.

There is no sharp indication of the end of the process. Samples have to be taken, and the decision as to when the blow is complete rests on the judgment of the foreman in charge as to the appearance of the fracture; and in some cases, where the sample shows that the phosphorus is almost removed, so that if the converter were turned up again and blown, even for the shortest time, the metal would be over-blown, it must be a difficult question to decide which course to take. There is therefore some difficulty in making absolutely uniform metal.

Then the addition of the ferro-manganese always causes a reduction of phosphorus to a certain extent unless the slag is completely removed, and this is not practicable. Much basic Bessemer steel contains, even when carefully made, over ·08 per cent of phosphorus, and this is the limit fixed by many engineers for steel rails, whilst others specify the phosphorus to be as low as ·04 per cent; and whilst it is quite easy to obtain even this in occasional charges, it is not by any means easy, even if it be possible, to obtain a regular output of steel so low in phosphorus.

It is, however, only in cases where the absence of phosphorus is of great importance that any doubt need be felt as to the use of basic Bessemer steel; for all other purposes it is quite as good as any other form.

THE OPEN-HEARTH PROCESS.

The Siemens or open-hearth process owes its possibility to the introduction of the gas producer and the Siemens regenerative furnace. The process is very like puddling, except that the furnace is much larger, larger quantities of material are worked in one charge, and that the temperature is so high that the resulting carbon-free iron does not "come to nature," but remains liquid. As the process is usually conducted, the carbon is completely, or almost completely, removed, and the metal is re-carburised to the required extent by the addition of ferro-manganese, as in the Bessemer process.

Siemens Furnace.—The furnace is of the reverberatory type, but, instead of a fireplace, is provided with gas and air ports at each end. It is also provided with four regenerators. There are chambers filled with a chequer work of firebrick, and are placed in any convenient position, but usually under the furnace. The products of combustion on their way to the chimney pass through two of these, the air and gas on their way to the furnace passing through the other two. The direction of the gases is reversed about every hour, so that two regenerators are always being heated by the waste gases, and two are heating the gas and air. By passing through the regenerators the gas and air are strongly heated; and the temperature being further raised by combustion, the furnace becomes intensely hot—hot enough, in fact, to keep the carbon-free iron in the fused condition.

The hearth of the furnace is constructed of iron plates, so arranged that air can circulate freely beneath, and on this is laid a layer of bricks, and on this the working bottom of sand, which must be very refractory, yet fusible enough to be fritted into a solid mass at the intense heat of the furnace. Siemens furnaces are now made of very large size, capable of holding 20 to 40 tons of metal. Fifty-ton furnaces are in use, and much larger sizes have been proposed.

The Process.—The furnace being hot from the previous charge, the metal, which may be either all pig iron or a mixture of pig iron and scrap, is put in, and the temperature is raised till the whole is melted. When the mass is in the molten condition, oxide of iron in the form of hæmatite ore, as free as possible from silica, is added in small portions at a time. At first the ore is dissolved, and slag accumulates over the metal; then, as more is added, the whole seems to boil, from the rapid escape of carbon-monoxide. As the boil diminishes, and ultimately ceases, a point is reached when the operation is judged to be over, and when, if the temperature were lower, the metal would come to nature. A sample is then taken by means of a small ladle sent to the laboratory, and the carbon is determined colorimetrically, which can be done in a very short time, the flame being so adjusted during the interval that the metal undergoes as little change as possible. If the carbon removal be sufficiently complete, the metal is tapped into a large ladle, capable of holding the whole charge, and as it flows the necessary amount of ferro-manganese or spiegeleisen is thrown in, and the metal is run into the moulds exactly as in the Bessemer process.

The Plant.—The plant consists of the furnace, as already described, with the gas producers and regenerators, the ladle which must hold the metal and the slag, the casting pit, and the moulds As already mentioned, the furnace is usually placed above the regenerators, and, where possible, it is built against a bank, so that the front is high enough to be convenient for working, and the back low enough to allow the ladle and its car to be run under the tap hole to receive the metal. The ladle is exactly similar to that used in the Bessemer process, but is usually carried on a truck running on rails, instead of on a rotating ladle crane. The casting pit is usually a longitudinal pit between the rails on which the ladle car runs, and the moulds are arranged in a row, so that as the ladle car is drawn along by an engine the metal can be run into them. The crane for lifting the ingots and moulds usually travels on a line of rails alongside that on which the ladle car runs, and is often used for drawing it along.

Chemistry of the Process.—The chemistry of the process is so simple that after what has been said of the other processes it hardly needs description. During the melting down the iron becomes partially oxidised, and the oxide thus formed removes some of the silicon. The process could be conducted exactly in the same manner as puddling—that is, oxide formed by atmospheric oxidation could be allowed to act on the silicon and carbon ; but this would take far too long for a large charge of pig iron, so oxide of iron is added. This rapidly oxidises the silicon, forming ferrous silicate, which enters the slag, the amount being no doubt increased by the action of oxide of iron on the sand bottom. When the silicon is removed the carbon is attacked, and the boil commences, and ceases when the carbon is all out. When the ferro-manganese is added, most of the manganese is oxidised in the removal of oxygen that may have been taken up and the remainder dissolves in the metal, and the carbon enters the metal. The whole operation lasts from eight to twelve hours, the time depending on the quantity of the elements which have to be oxidised out.

The great advantage of this process is that it is completely under control, and for this reason it has been generally adopted where it is required to make steel of perfectly definite composition. Samples can be taken and tested, the charge being meanwhile kept melted, so that any further addition of ore or pig that may be found necessary to bring the metal to the required composition can be readily made. Steel can not only be made of perfectly definite composition, but it can be made milder than is possible by the Bessemer process, because but little oxygen is taken up, and therefore only a small quantity of ferro-manganese need be added. On the other hand, a harder steel may be made without the addition of an undue quantity of ferro-manganese, by stopping the process after the silicon has all been removed, but before all the carbon has gone.

The silicon and carbon are completely oxidised out, but the heat evolved by their combustion does not materially help the process, as it is distributed over a long time, instead of being concentrated into a few minutes, as in the Bessemer converter. Phosphorus and sulphur are not removed, so that only hæmatite pig can be used, and the ore added must also be free from phosphorus; but a much wider range of composition is allowable in other respects than with pig for the Bessemer process, because the impurities have merely to be got rid of, and play no part in the operation.

Modifications of the Process.—The process may be modified in various ways. In the original Siemens process pig iron and ore only were used, and in the Siemens-Martin process pig iron and scrap only. In the latter case the operation takes a shorter time; the carbon and silicon are oxidised out by means of oxides formed by atmospheric oxidation, and the quantity of pig iron used is small in proportion to the quantity of scrap. The process now generally used is a combination of the two forms, pig iron, scrap, and ore being used; hence it is sometimes called the Siemens and sometimes the Siemens-Martin process. The former name, however, should be used in cases where ore is added to the charge.

Siemens Steel.—This is probably the most generally favoured form of mild steel, and the reasons for the preference have been indicated above. It may contain any amount of carbon from ·1 to about ·6, or even more, and it can be made to specification of definite carbon content to within a few hundredths per cent, which is not generally possible by the Bessemer process. There is also less likelihood of the metal containing silicon than when it is made in the converter.

THE BASIC OPEN-HEARTH PROCESS.

The ordinary Siemens process in one respect labours under the same disadvantage as the Bessemer—that is, only non-phosphoric pig irons are available for steel making by it. This is probably not a matter of very great importance, as hæmatite pig suitable for either process is now made in very large quantity, and can be obtained at a reasonable price, The process can, however, be modified by using furnaces lined with a basic material, so that ordinary phosphoric pig irons may be used. It is then called the basic Siemens or basic open-hearth process.

The Basic-lined Furnace.—This does not differ in any important particular from the acid furnace, except that the working bottom, instead of being made of sand, is made of some strongly basic material, such as calcined dolomite or magnesite. As bricks made of this material are not strong enough to use for building the sides and roof of the furnace, these must be built of ordinary acid links.

Since calcined dolomite would at a high temperature form fusible silicates with the silica of the bricks, and thus flux them away, the two materials must not be allowed to come in contact, but must be separated by a layer of neutral material. This separation of the acid and basic portions of the furnace has been one of the greatest difficulties in the construction of furnaces for the basic open-hearth process. The materials usually used are graphite or chromite (chrome iron ore), neither of which is attacked by silica or basic materials. If calcined magnesite be used for the hearth, the separating layer is not essential; but this material is of comparatively rare occurrence, and therefore is expensive.

The Process.—The working of the process is very similar to that of the ordinary Siemens. The pig iron is charged into the furnace with a considerable quantity of lime, and is melted down. Oxide of iron is then added, and the process is continued in the ordinary way. The silicon is oxidised rapidly, and, owing to the basic nature of the slag, is so completely removed that no trace of it is left. The carbon may also be almost completely removed. The phosphorus passes into the slag as phosphate of lime, and may be almost completely removed. As the phosphorus removal does not take place to any extent till the carbon is reduced to about ·08 per cent, the carbon must be wholly removed, and that which is required for the steel must be subsequently added in ferro-manganese. Samples are taken and tested so as to determine when the oxidisation has gone far enough. To prevent reduction of the phosphorus, the slag is removed as completely as possibly before the re-carburiser is added.

Basic Open-hearth Steel.—It is possible to make a milder steel by this process than by any other. The carbon and silicon may be completely removed, and the phosphorus almost so. The slag can be nearly completely separated; therefore there is much less chance of the re-reduction of phosphorus than in the basic Bessemer process. The whole process is under perfect control, and samples may be taken and tested or analysed at any stage, and the phosphorus can be almost completely eliminated without the danger of oxidising the metal. Basic open-hearth steel does not differ in any essential from ordinary open-hearth steel, and, now that the manufacture is well understood, is quite as trustworthy. The basic open-hearth process is not being very largely used in this country, because it is necessarily somewhat more expensive than the acid process, and Bessemer pig now is very cheap, and the supply of non-phosphoric ores abundant. The prejudice against basic steel, which was at first very strong, is now disappearing.

Combination of Steel Processes—It has been very frequently suggested to combine the various processes: for instance, to commence in an acid-lined Bessemer converter, and to finish in one with a basic lining; to commence in the converter, acid or basic, and finish in an open-hearth furnace; or to commence in an acid-lined open-hearth furnace, and finish in one with a basic lining. Whilst these may be advantageous under certain conditions, as, for instance, where it is desired to use an iron unsuitable for any single process, these modifications are not likely to seriously modify the quality of the steel produced; they are, therefore, of metallurgical interest only.

HIGH-CARBON STEEL BY MODERN PROCESSES.

The difficulty in the production of high-carbon steel, by the Bessemer or open-hearth process, lies in the use of ferromanganese, or similar alloys, for re-carburisation, because, if enough of these be added to give the requisite amount of carbon, other impurities are introduced in such large quantity as to deteriorate the steel very seriously. Mr.

Darby has suggested carburisation—after the addition of the necessary amount of ferro-manganese to remove oxygen—by running the metal over charcoal. This method seems to be satisfactory, but it has not come into practical use.

Selection of Steel.—The engineer frequently specifies steel made by a particular process, and this is often objected to on the ground that, if the engineer gets a material which will pass his tests, it is a matter of no moment to him how it is prepared. This is, however, not strictly the case. That the engineer only needs to obtain a suitable material is undoubtedly true; but as every piece of metal cannot be tested, he is perfectly justified in deciding not to accept steel made by a process in which there is any likelihood of either the introduction of injurious constituents or the production of steel of irregular composition and qualities. There is, however, unfortunately no doubt that engineers often specify steel to be made by a particular process from habit or fancy, without any clear idea as to why the metal made by that process should be better than that made by any other. Such specifications have lowered engineers very much in the eyes of practical metallurgists, and have made the latter think that only too often the former do not know exactly what they want. Architects are perhaps even worse sinners in this respect than engineers, it being no uncommon thing for girders and other articles of structural steel to be specified as to be made of "mild steel," without any restriction as to composition or provision for testing.

CHAPTER X.

THE FOUNDRY.

IRON and steel are converted into the forms required for use by two methods: First, by casting, in which the metal is melted and run into moulds of the required form; and second, by forging, the metal being heated till it is plastic, and then hammered or rolled into the required form. The first method is available for cast iron and all varieties of steel, whilst the second can be used for malleable iron and steel.

For casting, the metal may either be run direct from the furnace in which it is made to the mould, or it may be cast into ingots and afterwards re-melted in a cupola, or a reverberating or crucible furnace. Cast iron and the harder steels are almost always re-melted, whilst mild steel is usually cast direct from the steel-making furnace.

The conditions of casting of cast iron, mild steel, and hard steel are so different, that they must receive separate consideration.

CASTING CAST IRON.

Cast iron is almost always obtained from the blast furnace in pigs, and is then re-melted in the foundry cupola. In some cases, however, as in casting the large ingot moulds for the steel foundry, the metal is sometimes run direct from the blast furnace.

The Cupola.—The foundry cupola is a small blast furnace. It may vary much in form and size. Fig. 9 represents one capable of melting about three tons of iron per hour. As the temperature is never very high, slag will frequently remain unfused, and accumulate at the bottom; this must be removed either through a breast opening, which is bricked up temporarily while the furnace is at work, or, as in the illustration, by means of a "drop bottom" of iron plates, which is opened at the end of the run. The furnace may be cylindrical in section, or it may be narrowed at the tuyere

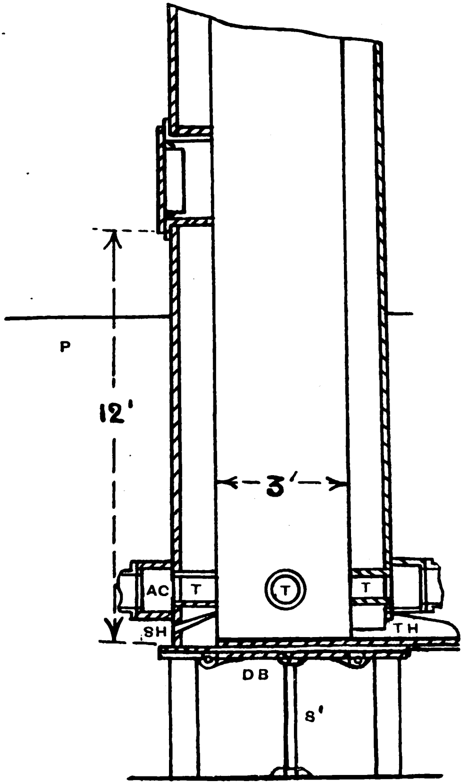

FIG. 9.—Iron foundry cupola.

P—charging platform.
AC—air chest.
T—Tuyeres.
SH—Slag hole.
TH—Tap hole for metal.
DB—Drop bottom.
S¹—Support for D.B.

level, in which case, as a large hearth is required to hold the metal, it is widened to its full diameter below. The air is supplied by a row of tuyeres near the bottom, or, in some American cupolas, by a centre tuyere, fig. 10.

Working the Cupola.—The cupola having been cleaned from the previous charge, a fire is lighted on the bed, and on this is laid a layer of coke, and then layers of coke and iron alternately. When the fire has burnt up the blast is put on, gently at first, then full, and the metal soon begins to melt.

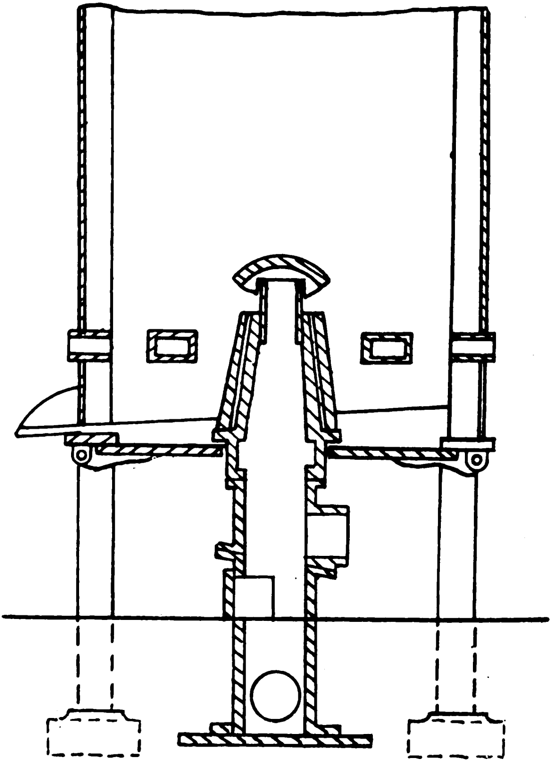

Fig. 10.—Centre blast cupola.

As the charge sinks more iron, flux, and fuel are added. When enough metal has accumulated in the hearth, it is tapped into a ladle for use, and when the run is over, and all the metal tapped out, the solid or pasty residue is removed through the breast opening, or by means of the drop bottom. Since the only object is to melt the metal, a very small quantity of fuel is required, the amount varying with the size of the cupola and the amount of iron melted during the run, from 1½ cwt. to 5 cwt. per ton of iron melted, the amount being, of course, largest with small cupolas which are worked only on short runs at considerable intervals, and least with large cupolas which run almost continuously.

Chemistry of the Cupola.—The amount of fuel used is small, and the amount of air supplied is large, so that the carbon is to a large extent burnt to carbon-dioxide. No doubt at the tuyere level a considerable quantity of carbon-monoxide is formed, owing to the high temperature; but as the gases rise they cool, and the carbon-monoxide is further oxidised to carbon-dioxide, so that ultimately the combustion is almost complete. Owing to this the atmosphere is not powerfully reducing, as in the iron-smelting blast furnace, but is rather oxidising, and thus changes are brought about in the character of the metal.

The pigs, as charged, always have sand adherent to them, and the coke used always leaves a considerable quantity of ash; so to prevent undue loss of metal by the formation of silicate iron, limestone is added as a flux, to the extent of 7 lb. to 10 lb. for each ton of iron melted.

The chemical changes which may take place in the cupola are of two kinds: (1) Constituents may be removed from the iron by oxidation, and (2) impurities may be taken up by the iron from the fuel.

As already mentioned, where iron is heated in an oxidising atmosphere, the silicon is the constituent to be first removed, passing into the slag as silicate of iron or lime. The removal of silicon is well marked, but, as a rule, the amount of carbon is scarcely, if at all, reduced. This may be because any carbon oxidised out may be replaced by that which may be taken up from the fuel.

The following table, by Mr. T. Turner, will show the nature of the changes which are produced by repeated meltings :—

No. of melting.	Total carbon.	Combined carbon.	Silicon.	Sulphur.	Manganese.	Phosphorus.
1	2·67	0·25	4·22	0·03	1·75	0·47
8	2·97	0·08	3·21	0·05	0·58	0·53
12	2·94	0·85	2·52	0·11	0·33	0·55
14	2·98	1·31	2·18	0·13	0·23	0·56
15	2·87	1·75	1·95	0·16	0·17	0·58
16	2·88	....	1·88	0·20	0·12	0·61
18	....	2·20	....	....	....	....

Though the carbon is not reduced, the removal of the silicon profoundly affects the condition in which the carbon will be present in the metal after solidification, for as the silicon falls the carbon tends to pass into the combined condition, and thus to whiten the iron.

Manganese, if present in any quantity, is soon removed by oxidation.

The only constituent likely to be taken up from the fuel, except perhaps a little carbon, is sulphur, and whether this will be absorbed or not will depend on circumstances. Whilst there is a considerable quantity of silicon present no sulphur is taken up, but as the silicon is reduced below 1·5 per cent sulphur passes into the iron, and thus helps to throw the carbon into the combined condition and whiten the metal, this absorption of sulphur being no doubt also facilitated by the removal of the manganese.

The tendency of melting is therefore to reduce the percentage of silicon and manganese, and increase that of sulphur; so that if the iron has been many times melted, it frequently becomes white.

Whether melting will improve an iron or not will obviously depend upon circumstances. If it contains more silicon than is good for the purpose for which it is required, melting will improve it; but if it only contains the right amount of silicon, then melting will deteriorate its quality. As most foundry pigs are high in silicon, they are usually improved by one or two meltings.

If the iron be very high in silicon, this may be reduced by melting the metal in a reverberating furnace, and keeping it in contact with air for some time, much more conveniently and cheaply than by repeated re-melting in the cupola.

If the iron tends to go white on melting, it may be readily brought back by the addition of silicon, in the form of silicon-iron. This will throw the carbon into the graphitic form, and thus make the iron grey. Aluminium has a similar but much more energetic action, so that a small quantity only is needed to keep the iron grey.

Many substances have been suggested for the removal of sulphur from pig iron, and for preventing its absorption from the coke. Since sulphur cannot exist in iron in any quantity in the presence of much silicon, the addition of silicon tends to remove sulphur. Manganese has also been suggested, and more recently ferro-sodium, an alloy of iron and sodium, has come into use.

The amount of change which will be produced by melting will depend on many circumstances. The more air is given, the more "cutting" will be the blast, and the more rapidly will oxidation take place. This will not only cause a more rapid whitening of the iron, and also a much greater loss of metal, by the formation of a ferrous-silicate slag; whilst on the other hand, if the blast be too "soft," the action will be too slow, and the resulting temperature will be too low.

Selection of Pig Iron.—A consideration of the changes which take place in the cupola renders the selection of a suitable pig for any purpose comparatively easy. Since the phosphorus and carbon are very little changed by the melting, the pig should contain about the amount of these which is required in the casting; and as the silicon will be reduced, the pig should contain a little more of this element than is best for the finished casting.

As a rule, founders use a mixture of various brands of pig iron for their castings. As no check is kept on the composition of the pig sent to the cupola, the use of mixtures certainly helps to prevent sudden variations, since it is not likely that all the brands used would vary in composition in the same direction, at the same time; but it has no other advantage. It would be far better if founders insisted on having a pig—or, if they prefer it, a mixture of pigs—of a composition to suit their work.

When white scrap has to be used, silicon-iron should be added. When the iron is too siliceous, it may be improved by the addition of malleable iron scrap. This will serve to dilute the silicon, whilst it will not have much effect on the carbon, because some of that element will be taken up from the fuel. Melting wrought iron or mild steel with pig iron in the cupola can only give cast iron, and under no circumstances are such mixtures entitled to be called cast steel.

Chill Casting.—When cast iron not too high in silicon or phosphorus is quickly cooled, solidification takes place so rapidly that the carbon has not time to separate as graphite, but remains in the combined condition, thus making the iron white. Advantage is taken of this in "chill casting," the mould for the part of the casting to be "chilled" is made of metal, so that the iron as it comes in contact with it is quickly solidified. Iron for chilling should not be too high in silicon or phosphorus, as these favour the separation of graphite, the former by its direct action, the latter by the increased fusibility it gives to the pig. Ordinary foundry pig is therefore quite unsuited for chill casting.

CASTING MILD STEEL.

The casting of mild steel presents much greater difficulties than that of cast iron, and these are of a different character.

The steel is almost always run direct from the furnace in which it is made into a ladle, and thence the moulds, and owing to its high melting point it must be cast at a very high temperature. The metal may either be cast into large ingots, which are subsequently to be rolled down into bars or other forms, or it may be cast in moulds, so as to produce an article of any required form direct, as, for instance, a railway car wheel.

Gases in Steel.—Steel during the process of manufacture is, in the Siemens process, kept for a long time in the molten condition in contact with air and the various products of combustion, whilst in the Bessemer process air is blown through the metal. Under these conditions a large quantity of gas is dissolved by the metal, and is in such a condition that a considerable portion is given out on solidification. This phenomena—*i.e.*, the absorption of gas by the liquid and its evolution on solidification—is also seen to some extent with cast iron, but the results are in that case far less serious, and therefore have not attracted so much attention.

Mould Gases.—The gas which is evolved during solidification in the mould may be called mould gas (Howe), and it is to this that the blowholes so common in steel castings are due. The composition of this gas may vary very much. It, however, almost always consists principally of nitrogen and hydrogen, with smaller quantities of carbon-monoxide and carbon-dioxide, and the volume of gas given off may be several times the volume of the metal.

When the ingot is poured into the mould, it may behave in one of several ways. It may solidify with little apparent escape of gas, and without the formation of blowholes, in which case the ingot will probably pipe—that is, the centre of the top will become depressed. This is specially the case with the harder steels. It may rise in the mould so that the portion of the ingot at the top may become honeycombed or porous, whilst the body of the casting is free from blowholes, or it may not only rise, but also may yield a casting containing blowholes. In some cases the escape of gas is so violent that the metal not only rises, but is scattered, the mould being sometimes partially emptied.

Formation of Blowholes.—The separation of gas commences immediately the metal begins to cool, and some gas will therefore be given off whilst it is in a perfectly liquid state. This will at once rise to the surface through the liquid mass and escape, and if in sufficient quantity may make the metal boil, or, if the escape be very rapid, scatter. If the metal be cast at a very high temperature, much gas may thus escape, and the iron may be very "wild." Gas so evolved escapes so readily that it is not likely to cause blowholes. The gas which is evolved when the metal is in a more or less pasty condition behaves differently. Being unable to escape through the iron, the gas by its pressure forms a cavity or blowhole in the still soft metal; and since the evolved gas must occupy space, there must be an increase of volume, and therefore the metal will rise. This rising may sometimes be so serious that, "even if the mould was originally but half filled, the top of the ingot may eventually protrude above that of the mould."*

In many cases, even where gas is separated from solution in a liquid, if it be in contact with a solid, it clings to the solid in bubbles instead of rising freely through the liquid, and by this action the solidification of the metal round the bubbles may form blowholes. The arrangement of the blowholes is invariably such as would be indicated by the separation of the gas in the manner above indicated. The escape of gas from the ingots continues long after they have solidified, gas having been obtained from ingots hours after casting and long after it must have been solid throughout. No doubt at the high temperature the metal is more or less porous to gas, so that any that is liberated can diffuse out.

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* Howe, "Metallurgy of Steel," page 126.

Boring Gases.—The whole of the gas is not evolved during solidification, and if the cold metal be bored under water, a further quantity may be obtained. The volume of gas obtained is almost always less than that of the metal, and consists mainly of hydrogen and nitrogen, with a smaller quantity of carbon-monoxide. On heating the solid metal in vacuo, the gas is completely evolved, and the volume of gas obtained in this way is often many times greater than that of the metal.

Prevention of Blowholes.—Many methods have been suggested for preventing the formation of blowholes, some chemical and some physical. Silicon is very frequently added. If a little ferro-silicon be thrown into a ladle of metal which is evolving gas, the metal at once quiets down and becomes tranquil, and the same result is obtained by the addition of a very small quantity of aluminium. It is not quite certain how these elements act, but the most satisfactory explanation is that they increase the solubility of the gas in the solidifying metal, and thus retain it in solution after solidification. Aluminium is now almost universally used for this purpose in the manufacture of mild steel castings.

The mechanical methods are of three kinds. (1) The metal may be agitated in the ladle, so as to release as much gas as possible. (2) The cooling may be made to take place very slowly, or the solidification at the surface may be retarded, so as to give as long a time as possible for the escape of the gas, and this is no doubt one of the results of closing the top of the mould with sand and a metal plate as soon as the steel has been run in, which is common in steelworks. (3) The metal may be cast under great pressure, pressure tending to retain the gas in solution, the pressure being obtained by means of a head of metal, by a hydraulic press, or even by the pressure of steam or another gas. In the Whitworth press the metal is cast under a pressure of up to twenty tons on the square inch of horizontal surface of the ingot.

Small Steel Castings.—Small castings of very mild steel are difficult to make, first on account of the high temperature at which the metal must be cast, and, second, because the amount of gas evolved makes the castings porous. If a small quantity—about ·1 per cent—of aluminium be added just before teeming, very fine castings can be made even of the mildest steel. This is the process by which the well-known mitis castings are made. The exact action of the aluminium is at present unknown.

Segregation.—Steel is not one substance of perfectly uniform composition. Whilst it is in the liquid condition all the constituents may be uniformly distributed, but as soon as solidification begins this ceases to be the case, for the elements present will at once commence to rearrange themselves so that compounds of the highest melting points will separate out first, others will follow, and the portions last solidified will be those which are most fusible. As most of the constituents in steel form with iron compounds which are more fusible than pure iron, it follows that the iron, or at anyrate portions containing smaller quantities of impurities, will solidfy first, and compounds with larger portions of these constituents will be the last to solidify. It might be expected that segregation would be most marked in high carbon steels, but this is by no means the case. The amount of segregation that takes place will vary very much according to the composition of the metal and the rate of cooling. In one case given by Campbell* the following results were obtained :—

	Carbon.	P.	S.	Si.
Top of ingot..........................	·941	·015	·012	·09
One-fourth way down the ingot	·990	·019	·010	·10
One-half way down the ingot	·991	·017	·012	·09
Three-quarter way down the ingot....	·982	·020	·010	·11
Bottom of ingot.......................	1·012	·016	·010	·11

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* "Structural Steel," page 189.

Crucible Cast Steel.—Steel made by the cementation process is melted in crucibles to form crucible cast steel. The method of casting steel was discovered by Huntsman, about 1760.

The bars of blister steel are broken up and melted in clay or graphite crucible, each holding about 80 lb. of metal. The metal is melted, and then is kept in a state of fusion for some time, the second stage being called the "killing," and the metal when ready for pouring is said to be "dead melted." If the metal be poured too soon, it rises, and is porous and full of blowholes; and if it be left too long in the fire, it yields very solid ingots, which, however, are hard and brittle. Great care must be taken that no coke falls into the crucible, or carbon and sulphur will be absorbed, and the metal will be spoilt.

The process may be divided into the two stages—melting and killing.

During the melting-down stage oxidation will always take place to a small extent, the carbon and silicon being somewhat reduced. The oxidation is brought about by the air which is present, and by the small quantity of oxide scale that always adheres to the bars.

During the killing stage no oxidation takes place. The metal, however, slowly absorbs silicon and carbon from the crucible, so that the amount of these elements increases. The object of the killing, as remarked above, is to enable the metal to give solid ingots. It is usually thought that this is brought about by the escape of the gas from the liquid metal. Howe thinks that the quieting is not so much due to the escape of gas as to the taking up of silicon from the crucible, this increasing the solvent power of the metal for the gases, and thus preventing their escape.

CHAPTER XI.

WORKING IRON AND STEEL.

MALLEABLE iron and mild steel are reduced from the bloom or ingot to the form required for use by hammering or rolling. Malleable iron is infusible—or rather, if it were melted, it would cease to be malleable iron; and mild steel is for many reasons better worked than cast direct. As a rule the working is carried out on the red-hot metal, but in some cases—as, for instance, wire drawing—it is completed at ordinary temperatures.

Effect of Hot Working.—It is quite evident that working cannot produce any chemical change in the metal except that which may be due to the re-arrangement of the elements present, but there is no doubt that it profoundly modifies the physical properties. Metal which has been well worked is stronger than that which has not been so treated, and therefore thin sheets or other articles which have been subjected to a considerable amount of work are stronger than those on which less work has been put; and this is true as much of mild steel, which has no fibre, as of malleable iron, in which a distinct fibre is developed. What is the exact nature of the change produced it is impossible to say.

Effect of Cold Working.—Wire drawing or cold rolling also greatly increases the tenacity of iron and steel, the extensibility decreasing and the hardness increasing at the same time, this being so marked that the metal soon becomes so hard that further work is impossible, and it has to be annealed. Here, again, the nature of the change is uncertain, but it has been suggested that the iron may pass into an allotropic, harder modification (δ iron), which may or may not be identical with the β iron, to which the hardness of steel is thought by many to be due.

Annealing.—Cold working renders the metal brittle, but this brittleness can be removed by heating to redness, and cooling slowly or annealing. The *rationale* of annealing seems to be, that as the metal reaches the plastic condition the molecules have a certain amount of free play, so that they can re-arrange themselves, and thus relieve the stress set up by the work. This re-arrangement may, of course, involve changes in the way in which the constituents are united, or in the allotropic condition of the metal itself. The annealing does not remove the whole of the effects of work, and, therefore, in the case of hot working it is the whole work which has been put on the piece, and not only that which is put on during the last working, that affects the quality.

Annealed steel is softer than natural steel—*i.e.*, in the condition which it leaves the mill—the difference depending somewhat on the temperature at which the working was finished. The tensile strength is also decreased, as is the elastic limit, whilst the elongation is only slightly increased.

Some authorities have contended that the method of annealing has a very important effect, and that the metal is deteriorated if heated by an open flame, whilst it is improved if heated in a closed vessel. This does not seem to be always the case, but no doubt a flame is subject to greater variation than the heat in a muffle or box, and therefore other changes besides true annealing may take place.

Welding.—The property of welding is closely allied to that of plasticity. When the metal becomes so plastic that the molecules can be forced so near one another as to come within the range of molecular attraction, this will come into play, and the two pieces will be united. The power of welding is eminently characteristic of wrought iron and mild steel; the former, as already remarked, being built up by the welding together under the hammer, and in the rolls, of separate portions of nearly pure iron.

Any constituents which tend to harden the metal, and decrease the freedom of motion of the molecules, tend also to hinder welding. This influence may be shown in extreme cases by the impossibility of welding at all, and in others by the unsoundness of the weld.

The constituents which most interfere with welding are sulphur and carbon, then silicon, arsenic, and copper. The effect of most of these has been much disputed, and at present it is impossible to say what would be the effect of each one present by itself, or the exact limit for them which is allowable in metal to be welded. As a rule it may be stated that the purer the metal, the better it will weld.

Wrought iron and mild steel of similar composition weld equally well, and even steel containing ·15 per cent of carbon may be welded with ease. It must be remembered, however, that the best temperature for welding will depend on the composition of the metal; the purer it is, the higher being the temperature at which it can be welded, and the greater the range of temperature during which welding is possible. It is therefore, as a rule, much easier to weld two pieces of similar metal, than it is two pieces of widely different composition, and in the latter case it may be impossible to secure a good weld, even though both metals would weld readily enough to metal of like composition.

Conditions of a Good Weld.—In order to secure a good weld it is essential (1) that the metal should be at a suitable temperature, and (2) that the surfaces in contact should be absolutely clean. This latter condition can be secured by the use of suitable fluxes. When the pieces to be welded are brought together at a high temperature, the air will always oxidise the hot surfaces to some extent, and the oxide thus formed, being solid, would prevent a good weld being made. A flux must therefore be added to dissolve or liquefy this oxide, and when the weld is being made the liquid will squeeze out. For welding steel borax is very frequently used; this melts at a very moderate temperature and dissolves, and this dissolves and carries away the oxide. For ordinary work sand is used. Sand is nearly pure silica, which itself is infusible, but in contact with oxide of iron forms a readily fusible ferrous silicate, which can be squeezed out. When welds are being made at or near a white heat, no flux is necessary, as the oxide itself melts at that temperature. Wrought iron and very mild steel can be welded quite readily without any flux.

Other fluxes have been suggested, and are sometimes used, such as clay, or mixtures of clay and sand, potassium, ferroganide, &c., but none of these have come largely into use.

Electric Welding.—Electricity may be used as the source of heat for welding, and two methods of carrying this out are in use.

The Thomson process depends on the evolution of heat when an electric current passes through a conductor. The heat evolved depends upon the resistance of the conductor and the strength of the current. If two iron wires, for instance, be brought together, each connected with one of the poles of a suitable dynamo, the current will rapidly heat them to welding temperature, and if the ends be kept in contact a weld will be made. Wires or tubes can be welded, end on, by this process, and brass or other metal can be welded to iron. Only comparatively small articles can be welded, for the resistance, and therefore the heating power of the current, diminishes in proportion to the area of the conductor through which the current has to travel. According to Howe, the largest articles welded by this process are 2·5 in. iron bars, but no doubt larger sizes could be worked. To weld a 2 in. bar, Howe gives the current required as being 20,000 amperes, to generate which 40 horse power would be required.

The Bernados process is based on the use of the electric arc. Chips or small pieces of metal are placed between the pieces to be united, and these are made the negative pole for a powerful current, the positive pole being a carbon rod, which is moved about into the required position. The heat of the arc melts the chips, and thus solders the two pieces together.

Effect of Welding.—The weld, whether made in the ordinary way or by electricity, is rarely, if ever, as strong as the metal itself; the hammering in the ordinary method tends to give an increased strength, which is lacking when the welding is conducted by the electric processes, as in that case no work is put on the metal.

INFLUENCE OF CERTAIN ELEMENTS ON IRON AND STEEL.

Special Steels.—The influence of the ordinary constituents on iron has been already discussed. Within the last few years special alloys containing metals not commonly found in steel have been introduced, and as very important properties are claimed for some of these, a brief consideration of their character is necessary.

Manganese Steel.—By the addition of an excess of ferro-manganese to the mild steel in the ladle alloys can be obtained containing up to 20 per cent of manganese. These alloys—manganese steels as they are called—have important properties, which have led to their use for special purposes. Steels containing 14 or 15 per cent of manganese melt to a very fluid liquid, and make good castings, free from blowholes, the casting breaking with a highly crystallised fracture. The metal is hardly, if at all, weldable, and in the natural condition is brittle, but by being heated to whiteness and quenched it becomes very hard, tough, and strong; so hard, indeed, that it is almost impossible to machine it. The tensile strength of a 14 per cent steel—which is about the maximum strength and toughness—was in one case found to be about 36 tons in the natural condition, and this was increased to about 67 tons by quenching, and reduced somewhat by annealing. The elongation of the natural bar was little, but on the hardened bar it became about 44 per cent on an 8 in. test piece, and when annealed about 14 per cent. This combination of strength and elongation is stated by Howe to be "far greater than any other I have met with." Forging destroys the crystallisation of the metal and increases the toughness, but cold work makes it very brittle, the toughness being restored by heating and quenching. The elastic limit of the metal is low, and thus a permanent set is given by a moderate load—under 16 tons in the case of a metal giving an ultimate strength of 56 tons; it is therefore brittle to bending tests. Manganese steel is almost unmagnetisable, and on cooling it shows no point of recalescence. Manganese steel has not come largely into use, but it will no doubt be useful in cases where hardness, toughness, or low magnetic permeability may be of advantage, but its use is greatly hampered by the extreme difficulty of machining, and apparently also of forging it.

Nickel Steel.—This is an iron nickel alloy containing carbon, made by adding metallic nickel to molten mild steel; the metal pours well, and yields solid castings. It forges readily, but cannot be welded, when the nickel is much above 1 per cent. The metal breaks with a fibrous fracture, and it is hard and tough, the hardness increasing up to about 20 per cent of nickel, but is then less hard than manganese steel. The tensile strength is increased greatly by forging, the elongation is considerable, and the elastic limit is high.

Nickel steel is gradually coming into use for armour plates and other purposes where hardness and strength are required. The high cost of nickel, however, makes it expensive.

Chrome Steel.—Chrome steel is made by adding ferro-chrome to the molten mild steel, or by melting steel and ferro-chrome in crucibles, in either case the loss of chromium by oxidation being considerable; chrome steel does not cast well, and the metal, unless very low in chrome, is difficult to work and weld. When quenched it is extremely hard, and also has a great power of resisting shock. The amount of chromium present is about 2 per cent or less.

Silicon Steel.—This is made by melting steel and ferro-silicon in crucibles. With 1 per cent of silicon it can be forged, and is fairly hard.

Tungsten Steel.—This steel is excessively hard, and therefore makes very durable tools for cutting hard metals. The amount of tungsten present is about 2 per cent. It is usually of very fine grain.

Many other alloys have been tried or suggested, but those mentioned above are the only ones which seem to have the promise of special usefulness. With some of them, more experimental data is needed before it is possible to decide the conditions under which they can be used. The student or engineer who desires further information, must refer to the original papers, in which the full details of experiments will be found.

CHAPTER XII.

Corrosion and Protection of Iron and Steel.

The action of air, oxygen, and moisture on iron has already been briefly considered, and it was pointed out that rusting was due to the combined action of moisture, usually condensing on the surface of the metal, carbon-dioxide, and oxygen, and only took place when all three acted together; the result being the formation of a brown ferric hydrate, or rust.

Iron Rust.—Iron rust is chiefly hydrated ferric oxide, but it always contains some magnetic oxide, the quantity sometimes being very considerable; two analyses of rust from the Conway Bridge and from Llangollen by the late Professor F. Crace Calvert may be quoted in illustration. The ferrous oxide was in all probability not present as such, but combined with ferric oxide to form magnetic oxide:—

	Conway Bridge.	Llangollen.
Ferric oxide	93·094	92·900
Ferrous oxide	5·810	6·177
Ferrous carbonate	·900	·617
Silica	·196	·121
Ammonia	Trace	Trace
Calcium carbonate	—	·295

Assuming the ferrous oxide to be present as magnetic oxide, the figures would be—

Ferric oxide	80·322	79·174
Magnetic oxide	18·582	19·903

These analyses, of course, represent the dry oxides ; the rust as produced would contain in addition a large quantity of water. The rust is very bulky, Bauerman stating that malleable iron produces about ten times its own volume of iron rust.

Action of Water.—When iron is exposed to the action of natural waters, such as river or sea water, it is more or less corroded. All waters contain carbon-dioxide and oxygen in solution, and sea water, in addition, contains various salts. These agents produce rusting, and in sea water the metal may be dissolved away without the formation of visible rust. Sea water has a much greater corrosive action than fresh water, usually in the ratio of from 6 : 1 to 9 : 1, though it may be much higher or lower. The action is, however, very irregular, and varies much with varying circumstances. The presence of sewage matter greatly increases the corrosive action, probably on account of the presence of sulphides. As a rule iron corrodes more readily in sea water than in air, though this is not by any means always the case, as the action of the atmosphere depends so largely on its hygrometric condition, and especially on the water deposited as dew or otherwise on the metal surface.

Causes of Rusting.—The production of rust by the direct chemical action of air, moisture, and carbon-dioxide has been discussed above. There are, however, many causes which tend to retard or accelerate the action, the principal accelerating agent being probably electric action set up by contact of the metal with other substances. When two substances are brought in contact an electric disturbance is set up, and if they be conductors, the one becomes electro-positive and the other electro-negative. In presence of a solution through which the current can pass chemical action at once begins, and the electro-positive element is attacked. The chemical reaction depends on the bodies in contact, and the amount of action depends largely on the conducting power of the liquid. The increased corrosion which takes place in sea water is probably to a large extent due to it being a much better conductor on account of the large amount of salts in solution.

The substances which are likely to come in contact with iron are mostly electro-negative to it, and thus tend to cause corrosion—lead, copper, carbon, and iron scale, or even iron rust, any one of which will determine rapid corrosion. If a piece of iron or steel, on the surface of which are specs of scale, be immersed in water, or exposed to the air, it will rapidly pit, spots of rust being formed round each particle of scale. Similarly, a little rust, once formed, will continue to increase rapidly by the same action. When iron railings are fixed into stone by means of lead, the iron is rapidly corroded away, and articles coated with copper, tin, or magnetic oxide of iron, for preservation, rust very rapidly when the protecting film is broken through. On the other hand, zinc is electro-positive to iron, so that it acts as a preservative, and is oxidised before the iron. Iron oxidises very readily in railway tunnels and similar positions. This is no doubt largely due to the moisture and the acid fumes from the combustion of the fuel, but it may also be due—to some extent, at least—to electric action set up by carbon deposited from the smoke.

Relative Corrosion of Different Forms of Iron.—This is a question which has been very fully discussed of late years, and on which innumerable experiments have been made. Unfortunately there is no accord between the results obtained by different experimenters, or between these and the facts observed in practice. It must be remembered, also, that the relative corrosion may differ very much under different conditions.

Under atmospheric conditions, it seems that cast iron is least easily acted on provided it be left with its skin on, but that if this be removed, it rusts just as rapidly as other forms of iron. Wrought iron is usually stated to corrode less easily than mild steel, and common wrought iron less readily than the best; but these conclusions have never been demonstrated, and are probably not correct. In sea water and in fresh water there seems to be little, if any, difference between iron and steel, and the evidence is now conclusive that in actual practice, whether for boiler or ship plates, steel does not corrode any more rapidly than iron.

The influence of impurities when present in small quantities seems to be slight, but when present in considerable quantity they may either accelerate or retard corrosion. Ferro-manganese, for instance, and to a less extent manganese steel, rusts very rapidly, whilst silicon iron, chrome iron, and nickel steel resist the corrosive action of air and moisture far more powerfully than ordinary steel.

Action of Acids.—The action of dilute acids is of some importance, as in many operations in the arts iron vessels have to be used. All ordinary varieties of iron and steel are readily acted on, white cast iron less than any other form; but iron containing a little chromium, silicon, or phoshorus resists acids much more strongly. Pans of phosphoric iron are used for the solution of silver in sulphuric acid, in parting gold and silver.

Removal of Rust.—Once rust has formed, its removal is extremely difficult. It may be rubbed or scraped off, but the surface of the metal is always left rough. The sand blast might be efficacious for use on structures where other means are not easily applied. For small articles pickling in alkali and then polishing has been used, and Vosmaer suggests the use of a solution of stannous chloride (protochloride of tin), in which the rusted article is to be soaked for twelve to twenty-four hours.

Protection from Rust.—Many methods of protecting iron

from rusting have been suggested, all consisting in coating the metal with a layer of some protecting material.

1. **Coating with other metals.**
2. **Coating with oxide films.**
3. **Coating with paints or varnishes.**
4. **Enamelling.**

COATING WITH OTHER METALS.

These methods are very largely used, the principal metals employed being zinc and tin, and to a smaller extent nickel, copper, or brass.

Galvanising.—The operation of coating iron with zinc is—very absurdly—called galvanising The usual method of "galvanising" is to pickle the article to be coated by dipping it in hydrochloric acid, so as to remove all scale, and then to pass it into molten zinc. Sheets are passed through the bath; other articles are dipped and left in for a short time. The molten zinc alloys with the iron, and forms a uniform protective coating. The articles are usually galvanised after they are completed, and small articles such as nails, &c., are put into a bag of wire netting and immersed. Quite recently galvanising by the deposition of zinc on the articles by an electric current has been introduced, and is now used to a considerable extent.

Galvanised iron articles are very largely used for many purposes, household utensils, large water tanks, &c., the size of the article being limited only by the size of the vessel of zinc available for dipping it. Galvanised sheets of corrugated iron are largely used for the erection of temporary buildings all over the world.

Zinc is an excellent protective agent under some conditions. Being electro-positive to iron, it has no tendency to produce rust, even should some of the coating be scratched off or worn away. It is slowly acted on by air, but the oxide formed is insoluble, so that the action soon ceases. Both the metal and the oxide being very soluble in acids, it does not stand well in towns, or in situations where it is exposed to acid fumes.

Tinning.—Tin plate, which is sheet iron—or rather now almost always thin sheets of Bessemer steel—coated with tin, is very largely used, especially for the manufacture of small articles for household and other purposes. The sheets are tinned, and the articles made up from the "tin plates," instead of being dipped after manufacture, as in galvanising. The plates are tinned by being passed through a bath of molten tin, usually by mechanical means ; the tin alloys with the iron, and thus forms a strongly adherent coating.

Tin resists atmospheric oxidation, but when the coating becomes broken through the iron rusts very rapidly. Tin plate is rarely used, except for comparatively small articles. The interior of iron water pipes is occasionally tinned.

Copper and Nickel.—These metals are only occasionally used, and for small articles. They are always thrown down from solution by an electric current. Electro-deposited metals are usually very porous, and allow air and moisture to penetrate through them. They are therefore very inefficient as protectors from corrosion, oxidation frequently going on underneath, and ultimately pushing off the layer of metal. With copper this difficulty may be overcome by burnishing under considerable pressure, but nickel is too hard to allow of this.

COATING WITH OXIDE FILMS.

The oxide used is always magnetic oxide, Fe_3O_4. The method was first introduced by Professor Barff, in 1876, and the next year Messrs. Bower patented a somewhat similar process. In the Barff process the articles were heated in a muffle to about 600 deg. Fah., and then steam superheated to about 1,100 deg. Fah. was blown in ; in the Bower process the articles were first heated in the products of combustion of coal, mixed with excess of air, and then in carbon-monoxide. The process as now carried on is a combination of the two forms, and is usually called the Bower-Barff process. The articles are heated to the required temperature in a closed chamber by the flame of ordinary producer gas; the gas is then turned off, and superheated steam is sent into the chamber for one or two hours.

The apparatus used is shown in cross-section in fig. 11, which will give an idea of the arrangement, though it is impossible to show the various valves in one view. The operation consists of two stages. During the first the articles are being heated, and during the second they are being oxidised

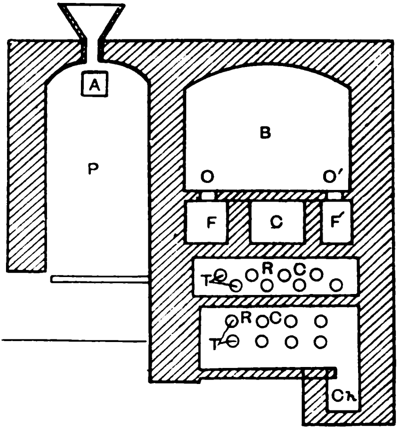

FIG. 11.

with steam. Gas is generated in the producer P, which is of the ordinary bar-bottom type, passes away by the opening A, and is brought by a suitable passage to one end of the combustion chamber C, into which air is also admitted, so that the gas is burned; the products of combustion pass from the other end of the chamber C into the flue F, thence by the opening O into the large chamber B, in which the articles to be oxidised are placed, and thence by a flue, not shown, to the regenerative chambers R C, which are crossed by a large number of tubes T, which thus become intensely heated, and away to the chimney by the flue C*h*. When the chamber and its contents are hot enough, the gas supply is stopped by means of a damper, and steam is blown through the tubes T, in which it becomes strongly superheated, to the flue F^1, thence by the openings O^1 to the chamber B, and finally through the chamber R C away to the chimney. When oxidation has been going on sufficiently long the articles are drawn, and the chamber is heated up again ready for the next charge.

Cast-iron articles are heated to a temperature of about 900 deg. Fah., whilst for wrought iron or steel a much higher temperature is used. The film of oxide deposited is dead black, smooth and coherent, and forms a perfect protection against corrosion whilst it remains unbroken. The articles must, of course, be coated after they are completed, as otherwise the film of oxide would be broken by the work, and, then being negative to the iron, would cause rapid corrosion. The process is principally used for articles of small size.

COATING WITH PAINTS OR VARNISHES.

This is the almost universal method of protecting iron and steel, especially in structures, from atmospheric corrosion.

Paints.—Painting is the most general method of protecting iron from corrosion. In many cases it is the only one possible, and on the whole, if well done, is fairly satisfactory.

Paints are composed of a colouring agent or pigment—a base to give body or covering power—and an oil.

The oil used is almost always boiled linseed oil. On exposure to the air this undergoes oxidation, forming a more or less transparent somewhat elastic body, which is insoluble in water, and is not acted on by atmospheric influences. Very frequently "driers," which are substances which facilitate the hardening, are also added.

The colouring matter will depend on taste, and the base is only necessary when the pigment is deficient in covering power. Of all the pigments, the most suitable when the paint is required as a preservative is red oxide of iron. This is very stable, has no action on the metal, and has good body, The oxide is usually artificially prepared by heating ferrous sulphate, but the natural oxide is occasionally used.

Red lead, for red paint, and white lead, for white, and the latter, mixed with pigments, for other colours, have been largely used, though they are much less popular than they were in cases where the object is protection from rust. They are readily dissolved by water containing carbon-dioxide, sulphurous acid, &c., and they are rapidly discoloured by many sulphur compounds, especially sulphuretted hydrogen. Where durability is required, the white lead is often replaced by zinc oxide, or mixtures of zinc oxide or sulphide, and barium sulphate. Barium sulphate and calcium carbonate are often used as bases to give body; they are both very objectionable, the latter especially, as it is readily acted on by moisture and carbon-dioxide, and dissolved away.

Great care should be taken that all the materials used for paints are of good quality, and that the paint contains no material likely to be destroyed by atmospheric influences, otherwise it is impossible that it should form a durable protective coating. As a rule, very little attention is paid by engineers to the chemical character of the constituents of a paint, provided it has the right colour, and covers well, which, after all, are matters of secondary importance. The surface of the metal should be quite clean and free from scale when the paint is applied, or it cannot be durable.

Bituminous Varnishes.—These have been largely used. The simplest is a layer of coal tar, which forms an excellent preservative. The late Dr. Angus Smith proposed a method known by his name, which has been largely used for cast-iron articles, especially iron gas and water pipes. The articles are cleaned, and then dipped into a hot mixture of pitch and oil, at a temperature of about 400 deg. Fah., in which they are left for fifteen or twenty minutes. This preservative acts well, especially in damp situations.

For the protection of submarine cables, a mixture of 65 parts mineral pitch, 30 parts silica, and 5 parts tar has been used.

Applying Paints and Varnishes.—Mr. Lindsay says: "In the case of cast iron, castings should immediately, on being removed from the mould, and while warm, be cleaned and dressed, and then receive a coat of, or be dipped in, hot boiled linseed oil." "Before leaving the workshop the casting should receive a priming or first coat of pure red oxide of iron paint, and after erection two coats of protective paint, finishing with a layer of copal varnish."

"In the case of iron and steel, the most effective method of preparing and coating them would be to remove the outer skin of unstable magnetic oxide and incipient rust, heat the parts to about 450 deg. Fah., dip them in a bath of hot linseed oil, and then give them a 'priming' coat of red oxide of iron paint, after manipulation in the workshop, and before leaving it. The oxide may be removed by dipping the parts in dilute acid, and afterwards washing all traces of the acid away. When erected, the work should be coated as described for cast-iron work."*

Enamelling.—This is the most recent and the best method of protecting iron surfaces where it is applicable, but it can only be used for comparatively small articles, and the coating must be applied after the article is finished, as working would break away the enamel. It is very largely used for small household articles, baths, and iron notice plates. The enamels used are much of the nature of ordinary pottery glazes, but they should contain but little lead. Two methods are used: The first is to cover the metal with a transparent glaze, on which an opaque enamel is afterwards put. A frit is prepared by fusing together such materials as felspar and borax. This is powdered, mixed with china clay, felspar, and magnesium carbonate, and the whole made into a paste with water, and spread over the iron to be

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* "The Corrosion and Preservation of Iron and Steel."

enamelled. A fusible opaque glaze, made of such materials as quartz, borax, tin oxide, and carbonate of soda, is sprinkled over this, and the article is then fired at a high temperature in a muffle furnace. The second method is to put an opaque porcelain body on the metal. This is fired, drawn from the muffle, sprinkled with a transparent glaze, and again fired.

Enamelling is largely carried out, but each works has its own mixtures and methods, which are usually kept secret. The enamel is often easily chipped off, and the exposed surfaces rapidly rust, causing further breaking away, but while the layer of enamel remains intact the protection is perfect.

Miscellaneous Preservatives.—Various methods are used for the protection of small and ornamental ironwork, such as japanning, which is simply covering with a varnish and heating in an oven. This is largely used for bedsteads, bicycle fittings, grate fronts, &c.—covering with ordinary gum varnishes, coating with copper, brass, or nickel by electro-deposition, as in ornamental stove fronts. The commonest method of preserving bright ironwork for a short time is to rub it over with a layer of oil, vaseline, or similar substance. Very small articles such as coils of fine wire may be preserved by covering with dry lime; this absorbs both the moisture and the carbon-dioxide from the air, so that rusting cannot take place.

CHAPTER XIII.

MICRO-STRUCTURE OF IRON AND STEEL.

THE application of the microscope to the examination of iron and steel was first proposed by Dr. Sorby, who, as far back as 1864, published the first of his invaluable papers on the subject. Since that time a large amount of work has been done by various observers, methods have been perfected, and much valuable information has been obtained.

Method of Working.—It is impossible to grind a piece of iron so thin that it will become translucent, and thus allow of examination by transmitted light. Therefore, the methods used for the microscopic examination of rocks are not applicable, and the sections must be examined as opaque objects by reflected light. With high powers the objective has to be so near the object itself that all light would be cut off; therefore special reflectors are arranged in the microscopic tube to throw the light down on the subject being examined.

A small piece of metal is cut off, and by grinding or filing reduced to suitable size and shape. The surface to be examined is then polished carefully, first with emery of different degrees of fineness, and then with the very finest rouge. If the constituents are of very different degrees of hardness, the structure may be brought out to some extent by finishing the polishing with rouge on a soft surface, but usually the surface to be examined is etched with acid, washed, and dried. The less readily attacked constituents are left standing in slight relief, and the structure is thus rendered visible.

Structure of Iron and Steel.—When examined under the microscope, iron and steel are found to be by no means homogeneous, but to be made up of crystalline material, more or less irregularly arranged; these having separated either during solidification or whilst the metal was sufficiently plastic to allow of molecular change, the whole structure being much like that of an igneous rock which has solidified from fusion. This heterogeneity is hardly surprising, for in some irons—gray cast irons, for example—some of the constituents are in large enough portions to be seen without a microscope.

Seven constituents have been made out as being regularly present in one or other of the varieties of iron and steel, and there are others which are more rarely found.

1. *Ferrite.*—This is pure, or nearly pure, iron. It may be present in large quantity, as in malleable iron or mild steel, or it may be entirely absent. It forms distinct crystals, the

separating planes of which are made visible by the etching. The sections of these are of irregular form, as the crystals have not been free to develop, but have pressed upon one another, and also because of stresses set up during cooling. The crystals belong to the cubic system.

2. *Cementite.*—This is so called because it was first detected in steel made by the cementation process. It is a very hard substance, and occurs diffused through the iron in very small particles, or in plates or granules, though sometimes it is aggregated into larger masses. It is the normal carbide, Fe_3C, though the iron may perhaps be partially replaced by other metals.

3. *Pearlyte.*—This is the most striking object in many micro-sections of steel, sometimes causing a beautiful play of colours, with a pearly lustre, whence it was called by Sorby the pearly constituent. It occurs in minute plates, sometimes straight, sometimes wavy, varying much in thickness and distance apart, each being made up of alternate layers of cementite and ferrite.

4. *Hardentite.*—This substance, which makes up almost the whole mass of hardened steel, and is absent from annealed steel, consists of very minute crystals. On etching it becomes covered with a dark-coloured carbonaceous deposit. According to Osmond's theory, this is β iron changed with dissolved carbon, but Arnold contends that it is a definite carbide, having the formula $Fe_{24}C$, which contains ·89 per cent of carbon. It is intensely hard, and is capable of permanent magnetisation.

5. *Sorbite.*—Deep blue and deep red crystals which were detected by Sorby (after whom they are named) in many cast irons, and which have been found nowhere else; according to Sorby, they are probably either silicon or nitrate of titanium.

6. *Graphite.*—This only occurs well developed in grey cast irons, where it is present in characteristically curved plates. In steel it occurs in minute dots or elongated fragments,

showing no plate-like structure, and which have been called "temper carbon."

7. *Slag.*—This is found in those varieties of iron which have been aggregated from pasty masses without fusion, such as wrought iron. It occurs in irregular masses, which at high temperatures "probably tend to draw together, for it has been found in perfect spheres within half-inch crystals of iron, probably ferrite."

Pure Iron.—The purest iron attainable is found to have a distinctly crystalline structure, and to be made up almost entirely of ferrite, with only here and there small quantities of other constituents in the places between the crystals.

Wrought Iron.—In wrought iron the mass of the material is ferrite, which occurs in distinct crystals or grains, with a small quantity of diffused carbide, and here and there black patches of slag. When the bar is rolled the structure of the iron itself undergoes very little change, but the slag portions become elongated into threads in the direction of rolling. At a red heat the iron crystals seem capable of re-arranging themselves, so that whenever iron is heated to welding temperature it assumes its normal structure. When iron is rolled cold, so that the metal is not free to crystallise, the crystals are drawn out and the structure is completely broken down.

Mild Steel.—Very mild steel shows a structure very like that of pure iron, through which are scattered black spots of normal carbide. When the steel is annealed the crystal structure becomes larger and more distinct, and the carbide gathers together into larger patches of pearlite, which are surrounded by a layer of the crystallised carbide. As the percentage of carbon increases the areas of carbide become much larger, and when the carbon reaches about ·9 per cent, the whole mass consists of iron containing disseminated carbide, the two not being separated into distinct areas. When such a steel is annealed the section is composed entirely of the pearly constituent. When the carbon is higher still the unannealed steel shows an intimate mixture of iron and carbide broken up by meshes of carbide, which become more marked as the percentage of carbon increases, and the annealed specimens show pearlyte surrounded by carbide, with patches of graphite, each of which is surrounded by a small patch of iron.

Hardened steels differ very much in structure from the same steel annealed. When the carbon is low they show two distinct constituents, free iron and a hard amorphous or very finely-crystalline substance ($Fe_{24}C$, Arnold). When the percentage of carbon is ·89 per cent, the structure is almost uniform, consisting entirely of the hard, finely-crystalline substance, and when the carbon is higher still the structure is much the same, with the addition of dividing lines of normal carbide.

Grey Cast Iron.—In this the most striking feature is the innumerable small curved plates of graphite embedded in a ground mass of varying constituents, sometimes containing considerable quantity of ferrite, especially in very grey irons, pearlite, and a metallic residue full of foreign matter.

Cast iron is a very complex material, and evidently the graphite crystallises out first, then ferrite and pearlite, and the metallic residue is the material rejected from the various crystallisations, and solidifies last.

White Cast Iron.—This is largely made up of pearlite, crystallised in feathery crystals, graphite is absent, or present only in small irregularly scattered flakes, and the residue is a hard ground mass from which the pearlyte has crystallised.

The miscroscopic examination of iron and steel is of the utmost importance, not only as revealing the nature of the metal, but also for practical purposes. Some of the problems on which chemical analysis has been able to shed very little light are being rapidly elucidated by means of the microscope, and many uncertainties are being cleared away. The engineer or student who desires a real knowledge of iron and steel must, at anyrate, make himself familiar with the literature of micro-metallography, which is now becoming very extensive, and he should also learn something of the actual methods of work, and see for himself the appearance of the different varieties of metal under the microscope. No illustrations have been given, because any that were possible would not add anything to the knowledge of the student, which on such a subject, to be of real use, must be acquired at first hand.

CHAPTER XIV.

COPPER.

COPPER is, next to iron, the most important metal with which the engineer has to deal, though it falls enormously behind iron in usefulness, having comparatively few applications.

Physical Properties.—Copper has a characteristic copper-red colour and metallic lustre. It takes a high polish, but does not retain it on exposure to the air. Its specific gravity is about 8·92, but varying numbers have been given by different observers. Its melting point is about 1,121 deg. Cen. (2,050 deg. Fah.), standing, therefore, as to fusibility between silver and gold. It is somewhat volatile at a white heat, but to such a small extent that it may be classed among the fixed or non-volatile metals. Its specific heat is 0·09515, and its coefficient of linear expansion is ·00019188.

Copper is very malleable and ductile both at ordinary temperatures and at a red heat, and therefore can be worked either hot or cold, but at a temperature just below its melting point it becomes extremely brittle. The most striking property of copper is its high conductivity for heat and for electricity, and one of its important uses is the manufacture of conductors for electric purposes. For this purpose the metal must be very pure, as minute quantities of impurities impair the conductivity very much.

Chemical Properties.—Copper is stable in dry air or oxygen; exposed to moist air in presence of carbon-dioxide, it becomes covered with a green coating of basic carbonate, often, though improperly, called verdigris.* Exposed to air and seawater, it becomes covered with a film of oxychloride, and a similar body is formed when the metal is heated in presence of hydrochloric acid and oxygen, as when the products of combustion from coals containing sodium-chloride are passed through copper or brass boiler tubes. At a red heat it combines readily with oxygen, forming "copper scale," which is a mixture of the two oxides, Cu_2O, the red oxide, and CuO, the black oxide. Finely-divided copper—*e.g.*, copper precipitate—in presence of air and moisture, oxidises rapidly, considerable heat being evolved, and the resulting oxide being mainly CuO.

At a red heat copper combines readily with sulphur, phosphorus, arsenic, &c., forming fusible compounds, and molten copper will dissolve a considerable quantity of these compounds, and also of cuprous oxide, Cu_2O. Dilute sulphuric or hydrochloric acids have little action on copper in the absence of air, but in the presence of air the latter slowly dissolves on it. Hot strong sulphuric acid dissolves it readily, forming copper sulphate, and evolving sulphur dioxide, $Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$. Nitric acid dissolves it readily, $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + N_2O_2$. Most organic acids attack copper, especially in presence of air; hence it is quite unsuited for the manufacture of cooking utensils.

Copper forms two series of salts: The cupric, such as $CuCl_2$; and the cuprous, such as Cu_2Cl_2. The former are the stable salts at ordinary temperatures; they are mostly soluble, and give blue or green solutions. The latter are more stable at high temperatures; they are mostly insoluble, or are converted by solvents into cupric salts and metallic copper. Many cuprous compounds occur in nature. Cuprous chloride, Cu_2Cl_2, is a nearly white body, closely resembling silver chloride, insoluble in water and

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* Verdigris is a basic acetate of copper.

dilute acids, but soluble in strong hydrochloric acid, yielding a dark-green solution, from which the salt is precipitated on dilution. A solution of cupric chloride dissolves copper with the formation of cuprous chloride, $CuCl_2 + Cu = Cu_2Cl_2$.

SOURCES OF COPPER.

Copper ores are widely distributed.

Native Copper occurs in various parts of the world, and is largely worked in the Lake Superior copper region, yielding a very pure copper. The yield of this district is about 70,000 tons annually.

Oxidised Copper Ores, such as cuprite, Cu_2O, malachite, $CuCO_3$, CuO, H_2O, and azurite, $2CuCO_3$, CuO, H_2O, occur in various districts, and have been extensively worked. They are, however, almost always the products of the surface oxidation of underlying sulphide ores, and therefore are soon exhausted. Silicates and oxy-chlorides are also known, and have been worked.

Sulphide Ores.—These are the most abundant ores of copper, and those which are generally worked. The more important are redruthite (copper glance), Cu_2S; copper pyrites, $CuFeS_2$, the most abundant ore, characterised by its fine yellow colour and metallic lustre, frequently with an iridescent tarnish, and containing, when pure, 34·57 per cent of copper; and bornite (erubesite), Cu_3FeS_3.

There are also many complex ores, containing sulphide of copper and sulphides of arsenic and antimony. These are rarely worked for copper only, but as they often carry gold and silver, they are worked for these metals, and the copper is also obtained.

The sulphide ores are usually mixed with varying quantities of iron pyrites, and as, owing to the similarity of specific gravity, this cannot be separated by dressing; separation must take place during smelting.

Iron pyrites, which is burnt for the manufacture of sulphuric acid, often carries 2 to 4 per cent of copper, and the residue, or burnt ore, is then worth working for that metal.

METALLURGY OF COPPER.

Native copper needs only refining. Oxidised ores may be smelted in blast furnaces with coke, but as these do not occur largely, almost all smelting processes are arranged for the treatment of sulphides, oxidised ores, if available, being added at various stages of the process.

THE WELSH PROCESS.

This is the process on which all other processes are based, and it may be taken as a type. It is a complex process, consisting of six or more distinct operations, in which the copper is gradually concentrated in a smaller and smaller quantity of material, and ultimately separated and refined. The reactions on which the process is based are as follow:—

1. When sulphides are roasted, with free access of air, the sulphur is removed as sulphur dioxide, and oxides are left; *e.g.*,

$$Cu_2S + 4O = 2CuO + SO_2$$
$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2.$$

2. When mixtures of sulphide and oxide of copper and sulphide and oxide of iron are melted together, all the copper will be converted into sulphide provided there be enough sulphur present, the oxygen going over to the iron, thus: $3Cu_2O + Fe_2S_3 = 3Cu_2S + Fe_2O_3$, or similar reaction, according to the composition of the oxides and sulphides present.

3. Oxide of iron in a reducing atmosphere, and in presence of silica, forms ferrous silicate, which is fusible, $Fe_2O_3 + CO + SiO_2 = 2FeO, SiO_2 + CO_2$.

4. When sulphide of copper and oxide of copper are melted together in suitable proportions, copper is separated, any small excess of sulphide or oxide dissolving in the metal, $CuS + 2CuO = 3Cu + SO_2$.

If the excess of sulphide be large, it will remain, forming a separate layer of regulus, whilst excess of oxide will combine with silica, forming a cuprous-silicate slag.

In the Welsh process advantage is taken of these reactions, as follows:—

The ore consists essentially of copper sulphide, iron sulphide (pyrites), and silica, and should contain about 12 per cent of copper.

1. The charge is roasted so as to remove some of the sulphur, and convert some of the copper and iron into oxides.

2. The roasted charge is melted. The copper is thus converted completely into sulphide, which, combining with the residual sulphide of iron, forms a double sulphide or regulus of copper and iron (coarse metal), containing (if the roasting has been properly conducted) about 30 per cent of copper, whilst the silica combines with the oxide of iron, and forms a ferrous silicate slag, carrying only a trace of copper.

3. The coarse metal is ground, and roasted to remove more sulphur.

4. The roasted coarse metal is melted down. The sulphur again goes over to the copper, and a regulus (white metal) of cuprous sulphide (Cu_2S), with a little iron sulphide, containing about 70 per cent of copper, is formed, the oxide of iron combining with silica from sand adherent to the coarse metal pigs (which were cast in sand moulds), or from the furnace lining, forms a silicate of iron slag. If sufficient sulphur has not been removed, the regulus will contain less than 66 per cent of copper. It is then called blue metal, and the roasting and melting must be repeated.

5. The white metal is melted down with free access of air; the sulphur is partially oxidised, the oxide formed reacts on the sulphide (as in 4, above), and copper is separated, the small quantity of residual sulphide dissolving in the metal.

6. The metal or coarse copper is then refined.

Recently the process has been modified in various ways, the most important being the introduction of Bessemerising.

Coarse metal is made as above described, a blast furnace being used for the fusion. It is then run into a suitable Bessemer converter, and air is blown through the molten mass, the oxidation of the sulphur evolves enough heat to keep the whole melted, the oxide formed reacts on the sulphide, and copper separates. The oxide of iron formed attacks the silica of the converter lining, and forms a silicate of iron slag. Bessemerising thus, by combining operations 3, 4, and 5 into one, shortens the process materially. It has come into use to a large extent in the United States, the first regulus being usually made somewhat richer than our coarse metal.

REFINING THE COPPER.

Two methods of refining are in use. Poling, and the electrolytic method.

Poling.—The coarse copper obtained by the process above described still contains a little sulphur, which must be removed. To effect this, the bars of copper are placed on the hearth of a furnace, and melted with free access of air. The air soon oxidises out the sulphur, but it also oxidises some of the copper, forming cuprous oxide, and when the copper melts this dissolves, making the metal very brittle or "dry," and if cast in that condition it would break, with a dull red fracture, and would be quite useless. To remove the oxygen, a pole of wood is plunged under the surface of the metal ; decomposition at once begins, and the reducing gases as they rise through the copper remove the oxygen. The refiner takes samples from time to time, cools and breaks them, and when the fracture shows the metal to be tough enough, the pole is at once removed, and the metal is ladled into the moulds. If the pole were left too long in the metal it would be overpoled, and would again become brittle.

Electro Refining.—Electro refining is based on quite different principles, and has some advantages. A bar of crude copper is immersed in a solution of copper sulphate, and is made the anode for an electric current, the cathode being a thin sheet of electrotype copper. Copper is dissolved from the anode, and is precipitated in a nearly pure form on the cathode. Iron and certain other metals also dissolve, but are not re-precipitated, whilst silver, gold, and some other metals are not dissolved, but settle to the bottom of the vat in the form of a black powder, which can be collected and smelted. Thus any silver and gold present in the copper can be recovered.

THE WET METHOD OF EXTRACTING COPPER.

Enormous quantities of iron pyrites containing from 2 to 4 per cent of copper are imported from Spain and elsewhere for the manufacture of sulphuric acid. When the sulphur has been burned out, the residue, or "burnt ore," contains the copper, together with a small quantity of silver and a trace of gold, and these metals can be profitably recovered.

The burnt ore is mixed with salt, ground, and roasted for some time, with free access of air. A somewhat complex series of reactions takes place by which the copper is converted into soluble cupric chloride, $CuCl_2$, and the silver into silver chloride, $AgCl$, which, though insoluble in water, is soluble in the brine which is produced by the solution of the excess of salt in water. The chloridised ore is transferred to vats, and washed with hot acidified water till the soluble salts are dissolved. The silver is separated from the solution as silver iodide, AgI, by means of an iodide, and the copper is precipitated in the metallic form by means of scrap iron. The precipitated copper is separated from fragments of iron, dried, and sent into the market as "copper precipitate." Copper precipitate is a red or black powder, consisting of metallic copper and oxide of copper, and usually contains 80 to 85 per cent of copper, with more or less iron, arsenic, and other impurities. It is melted in a reverberating furnace, and refined.

COMMERCIAL COPPER.

Copper comes into the market in various forms.

Chili Bar is a crude copper resembling blister copper, except that it contains more sulphur. It contains about 98 to 99 per cent of copper, and is usually cast into ingots or bars weighing about 2 cwt. It has to be refined before it can be used.

Tough Copper.—This is the ordinary form of commercial copper. It is tough and strong, and breaks with a fibrous or silky fracture. It often contains considerable quantities of arsenic and other impurities.

B.S. Copper.—Best selected or B.S. copper is the purest form of copper which comes into the market. It was at one time always made by a process called "selecting," whence the name; but now it is more generally obtained by using pure ores. It is very pure, and should not contain more than ·05 per cent of arsenic and a trace of antimony. For many purposes B.S. copper has no advantage over ordinary tough copper, whilst for electric purposes only the very purest varieties of B.S. can be used.

Bottoms.—This is a very impure form of copper, containing a large quantity of arsenic, antimony, and sometimes tin, obtained in the manufacture of B.S. copper by the Welsh selecting process.

Copper is usually sent into the market in the form of ingots weighing 14 lb. to 28 lb., cast with one or more nicks across the bottom, so that they can be readily broken.

IMPURITIES IN COPPER.

Copper is never pure, but always contains larger or smaller quantities of various impurities. Since arsenic and antimony are very difficult to remove, great care is taken to select pure ores when B.S. copper is to be made. The purest copper in commerce is that which is electrolytically refined, or made from the Lake Superior native copper. Some copper precipitates and some Chili bars are very pure, whilst others contain a considerable percentage of arsenic and antimony; Australian copper is usually very pure. The following analyses will give an idea of the impurities usually present in copper :—

	Copper precipitate.	Chili bar.	Tough.	B.S.	Lake Superior.
Copper	78·212	98·50	99·15	99·90	99·83
Arsenic	·932	·10	·50	·05	Trace
Antimony	·015	Trace	·02	Trace	Nil
Lead	·720	Trace	Trace	Trace	·016
Iron	5·684	·40	·01	·01	..
Sulphur	·435	1·00	Nil	Nil	Nil
Chlorine	1·564	..	Nil	Nil	..
Silver	..	..	Trace	Trace	·026
Nickel Cobalt Zinc	·250	..	·20 Nil	·02 Nil	.. ..
Silica and Alumina	·105	..	..	..	..
Oxygen	12·033	..	·02	·02	·15
	100·00	100·00	100·00	100·00	100·02

Oxygen.—One of the most important impurities in copper is undoubtedly oxygen, though from the great difficulty of making an accurate determination, this is very often overlooked in analyses. When copper is melted in presence of air, cuprous oxide is formed, and is dissolved in the metal, profoundly modifying its character. When the amount is large the metal becomes "dry." It is then extremely brittle, and breaks with a dull brick-red fracture. Heated in a reducing atmosphere, the oxygen is removed, and the metal becomes tough, whilst on further deoxidisation it again becomes brittle; this brittleness not being due to the taking up of any additional constituents, but to the removal of the oxygen, the presence of a small quantity of which modifies the influence of the other elements to an important extent. Sometimes, therefore, the presence of oxygen is decidedly advantageous, whilst in other cases deoxidised copper is preferable. The influence of oxygen in thus neutralising the action of impurities is usually explained by assuming that in the presence of oxygen the impurities are present as oxides, which have less effect on the character of the metal than the elements themselves. This does not seem very likely, but there is no doubt as to the modifying influence of the oxygen. When copper free from oxygen is required, it is best obtained by the addition of a small quantity of phosphorus—usually as copper phosphide. This at once removes excess of oxygen, and if the phosphorus be in slight excess it prevents any absorption of oxygen during pouring. The amount of oxygen in copper varies very much, but very little reliance can be placed on most of the figures that have been published. Thurston gives two samples, containing respectively 1·3 and ·404 per cent of oxygen. An analysis of a copper firebox plate, attached to the second report of the Alloys Research Committee of the Society of Mechanical Engineers, gave ·0181 per cent, and in a series of eighteen analyses of firebox plates, published in the Proceedings of the Institution of Mechanical Engineers, in 1893, the oxygen varies from ·019 to ·248.

Arsenic.—This is usually regarded as being the most important impurity in copper ; but its influence has been much over estimated. It is always present, though some exceptionally pure coppers do not contain much more than a trace. B.S. copper, which is to be used for making brass to be cold drawn, must not contain more than ·05 per cent ; but tough copper frequently contains above ·5 per cent.

The influence of arsenic on copper seems to be to harden it somewhat, to increase its tensile strength, and diminish the extension before rupture, and the action seems to be much the same whether the copper contains oxygen or not.

Dr. Watson* gives the following results of experiments

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* Proceedings of the Institute of Mechanical Engineers, 1893, page 70.

with copper, containing various quantities of arsenic, which had been deoxidised by phosphorus :—

	Tensile strength per square inch.	Elongation in 2 in.
Pure copper	14·38	62·5
0·05 per cent arsenic	14·39	60·0
0·11 „ „	14·39	61·0
0·188 „ „	14·39	61·0

The influence of small quantities of arsenic thus not being noticeable.

Copper is largely used for firebox plates for locomotives, and is there subjected to temperatures higher than that of the atmosphere. The tenacity of pure copper rapidly decreases at elevated temperatures. "At 400 deg. Cen. or 750 deg. Fah., a temperature which may be attained in the fireboxes of locomotives, pure copper is singularly liable to disruption. Its very ductility is a source of danger, for even the deformation produced by successive expansions and contractions will destroy it."* The presence of impurities, by hardening the metal, and thus reducing the ductility, may therefore make it much more durable. A firebox plate, mentioned in the report of the Alloys Research Committee of the Society of Mechanical Engineers as having shown exceptional durability, having run 500,000 miles, contained ·3726 per cent of arsenic and ·0346 per cent of antimony.

Antimony.—This element is almost always present in copper, but usually in much less quantity than the arsenic. Its effects are much the same as those of arsenic, but are somewhat more marked. B.S. copper should not contain more than a trace.

Lead.—Lead is never present in copper as it comes from the refining furnace, but is added subsequently to facilitate rolling, so that worked copper always contains a small quantity of lead. The presence of lead is not objectionable till it reaches above ·25 per cent.

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* Roberts-Austen, Report of Alloys Research Committee. Proceedings of the Institute of Mechanical Engineers, 1893, page 124.

Bismuth.—The most objectionable constituent in copper for many purposes is bismuth, but fortunately it is rarely present except in minute quantities. Copper containing ·1 per cent of bismuth is too brittle to work, and has only a tenacity of about 8 tons per square inch As the temperature rises, the fall of tenacity is very rapid, and there is but little elongation. A sample of copper, containing ·1 per cent of bismuth, at 15 deg. Cen. (59 deg. Fah.), showed a tensile strength of about 8 tons, and an elongation of 20 per cent at 292 deg. Cen. (558 deg. Fah.). The tensile strength was about 1·2 tons, and the elongation ·5 per cent. Bismuth destroys the fibrous structure of copper, and gives a columnar crystalline fracture. Even ·01 per cent of bismuth has a marked influence. The cause of the action of bismuth seems to be that metal containing it never solidifies as a whole, but always has two solidifying points. "A portion of the bismuth, containing perhaps a little copper, always remains fluid until the temperature of the mass has fallen to 268 deg. Cen., or 516 deg. Fah., the point at which bismuth itself solidifies."*

Nickel and Cobalt are often present, but only in small quantities, and have no effect on the properties of the copper.

Tin, *Zinc*, *Iron*, and *Silver* are also often present in very small quantities. When the copper has been deoxidised by phosphorus, traces of that element may be present.

Most of the older published analyses of copper are not to be depended on, and very many analyses now made for engineers are valueless, the accurate analysis of copper presenting considerable difficulties to those who have no experience of it.

WORKING COPPER.

Copper can be worked either hot or cold, and can be forged, rolled, or drawn into wire. Cold working very soon makes the metal hard, and greatly increases its tensile

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* Alloys Research Committee Report, 1893.

strength. Frequent annealing is therefore necessary during cold working. It is of no importance whether the metal be cooled slowly or quickly in the case of ordinary commercial copper, though with pure copper the strength seems to be somewhat greater when the metal is cooled slowly. Copper for structural purposes is always annealed, as otherwise it is apt to fail. Annealing causes a diminution of tensile strength of about 10 per cent, and an increase of the elongation by about 16 per cent. Hot or cold working greatly increases the strength of the metal, and in the latter case annealing does not remove all the effects of work, the annealed metal being stronger than a casting.

The annealing of copper requires the greatest care, or the metal may be injured. As already remarked, if during refining the metal be exposed too long to the reducing action of the "pole," it becomes brittle. The same effect can be produced by heating the solid copper in a reducing gas, such as hydrogen or carbon-monoxide. If, therefore, copper be annealed by heating in a powerfully reducing atmosphere—as, for instance, in a smoky flame—the same change may brought about, and the metal becomes brittle and unworkable. It is probably rendered too completely free from oxygen, and the impurities present thus have full power to exert their greatest influence.

Casting Copper.—Under ordinary conditions copper does not yield sound castings. Whilst in the liquid condition it dissolves gas, and this being given off during solidification causes blowholes, and renders the casting unsound. When the casting is rolled down, the blowholes do not close up, but become extended into cracks, which are sources of weakness. Sound castings may, however, be readily made by the addition of a small quantity of phosphorus—best as phosphide. The phosphorus either removes the gas or prevents its evolution, and thus the formation of blowholes is prevented. Castings, however sound, are deficient in strength, having only a tenacity of about 8 tons on the square inch.

The melting and casting of copper requires the greatest care, as owing to the readiness with which the quality of the metal is altered, either by oxidising or reducing agents, it is very easily spoiled.

Conductivity.—Pure copper is the best conductor of electricity known, with, perhaps, the single exception of silver. A standard pure copper is taken as 100 per cent conductivity, but much copper is now made so pure that it has a higher conductivity up to 102 per cent. The presence of the smallest quantities of impurities reduces the conductivity very much, so that only the purest copper can be used for electric purposes. A very small quantity of arsenic, for instance, will reduce the conductivity to 60 per cent, whilst with 2·8 per cent of arsenic it is as low as 13·66 per cent; 0·13 per cent of phosphorus reduces it to about 70 per cent; 0·48 per cent of iron reduces it to about 36 per cent, and other impurities have a similar effect.

TESTS FOR COPPER.

The chemical composition of copper is, of course, the best guide as to its quality, but this involves an elaborate process of analysis; the ordinary physical tests for tensile strength, elongation, &c., may also be used. Where high purity is required, electric conductivity is an excellent test; indeed, for electric purposes, it is the only one available, and shows the presence of impurities in such small quantity that it would be extremely difficult to detect them by chemical means. Other tests, depending upon the preparation of certain alloys, are also used for special purposes.

USES OF COPPER.

Copper is not very extensively used in structural work. It is used for the manufacture of fireboxes for locomotives, and copper pipes for various purposes, and for other purposes where the temperature is high; also for rollers for calico printing, as it is not acted on by the colours used.

These rollers are usually made of solid copper, but sometimes they are of iron covered by electro-deposited copper.

Copper wire is manufactured on a very large scale, and is used for electric and other purposes, and copper rod is used for staying copper fire boxes, and other purposes. The most extensive demand for copper is for the manufacture of brass bronze and other alloys.

CHAPTER XV.

LEAD, ZINC, TIN, ETC.

LEAD.

LEAD is only used to a limited extent by the engineer.

Physical Properties.—Lead has a blue-grey colour. The freshly-cut surface has a bright metallic lustre, but it tarnishes superficially with great rapidity on exposure to the air. It is the softest of the metals used in engineering, and can be scratched with the nail, and it marks paper. It extends readily, and takes a permanent set under even slight stress. It has a very low tensile strength (about 1 ton per square inch), and is very malleable and ductile, though on account of its low tenacity it is difficult to draw it into fine wire. Just below its melting point it becomes brittle, but at slightly lower temperatures it is so malleable that it can be squeezed or squirted into tube or rod. Its specific gravity is about 11·4. It melts at about 620 deg. Fah. (327 deg. Cen.), and at high temperatures it is sensibly volatile. Its specific heat is about ·03 at ordinary temperatures, and its coefficient of linear expansion is about ·00003. It is a poor conductor both of heat and electricity.

Chemical Properties.—Though a clean surface of lead soon loses its brightness in air, oxidation only takes place to a very limited extent, lead being one of the most stable metals in this respect. Moist air containing carbon-dioxide forms a superficial coating of carbonate, and in presence of acetic acid vapour this action goes on rapidly till the whole of the metal is converted into carbonate. The carbonate produced is a basic carbonate ($2PbCO_3PbO, OH_2$), which is known as white lead. At a red heat lead is readily oxidised by air, forming litharge, PbO, and red lead, Pb_3O_4.

Lead is soluble in nitric acid, and is attacked to some extent by hot strong sulphuric acid, and by many organic acids. It is but little acted on by dilute acids, and hardly at all by dilute sulphuric acid. It is therefore used in the construction of the lead chambers for the manufacture of sulphuric acid, evaporating pans for sulphuric acid, and other appliances used in chemical works. It is slightly dissolved by pure water, and by water containing carbon-dioxide, so that it must never be used for condensers for distilled water; even some natural waters are pure enough to dissolve traces of the metal. The solubility is much less in water containing salts in solution, so that it may safely be used for water pipes under ordinary circumstances. Molten lead dissolves many metals very readily, and it is used for collecting gold and silver in some smelting operations.

Sources of Lead.—Lead is widely distributed in nature, and is smelted in most countries, the largest supplies at present coming from the United States and from Spain, though there are many mines working in Great Britain.

The principal ore is galena, lead sulphide, PbS, which occurs in all lead districts. Of less importance are cerrusite, or white lead ore, $PbCO_3$, and anglesite, $PbSO_4$. These have been produced by oxidation of galena at the surface, by the action of air moisture and carbon-dioxide, and are therefore usually superficial, passing into galena at greater depths.

Lead Smelting.—Oxide ores are easily reduced by carbon at a moderate temperature, but galena is not acted on under these conditions. Galena is very dense (sp. gr. 77), so that under ordinary circumstances it can be readily separated from the lighter gangue by dressing. The galena as sent to the smelter, therefore, often contains as much as 84 per cent of lead, and is nearly free from gangue.

Two methods of smelting are in use, the air-reduction or Flintshire process, and the iron-reduction process.

The air-reduction process depends on the following reactions :—

Galena, when roasted in air, is oxidised, oxide and sulphate being formed, $PbS + 3O = PbO + SO_2$, $PbS + 4O = PbSO_4$. When lead oxide or sulphate are melted with excess of sulphide, lead is separated. $PbS + 2PbO = 3Pb + SO_2$, $PbS + PbSO_4 = 2Pb + 2SO_2$.

The ore is therefore roasted so as to convert the galena partially into oxide or sulphate. The mixture is then melted down. The unreduced residue is mixed with lime, spread on the hearth of the furnace again, roasted, and again melted. About 80 per cent of the lead is thus obtained ; of the remainder, part is the slag and part is the fume carried away from the furnace, both of which are afterwards smelted. In Flintshire, and in many parts of Europe, this process is carried out in reverberatory furnaces, and in Scotland and the north of England shallow hearths are used. This process is only applicable to pure ores, nearly free from siliceous gangue. In the presence of silica, fusible lead silicates, such as $2PbO, SiO_2$, are formed, which interfere with the roasting, and are not reduced at the temperature of the furnace.

The iron-reduction process depends on the fact that iron will remove sulphur from galena at a red heat, forming iron sulphide and liberating lead, $PbS + Fe = FeS + Pb$. The charge, with or without previous roasting, is mixed with scrap iron, or with iron oxide, which on reduction will give metallic iron, and, strongly heated, the lead being thus reduced. In Cornwall this process was carried out in reverberatory furnaces, but blast furnaces are now almost invariably used. The ore is usually roasted, so as to remove some of the sulphur, and thus reduce the consumption of iron, and at the same time to melt it, so that the fused mass after solidification may be broken into pieces of convenient size for blast-furnace use.

The lead obtained by this process is usually harder and more impure than that obtained by the air-reduction process.

Lead is so volatile that long flues or condensers are always attached to the furnaces, and the lead fume which is condensed is afterwards smelted.

Desilvering Lead.—Lead always contains silver. It may be as little as 1 ounce to the ton, or as much as 500 ounces, or even more, as all lead ores carry silver, and the silver passes into the lead. Two processes of desilvering are in use. The Pattinson process, which was at one time universal, consists in melting a large quantity of the lead, allowing it to cool slowly, and fishing out the crystallised lead as it forms. The crystals are much poorer in silver than the liquid residue which is left, and by repeating the process several times, desilverised (D) or market lead is obtained, containing about ½ ounce of silver per ton, and a rich lead containing, perhaps, 800 ounces to the ton, which is cupelled.

The zinc process, which is now in general use, depends on the fact that zinc and lead do not alloy, so that if the molten metals be stirred up together, and then let cool, the zinc will rise to the top, and will carry with it all the silver.

The lead is melted in a large iron pot, and heated above the melting point of zinc ; the necessary amount of zinc is added, and well stirred in, after which the mass is allowed to cool. As the zinc rises it is skimmed off with a perforated shovel, and drained. The zinc is distilled and used over again, and the residue left in the retort is lead, containing all the silver. The lead left in the pot after desilverisation retains about 2 per cent of zinc, which must be removed by softening.

The rich silver lead obtained by either process is melted on a bone ash cupel, and a stream of air is blown over the surface; the lead oxidises to litharge, and partly flows over the edge of the cupel, and is partly absorbed, whilst the silver is left.

Softening the Lead.—Lead as obtained from the furnace often contains small quantities of antimony, copper, zinc, and other metals, which interfere with its ductility or make it hard, and when it has been desilvered by the zinc process there is a considerable amount of zinc left. To remove these impurities the lead is softened. From 10 to 50 tons is melted in a large reverberatory furnace, and kept melted and exposed to the air for many hours, with frequent stirring. The metals present are mostly more oxidisable than the lead. They therefore oxidise more rapidly, and pass into the scum with a considerable quantity of oxide of lead. This is skimmed off from time to time, and the process is continued till the lead is quite soft.

Commercial Lead.—Commercial lead is cast in "pigs," each weighing about 1 cwt. It is usually very pure, and rarely contains any constituents which injure its quality. Impurities are easily removed, and most, if left, would interfere more with the manufacture than the use of the metal. The presence of a minute trace of zinc renders the metal less powerfully resisting to the action of the acid. Chemical lead—*i.e.*, lead for making sulphuric acid chambers—is always desilverised by the Pattinson process.

Uses of Lead.—Lead is largely used in the form of sheet for roofing and other purposes, its power of resisting atmospheric corrosion rendering it valuable. It is also largely used for acid chambers and other appliances in chemical works, on account of its power of resisting acids, and for gas and water pipes. A lead sheet ·1 in. in thickness weighs about 6 lb. per square foot.

Litharge (PbO) has many uses in the arts. Red lead (Pb_3O_4) is used as a pigment, and white lead ($PbCO_3PbO, OH_2$) is used for the same purpose, and as a base for paints.

TIN.

Tin is not much used by the engineer.

Physical Properties.—Tin is nearly silver white in colour, and has a bright metallic lustre. It is malleable, and can be rolled into very thin sheets (tinfoil), which are used for packing and other purposes. Its tensile strength is only about 2 tons per square inch, and therefore it is not easy to draw it into fine wire. It melts at about 230 deg. Cen. (446 deg. Fah.), and boils at a bright red heat. At very low temperatures it crumbles into a grey friable mass, which is usually thought to be an allotropic modification of the metal. The specific gravity of pure tin is about 7·3, that of commercial tin somewhat higher. Its specific heat is ·0502, and its coefficient of linear expansion ·0000193. It is a poor conductor both of heat and electricity.

A stick of tin when bent emits a peculiar crackling sound, called the "cry" of tin, and as the presence of a very small quantity of lead destroys this, it is often taken as a test for the purity of the metal. Tin is very highly crystalline, and the cry is no doubt due to the breaking down of this structure.

Chemical Properties.—Symbol Sn, atomic weight 118. Tin occupies a position on the borderland between the metals and the non-metals, and in many of its chemical characters it is more nearly allied to the latter. It does not tarnish in air at ordinary temperatures, even in presence of moisture and carbon-dioxide. Above its melting point it oxidises readily, forming the dioxide SnO_2, which is commercially known as putty powder, and at very high temperatures it burns. It dissolves readily in hydrochloric acid, or aqua regia, forming chlorides; dilute nitric acid dissolves it partially as stannous nitrate, but the strong acid converts it into an insoluble hydrate of stannic oxide, known as meta-stannic acid.

The oxide is reduced by carbon or other reducing agents at moderate temperatures, but in presence of silica stannic silicates are formed, which are not decomposed by carbon, and in presence of strong bases fusible stannates may be formed. It alloys readily with most metals.

Sources of Tin.—There is only one ore of tin which is worked for the metal. This is cassiterite, or tin stone SnO_2, which always contains, or is mixed with, various impurities. In the early days of tin smelting in this country, and still to a large extent in other parts of the world, the ore was found in the form of pebbles in the streams in tin districts, its hardness having prevented it being broken up, and its density (sp. gr. 7) having prevented it from being carried away, by the running water, and it was called "stream tin." Now the ore is mined from the veins in the usual way. Tin ore is not widely distributed, but occurs only in comparatively few localities. For a long time Cornwall was the chief source of the tin supply of the world, but this has fallen off very much, and most of the tin used is now imported from the Straits Settlements, Australia, and elsewhere.

Tin Smelting.—Tin oxide is easily reduced, but other metallic oxides present with it would be reduced at the same time, and the metals would pass into the tin, rendering it impure; and as owing to the easy oxidisability of the tin they could not be removed by oxidation, only fairly pure tin stone can be smelted. The usual stages are the following:—

1 *Dressing.*—The ore is crushed and washed with water in suitable apparatus, so as to wash away as far as possible all impurities lighter than the tin stone itself—especially silica. If pyrites, or arsenical pyrites, be present, the washed ore is roasted to burn out the sulphur or arsenic, and again washed to remove the oxide of iron and to dissolve out any salts, such as copper sulphate, which may have been formed.

2. *Smelting.*—The ore is mixed with coke or coal, and, heated either in a reverberatory or blast furnace, the metal is reduced and tapped out.

3. *Liquation.*—The metal is heated on the hearth of a reverberatory furnace, or otherwise, above the melting point of tin. Nearly pure, melts and runs away, and a residue consisting chiefly of an alloy of iron and tin is left.

4. *Refining.*—The impurities are removed by oxidation. This is brought about in one of two ways. (1) By tossing, the metal being lifted in ladles and poured through the air back

into the pot, or (2) by poling or boiling, when a billet of green timber is plunged into the molten metal, and the evolved gas keeps the metal in agitation. By either process the impurities and some of the tin are oxidised, and rise to the surface as dross, which can be skimmed off.

Commercial Tin.—Tin is usually cast into small ingots, weighing from ½ lb. to 25 lb. each; or often, for the convenience of users, into sticks. The tin in ingots is known as block tin. Tin, when heated to near its melting point, becomes brittle, and if an ingot of tin be so heated, and then be allowed to fall upon a stone block, the metal breaks into columnar fragments, which are known as grain tin. Tin should be white in colour, and a piece, if nicked on one side, should bend over without fracture, and show a fine, silky texture. On bending, a stick should give a distinct cry. Commercial tin is never pure, though the amount of impurities is always small, the percentage of pure tin being often as high as 99·95, and in good tin being rarely below 99·9. The principal impurities are iron, lead, copper, and antimony, but there should be little more than a trace of any one of them.

Uses of Tin.—Tinfoil is used for packing tobacco and other materials, and for silvering the backs of mirrors by amalgamation with mercury. Tin is largely used for making alloys, such as bronze, pewter, &c., but the most important use is in the manufacture of tin-plate and other tinned articles, an industry which has increased enormously since the development of the canning industries.

In tinning, the plates of iron or steel are dipped, usually by machinery, into molten tin; the tin alloys with the iron, and forms a bright, adherent coating, which should be quite even and free from spots or pin holes. Lead pipes and copper and iron articles are often tinned. Dyers' kettles and other utensils are sometimes made of tin, and tin pipes are occasionally used where lead is considered objectionable.

ZINC.

Physical Properties.—It has a bluish-white colour and a metallic lustre. It is malleable and ductile at temperatures above 100 deg. Cen., but is brittle at lower temperatures. At about 200 deg. Cen. it again becomes brittle, and near its melting point can be powdered. It melts at about 420 deg. Cen. (788 deg. Fah.), and at a red heat it boils; indeed it is so volatile that it is always prepared by distillation. Its specific gravity is about 7·3, its specific heat ·0955, and its coefficient of expansion ·00002976. On solidification from fusion it forms a very crystalline mass, and breaks with a highly crystalline fracture, whence its brittleness.

Chemical Properties.—Symbol Zn, atomic weight 65. Zinc tarnishes slowly at ordinary temperatures on exposure to moist air containing carbon-dioxide, carbonate being formed. At the boiling point it burns with a bright greenish flame, and deposits clouds of white oxide of zinc, which, when so formed, has been called "philosophers' wool." It is very readily soluble in all acids usually with the evolution of hydrogen and the formation of zinc salts, and being the most electro-positive of the metals in common use, it precipitates most of the other heavy metals from solution. It alloys readily with most metals, and dissolves silver even from its solution in lead, but does not alloy with lead, a mixture of the two, on cooling, separating into layers—the lead below, the zinc above.

Sources of Zinc.—Several ores of zinc are known. The sulphide, ZnS, Zinc-blende, is one of the most important; then the carbonate, Calamine, $ZnCO_3$, and the silicate, Smithsonite, Zn_2SiO_4, H_2O. The ores are widely distributed, but only occur in few localities in large enough quantity to be worked for zinc. Blende very generally occurs with galena, and the separation is somewhat difficult. Zinc smelting is only carried on on a comparatively small scale in this country, most of the zinc now used being imported from Belgium and elsewhere.

Zinc Smelting.—Zinc is so volatile that it can only be obtained by distillation. The ore is roasted to convert the metal into oxide by removal of sulphur in the case of blende, $ZnS + 3O = ZnO + SO_2$, or carbon-dioxide in the case of calamine. Roasting only expels water from the silicate, and as the residue is difficult to reduce, it is rarely used when other ores are available. The roasted ore is mixed with charcoal and heated in a suitable retort, the zinc, which distils over, being condensed in suitable condensers. Most of the metals occurring in the ore, being non-volatile, are left behind, but some lead is always carried over. When the ore contains much cadmium, that, being more volatile than zinc, comes over first. The zinc needs no refining, but is melted and cast into ingots. Where great purity is required, it may be re-distilled.

Commercial Zinc.—Zinc is sent into the market in flat cakes about 1½ in. thick, in which form it is usually called spelter, and in rolled sheets. The cakes are very brittle, and should break with a fracture showing large facets, which should be quite free from spots ; if the zinc contains a moderate quantity of iron, the surface of the facets will show dull specks, and when the quantity of iron is considerable, the facets will be rough and the crystals much smaller. Owing to the narrow range of temperature through which zinc is malleable, the rolling is attended with considerable difficulty. The best temperature for rolling is about 120 deg. Cen.

A sheet of zinc ·10 in. thick weighs about 3·8 lb. per square foot.

Commercial zinc is never pure, but usually contains only about 98·5 per cent of zinc. Lead is always present. Molten lead and zinc mix perfectly, but as solidification takes place they separate, and the slower the cooling the more perfect will be the separation. When the cooling is sufficiently slow to allow of complete separation, the zinc retains about 1·5 per cent of lead. When the percentage of lead in a sample is much larger than this, shots or plates of lead can often be detected in the metal. It is impossible to obtain spelter free from lead, as even on repeated re-distillation it carries over about ·2 per cent.

Iron is always present. Freshly-distilled zinc contains but little, but it is dissolved from the iron vessels, in which the metal is subsequently melted, and the rods used to stir it. Iron is a very objectionable constituent in zinc, and good zinc should not contain more than ·15 per cent.

Tin is often present in considerable quantity, and so is copper, whilst arsenic and cadmium are rarely present except in very small quantity. The quality of zinc can, to a certain extent, be judged from the fracture, as above described.

Uses of Zinc.—Zinc sheet is sometimes used for roofing purposes. It resists atmospheric oxidation very well, but one objection to its use is the readiness with which it burns at high temperatures; it is also used for making domestic utensils of various kinds, lining cisterns, &c. It is quite unsuited for the manufacture of articles for domestic use, as it is readily acted on by even the weakest acids, by alkalies, and by soap. Sheet zinc is also used for the negative plate in electric batteries. Zinc yields excellent castings; it melts readily, and when cast fills the minutest crevices of the mould. It is largely used, therefore, in the manufacture of ornamental articles of various kinds; these are usually coloured to represent bronze, and are known as French bronzes. Zinc castings are also largely used for architectural ornaments. In casting, the temperature must not be much above the melting point of zinc, or the castings are brittle.

A large quantity of zinc is used in the manufacture of galvanised iron. The articles to be galvanised are simply dipped in molten zinc, which alloys with the iron, and forms a coherent coating. Owing to its position in the electric series, the zinc is attacked by oxidising agents before the iron, and thus prevents the latter rusting.

Zinc oxide and zinc sulphide are used as white pigments, having the advantage over white lead that they are not blackened by sulphur compounds.

ALUMINIUM.

Physical Properties.—Aluminium is a silver-white metal, with a high lustre, the colour varying somewhat according to the purity of the metal and the temperature of casting. It is malleable and ductile, but hardens rapidly when worked, so that it requires frequent annealing. Its tenacity is low, being only about 6 tons for castings and 12 to 15 tons for the rolled metal. The worked metal is hard and brittle, but annealing softens it, at the same time reducing the tenacity by about one half; the strength also diminishes rapidly as the temperature rises. A sample which had a tensile strength of 11·68 tons at 15 deg. Cen., fell to 9·5 tons at 100 deg. Cen., and 6·3 tons at 200 deg. Cen. It melts at about 700 deg. Cen. to a fluid liquid, which casts well, but shrinks considerably on solidification. Its specific heat is very high—·225; hence it melts and solidifies very slowly. The conductivity for heat and for electricity is low; at ordinary temperatures about one-third that of copper.

The most remarkable property of aluminium is its extreme lightness, its specific gravity being about 2·67. It is therefore only about one-third the weight of iron or steel; one-ninth the weight of platinum.

Chemical Properties.—Symbol Al, atomic weight 27. Dry air or oxygen has no action on it, but in moist air it becomes covered with a thin film of oxide, which dulls the surface only, and does not increase, and even in presence of carbon-dioxide no serious oxidation takes place. At a red heat it does not oxidise in air unless finely divided, but at a white heat it takes up oxygen. The powdered metal projected into a flame burns with a brilliant light. Water has no action at ordinary temperatures, but sea water attacks it slowly. It dissolves readily in hydrochloric acid, but other acids act on it only slowly; organic acids do not seem to attack it, except in presence of salt, but alkalies attack it readily.

It alloys readily with most metals, and at high temperatures decomposes most metallic oxides, and even silica or boric anhydride, the silicon or boron dissolving in the aluminium.

Occurrence of Aluminium.—Aluminium is most widely distributed, occurring in all clays and in most rocks, but as these also contain silica, they are not available as sources of the metal. The materials used are bauxite, a hydrated oxide of aluminium and iron—xAl_2O_3, yFe_2O_3, zH_2O—or cryolite, a double fluoride of aluminium and sodium, which occurs in Greenland; but the latter is now little used.

Extraction of Aluminium.—Various processes have been used for the extraction of the metal, but all have given place to the electrolytic method, which was introduced in 1887. A mixture of alumina with a suitable solvent flux, such as cryolite, is put into a large crucible lined with carbon, and a powerful electric current is passed through from a carbon pole as the anode, the crucible itself forming the cathode. The heat evolved by the passage of the current melts the flux and the alumina, which is then decomposed by the current, aluminium being separated at the cathode, and oxygen being separated at and attacking the anode.

As other elements would be reduced by the current, and would dissolve in the aluminium, pure alumina must be used. The bauxite is therefore subjected to a preliminary purifying process for the removal of the iron, silica, and other reducible substances that may be present.

Commercial Aluminium.—The aluminium as now made is usually very pure, some samples containing 99·9 per cent of aluminium. The principal impurities are iron and silicon, and copper and lead are sometimes present. Both silicon and iron are very objectionable, but especially the former, as it impairs the colour, the malleability, and the fluidity of the metal.

The metal is sent into the market in small bars or ingots of any required size.

Uses of Aluminium.—The value of aluminium has been much overrated. It is not at all likely ever to come into use for structural purposes, but no doubt will be largely used for the manufacture of smaller articles of various kinds.

It casts well, but as it shrinks much on cooling, due allowance must be made for this in the preparation of the moulds. For cooking utensils it is well suited if they are handled only by those who know something of the character of the metal, but it must not be cleaned with soap, as the alkali attacks it and dulls and roughens the surface. Owing to its sonorousness, it is well suited for making bells; and owing to its lightness, it may be satisfactorily used for making opera-glass or telescope mounts, or musical instruments which have to be carried, &c.

It is most largely used in the preparation of alloys, some of which have remarkable properties. It is also used in the steel foundry to quiet steel that is giving off gas, and so prevent blowholes and make sound castings, and for other purposes.

There are many other purposes for which the metal may be used, but they are mainly those where cost is of little moment, and lightness is of great importance, as in building racing yachts, &c.

NICKEL.

This is a nearly silver-white metal, having a distinctly bluish tinge. Its specific gravity is about 8·5; it fuses with very great difficulty, and is malleable and ductile. It does not tarnish on exposure to the air. It can be either cast or forged, though the addition of a little magnesium seems essential to the production of good castings.

Nickel is obtained from various minerals which contain it in small quantity: a silicate of magnesia in New Caledonia and pyrites in Canada. The metal is obtained by a somewhat elaborate series of processes—partly metallurgical, partly chemical.

Nickel is only used to a very small extent in its pure form. It is largely used in the manufacture of German silver and other alloys, and for coating metals by electro-deposition. Electro-deposited nickel has a brilliant lustre, but it is so porous that moisture can find its way through to the metal beneath, and it is so hard that it cannot be rendered more compact by burnishing.

CHAPTER XVI.

ALLOYS.

MOST of the metals unite readily with one another under certain conditions, forming alloys. These alloys are distinctly metallic in character; they have a metallic lustre, and both in the solid and the liquid condition conduct electricity more or less readily. Alloys have been known from a very remote period, and it is generally supposed that bronze—an alloy of tin and copper—was the first metallic material with the use of which men were acquainted. In several cases alloys were in general use before the metals of which they are composed had been separated.

A great deal of attention has recently been paid to the alloys, as they present some very interesting problems, which are at present only in process of solution.

It two metals are melted together, as a rule—to which, however, there are exceptions—they will remain mixed uniformly so long as they are kept in the liquid condition, but only in the rarest cases will this uniform distribution continue, as the mixture solidifies. With some metals, in some proportions, there is no tendency to separate on cooling, but usually the mixture, on solidifying, will tend to separate into different portions, which may be either the metals themselves or alloys, and, therefore, most solidified alloys are either indefinite mixtures or solidified solutions.

Alloys vary very much in nature, properties, and chemical structure. In the liquid state the alloy may consist of definite chemical compounds of the metals, or of solutions of one metal or of definite compounds of the metals, in the other metals, or in compounds of them.

Matthiessen classifies solid alloys into eight groups:—

1. Solidified solutions of one metal in another.
2. Solidified solutions of one metal in an allotropic modification of another.
3. Solidified solutions of allotropic modifications of the metals in one another.
4. Chemical compounds of the metals.
5. Solidified solutions of chemical metallic compounds one in another.
6. Mechanical mixtures of solidified solutions of one metal in another.
7. Mechanical mixtures of solidified solutions of one metal in allotropic modifications of another.
8. Mechanical mixtures of solidified solutions of two allotropic modifications of metals in each other.

It is quite obvious that if alloys vary so much in nature it will be quite useless to attempt to determine their properties from those of their constituents, and, also, that investigating the properties of any particular set of alloys must be attended with considerable difficulty. Ultimate chemical analysis can only give the relative proportions in which the constituents are present; it cannot give any information as to how they are combined, and there is at present no method of proximate analysis which is available for the purpose.

If the metals have combined to form definite compounds, they must be present in equivalent proportions, but this is very rarely the case with alloys, and although many such compounds do exist, they are usually present, dissolved, in excess of one or other of the metals.

As a complex mass of material cools from fusion, many changes, combinations, decompositions, and recombinations may take place, and it is usually only in the case of an element or a definite chemical compound that solidification takes place, as a whole, at one definite temperature. When, for instance, a mass of igneous rock solidifies, rearrangements take place, definite minerals crystallise out, till ultimately a residual mass, which is probably not a definite compound, is left, which solidifies and forms the ground mass of the rock, and such rocks can be seen either by the naked eye if the crystals are large, or by the microscope if they are small, to be built up of masses of crystals formed during solidification, often embedded in a ground mass, which is very frequently glassy.

So in the case of cast iron, to which reference has already been made. Whilst in the liquid condition the carbon is all either in combination or solution, but as solidification goes on it is thrown out, first as graphite, then as definite compounds of carbon and iron, and, lastly, the ground mass in which all these are embedded solidifies. The same series of changes takes place in the solidification of alloys. Only in the rarest cases do they solidify as a whole at one definite temperature, but as the temperature falls certain compounds fall out; then a re-distribution again takes place in the molten mass; after a time other compounds separate, till at last the whole mass becomes solid. The portions which fall out are not usually definite compounds, but may be solutions of these in excess of one of the metals. They represent the most fusible solution of that compound and metal, and are called eutectic alloys. It is obvious that if solidification be sufficiently slow, and if the solidified portions be very different in specific gravity from the portion remaining liquid, actual separation may take place, the solid portion either rising or sinking, according as it is lighter or heavier than the still liquid portion. This separation, or liquation, is familiar to all who are practically engaged in casting alloys, and sometimes it gives considerable trouble. As a very grey cast iron solidifies, the ejected carbon and some iron carbide rise to the surface, forming a layer of "kish," and in casting bronze articles the metal at the top of the mould tends to be poorer in copper, and richer in tin, than that lower down. By very rapid cooling the liquation may be prevented, the constituents remaining so intimately mixed that the solid appears to the eye to be homogeneous. Very frequently, however, if the temperature be raised to the melting point of the more fusible of the constituents, it will melt and "liquate" or "sweat" out in the liquid condition, and the separation may be much facilitated by the application of pressure.

Properties of Alloys.—The properties of alloys in many cases seem to bear very little relation to those of their constituents.

Colour.—Whilst alloys of the white metals one with another are always various shades of white, the colour may be little altered, or may be very much modified, by the introduction of the coloured metals, such as copper or gold, but the alteration of colour does not seem to vary in any definite proportion with the amount of coloured metal. An alloy of copper with 10 per cent of aluminium has a fine yellow colour, resembling gold (aluminium gold). The alloys of copper and zinc are various shades of yellow when the percentage of copper is more than 50, but when this falls to 40 the alloy is silver white (white brass). A very small addition of tin to copper destroys the red colour, and produces bronze; in other proportions the alloy is white (speculum metal), and an alloy of copper and antimony (regulus of venus) has a fine violet colour. The most striking change of colour is that of an alloy of gold and aluminium, discovered by Professor Roberts-Austen, which is ruby red.

Crystallisation.—From what has been said above it will be seen that most alloys must have a crystalline structure. In some cases the crystals are small, and aggregated into granules, giving a granular structure, whilst in others they may be very large and distinct, as in speigeleisen, &c. Very slow cooling tends to the production of large crystals, whilst work tends to break them down.

Specific Gravity.—When metals are alloyed, there is almost always either expansion or contraction, so that the specific gravity of the alloy differs from that which a mere mixture of the metals in the same proportions would have. The copper-tin, copper-zinc, and many other series of alloys have a density greater than that of a mean of their constituents, whilst the copper-silver alloys have a less density.

Fusibility.—The melting point of an alloy is almost invariably lower than the mean of that of its constituents, and in some cases it is lower than that of any one of them. This is not peculiar to alloys, as in many other cases mixtures are more fusible than their constituents, as, for example, the mixture of sodium and potassium carbonates, so largely used in the laboratory. The most marked examples of the lowering of the melting points, among the metals, is that of the fusible metals. These contain lead, tin, bismuth, and sometimes cadmium, and when of suitable composition will melt readily in boiling water.

Alloys, as a rule, solidify at the same temperature as that at which they melt, though there are—at anyrate apparent—exceptions. Most alloys, as already remarked, do not solidify as a whole, but have a series of freezing points, as the different constituents solidify.

Specific Heat.—The specific heat of alloys seems to be the mean of that of their constituents. There are apparent exceptions to this, but the subject needs fuller investigation.

Expansion by Heat.—As a rule, this seems to bear no relation to the expansion of the constituent metals.

Heat Conductivity.—The conductivity for heat of alloys does not seem to bear any definite relationship to that of its constituents.

Electric Conductivity.—In some few cases the electric conductivity of alloys is a mean of that of its constituents, but in almost all cases the alloys are worse conductors than either or any of the metals of which they are composed; the addition of even a small quantity of a foreign metal often reducing the conductivity enormously.

Oxidation, &c.—As a rule, alloys oxidise less readily than the metals of which they are composed. Bronze and phosphur bronze, for instance, resist atmospheric oxidation very strongly. Many alloys also resist the action of acids more powerfully than the constituent metals do. Some alloys of copper and tin are less readily acted on by nitric acid than copper itself, and an alloy of iron and chromium is almost unaltered by acids. There are, however, many exceptions.

In some cases the more soluble metal is dissolved out, the less soluble being left, as in the parting of gold from silver by means of nitric or sulphuric acid, and sometimes the presence of an excess of a soluble metal may determine the solution of a metal which by itself would be insoluble; as, for instance, when an alloy of silver with a small quantity of platinum is acted on by nitric acid, the whole dissolves, though platinum alone would be quite unacted on and the presence of a small quantity of mercury in aluminium will determine the oxidation of the aluminium, though it alone would be quite stable.

When alloys containing easily-oxidisable metals are melted with free access of air, the easily-oxidisable metal will oxidise most readily, and in some cases may be completely separated, as in the case of lead containing silver or gold.

Structure of Alloys.—The structure of alloys cannot be determined directly, but the problem has been approached by different lines by different workers, and valuable indications have in many cases been obtained.

When an alloy has a definite composition, and, at the same time, a fixed freezing point and other definite properties, it may be assumed to be a chemical compound, but, on the other hand, if it shows more than one solidifying point, or if it separates into two portions on slow cooling, it can only be a mixture or a solution of one substance in another. Definite chemical compounds of the metals undoubtedly exist, but few, if any, of them are alloys of commercial importance.

The electrical relations of an alloy give valuable evidence as to its structure. If the electric conductivity of a metal falls or rises steadily as another metal is added, the resulting alloy is probably only a mixture; if, on the other hand, the fall or rise shows distinct breaks or critical points, then some change must have taken place at these points, probably the formation of definite compounds, and the resulting alloy will not unlikely be a mixture of such compounds with one another, or one of the metals, or a solution of some of these in the other.

All the alloys in the molten condition conduct electricity like metals, and they do not in any case undergo electrolytic decomposition, as all other fused compounds do. It is probable, therefore, that fused alloys are mixtures or solutions, and that definite chemical compounds are only formed on solidification.

The electrolytic relations of the metals and alloys, as indicated by the electro-motive force (E.M.F.) generated, when they are immersed in dilute acids and connected by a wire, is also important. Laurie found that "if the zinc plate of a Daniel cell be replaced by a compound plate formed by joining copper and zinc, the cell has the same electro-motive force as one in which zinc alone is used. This is true even if the zinc surface be only $\frac{1}{1000}$ part of the copper surface. If the zinc plate be replaced by copper-zinc alloys, no deflection of the galvanometer needle is observed as long as the alloy contains less than 67 per cent of zinc. At this point, however, a considerable deflection, practically equivalent to that given by zinc, is suddenly obtained. This result, in his opinion, may be taken as evidence of the existence of a compound of the two metals of the formula $CuZn_2$."

Allotropic Modifications of the Metals.—Many elements, both metals and non-metals, can exist in more than one form, these different conditions being called allotropic, and the change from one form to the other is often produced by apparently very slight causes. The changes produced by the addition to a metal of minute quantities of foreign constituents are sometimes so great as to make it almost impossible to imagine that they are produced directly by the small quantity of added element, and in such cases it seems much more likely that the metal itself has passed into an allotropic modification. As examples, may be mentioned, the action of a minute quantity of tin on copper, or carbon on iron. Allotropic modifications of some of the metals have been proved to exist. Metals are often liberated from their alloys, by solution, in forms very different to those in which they usually occur. Gold, for instance, is liberated from its alloy with the alkaline metals by water, and from those with some other metals by acids, in the form of a black lustreless powder, which, on heating to redness, passes into the usual yellow form.

Preparation of Alloys.—Alloys may be prepared by various methods, but fusion is by far the most general, so much so, indeed, as to be almost universal.

1. The metals may be mixed in crucible, covered with a layer of charcoal or other material to prevent access of air, and then melted together. This method is only available when the metals are non-volatile, and melt at temperatures not very far removed from one another.

2. One metal is melted, and the other is then added and stirred in. This is the most usual method of making commercial alloys. The metal of highest melting point is first melted under charcoal; the other metal is then added in small portions at a time and stirred in. Care must be taken not to add the cold metal in too large portions at once, or some of the molten metal may be "frozen"; and as the melting point of the alloys is usually much lower than that of the least fusible metal they contain, it would be difficult to melt again.

In the case of complex alloys, very frequently two alloys are made, which are then melted together, or one is melted and the other added to it. In making German silver, for instance, the nickel is alloyed with part of the copper and the zinc with the other part; the nickel-copper alloy is then melted and the copper-zinc alloy stirred in.

The order in which the metals are melted, the temperature to which they are heated, and the length of time they are kept melted, have some influence on the property of the alloy.

3. At one time some alloys were made by melting together a metal and an oxide, or two oxides, with reducing agents; thus brass was made by melting together copper, zinc carbonate, and charcoal; the zinc was reduced and alloyed with the copper. Brass—known as calamine brass—was prepared by this process before zinc had been obtained in the free state.

4. Alloys may be made by subjecting the constituents in a fine state of division to great pressure. This has, however, only been done in a few cases, and then only experimentally.

5. Alloys may be precipitated by an electric current from solutions containing both metals. The solution must be of a suitable kind and strength, and the metals must be of such character that in the solution they can both be precipitated by the same current. This method is used in electro-bronzing, electro-brassing, and similar operations.

BRONZE.

Bronze is essentially an alloy of copper and tin. These metals alloy readily in all proportions, but most of the alloys liquate on slow cooling, the top of the casting being poorer and the bottom richer in copper.

There are at least two definite compounds of copper and tin—$SnCu_3$, containing 61·8 per cent of copper, and $SnCu_4$, with 68 2 per cent of copper. Both these contain less copper than the commercial alloys, which may therefore be regarded as solidified solutions of these compounds in an excess of copper.

As tin is added to copper the electric conductivity falls rapidly till the alloy contains nearly 10 per cent of tin; it then falls more slowly till the composition $SnCu_4$ is reached; then it rises slightly till the composition is $SnCu_3$, after which it remains nearly constant. The heat conductivity is somewhat similarly affected, though there are more breaks in the line, but the minimum conductivity is reached when the composition is $SnCu_4$.

The E.M.F. of a copper and copper tin alloy couple is almost nil whilst the copper is in excess of that required for the formula $SnCu_3$; when that composition is reached it rises suddenly to that of copper and tin, and remains constant as the copper is further diminished.

These facts are well shown by fig. 11, which is from the third report of the Alloys Research Committee of the Society of Mechanical Engineers.

Prof. Roberts-Austen has also shown that the copper-tin alloys, as a rule, do not solidify as a whole, but in stages. As tin is added to pure copper the freezing point falls till when 10 per cent has been added ; "while the alloy as a whole freezes at 1,000 deg. Cen. or 1,830 deg. Fah., a small portion remains liquid until 770 deg. Cen. or 1,420 deg. Fah. is reached. Alloys containing about 80 per cent of copper solidify in three distinct stages, and those containing from 50 to 75 per cent of copper have no fewer than four separate freezing points."*

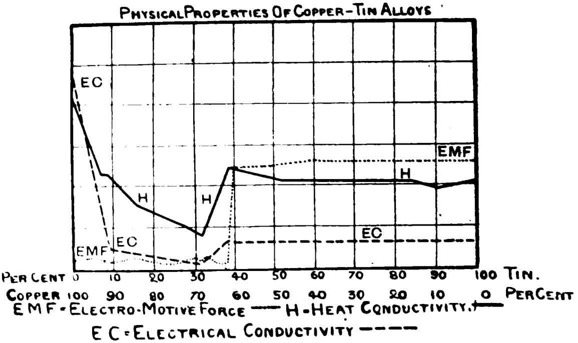

Fig. 11.

The tenacity of copper is slightly increased by the addition of tin, the maximum being reached with over 10 per cent, after which the tenacity falls. The elongation falls

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* Stansfield. Proceedings, Inst. Mech. E., 1895, p. 270.

away much more rapidly. These changes are well shown in fig. 12, which is from the report already mentioned, both these changes being probably due to the hardening influence of the tin. The upper, stronger, members of the series break with a granular fracture, but with the lower members (below 80 per cent copper) there is but little grain, the fracture being often smooth and conchoidal. The higher members of the series are malleable and ductile. With 5 per cent of tin the alloy can be worked cold; above this it can be forged hot or cold, till, when the percentage of tin passes 12 deg., it ceases to be workable at any temperature. The alloys cast well, but usually are subject to liquation on slow cooling. The alloy $SnCu_3$, however, liquates very little, and is not altered by repeated fusions. It is the densest of the alloys, and is so brittle that it can be pounded in a mortar.

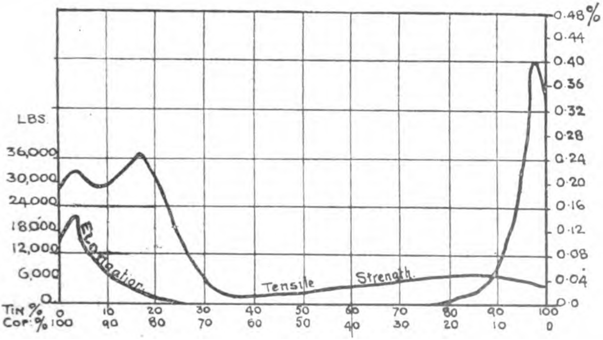

FIG. 12.

Tin very rapidly destroys the colour of copper. When the quantity of tin is small the alloy has a bronze yellow colour, but when the percentage of tin reaches about 30 per cent the metal becomes white.

Bronzes are annealed or softened by being heated to redness and suddenly cooled. This seems to be characteristic of alloys which contain a very fusible constituent, and therefore speculum metal ($SnCu_4$), which solidifies "almost entirely at its higher melting point, is nearly unaffected by slow or rapid cooling."

Very small quantities of impurities have considerable effect on bronze, often tending to make it brittle; sulphur, arsenic, antimony, and lead being the most objectionable impurities. Sulphur is never present unless dirty scrap has been used in the manufacture, and where great strength is required the bronze should be rejected if it contains more than the smallest trace. Lead tends to liquate, and thus produce weakness, so that only a very small quantity should be present—not more than ·1 per cent; whilst arsenic should not exceed ·01, and antimony a trace.

Bronze is strong, hard, and durable. It is not readily acted on by corroding agents, but on exposure to air and moisture it becomes covered with a green film of basic carbonate of copper; the action, however, soon stops.

PREPARATION OF BRONZE.

Bronze is made either in crucibles or reverberatory furnaces, preferably the former. The copper is melted, then any scrap which is to be used is added, and lastly the tin, the whole being covered with charcoal to prevent oxidation. There is always some loss of tin, especially when old bronze is re-melted, as the tin oxidises more readily than the copper. The tin oxide rises to the surface, but a trace may remain entangled or dissolved in the metal. Bronze, like other metals, dissolves gases to some extent, these being given out as the metal solidfies. As bronze may separate into layers of different composition, even when in the molten condition, the metal should be poured as soon as melting is complete, and should be well stirred before pouring.

VARIETIES OF BRONZE.

Coin Bronze.—Bronze has been used from a very remote period, and ancient bronzes are very similar to those used to-day. Greek and Roman bronze coins often contained copper 96, tin 4, and a similar alloy is now used for the manufacture of bronze medals, though many so-called bronze medals are copper with an artificial surface bronzing. Our bronze coinage is not a pure bronze, but contains a little zinc.

Gun Metal.—At one time field pieces were largely made of bronze, usually containing about 90 per cent copper and 10 per cent tin, whence this alloy has been called gun metal. It is stronger and harder than copper, casts well, and can be worked hot. It is very durable, as it resists atmospheric and other corroding influences powerfully. The bronze used for statuary is usually gun metal. It is also well suited for bearings that are subject to great friction.

Bell Metal.—This alloy is largely used for casting bells and other purposes. The composition usually given is copper 80, tin 20, but the alloy used by various founders of bells often differs considerably from this. It is used for bells on account of its sonorousness, and as this property is greatly impaired by the presence of lead, great care must be taken as to the purity of the metals used. Heating the metal to redness, and cooling suddenly, softens the metal, but its hardness and sonorousness are restored by hammering.

Speculum Metal.—This alloy is only used for the manufacture of metallic mirrors. It is silver white, very hard, and brittle, and takes a fine polish. The usual composition is copper 66, tin 34, a little arsenic being also often added.

PHOSPHOR BRONZE

The addition of a small quantity of phosphorus to a copper-tin alloy has a remarkable effect upon its properties, an effect out of all proportion to that which one would expect to be produced by the very small proportion of phosphorus which remains in the alloy. The action is therefore probably to a large extent indirect. The alloy of copper and tin may—indeed, probably does—contain various oxides, such as oxides of copper and tin in solution, and these impair its strength.

The phosphorus, acting on these oxides, decomposes them, forming oxide of phosphorus and liberating the metals. At the same time, considering the effect of very small quantities of other elements in alloys, the residual phosphorus may exert a direct action on the metals. It is certain that the bulk of the phosphorus passes out, the residual amount in three cases given by Brandt* being ·76, ·196, and ·053. The tensile strength of phosphor bronze wire may be up to 70 tons on the square inch in the hard condition, and about one-third of that after annealing. Castings are, of course, much weaker, the tensile strength being about 20 tons or more. Figures such as these are, however, of very little value, since the strength will necessarily vary with the composition of the bronze itself. It is sufficient to say that the phosphor bronze is stronger, tougher, more elastic, and resists corrosion far better than a similar bronze made without the addition of phosphorus ; or, as Thurston expresses it : "The phosphor bronzes greatly excel the unphosphoretted alloy in every valuable commercial quality, and they are very extensively used for every purpose for which such alloys are fitted."†

Phosphor bronze can be rolled, forged, or drawn into wire, It melts at about the same temperature as ordinary bronze. but the surface does not oxidise, and the quantity of tin is not reduced by re-melting, till all the phosphorus has been removed. The phosphorus is usually added to the metal in the form either of phosphor-tin or phosphor-copper.

Phosphor-tin is a highly crystalline alloy, containing about 11 per cent of phosphorus. It is made by pouring molten tin on to phosphorus ; best contained in a closed vessel, to avoid loss of phosphorus. Phosphor-copper is a brittle granular substance, made by pouring molten copper on to phosphorus.

The alloy is made exactly in the usual way, except that a portion of the tin or copper is replaced by the phosphor-

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* "Alloys," page 203.

† "Materials of Engineering," vol. iii., page 143.

compound, the amount of phosphorus added being usually between 1 and 2 per cent.

Silicon Bronze.—If the principal function of phosphorus is to remove oxygen, any other element which has a great affinity for oxygen might be substituted. This is found to be the case, but the small amount of residual deoxidiser left gives each bronze a character of its own.

Bronze containing a small quantity of silicon is prepared by fusing copper with potassium silico-fluoride, and sodium. It is very similar to phosphor bronze, very strong and tough, and is a much better conductor of electricity than phosphor bronze or ordinary bronze. It is therefore largely used for telegraph and telephone wires, it being both stronger and a better conductor than mild steel.

Manganese Bronze is made by adding manganese or ferro-manganese to bronze; its properties are very similar to those of the other bronzes described. The amount of manganese left in the alloy is very minute, but if ferro-manganese is used a considerable quantity of iron is left.

BRASS.

Brass is the most largely used and most important of all the alloys used in the arts. It consist essentially of copper and zinc, small quantities of other elements being often added or being present as impurities. Copper and zinc alloy in all proportions, and two definite compounds, CuZn and $CuZn_2$, probably exist, but neither of them corresponds to any useful alloy. The alloys used for engineering purposes contain more than 55 per cent of copper, and within this range there is a very great variation in properties, so that by careful selection alloys suitable for many purposes may be obtained. The tensile strength may vary from 30 tons or more down to 10 tons or less, and the extensibility from 50 per cent to almost nil, and with other properties the variations are almost as great.

The physical properties vary with the chemical composition, but in this, as in so many other cases, the variation is by no means proportional to the percentage of either metal; for the properties depend on the proximate, not on the ultimate composition. As already remarked, the composition of alloys is often very complex, and as there are no known methods of proximate chemical analysis which are applicable, other means have to be adopted to ascertain the chemical structure.

The solid alloys are not homogeneous, but as they solidify separate portions crystalise out. This is the case with the alloys of copper and zinc, just as with those of copper and tin, there being several distinct freezing points at which during solidification definite "eutectic" alloys separate. These alloys do not contain the metals in atomic proportions, and therefore are not definite chemical compounds, but may be solutions of these compounds in excess of one of the metals. The presence of a eutectic alloy of low melting point is always a source of weakness in an alloy.

Tensile Strength.—As zinc is added to copper the tensile strength increases, but not by any means uniformly, till a maximum is reached, when 40 per cent is present. After this, it falls away very rapidly, and when the alloy contains 60 per cent of zinc it is extremely weak, probably because the compound CuZn is now mixed with an excess of zinc instead of with free copper. As the percentage of zinc is increased the tensile strength rises somewhat. These variations in the tensile strength with the composition are well shown in the curves, fig. 13, from the fourth report of the Alloys Research Committee of the Institution of Mechanical Engineers. The alloy of maximum strength has only one freezing point—that is, it solidfies as a whole at about 900 deg. Cen. (1,650 deg. Fah.)

The results which have been obtained by previous observers differ in many respects very widely from these figures, but the tables have often been collated from isolated experiments by different observers, and in many other cases, where series of experiments have been made, so little care has been taken to ensure the purity of the metals used and

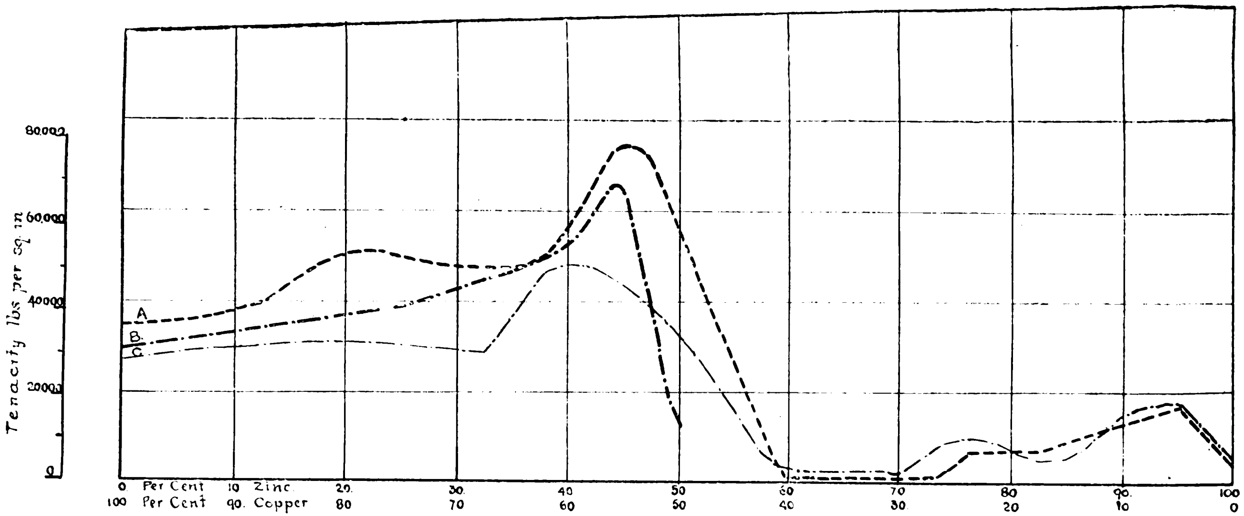

FIG. .

A—Alloys Research Committee (worked rods of brass). B—Charpy (annealed brass). C—Thurston (cast brass).

identity of the conditions of experiment, that the results are valueless.

Extensibility.—As zinc is added to copper the extensibility increases very much, as does the tensile strength, but the maximum is reached when the alloy contains about 30 per cent of zinc, after which it falls away, the fall being very rapid after 40 per cent of zinc has been reached. This alloy of maximum ductility coincides with the first appearance of the upper eutectic which falls out from the alloy that contains 71 per cent of copper. This eutectic probably consists of a mixture of copper with the compound CuZn. The mixture of the soft and hard substances produces great strength, as is evident from the fact that the strongest alloy of the series consists almost entirely of this eutectic, but the presence of the eutectic naturally diminishes the extensibility of a mass which contains more than a small amount of it.

Effect of Work.—The strength of brass castings is greatly increased by work, and also by annealing, as is well shown by the three curves in fig. 13, and the two in fig. 14. Working makes the brass hard, and annealing softens it, and at the same time reduces its strength. Annealing takes place at about 900 deg. Fah. (500 deg. Cen.). "Heating brass to 1,650 deg. Fah. (900 deg. Cen.) causes a rapid diminution of the extensibility of the alloy, and in commercial alloys which contain 0·15 per cent of tin and 0·2 per cent of lead this effect, which is technically known as burning, is produced at a temperature below 800 deg. Cen., or 1,450 deg. Fah."*

Other Impurities.—Brass is harder than copper, but the relationship existing between hardness and composition has not been made out. According to Mallet, the hardest brass is that containing 66·6 per cent of copper. Methods of measuring hardness are, however, somewhat unreliable.

The melting point of brass, as far as a definite melting

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* Report of Alloys Research Committee. Proc.Inst.Mec.E., 1897, page 38

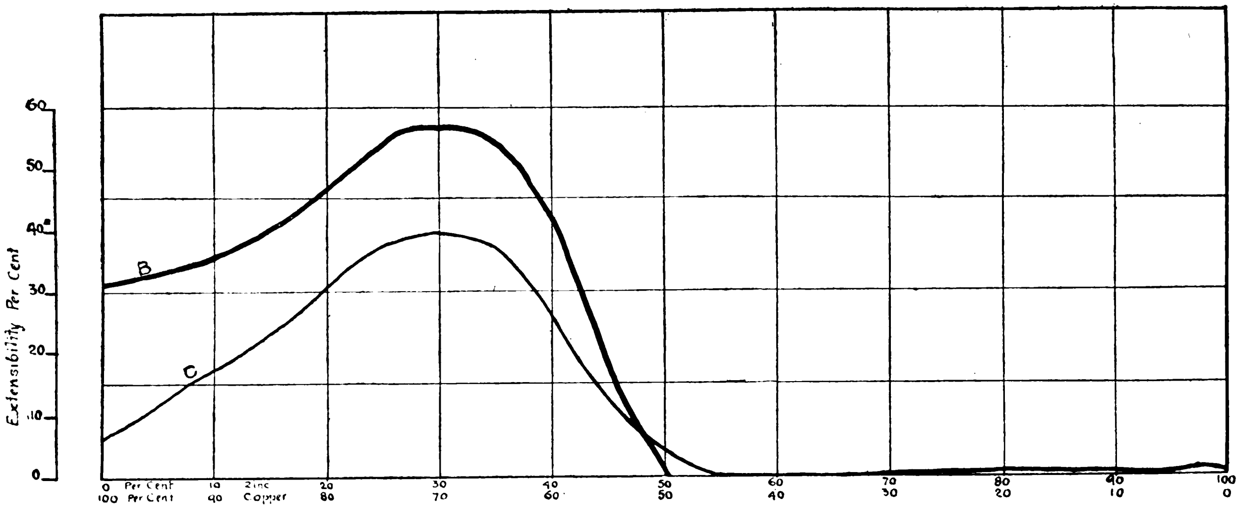

FIG. 14.

B—Charpy. C—Thurston.

point can be determined, is less than the mean of that of its constituents, and falls steadily with decrease of the percentage of copper.

The colour of the alloys varies very much. A very small quantity of zinc destroys the red colour of the copper. The colour becomes brass yellow, being strongest when the metals are present in about equal quantities; then it becomes rapidly paler, and when the copper falls to 40 per cent it is almost silver white, after which it becomes greyer, and approaches more nearly the colour of zinc.

Brasses containing less than 33 per cent of zinc can be worked hot or cold, and are malleable and ductile; when the quantity of zinc is much increased they become very brittle. Brass containing 40 per cent of zinc can be worked hot, but with a higher percentage it is brittle enough at a high temperature to be pounded in a mortar.

Brass shows usually a decidedly crystalline structure, the most crystalline being the common brass, with about 50 per cent of copper. The presence of a small quantity of impurities, especially antimony, hardens the metal, induces a crystalline structure, and reduces the malleability and ductility very much. Crystallisation is induced by work; hence the necessity for repeated annealing when the metal is worked cold, and brass which is subjected to repeated shock is said to become crystalline and brittle. Thurston states that brass is liable to flow under stress, and therefore should never be used for chains or tie-rods which have to carry heavy loads. Brass that has been hardened by work is much less liable to flow than that which has been annealed, or a casting. Some varieties of brass are elastic enough for springs, but they are only suitable for intermittent use, as the alloy is very liable to take a permanent set.

Impurities in Brass.—Brass should consist only of copper and zinc, but other constituents are always present, either as impurities or intentionally added. The most objectionable impurities are arsenic, antimony, bismuth, and sulphur. These all tend to harden the metal and decrease its ductility, and therefore are far more injurious in brass which is to be rolled than in that which is to be cast. Sulphur is never present except when dirty scrap has been used in the manufacture of the alloy. When brass is to be cast, about 2 per cent of lead is often added, as this hardens the metal and makes it work more easily with the tools ; but such brass must be cooled rapidly, or the lead will liquate out. A little tin is also often added.

VARIETIES OF BRASS.

A large number of varieties of brass are used in the arts, and very often several names are given to the same alloy by manufacturers for trade purposes, so that the number of names is far larger than the number of alloys to which they refer. Only the more important will be mentioned here, and these will be better designated by the relative proportions of the metals than by any special names.

90 and 10. Alloys containing about 90 per cent of copper are sometimes made for rolling into leaf, and other purposes. They are usually known by the name "Tombac." When the alloy is pickled in acid the zinc is partially dissolved away, leaving the surface of a more or less copper-red colour, whence it is called "red brass."

80 and 20. An alloy of this composition is largely made. Hammered into thin sheets, it is used for gilding (gilding metal), and it is drawn into tubes for marine and other boilers.

70 and 30. This is the most malleable and ductile brass, and it is largely used for the manufacture of solid-drawn brass tubes for boilers, rolling into sheet for the manufacture of brazed tubes and other purposes, and drawing into wire. It may be stamped or spun, and is in general the best brass for working.

68 and 32. Brass of this composition is often used for the manufacture of solid-drawn brass tubes.

66 and 34. This is the poorest brass which is ductile enough to be drawn into tubes.

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60 and 40. This alloy, which is known as "Muntz" metal, can be rolled and forged at a red heat. It is largely used for sheathing wooden ships, and has displaced copper for this purpose. It keeps the bottom of the ship cleaner, this being due, according to Mr. Muntz, to the slow, uniform corrosion of the zinc by sea water.

50 and 50. This is the common yellow brass which is largely used for castings. It melts readily, makes clean castings, it has a fine yellow colour, but cannot be forged.

45 and 55. This alloy, containing 40 to 45 per cent of copper, is white in colour, whence it is usually called "white brass." It casts well, and is frequently used for making small castings, but it is very brittle. White brass has a fine grain, a silver-white colour, a metallic lustre, and breaks with a smooth or conchoidal fracture.

Brass Solders.—Brass and copper articles are frequently made by uniting the edges of plates by soldering or brazing. To do this it is necessary to use some alloy which melts at a lower temperature than the pieces to be united and which will alloy with them, and for convenience it must be in a fine state of division. For soft soldering a tin-lead solder is used, but for hard soldering or brazing the solder is always a copper-zinc alloy poorer in copper than the pieces to be united. For brazing copper or rich brasses a solder containing as much as 55 per cent of copper may be used, but for poorer brasses one containing from 50 down to 35 per cent of copper will answer the purpose, and, where a very fusible solder is required, tin may be added.

The brass solder is cast into cakes; these are heated to a temperature at which the alloy becomes brittle (usually just below redness), powdered in a large iron mortar, and passed through a sieve of the required mesh.

MANUFACTURE OF BRASS.

Brass is always made by melting the copper in a crucible, and adding the zinc in pieces of moderate size, stirring it very cautiously. Great care must be taken not to add too much zinc at a time, or it may cause some of the copper to set, and, as the melting point of copper is higher than that of the alloy with which it is surrounded, it would be impossible to melt it without a serious loss of zinc by volatilisation.

As zinc is very volatile, there is always some loss, and a little extra zinc is added to compensate for this. In a 70 and 30 brass about 2 per cent of zinc is added in excess of that which should pass into the alloy—that is, for each 100 lb. of brass 70 lb. of copper and 32 lb. of zinc would be used.

BRASS WITH OTHER METALS.

Very frequently in the manufacture of brass small quantities of other elements are added.

Iron.—The additon of a small quantity of iron (1 or 2 per cent) has a great influence on the properties of the alloy, greatly increasing its strength, density, and power of resisting corrosion. The influence of iron has been known for a long time, but there were difficulties in the way of the manufacture of the alloys which prevented them coming largely into use. These difficulties were overcome by Mr. Dick, and the alloy he introduced is known as "Delta" metal. Zinc is saturated with iron, and some of this alloy is added to the copper with the zinc in the manufacture of the brass, a little phosphorus being also added to prevent oxidation. The alloy casts well, can be readily forged, and has a tensile strength up to 35 tons on the square inch, with an elongation up to 30 per cent on an 8 in. test piece ; it also resists corrosion more strongly than ordinary brass. The influence of iron seems to be due to its entering into combination with the eutectic, raising its freezing point considerably.* The apparent melting point of brass containing iron is higher than that of iron-free brass of the same composition. Sterro metal and Aich metal are brasses containing iron.

Tin.—Many brasses used in machinery contain a little tin, which hardens and strengthens the alloy.

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* Fourth Report, Alloys Research Committee.

Aluminium.—The addition of aluminium to brass greatly raises its tensile strength and elongation, makes the fused metal more fluid, and renders the alloy less susceptible to oxidation.

An aluminium brass containing 66 per cent of copper and 1·36 per cent of aluminium is stated to have been tested by Professor Tetmajer, of Zurich, and to have shown a tensile strength of 38 tons per square inch. The amount of aluminium added to brass may vary from ¼ to 3½ per cent, the strength and hardness increasing with each addition of aluminium. The more zinc the alloy contains, the less is the amount of aluminium that can be added without inducing brittleness. The alloys cast well, and can be forged, stamped, or rolled at suitable temperatures. An alloy with 33 per cent of zinc and 3 per cent of aluminium works well at a cherry-red heat. The aluminium is stirred into the molten metal before or after the zinc.

ALUMINIUM BRONZE.

This alloy—which contains only copper and aluminium, and, strictly speaking, therefore is not a bronze—is one of the most valuable and generally useful of the copper alloys. The amount of aluminium in the commercial aluminium bronzes is usually from 5 to 10 per cent, though for special purposes alloys either richer or poorer may be made. The alloy with 10 per cent of aluminium has a fine golden-yellow colour, and is largely used in the manufacture of articles of jewellery to resemble gold, and these are sold under many fancy names.

The strength of the alloy varies with the proportion of aluminium present and with the way in which it has been treated, forgings—as is usually the case—being much stronger than castings. With 10 per cent of aluminium the tensile strength may reach 50 tons on the square inch, and with wires of this composition a strength of over 60 tons has been obtained. The alloy is very ductile and malleable, can be forged or rolled at a red heat, or drawn into wire. It casts well, but shrinks very much, the lineal shrinkage being 1·8 to 2 per cent, so that allowance must be made for this in making the patterns. The less aluminium the alloy contains, the higher is the temperature at which it can be cast. Five per cent aluminium bronze can be soldered with soft solder, but for higher grades a hard brass solder must be used.

Aluminium bronze resists atmospheric oxidation very strongly if it be free from silicon, but tarnishes rapidly if it contains that element. It is attacked by dilute and organic acids, moisture from the fingers, &c., but less readily than most other copper alloys; it also resists the corrosion of sea water very well.

GERMAN SILVER.

Copper and nickel alloy very readily, and such alloys, with or without the addition of zinc and other metals, are known as German silver or white metal, and are largely used for the manufacture of table ware and other small articles, fancy names, such as silveroid, silverite, electrum, Nevada silver, &c., being very often given.

The metals alloy in all proportions, but the composition of the commercial alloy does not vary very much. Commercial proportions are copper 50 per cent, nickel 25 per cent, zinc 25 per cent, to copper 60 per cent, nickel 20 per cent, zinc 20 per cent.

German silver has a white colour, takes a high polish, and is hard, tough, and malleable. Solders for German silver contain less copper and nickel and more zinc, so as to make a more fusible alloy.

WHITE BEARING METALS.

White metals are very largely used for filling journal boxes, so as to give a surface on which a shaft can run with but little friction. A good bearing metal should be durable, should not become heated, should be sufficiently soft to adapt itself to the surface which runs on it, and should be fusible enough to be readily melted out of the box. These qualities are all possessed in a high degree by several of the commercial alloys. As the alloy must be soft and fusible, the basis must be one of the soft, fusible metals, tin or lead, preferably the former, and, since these alone would be too soft, other constituents must be added to give the necessary hardness. The alloys may therefore vary very much in composition, and in hardness, durability, and other properties. Many of the commercial alloys are sold under fancy names at a high price, and too often ridiculous claims of superiority are made for them. In this, as in other cases, but little reliance can be placed on the statements made in advertisements. A few only of the best known bearing alloys will be mentioned.

Babbitt's Metal.—This is probably the most largely used of these alloys. It usually contains about—Tin 81 per cent, copper 4 per cent, and antimony 7 per cent, but as there is no absolute standard, the "Babbitt" of different makers varies very considerably in composition. Another alloy, also known as Babbitt's metal, contains—Tin 90 per cent, copper 10 per cent. As tin is a very expensive metal, it is often replaced by the cheaper lead, antimony being added to harden the alloy.

Fenton's Metal contains about—Zinc 80 per cent, tin 15 per cent, copper 5 per cent.

Durance's Metal contains about—Tin 33 per cent, copper 23 per cent, antimony 45 per cent.

Hoyle's Metal contains about—Tin 46 per cent, antimony 12 per cent, lead 42 per cent.

One of the best known and most largely advertised of the special bearing metals is Magnolia metal, and this, from tests made by various independent engineers, seems to stand far ahead of the ordinary alloys. It consists mainly of antimony and lead, with a small quantity of iron, and a trace of bismuth.

Professor Goodman has recently investigated the properties of anti-friction alloys, but the whole of his results are not yet published. He points out* that some of the alloys with which he experimented, though supposed to be the same, gave frictional results differing by as much as 100 per cent. Analysis of the samples showed that the chief constituents were present in almost exactly the same proportions, but that there were differences in the small quantities of impurities present. Further investigation showed that very minute quantities of some elements had a marked effect on the friction, some increasing and others diminishing it; and further, that those elements of low atomic volume $\left(\frac{\text{atomic weight}}{\text{specific gravity}}\right)$ increased the frictional resistance, whilst those of high atomic volume decreased it, provided that they were present in small and definite proportions. The addition of ·1 per cent of aluminium, which has an atomic volume of 10·6, produced about 30 per cent increase in the frictional resistance, whilst the addition of bismuth, which has an atomic volume of 21·1, immediately reduced the friction. When bismuth was added to a bearing metal, ·025 per cent was sufficient to perceptibly reduce the friction, and it was further reduced by additions of bismuth till ·25 per cent was added, after which any further addition produced increased frictional resistance.

It is, therefore, very important that the metals used in making anti-friction alloys should be very pure, and that if foreign elements are to be present, they should be added in known and definite quantities. It has been stated that certain anti-friction metals contain graphite, but this is certainly not the case.

FUSIBLE METALS.

The melting point of an alloy is, as a rule, less than the mean of that of its constituents, and sometimes less than that of either of its constituents, and alloys can readily be prepared which melt at a comparatively low temperature. The so-called fusible metals, which melt slightly above or

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* Proceedings, Institution of Mechanical Engineers, 1895, p. 289.

below the boiling point of water, are always alloys of bismuth and tin, often with the addition of lead or cadmium. Among the best-known fusible metals may be mentioned—

Newton's Alloy, which contains—Bismuth 50 per cent, lead 31 per cent, tin 19·2 per cent, which melts at 202 deg. Fah.

Rose's Alloy contains—Bismuth 50 per cent, tin 25 per cent, lead 25 per cent, which melts at 197 deg. Fah.

Wood's Alloy contains—Bismuth 38·4 per cent, tin 15·4 per cent, lead 30·8 per cent, cadmium 15·4 per cent, which melts at 166 deg. Fah.

Fusible alloys are used for fusible plugs for steam boilers and for making small castings.

CHAPTER XVII.

WOOD.

WOOD is very largely used for structural purposes, both temporary and permanent, its strength, its elasticity, and, above all, the ease with which it can be worked, rendering it specially valuable.

Structure of a Tree.—Wood is the more or less hardened tissue of certain perennial plants—the timber trees—and as the chemical and physical characters of the wood are largely determined by the way in which it is produced, it is necessary to describe very briefly the structure and growth of the plant. All timber trees belong to the botanical class of the exogens or dicotyledons; the endogens or monocotyledons, such as the tree ferns, having a very different structure, and being quite useless for timber.

When an ordinary timber tree is sawn across, it is seen to be made up of a series of more or less concentric rings—the annual rings, or rings of growth—which surround a central small core, the pith, and the whole is enclosed by a more or less thick layer of bark. Through the mass of the wood pass a number of minute radial lines, the medullary rays, which begin at the outer surface of the wood and pass inward, some few reaching to the pith.

When the tree is living, the actually living growing part is confined to a thin layer—the cambium—lying between the wood on the inside and the bark on the outside, and forming both by the division of its cells. In this climate growth is at a standstill during the winter, but as soon as spring comes it re-commences, the cambium cells divide up and become specialised, forming on the one side the wood and on the other the bark cells. At first in spring, when the supply of nutriment is not very large, the cells are large and thin walled, whilst as the supply of nutriment becomes larger the walls of the cells become thicker, and therefore the cavities smaller; thus the outer portion of each annual ring is different in colour to the inner portion, and as the dark portion of one ring comes against the light portion of the next, the rings are clearly marked. In tropical countries, where growth keeps on all the year round, the distinction between the annual rings may be quite obliterated. The cells of the cambium become very much modified in form, the exact form varying with the nature of the wood, but the wood is always made up of elongated cells packed closely together, thus producing the fibre or grain of the wood, the fibres being more or less broken up by the cellular patches of

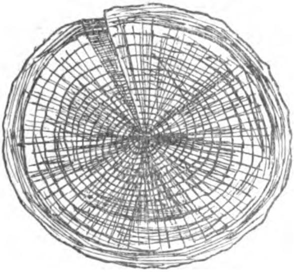

FIG. 15A.

the medullary rays, and through the mass running parallel with its fibres there may be ducts or passages, or long vessels.

Water in Wood.—When the tree is living it always contains a very large quantity of water (50 to 70 per cent), this being much greater in the younger parts of the plant than in the older, and greatest of all in the leaves. The amount of water varies with the season, and is always greatest when the growth is most active—in the summer. Even when there is most water present, however, the vessels are largely filled with air, so that the wood is lighter than water, and will float, though the materials of which it is composed are actually heavier.

Felling Timber.—When wood is to be used for timber it should be felled in winter or early spring, when vitality is least active, as then the amount of water present is much less than at other seasons. The bark is then stripped off, and the wood is left exposed to the air, lifted off the ground, and sheltered from the rain for months or years, till it becomes air-dried, and in this condition it may contain from 10 to 15 per cent of water. The more perfectly the wood is dried, the more durable is it likely to be when used in structures.

Shrinkage of Wood.—As the wood loses water it shrinks, and the shrinkage is greater in the case of the newer wood than the older, and as this new wood is outside, the contraction necessarily produces radial cracks. If planks be cut out of the wood before the shrinkage is complete, or if the wood be subsequently more thoroughly dried, they will warp, the warping always being determined by the greater contraction of the younger wood.

Dry wood exposed to moist air will absorb moisture, and this causes an expansion exactly the reverse of the contraction produced on drying. The absorption of water and resulting expansion is due to the presence of constituents in the cells which absorb water and expand in so doing. The expansion may be so great that the cracks in a dried disc completely close up.

Formation of Wood.—The cells in the living and growing cambium layer have thin walls of cellulose, and contain the nitrogenous matter known as protoplasm. As these cells become converted into woody tissue, the walls become very much thickened and changed in character. The protoplasm, to a large extent, disappears, and the cells and vessels contain various elaborated products, such as starch, resins, gums, &c., the nature and quantity varying with the plant.

Cellulose.—The primary constituent of the cell wall in the young and growing plant is cellulose, a substance which is to be had in a nearly pure form in cotton and unsized paper. It has the formula ($C_6H_{10}O_5$), and contains carbon 44·44 per cent, hydrogen 6·17 per cent, and oxygen 39·39 per cent. It is very inert to all ordinary decomposing agents, such as air and moisture, but is acted on by certain reagents, yielding products which are of commercial importance.

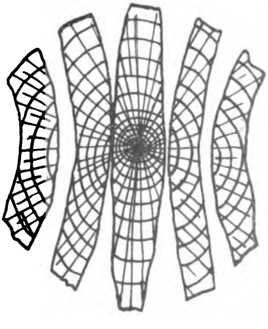

FIG. 15B.

When cellulose is treated with sulphuric acid, it is converted into an amorphous mass known as amyloid. Advantage is taken of this reaction in the manufacture of parchment paper, which is paper which has been partially converted into amyloid by the action of sulphuric acid.

When cellulose is treated with a mixture of nitric and sulphuric acids, it gives rise to nitro-substitution products, the most important of which, $C_{12}H_{14}(NO_2)_6O_{10}$, is called pyroxyline or gun cotton, and is a powerful explosive. Nitro-cellulose treated with camphor yields the substance celluloid, which is so largely used for the manufacture of small articles.

Treated with an ammoniacal solution of copper oxide, the cellulose is dissolved, and is re-precipitated from the solution on addition of acid. When such a solution is evaporated it leaves a gummy mixture of copper oxide and cellulose. Willesden water-proof paper is prepared by passing paper through the ammoniacal solution and then drying it. The amorphous layer of copper oxide and cellulose left on the surface is perfectly water-proof.

Composition of Wood.—As the growing cells become differentiated into the wood cells, and the walls become thickened, the cellulose undergoes very great changes. On the outer side of the cambium layer various complex adipo-celluloses are formed, and on the inner side various ligno-celluloses. Ordinary woody tissue is largely made up of ligno-cellulose, a mixture of cellulose and lignine. Lignine has the composition $C_{18}H_{24}O_{10}$, and contains, therefore, 55·5 per cent of carbon, and it is somewhat richer in hydrogen than cellulose. In addition, the cells contain, intermixed with the cellulose and lignine, small quantities of complex bodies containing nitrogen. The cells themselves may contain starch and other materials, stored up by the plant for its future use, and the vessels may contain resins and other complex bodies.

Wood, therefore, cannot be regarded as being a definite substance, but rather as being a mixture of substances, some of which are much less stable, and are more readily attacked by living organisms and inorganic reagents than others.

The average composition of dry wood is about—carbon 50 per cent, hydrogen 6 per cent, oxygen 41 per cent, nitrogen 1 per cent, and ash (mineral matter) 2 per cent, but all the constituents vary somewhat according to the nature, age, &c., of the wood.

Seasoning of Timber.—Wood, as has been mentioned above, is always seasoned before use. The object of the seasoning is to get rid of as much water as possible, and thus to reduce the weight and to dry up the more easily decomposable matters in the sap. Air seasoning is generally used. The wood is then stacked, so as to be protected from sun and rain, and so as to be freely exposed to the air on all sides, a free circulation of air being one of the chief essentials of good seasoning. Air seasoning may occupy from two to four years. In water seasoning the wood is kept under water for some time. In hot-air seasoning the wood is exposed to air artificially warmed to a temperature of from 100 deg. Fah. to 250 deg. Fah. Various other methods of seasoning are used occasionally.

Varieties of Wood.—Many woods are used for constructive purposes, and they vary very much in character and properties. Some are used on account of their strength, others on account of their colour or the grain which they show on the cut surface, and others for other characteristics.

The only classification of woods that need be mentioned here is that into soft and hard. The soft woods are chiefly derived from the coniferous trees, and contain various resins, though the birch, which yields a soft wood, is not a conifer. All the other timber trees yield hard woods. The hard woods are usually more durable than the soft woods.

Durability of Wood.—Wood, under suitable conditions, is very durable, but under others it decays rapidly. The constituents of wood are so inert that the decay is never brought about by the action of chemical forces alone, but always requires the aid of the lower forms of life; the conditions, therefore, which favour the decay of wood are always those which favour the growth and development of the organisms which produce it.

Dry Rot.—The best known disease of wood is that known as dry rot. The wood becomes darker in colour, decreases in weight, acquires a musty smell, and may become so soft that it can be cut with a knife "almost like cheese," if it be wet, but, if dry, crumbling under very slight pressure to a brown powder, and thus the wood becomes weak and thoroughly rotten. Dry rot is produced by the growth of a fungus (Merulius lachrymans), which lives on the wood, and ultimately destroys it. The spores of the fungus germinate on damp timber; their germinal filaments pass into the wood, pierce through the cell walls and among the cells, so as to draw nutriment from the nitrogenous matter, lignine, and other materials present on which they can live, and thus as it uses up part of the material of the wood it disintegrates and breaks up the remainder.

The conditions which favour the development of the fungus are of two kinds, those of the wood itself and those of the surroundings. The less perfectly the wood has been dried, the more readily will the fungus be able to find nutriment. Moisture is essential to the development of these forms of life, and unless this be present the "rot" cannot set in: "*Dry* timber *kept dry* is proof against dry rot."* One of the most prolific causes of dry rot is the use of wood not sufficiently seasoned. Professor Ward says: "It is clearly an act worthy of a madman to use fresh 'green' timber for building purposes; but it seems certain that much improperly dried and by no means 'seasoned' timber is employed in some modern houses. Such wood is peculiarly exposed to the attack of any spores or mycelium that may be near."

As to the surroundings, dampness is one of the most important favourable conditions; and if the wood itself be not damp, it may be in contact with damp masonry or other things, and may be surrounded by a damp, stagnant atmosphere. This with darkness and moderate warmth are just the conditions under which the fungus can grow and flourish.

Obviously, therefore, if dry rot is to be prevented, not only must the timber be put in dry, but it must be kept dry, and the space around it must be kept thoroughly ventilated.

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* Marshal Ward's "Timber and Some of Its Diseases," page 191.

It must be remembered that the disease is always propagated by the spores or mycelium of the fungus. As these spores are extremely small, not more than $\frac{1}{3000}$ of an inch in diameter, and are very light, they will be easily carried about, and one piece of timber may infect many others. Dry rot, as far as is known, only attacks wood in buildings, &c., and is unknown in the forest. There are, however, many other fungi which produce similar results. In a pine forest, it is frequently found that the stumps of the trees which have been cut down, whilst little changed in appearance, have become so rotten that they can easily be broken up, and often they fall to a powder under pressure. This change is due to the action of various fungi, the function of which in nature is, no doubt, to break up and destroy useless wood.

Wet Rot.—Growing trees are as subject to decay as cut timber, the heart wood being usually attacked, the tree being often left hollow. This is likewise usually, if not always, due to the action of a fungus, which, living on the nutritive portions of the wood, breaks up and destroys the remainder.

Other Cases of Decay.—Wood decays more or less rapidly in almost all positions, the decay being always the result of the growth of fungi, or other low forms of life, at the expense of the wood, since the constituents of the wood are so inert that, apart from the action of living organisms, there would be little tendency to alteration.

Preservation of Timber.—Obviously, if the decay of timber is produced by the action of living organisms, the decay can be prevented by destroying the organisms, or making the conditions such that they cannot thrive.

If the wood be perfectly dry, painting the surface, or covering it with a layer of some impervious material, may preserve the timber; but if it be at all damp, then such a coating will do more harm than good, for it will prevent the escape of moisture, even if the surface be exposed to the air. It very often happens, therefore, that a carefully-painted piece of timber will be destroyed, except for a thin external shell.

The fungus is killed by creosote, mercuric-chloride, copper sulphate, and many other mineral poisons; but the mere application of these to the surface of the wood is of little avail, as decay may still go on in the interior. Similarly, charring is only a very partial protection; the layer of charred wood gives some protection, and in charring the wood below the surface will be more or less thoroughly dried, but moisture will soon be absorbed again, and then decay may set in.

The only satisfactory method of preventing the "rot" is to thoroughly saturate the timber with the antiseptic solution—that is, the air in the cells and vessels must be completely, or at anyrate to a large extent, displaced by the antiseptic solution, so that the material on which the fungus has to feed is effectively poisoned.

In Bethell's process, which is perhaps the most generally used, the wood is dried, placed in an iron cylinder, and creosote is pumped in at a temperature of about 120 deg. Fah., and at a pressure of about 170 lb. per square inch. Very frequently the vessel is first exhausted of air, so as to facilitate the escape of air from the wood. Soft wood may absorb about 10 lb. of creosote per cubic foot, whilst hard wood, such as oak, will take very much less. Creosoting seems to be the most efficacious method of preserving timber.

Kyan's process (Kyanising) consists in saturating the wood with a solution of mercuric-chloride (corrosive sublimate); in Boucherie's process copper sulphate is used; and in Burnett's, zinc chloride.

Attacks by Animals.—Under some conditions wood is liable to be attacked by animals of various kinds, boring animals occurring both in earth and in water. For wood which has to be buried in earth charring seems to be a fairly good protection, and creosoting also answers very well.

CHAPTER XVIII.

STONE.

Stone.—Stone is very largely used for structural purposes; indeed, it may be said to be the natural material for permanent structures. The beauty and durability of suitable stone, and the readiness with which it can be worked to any required form, are very great advantages, whilst its only disadvantage is the cost, and the advantages so much outbalance the disadvantage that stone is invariably used for important structures, and even for ordinary work in all localities where it can be readily obtained.

Stone occurs in nature in such abundance, and in such great variety, that stone suited for any purpose can usually be obtained.

Classification of Stone.—Stone can be used for so many purposes, that it is sometimes convenient to have a classification based on purposes for which it can be used; *e.g.*:

1. Building stones. Those which are used for building purposes.
2. Ornamental stones. Those which are used for internal or external ornament, and for small structures such as tombstones.
3. Paving and roofing stones. Those which can be split into more or less thin layers, such as slates and flagstones.
4. Fire stones. Those that can be used in the construction of parts of furnaces which are required to withstand a high temperature.

It is quite obvious that these groups are not mutually exclusive, there being no reason why a building stone should not also be an ornamental stone or a fire stone, since the properties of the one are not incompatible with those of the other.

For practical and descriptive purposes, stones are best classified according to their geological character and mode of origin, each class being then subdivided according to chemical composition. A convenient classification on these lines is:

1. Igneous rocks, including such sedimentary rocks as have undergone sufficient metamorphic change to destroy the stratification and induce a crystalline structure, *e.g.*, granite, basalt, &c.

2. Sedimentary rocks, or those which have been deposited from water, and still retain their original structure, though they may have subsequently undergone some metamorphic change.

α Sandstones.
β Limestones.
γ Claystones, including slates.

The characters on which the value of a stone depends are many, and those which are most important depend on the purpose for which it is to be used.

Durability.—In most cases this is of primary importance, for stone is only used for structures which are intended to be permanent.

Stone used for building purposes is exposed to the air in all weathers, and is therefore subject to the corrosive action of air, moisture, carbonic acid, and of other acids in the atmosphere of towns, and to the disintegrating action of frost. The effect of these agents will depend both on the chemical composition and physical structure of the stone, and, therefore, whilst chemical analysis gives valuable information, it is not all that is required to enable a judgment to be formed as to the probable durability of a stone. It must be remembered that time is a very important factor in chemical change, and that very weak reagents acting for a long time may produce serious results, while during the short time over which a laboratory experiment can be extended no change whatever could be detected.

The action of atmospheric disintegrating agents varies very much. In the case of stones of uniform texture, the action may be uniform all over the surface, and may be shown only by a wearing away or rounding of projecting edges;

whilst if the texture be very uneven portions may be eaten away irregularly, the stone first becoming rough, and then being more or less completely disintegrated. Sometimes the material of the stone breaks away in flakes from the surface, and many stones, whilst they do not disintegrate in the ordinary sense, undergo changes of colour, often in irregular patches, by which their beauty is completely destroyed. Many stones which are permanent in the country discolour more or less rapidly in the atmosphere of towns.

Mechanical disintegrating agents such as the wind, blown sand, the mechanical action of rain, &c., are of little importance for ordinary building stones in this country, since their action will always be very small.

Organic disintegrating agents must not be overlooked, though no doubt their action on structures is usually slight. In country districts stone very frequently becomes covered with green, growing organisms, and these may attack the stone. In the case of limestones, the acid which they secrete in their rootlets, or the carbonic acid which they evolve during growth, helps to destroy the stone, but if the stone is not thus attacked, the growing layer may to some extent protect it from atmospheric corrosion.

The durability of a stone exposed to variations of temperature depends somewhat on its porosity. The more porous it is the more water it will absorb, and the greater will be the disintegration produced by the expansion of this water as it freezes. In this country the freezing of absorbed water is one of the principal causes of the disintegration of building stones.

The best method of determining the durability of a stone is, wherever possible, to examine an old building built of it.

Hardness.—For some purposes the hardness of a stone is of importance, as on this depends its power of resisting mechanical abrasion. For paving purposes, a stone which contains hard mingled with softer constituents is often well suited as the irregular wear produces a slightly rough surface, which gives a foothold, whilst hard stones, if of uniform texture, wear to a very smooth surface. When stone is required for positions where it is exposed to running water, a hard stone should be used, as the abrading action of water is considerable.

Strength.—The strength of stone for compression is of little moment, because wherever it is used for structural purposes this strength is much greater than is actually necessary. The weakest sandstones will bear a pressure of over 100 tons per foot of area, while strong stones, such as granite, will bear seven or eight times as much. The pressure on any stone in building is far below this; indeed, it has been stated that the greatest stress on any part of the masonry of St. Paul's Cathedral is about 14 tons per square foot.

Weight.—Stones vary somewhat in weight, usually ranging between 120 lb. and 170 lb. per cubic foot. The differences are, however, not sufficient to be of much practical importance.

Working the Stone, &c.—The sedimentary rocks have been deposited in more or less regular layers, and this stratification may in some cases be very distinct, whilst in others it may be quite unnoticeable; it is, however, almost always sufficiently marked to interfere with the durability of a stone if attention is not paid to it in the setting. Stone should always be set with the bedding horizontal—*i.e.*, either in the position in which it occurred in nature or upside down. Where stress has to be borne, as in arches, the stone should be cut so that the thrust is at right angles to the bedding.

If a stone be set with the bedding vertical, there will always be a tendency for it to scale under the influence of frost.

Many stones harden considerably on exposure to the air, being much softer and more friable as they come from the quarry than after they have been "seasoned." This is probably largely due to loss of water. Most stone is improved by being left exposed to the air, so that it can slowly dry before being used.

Testing Stone.—A judgment as to the character of the stone can be formed from its appearance, and from a few simple tests, but these are more or less uncertain, the only real test being that of actual use.

When the stone is broken, and the fractured surface is examined with a magnifying glass, it should appear solid and compact, the particles being well cemented together; "a dull earthy appearance betokens a stone likely to decay."

The amount of water which the stone will absorb when soaked for 24 hours or so is held by some to be a good test; the better the stone the less water will be absorbed. The amount of water absorbed may vary from ½ per cent to 20 per cent of the bulk of the stone. The amount absorbed by the crystalline stones such as granite or trap is very small. Limestones absorb up to 15 per cent, and sandstones up to 20 per cent. It is only with the last named that the test seems to be of any real value. It has been stated that durable sandstone should not absorb more than 10 per cent of water. The condition of the stone as to dryness, &c., before the test is made, will very much modify the amount of absorption, so that for the test to be of any value the stones tested must be in the same condition of dryness.

Acid Test.—Chips of the stone are immersed for some days in a 1 per cent solution of sulphuric or hydrochloric acid. This test is of no value except in the case of sandstones, and with them it only indicates whether or no the cement is soluble in acid. Other tests have been suggested, but they are of little real value.

VARIETIES OF STONE.

Granite.—Under the name of granite are included a considerable number of rocks, differing largely in appearance, properties, and mode of origin, but agreeing in their general petrological character. The granites are all distinctly crystalline, the size of the crystals varying from an inch or more in length, as in the porphyritic granites of

Shap, to an almost microscopic size in some of the very fine grained granites. Granite is composed essentially of three minerals: quartz (SiO_2), usually white and glassy; felspar (a silicate of alumina and potash, or some other base), often in large crystals; and mica (a complex silicate of alumina and other bases), in flaky crystals, usually of small size, and scattered through the mass there are very often crystals of garnet and other secondary or accessory minerals. The colour of the rock depends mainly on the colour of the felspar and the mica; when pink felspar (orthoclase) is present, the colour is pink, whilst, when the felspar is white and the mica black, the granite is grey. The colours vary considerably according to the proportions in which the various constituents are present.

Granite is usually classed as an igneous rock; but whilst it is probable that some of the granites have been formed by fusion, there are others which have certainly been produced by the metamorphism of stratified rocks without fusion, probably under the combined influence of heat, water, and pressure.

Granite is largely used for heavy work, where great durability is required, and for ornamental columns and other parts of structures, in this case it being usually polished. It is only used as a building stone in neighbourhoods where it occurs in abundance. It is hard and difficult to work, and therefore is expensive.

Granite is usually regarded as being a very durable stone; but whilst on account of its hardness it is undoubtedly good for resisting heavy wear, it does not resist the corroding influences of the atmosphere as powerfully as is often supposed. Felspar, especially the pink, potash variety, yields in time to atmospheric influences, breaking down ultimately to a soft, incoherent mass of kaolin or china clay, and it is by no means uncommon to find beds of granite which have been exposed to the air for ages so weathered to a considerable depth. The corrosion that has been observed in granite structures is, of course, much less, being mainly confined to a loss of the polish and a roughening of the surface, due to the corrosion of the felspar crystals. If iron be present in any form, it may accelerate decay, especially if it be irregularly distributed in the form of pyrites (FeS_2). This is indicated by the production of iron stains on the surface of the stone on exposure to the weather. As a general rule, the smaller is the grain of a granite the more durable it is likely to be, and at the same time the more easily will it be worked.

Syenite closely resembles granite, except that the mica is replaced by hornblende ; or if mica and hornblende are both present, it is a syenitic granite. The syenites are often darker in colour than true granites, and are hard and tough.

Igneous rocks other than granite are not used to any large extent, except in localities where they are abundant.

The porphyrites are compact rocks of igneous origin ; consisting of a felspathic base, in which crystals of quartz, felspar, and other minerals are developed. They contain from 50 to 80 per cent of silica, and vary very much in colour and in chemical and mineralogical composition. They are mainly used in this country for road metal.

Trap Rocks.—Under this head may be included a large number of rocks, the greenstones or whinstones (diorite- diabase, &c.), the basalts, and others. They are all of igneous origin, having cooled from fusion. They vary very much in chemical and mineralogical composition, and consist mainly of felspars, with hornblende or augite, and other minerals. The percentage of silica is low, so that the rocks are basic in character. The colour varies from grey or green to black, according to the colour of the minerals present, and they are fine grained, compact, and dense. Owing to the way in which the rocks are usually cracked, it is not easy to obtain large blocks of the stone, so that it is very little used for building purposes, but is well suited for road paving and road metal. Most of these rocks weather very readily, the surface becoming brown from the oxidation of the ferrous oxide present, the stone ultimately becoming soft and incoherent.

Sandstone.—Sandstone consists of larger or smaller grains of sand united into a solid mass by some cementing material, the most common being silica, carbonate of lime, and oxide of iron. Since sand is silica (SiO_2), which is very hard, and is quite unacted on by all ordinary re-agents, the durability of a sandstone will depend mainly on the nature of the cementing material, and, to some extent, on the nature of any intermixed substances that may be present. The sand has always been deposited from water, and the cementing of the particles has been due to subsequent changes.

The classification of sandstones is not by any means easy, as many terms are used—to describe varieties—which will not fall into any systematic classification. Thus, any stone which cuts and works well is often called a *free stone*, a sandstone in which the particles are large is called a *grit*, and a sandstone which will easily split into layers is called a *flagstone.* The most convenient classification for our purpose is probably that according to the nature of the cementing material :—

1. Siliceous sandstones, in which the cement is silica.

2. Calcareous sandstones, in which the cement is carbonate of lime.

3. Ferruginous sandstones, in which the cement is oxide of iron.

4. Felspathic sandstones, in which the cementing material is felspar.

1. The siliceous sandstones may contain as much as 99 per cent of silica. They are very hard and are extremely durable, indeed, they are apparently quite unacted on by atmospheric disintegrating agents. Sir A. Geikie points out that tombstones of this variety of sandstone, in Edinburgh, show distinctly the chisel marks on the polished surface after over 200 years exposure to the weather, a durability which is not equalled by any other stone. They are usually

white in colour, and they are well suited for building or for any purpose where durability is required.

2. Calcareous sandstone is usually white in colour, and the particles are cemented by carbonate of lime. While the sand is quite durable, the carbonate of lime is readily attacked by water containing carbon dioxide, soluble bicarbonate of lime being formed—

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2,$$

and thus the stone is soon disintegrated. Speaking of a monument of a stone of this class, erected in 1863, Sir A. Geikie says that the inscription is no longer legible (1882), the stone being eaten away at a rate equal to about $\frac{3}{4}$ in. in a century.

3. In felspathic sandstones the matrix is felspar. As this often weathers into a clay-like mass, such stones are not durable.

4. The ferruginous sandstones are characterised by their red colour, the cementing material being oxide of iron. They are largely used for building purposes, and are usually durable.

Colour.—The colour of sandstones varies very much; some are quite white, others are grey, and others are various shades of yellow and red. The red colour is due to the presence of ferric oxide, or a hydrate containing but little water, whilst the yellow colour is due to the presence of hydrated ferric oxides; blue or grey tints, especially in the calcareous sandstones, are due to the presence of ferrous carbonate and silicate, which, under the influence of air and moisture, may pass into the condition of ferric hydrate, thus staining the stone brown. The ferrous carbonate is often not distributed uniformly through the stone, but is in strings or nodules, which, when they weather, give the stone an irregular brown mottling, which is most disagreeable; in the atmosphere of towns, and, to a less extent, in the country, red sandstones gradually darken in colour and become unsightly.

Flagstones.—When the sand as it was deposited was mixed with mica, the flakes of this mineral settling into layers give the resulting stone a cleavage parallel to the lines of bedding. Such stones are easily cleaved into flat sheets suitable for paving, whence they are called flagstones or tilestones. These stones split so easily that they are unsuited for building purposes, and, if used, must always be set with the lines of bedding horizontal. Sir A. Geikie mentions a tombstone of such a material, erected in 1841, in which the lettering remains perfectly distinct, but the stone is breaking up in scales.

Altered Sandstones.—When sandstones have undergone metamorphosis they yield stones which are very hard and durable, but are difficult to work. They are well suited for grindstones, for furnace construction, and for various other purposes.

Limestone.—Limestone is composed principally of carbonate of lime, with small quantities of other impurities.

Limestones are very widely distributed in rocks of all geological ages, and are almost always composed of the calcareous shells of minute forms of life. They vary very much in texture and properties, from highly crystalline marble to loosely coherent chalk.

Limestones may be classified into the following groups:—

1. Limestone.
2. Marble.
3. Magnesian limestone.

1. *Limestone.*—Limestone may be fine grained and compact or oolitic, in which case it consists of distinct grains of carbonate of lime cemented together by crystallised carbonate of lime or other substance, the granules varying from a very small size in the true oolitic limestones, larger in the roestones, to as large as peas in the pisolites or pea stones; fossils are nearly always present, and when the limestone consists almost entirely of these, it is called shell limestone, often being named according to the shells which are present.

Limestones vary very much in colour according to the impurities that are present; they may be quite white if pure, blue or grey if organic matter be present, and red in the presence of oxide of iron; they also vary in density and in the amount of water they will absorb. Limestones are very largely used for constructive purposes of all kinds, the coarser grained stones for outside work, and the fine grained stones, from their evenness of texture, are specially suited for inside decorative carving.

Limestones are not very durable, as they are comparatively soft, and calcium carbonate being soluble in water containing carbon dioxide, they are more or less attacked on exposure to the air; sharp, projecting edges are thus rapidly destroyed, and therefore such stones should never be used for external ornamental carving. For large work this surface solution is of little importance, as in the case of stones of very even texture it may be fairly uniform all over the surface, and the weight of the stone will not be sensibly reduced except on very long exposure.

The disintegration of marble tombstones has been investigated by Sir A. Geikie, and as the disintegration of all limestones is much of the same character, the result of his researches is of considerable importance. He says: "The process of weathering in the case of this white marble presents three phases sometimes to be observed in the same slab, viz., superficial solution, internal disintegration, and curvature with fracture."

1. The first stage is brought about by the acids in the air—carbonic acid in the country, and in towns sulphuric and sulphurous acids in addition. The polish on the marble soon disappears, the mass is irregularly attacked, and the surface becomes loose and granular. In one case, that of a monument erected in 1864, the surface had become so rough by 1882 that the particles could be rubbed off with the finger. Just as in the case of etching with acids, this superficial action is often irregular and brings out the internal structure of the stone. The rate of this action

depends on circumstances, but on monuments erected in 1803 the lettering had become illegible by 1882.

2. Marble monuments sometimes become "covered with a dirty crust, beneath which the stone is found on examination to be merely a loose crumbling *sand* of incoherent calcite granules. This crust seems to form chiefly where solution is feeble." Whilst the film remains unbroken the slab appears little changed, but once the crust is broken the stone decays rapidly, it having been partially destroyed already. "The crust varies in colour from dirty grey to a deep black, and in thickness from that of writing paper up to at least a millimetre." The film seems to be calcium sulphate formed by the action of the sulphuric acid in the air entangling particles of soot; as the layer cracks the air and rain water find their way into the stone and the disintegration of the stone goes on beneath the crust owing to the action of the carbonic and other acids.

3. In many cases marble slabs used as tombstones become in the course of years bent, distorted, and cracked. This seems to be due to the freezing of water which the stone has absorbed.

These observations of Sir A. Geikie refer, of course, only to marble in the atmosphere of a town. No doubt other forms of limestone would behave similarly, and the action of country air, free from acid fumes, would have much less effect; nevertheless, limestones are, as a rule, to be avoided, though some of them are the best-known building stones.

Marble.—Marble is crystalline limestone. It is probably originally of organic origin, like the ordinary limestones, but having been subjected to the action of heat and other agents has become crystalline. Pure marble is white, colour being always due to impurities—iron oxide in the case of red marbles, organic matter in the case of black marbles. Many marbles are most beautifully marked.

Magnesian Limestone.—This rock is a mixture of carbonate of lime and carbonate of magnesia. It is often called dolomite, but this is the name of the mineral ($CaCO_3MgCO_3$)

in which the carbonates are present in equivalent proportions. The amount of carbonate of magnesia in these limestones varies very much, but the nearer the stone approaches the composition of a dolomite the more durable it is likely to be. Magnesian limestones vary in colour from white to buff, the latter colour being due to the presence of oxide of iron. They are attacked by water containing carbonic acid, in the same way as limestones, and they are, therefore, not suitable for fine work which has to be exposed to the air.

Argillaceous Stones.—The clays and shales are too soft for structural purposes, so that the only stones of this class that can be used are those which have undergone hardening, and of these the only ones of any importance are the slates. These are essentially clays from which the water of hydration has been expelled, and in which a cleavage has been induced by lateral pressure. This cleavage bears no necessary relation to the lines of bedding.

Slates are fine grained, vary in colour from grey to purple, green, or nearly black, and often show characteristic markings. They always are of the paleozoic age. Slates are exceedingly durable as they are not acted on by any ordinary re-agents.

ARTIFICIAL STONE.

Many attempts have been made to prepare building blocks which shall have the character and appearance of stone. They are always made of particles of some very durable stone, cemented together by a suitable cement, or by melting the material and casting it into blocks.

Ransome's Stone is made by mixing sand with silicate of soda and a little chalk or other similar material. The materials are incorporated in a pug mill, and are poured into moulds. The blocks are then saturated with a hot solution of calcium chloride. The calcium chloride soaking into the blocks comes in contact with the silicate of soda; a double decomposition takes place by which sodium chloride (common salt) and calcium silicate are formed; the latter binds the whole into a hard mass, and the former is washed out with water. This stone is fine grained, weighs about 120 lb. per cubic foot, is hard, durable, and resists corrosive agents.

Victoria Stone consists of finely powdered granite, the particles being cemented together with Portland cement, and the blocks hardened by immersion in a solution of sodium silicate for some weeks. No doubt the sodium silicate is decomposed by the lime in the cement, calcium silicate being formed and binding the mass together. It is mainly used for paving, and is said to be hard and durable.

Chance's Stone "is made by melting Rowley rag, a basaltic rock found in Staffordshire, and casting it into the shapes required for different architectural ornaments." Similar stones are made by melting blast furnace slag with or without the addition of other substances, according to the nature of the slag. Such materials are usually more or less glassy and brittle, owing to the rapidity with which they are cooled.

Preservation of Stone.—When a building has been erected of an unsuitable, non-durable stone, it may be necessary to treat it with some preservative to retard its disintegration. This frequently happens with limestones. A very notable case is that of the Houses of Parliament, London, in which the stone used was a magnesian limestone. A mere surface cover, such as paint, is of little use, as the disintegrating agents will soon find their way through it—besides which, paint destroys the character of a stone building—but the stone must be saturated with the preservative, so that its pores are filled up, and air cannot find access. The number of materials that have been suggested is almost innumerable, oil, paraffin, and many other similar substances having been used with more or less success. The only substance which seems to have been a success is soluble silicate, such as sodium silicate, either alone or mixed with a salt, such as calcium chloride. If sodium silicate alone be used, this is slowly decomposed by the carbon-dioxide in the air, silica being liberated. If after the sodium silicate has been used calcium chloride be applied, double decomposition will take place and calcium silicate will be formed.

It cannot be said that any of the preservatives are an unqualified success; indeed, it is difficult to see how they can be, especially when they have to be applied to the stonework of existing buildings, which cannot be either quite clean or quite dry, and which it is therefore impossible to saturate thoroughly with the preservative.

CHAPTER XIX.

CLAY AND CLAYWARE.

THE use of clay for structural and other purposes dates from the remotest antiquity. Men found in clay a material which, owing to its plasticity, could be moulded into any required form, and they were not slow to discover methods of using it. At first the articles made were only sun-dried, and, therefore, were very fragile, and would not withstand the action of water; then the art of making them permanent by burning was discovered, and, much later, the method of making them impervious to water by means of a glaze or enamel.

Burnt clay is probably the most durable of all materials. Engraved bricks nearly six thousand years old have been found in the ruins of Babylon and other great cities of antiquity retaining every mark as distinct as on the day that they came from the oven.

Clay.—The most striking properties of clay are the plasticity it acquires when it is mixed with water, and that the plastic mass becomes hard when the water is expelled by heating to redness. The first property allows of the ready manipulation of the clay into any required form, useful or ornamental, and the second enables these forms to be made permanent—qualities not possessed by any other material.

Clay rocks are abundant in all geological ages. Those of the paleozoic period have often undergone such changes that they have lost the power of becoming plastic when mixed with water. They are then hard and stony, and very frequently have developed a slaty cleavage. They are called clay slates, and are argillaceous rocks rather than clays.

The clay rocks of the upper paleozoic and mesozoic periods are soft, easily pulverised, usually of a dark colour, and with a talcy or soapy feel, and are called shales. They are not plastic as they occur, but on mixing with water acquire the property in a high degree. Most of the clays used in the manufacture of firebricks belong to this class. The clay rocks of the cainozoic (or tertiary) and recent periods usually retain enough water to be more or less plastic as they are got from the earth. Most of the ordinary brick clays belong to this class.

Clay is essentially a hydrated silicate of alumina, having the formula $Al_2O_3SiO_22H_2O$, and containing, therefore—alumina 39·7 per cent, silica 46·4 per cent, and water 13·9 per cent. In the pure form it is perfectly white, has a soapy feel, becomes very plastic when mixed with water, and is called kaolin or china clay. It loses water when heated, becomes hard, loses the power of becoming plastic with water, and is infusible at all furnace temperatures.

Kaolin is always produced by the atmospheric disintegration of felspar (orthoclase). This mineral has the formula $K_2OAl_2O_36SiO_2$. Under the influence of air, moisture, and carbon-dioxide it is broken up, the potash is dissolved out together with two-thirds of the silica, water is taken up by the residue, and kaolin is thus formed.

Pure kaolin can only be produced by the weathering of a pure felspar rock, and as these rocks are very rare, the kaolin is usually mixed with quartz, mica, and other materials, which were present with the felspar, but which resisted atmospheric disintegration more powerfully.

Clays are very rarely found in the places where they were formed. The kaolin, being light, is washed away by rain into the streams, and is thus carried out to sea; there it slowly subsides, and in time forms beds of clay, in which the kaolin will obviously be mixed with other materials and deposited at the same time. Clays are, therefore, often very impure, and the material is called a clay so long as it contains enough kaolin to become plastic when it is mixed with water.

Impurities in Clay.—That clays are impure is shown by their colour, since this is very rarely white. The most important impurities are:—

Silica.—The kaolin itself, of course, contains silica in combination, but there is generally, in addition, more or less intermixed free silica or sand. This is not by any means objectionable in most cases; it diminishes the plasticity, but at the same time it decreases the shrinkage which will take place on drying and firing the clay. It somewhat increases the fusibility, but not enough to interfere with the use of the clay for making firebricks; but if present in too large quantity, it may seriously diminish the strength of the brick. The most fusible mixture contains $Al_2O_3 17SiO_2$, or about 86·2 per cent of silica.

Ordinary fire clays contain from 45 to 70 per cent of silica, and from 0 to 50 per cent of uncombined silica or sand.

Alkalies (Soda and Potash).—These are always present, but usually only in small quantity. As they increase the fusibility of the clay very much, it does not take much of either of them to render a clay unfit for use in making firebricks. Snelus states that 1 per cent renders a clay too fusible for that purpose. For ordinary bricks the alkalies are of little importance unless present in unusually large quantity.

Sodium chloride is sometimes present, and is objectionable.

Lime.—The alkaline earths are nearly as objectionable as the alkalies, since they form fusible double silicates of lime and alumina, with the alumina and silica present. In large quantity, therefore, lime may make the clay so fusible that the bricks will soften and lose their shape, and even in small quantity it will render the clay quite unsuitable for firebrick making. In badly-made bricks lumps or pebbles of limestone are sometimes present. On firing the carbon-dioxide is expelled, lime being left, and this is not in close enough contact with the silica and alumina to enter into combination. It therefore remains in the brick as a lump of lime. When the brick is wetted and the water reaches the lime, calcium hydrate is formed, with a considerable evolution of heat and often sufficient expansion to break up the brick.

Oxide of Iron.—This is always present in larger or smaller quantity, and its influence varies much, according to the conditions to which the bricks are exposed. Heated in an oxidising atmosphere ferric oxide does not seriously impair the fusibility of the brick, since it is not readily fusible, and ferric silicates are not formed; but in a reducing atmosphere oxygen is removed, and ferrous oxide is formed. This combines at once with the silica, forming a very fusible black ferrous silicate. For firebricks the quantity of ferric oxide should not exceed about 1·0 per cent, though many good clays contain somewhat more.

Clays containing much ferric oxide are usually more or less yellow or red. Ferrous oxide is sometimes present, and is more objectionable than ferric oxide, as it can combine more readily with silica; it gives a green or black colour to the clay.

Iron Pyrites—FeS_2—is very frequently present in clay. In small quantities it is oxidised during burning; the sulphur is burnt out, ferrous oxide is left, which at once combines with the silica, forming black ferrous silicate, which is absorbed by the brick. The spot where the pyrites was, is thus left as a hole surrounded by a black stain. If the particles of pyrites are very numerous, the brick may thus be rendered too porous. Large fragments of pyrites may expand on oxidation sufficiently to break up the brick.

Organic Matter is often present, especially in coal measure clays. It gives them a black colour, but is not objectionable, and is burnt out when the clay is fired.

Action of Heat on Clays.—When a clay which has been mixed with water and moulded is dried, it shrinks very considerably, and often very irregularly; on firing, it loses the two molecules of water of combination, and again shrinks very much. The purer the clay, the more it will shrink. Pure kaolin shrinks so much, and becomes so distorted and cracked, that it can hardly be used without the admixture of other materials. Clays which contain a large quantity of kaolin, and which, therefore, shrink very much, are often called fat clays; whilst those which contain much intermixed matter, and therefore shrink less, are called lean clays. The fat clays are always mixed with some foreign material, usually burnt clay or sand, before moulding.

If the clay contain no fluxing material capable of combining with the silica to make fusible compounds, the burnt clay is open and porous; but if such substances be present, the granules of clay become fused or fritted together, and the resulting burnt clay is more or less vitrified. For some purposes this is an advantage; for others it is not. As the vitrification is semi-fusion, a clay which is to be used for bricks which are to be exposed to a high temperature should not show any signs of it on heating.

When a clay is fired the water of combination is expelled, the organic matter is completely burnt out, the iron is left in the form of ferric oxide colouring the brick red, unless the atmosphere be reducing, when, owing to the formation of ferrous silicate, the mass may become black and vitrified; the pyrites is oxidised as already described.

CLASSIFICATION OF CLAYS.

1. *Pottery Clays.*—These are free from impurities which will impart a colour after firing. They are fat clays, so that

they need the addition of some non-contracting material, and they should be free from fluxing constituents.

2. *Fire Clay.*—This must be free from all fluxing materials, and almost always contains silica much in excess of that present in pure kaolin, some fire clays containing so much free silica that they have barely enough plasticity to allow of moulding.

3. *Brick Clays.*—These are more or less impure clays, the amount of impurity allowable depending on the nature of the bricks to be made, and the conditions to which they are to be exposed.

α. *Plastic Brick Clays.*—These are fairly pure clays, containing but a small quantity of fluxing material, so that the mass is not much fritted after firing.

β. *Loams.*—These are clays containing a large admixture of sand. Such clays frequently require the addition of fluxing material, or the bricks, after firing, are likely to be weak. They also frequently contain gravel, which must be separated.

γ. *Marls.*—These are clays containing intermixed carbonate of lime, and often also sand. On firing, bricks made from such clays become partially vitrified, but care must be taken that the amount of fusible material is not so great that the brick will soften and go out of shape.

Effect of Physical Structure, &c.—The character of a clay cannot be altogether determined from its chemical composition, since the physical nature has some influence. This is specially the case in fire clays, bricks made from exactly similar clays sometimes differing in fusibility and in other characters: "The refracting nature of the clay depends to a great extent on the mechanical arrangement of the particles, for of the two materials having exactly the same chemical composition, one being coarse and the other fine, the coarse may be practically infusible, while the fine may be more or less easily fusible. The more porous the substance is, the more infusible it will be." *

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* Davis, "Bricks, Clay, &c."

The following analyses will be sufficient to show the general character of clays. They are mainly selected from Davis' excellent volume on bricks and clays.

	1	2	3	4	5	6	7
Silica (combined)	27·20	44·35	30·40	28·40	46·10	34·70	33·00
Alumina	23·30	35·30	24·68	24·11	35·24	31·34	23·80
Water (combined)	8·40	13·07	9·00	7·20	10·30	12·00	6·70
Silica (sand, &c.)	36·10	1·30	31·05	10·50	1·70	12·20	29·10
Potash, K_2O	..	·75	·20	0·95	1·96	·79	2·01
Soda, Na_2O	..	..	..	..	..	0·16	0·76
Lime, CaO	·73	..	..	..	..	..	..
Magnesia	..	..	·10	..	..	0·10	0·57
Ferric oxide, Fe_2O_3	1·80	1·60	1·67	0·79	2·26	·16	1·60
Water and organic matter	1·90	2·70	1·90	·70	3·00	8·00	4·94

1. Stourbridge clay. 2. Garnkirk. 3. Glenboig. 4. China clay, Redruth. 5. Derby clay. 6. American potter's clay. 7. Pipe clay.

BRICKS AND TILES.

Bricks and tiles used in engineering work may be divided into three classes :—

1. Building bricks.
2. Fire bricks.
3. Paving bricks and tiles.

These are all, with the exception of some forms of firebrick, made of some variety of clay.

Building Bricks.—These may be classed in various ways, according to the purpose for which the classification is intended, the usual arrangement being :—

a. Ordinary Bricks.

β. Cutters or Rubbers.—These are made softer than ordinary bricks, so as to allow of their being cut or rubbed into any form required for use.

γ. *Underburnt and Mis-shapen Bricks.*—These are fit only for inside work, and are called grizzle or place bricks.

Other classifications are used, which vary much according to the district, the treatment the clay has undergone before moulding, method of firing, &c., but these distinctions are of little importance.

A good brick should be free from flaws and cracks, and when broken should show a uniform fracture, lumps should be absent, and lumps of lime are specially objectionable. The firing should have been carried out at a temperature sufficient to produce incipient vitrification, and the bricks should be so hard as not to yield to the knife. They should be uniform in shape and size, the surfaces should be flat, and the edges sharp.

A brick should be capable of standing a pressure (compression) of 10 to 20 tons without cracking. Hard-burnt bricks may stand much more, while very soft bricks may yield with less. For large structures, arches, &c., where the pressure will be great, strong bricks should, of course, be selected. Bricks are usually very porous, and absorb one-sixth to one-tenth their weight of water, but where vitrification has partially taken place the amount absorbed may be much less.

Bricks can be made of any required form and size. Ordinary building bricks are about 8¾ in. long by 4½ in. wide by 2½ in. deep, and weigh about 7 lb., though the sizes used in different localities vary somewhat.

White Bricks.—These are made of clay containing very little iron. Sand is usually mixed with the clay, and sometimes chalk, if the clay will bear it. The addition of chalk allows the use of clay containing more iron. The bricks must be well burnt, and during burning must be protected from reducing agents.

Red Bricks.—The red colour is invariably due to the presence of ferric oxide. The colour, however, varies very much, according to the form in which the iron is present in the clay, and certain clays are famous for the fine colour of the bricks which they yield. Red bricks should be guarded from the influence of reducing agents during firing, or the colour may be impaired. Red bricks are now made by the addition of oxide of iron in a suitable form to white clay.

Blue Bricks.—These are made from clays containing a considerable quantity of oxide of iron. They are fired at a sufficiently high temperature and under such conditions as to ensure the reduction of the ferric oxide to the ferrous condition, the ferrous oxide then combining with the silica to form a ferrous silicate, which being blue-black gives the colour to the brick. Owing to the fusibility of the ferrous silicate these bricks are always vitrified, and they are strong, durable, and non-porous.

Manufacture of Bricks.—The manufacture of bricks is comparatively simple. The clay is allowed to weather—either alone or mixed with the other materials that are to be added to it—for some time. Stones are picked out, and the clay is ground to a coarse powder under edge runners or between rolls. It is then tempered by adding water and thoroughly mixing, either by turning over and beating, or in a pug mill. When the former method is used the operation takes a long time, and is usually carried out in the early months of the year, before actual brickmaking begins.

Moulding.—The moulds are rectangular frames of wood, often lined with metal, or of brass, so much larger than the brick is to be made as to allow for the contraction which takes place during drying and firing, which may amount to about 1 in. for each linear foot. This frame rests on a stock-board, which fits it, and in the middle of which is a projection to form the frog of the brick. The tempered clay is dashed into the mould, pressed home so as to fill every corner, and the surface is levelled by means of a straight-edge, which is drawn across the top of the mould. To prevent the clay adhering to the mould it is dipped in water (slop moulding) or sprinkled with sand (sand moulding) before use.

Hand moulding is being rapidly superseded by machine moulding, in which either the clay is automatically delivered to moulds and pressed, or it is delivered from the tempering machine in a continuous mass, which is cut up by wires into blocks of the required size. Bricks made by this process are, of course, without a frog.

Drying and Firing.—The moulded bricks are carried to the drying floors, and dried either by exposure to the air or by artificial heat. In the former case they are stacked in rows, and covered with boards to keep off the rain; in the latter they are spread on floors in covered sheds, heated by fires below. Drying by artificial heat is much preferable, but the temperature must not be high, and drying must be slow.

The dried bricks are fired in heaps (clamps) or in kilns.

For clamp burning a series of temporary flues are built up with burnt bricks, and over these are stacked the bricks to be burnt, the spaces between the bricks being filled up with breeze, and the whole enclosed in a temporary cover of burnt bricks. Fires are lighted in the flues, and are kept going for several weeks. The burning is often very irregular, the bricks near the fires being overburnt, and those farther away underburnt. The direction of the wind also has great effect in modifying the burning. When bricks are to be burnt in clamps breeze is sometimes mixed with the clay of which they are made. This, however, is objectionable, as it increases the porosity of the brick.

Kilns are of many kinds. The simplest form is simply a space enclosed by four walls, but almost always closed brick chambers are used, with a series of external fireplaces, often so deep as to be almost gas-producers, or they may be fired with gas. In ordinary coal-fired kilns the kiln is filled, the fires lighted, the temperature gradually brought up to that required, at which it is kept for several days, and then it is allowed to cool slowly, the whole operation lasting perhaps a fortnight. There is, of course, a considerable loss of heat by this process.

In the modern gas-fired kilns, such as Hoffman's or Dunnachie's, a series of chambers are so arranged that the air entering passes through several chambers containing burnt bricks, thus cooling them off, and itself becoming heated. It is then used to burn the gas in the kiln which is being fired, and the products of combustion pass through chambers containing bricks ready for burning. These will thus be thoroughly dried and heated by the products of combustion.

In the Hoffman kiln the chambers are arranged concentrically round the chimney; in the Dunnachie kiln they are arranged in two parallel rows. In either case there are usually about nine chambers, and when at work, whilst one chamber is being fired, three will be heating up, three cooling off, one loading, and one discharging, so that the work goes on continuously.

Gas kilns have very great advantages where the output is sufficiently large and steady to allow of continuous working.

The firing in kilns is much more even than that in clamps; the bricks are more uniform, there are fewer either over or underburnt, and as the heating is more uniform there is much less liability to warp or crack.

Pressed Bricks.—These are made in the usual way—generally by machinery—and are subjected to great pressure in the moulds before they are turned out to dry. They are, therefore, compact and smooth.

Dry-clay Bricks.—This method of making bricks is more largely used in the United States than in this country. The clay is dried in the sun, pulverised, and passed through a sieve, to remove particles which are too large, these being re-ground. It is then transferred to the moulds, in which it is subjected to great pressure. Such bricks require very little drying, and are fired in the usual way.

Enamelled Bricks.—Bricks with one or more surfaces covered with a white enamel are now largely used for various purposes. There are two methods of glazing. In the one the surface is covered with an opaque glaze containing oxide of tin; in the other a dead-white layer of china clay is first put on, and over this a transparent pottery glaze, preferably a felspathic, not a lead glaze.

Usually the brick is finished as usual, and the glaze is put on afterwards and it is again fired, but with a suitable clay a tin glaze may be put on the dried brick, and one firing may be made to do. This is, however, only possible with certain calcareous clays.

The difficulties in the manufacture of good glazed bricks are very considerable. Unless the clay and the glaze are of such a nature as to adhere firmly, and expand at about the same rate, the enamel is very likely to chip off, or the surface may become so cracked (or crazed) as to be unsightly. The enamel is impervious to moisture, but as the brick is only enamelled on the outer surface, moisture can still find access through the mortar, and if the brick becomes saturated with water, and is then subjected to the action of frost, the layer of enamel is very likely to be pushed off. Colouring matters may, of course, be added to the glaze or body as required. Great improvements have been made in the manufacture of enamel bricks.

A transparent glaze (salt glaze) is sometimes given to bricks by putting salt into the kilns during burning. The salt volatilises, and coming in contact with the clay forms a thin layer of fusible sodium silicate, which thus gives a glaze to the bricks.

Terra-cotta.—Ornamental work of terra-cotta is now very largely used for architectural purposes. Great care is required in the selection of suitable clay, and to reduce shrinkage it is mixed with as large a proportion of burnt clay as it will bear. The blocks are usually burnt in pottery kilns, enclosed in clay vessels or saggers, so as to prevent contact with reducing gases.

Durability of Clayware.—Burnt clay is one of the most durable substances known. It resists perfectly atmospheric chemical action, and the action of all ordinary reagents. It is subject only to mechanical disintegration, and the more porous it is the more likely is it to be broken up by the action of water and frost. Hence the advantage of at least partially fritting the material, thus making it less porous. Sometimes when the clay contains soluble materials these are dissolved out, and by the evaporation of the water on the surface are left as an efflorescence, causing unsightly markings.

FIREBRICKS.

Firebricks are bricks made of such materials that they will withstand a very high temperature. Clay is the basis of most firebricks, but of late years bricks have come into use made of other materials.

Clay Firebricks.—These are made of clay free from any materials which will impair the heat-resisting power. They therefore contain but little alkalies, lime, magnesia, or ferric oxide; indeed, the nearer the clay approaches the pure kaolin the more refractory will it be, though most fireclays contain a considerable excess of silica. Nearly all the fireclays in use for brickmaking belong to the carboniferous period.

Firebricks are made exactly in the same way as other bricks, except that greater care is exercised in some of the operations, and they are always fired in kilns.

Firebricks are usually nearly white or pale buff in colour, sometimes with yellow patches (oxide of iron), and often showing black specks with a hole in the centre, indicating the existence of specks of pyrites in the clay. They should resist a high temperature without softening or becoming weak or brittle, should not crack when exposed to sudden changes of temperature, and should resist the action of basic oxides.

Ganister, which is largely used for making bricks and for furnace linings, is an argillaceous sandstone, containing only enough clay to make it bind.

Silica Bricks.—These are made of siliceous materials, such as Dinas rock (about 98 per cent silica), calcined flints, &c. These are coarsely ground, mixed with about 1 per cent of lime, and water, moulded as usual, and are then fired at a high temperature. The lime combines with the silica at the surface of the particles, forming a fusible silicate of lime, which binds or frits the whole together. Such bricks are very refractory, but are weak, and are readily attacked by basic oxides.

Bricks are also made of *bauxite*, a hydrated oxide of iron and alumina, *chromite* (chrome iron ore), *magnesite* ($MgCO_3$), and *magnesian limestone* ($MgCO_3CaCO_3$). In the two last cases the material is burnt—so as to drive off the carbon-dioxide and convert the carbonates into oxides—and crushed. It is then mixed with anhydrous tar, moulded into bricks under great pressure, and the bricks are fired at a high temperature.

Acid and Basic Bricks.—Bricks which contain excess of silica are said to be *acid*; those which are composed of magnesia or magnesia and lime are *basic*; and those of chromite are neutral.

Acid bricks are attacked by basic materials at high temperatures; basic bricks are attacked by siliceous or acid materials; and neutral bricks are not attacked either by acid or basic substances.

PAVING-BRICKS AND TILES.

A brick to be used for paving purposes requires to be very hard, so as to resist friction, and strong and tough, as not to be broken up by the traffic passing over it. It must also be dense and non-porous. Suitable clays, usually containing a fair quantity of oxide of iron, are used, and they are fired at a temperature high enough to produce nearly complete vitrification. Such bricks are usually nearly black in colour, and very dense.

Tiles are usually used when an ornamental surface is required. The body is usually white and comparatively soft, and is pressed before firing. The pattern is made on the surface by means of coloured slip—*i.e.*, clay mixed to thin paste with water—and the whole is again fired; or the surface of the tile may have a pattern painted or printed upon it, and be afterwards glazed.

CHAPTER XX.

MORTAR AND CEMENTS.

BRICK and stone when used for building, except for the very roughest walls or "dry dykes," are always bedded either in mortar or cement. This bedding serves a double purpose, being soft and yielding it provides a uniform bearing surface, and compensates for inequalities in the surfaces of the stone or bricks, and by its subsequent hardening it binds the materials together, and so produces a firm and durable structure.

The essential quality of a mortar or cement is that it should harden more or less rapidly on exposure to the air or under water, according to circumstances.

These materials may be classified into—

1. Mortars, mixtures of lime and sand used for ordinary building purposes, which harden on exposure to the air.
2. Hydraulic cements, which will harden under water without access of air.
3. Miscellaneous materials.

MORTAR.

Mortar is composed essentially of lime and sand; it is therefore necessary to consider the properties of these materials.

Lime (*CaO*).—This is always prepared by heating calcium carbonate, $CaCO_3$, to redness, when carbon-dioxide is expelled and lime is left, $CaCO_3 = CaO + CO_2$. If a fragment of pure calcium carbonate, such as calcite or white marble be used, the residue will be an opaque white mass of pure lime. On addition of a little water, a vigorous action takes place, much heat is evolved, and the lump breaks down into a powdery mass of slaked lime, calcium hydrate, $CaO + H_2O = CaH_2O_2$. If this be treated with excess of water, it slowly dissolves, forming lime water. Made into a paste with water, and left exposed to the air, it harder somewhat on the surface from the formation of a superficial layer of calcium carbonate, by absorption of carbon-dioxide from the air, $CaH_2O_2+CO_2=CaCO_3+H_2O$, but as this crust is more or less impervious, the mass below may remain soft for a very long time.

The limestones used commercially for the preparation of lime are never pure, but always contain foreign constituents, and these often have great influence on the quality of the lime obtained. If the impurities are of such a nature as not to interfere with the slaking quality of the lime, they may be regarded as mere mechanical intermixtures, whilst if they are of such a character as enter into chemical combination with the lime, they will decrease the readiness with which it combines with water or slakes, and its solubility in water, thus altering the whole character of the material.

Limes which slake readily, and are almost completely soluble in water, are called fat limes, whilst those which slake less readily, and are less soluble in water, usually set under water, and are called hydraulic limes. The most important constituent for imparting hydraulicity is clay. A lime containing 5 to 12 per cent of clay is feebly hydraulic, whilst with 30 per cent it is strongly hydraulic, and will hardly slake at all except in the condition of powder. Artificial hydraulic limes may be made by calcining together an intimate mixture of clay and limestone, or clay and lime.

The hydraulic properties of a lime depend not only on the constituents present, but on the temperature at which it is burned. If too high a temperature be used the hydraulic power is destroyed.

Sand.—The sand should be a clean river sand, and should consist of angular—not rounded—grains of silica, as free as possible from foreign constituents. Sea sand is objectionable, as the salts which it contains are hygroscopic, and thus tend to keep the mortar moist, or these may effloresce on the surface.

Lime Burning.—The lime is always burnt in kilns. Many types of kilns are used; some of them very closely resemble the kilns used for calcining iron ores, which have been already described. In ordinary kilns the limestone is mixed with the fuel in alternate layers, as in the iron ore kilns, but this system has the objection that the lime is contaminated with the ash of the fuel. This is remedied in the "flare" kilns, in which calcination is effected by the products of combustion only. The kilns may be worked intermittently, being charged, fired, allowed to cool, and drawn; or they may be worked continuously, the charge being added at the top, and the burnt lime drawn at the bottom from time to time. Most modern kilns are worked continuously.

Mortar.—Mortar is essentially a mixture of lime and sand, sometimes with the addition of small quantities of other materials. The relative proportions in which the materials are mixed vary very much according to the nature of the lime, varying from one part by volume of lime to three of sand in the case of fat limes, to one volume of lime to two of sand in the case of hydraulic limes. Sand being much cheaper than lime, as much as possible of it is usually used.

The sand exerts no chemical action on the lime; at any rate, not until they have been in contact a very long time, so that its influence can only be mechanical. It seems to have a two-fold action—(1) diminishing the shrinkage, which would be very great if lime alone were used; and (2) producing a more open structure, so that air can find more ready entrance, and moisture can escape.

The setting of the mortar, therefore, depends entirely upon the lime, and is always brought about mainly by the action of the carbonic acid of the air.

When a pure or "fat" lime is used, the setting is very slow, the interior of the mass remaining soft for months, or even years, and when such a mortar has set it is never very strong, there being little cohesion between the particles.

Fat limes should, therefore, never be used except for rough work or that on which very little stress will be thrown.

With hydraulic limes the action is very different, the action of the atmospheric carbon-dioxide is supplemented by the setting power of the lime itself, due to the chemical changes which take place between the lime and the hydraulicising constituents. Mortars made with hydraulic limes, therefore, set much more rapidly, and become much harder than those made with "fat" limes. When masonry is to be exposed to moisture, a strong hydraulic lime should be used. When hydraulic limes are not available, Portland cement or plaster of paris is sometimes mixed with a fat lime to give it hydraulic properties.

In course of time, the mortar on a structure often becomes so well set and so hard that it is stronger than the brick or stone it is used to bind.

HYDRAULIC CEMENTS.

These materials possess the power of setting under water to a far greater degree than the hydraulic limes, indeed with them the action of carbon-dioxide is of little or no importance.

Hydraulicity.—The power of setting under water or hydraulicity seems to be due to the fact that in many cases anhydrous bodies are more soluble than the hydrated forms of the same substance. If such a substance be treated with water the anhydrous body will dissolve, but in the very act of solution it will become hydrated and at once crystallise out, thus binding the whole into a solid mass.

The best known example of a hydraulic material is ordinary plaster of paris. As is well known, if this be made into a paste with water, it sets very rapidly into a solid mass. The reaction is simple. The plaster consists of anhydrous, or nearly anhydrous, calcium sulphate, $CaSO_4$, which is much more soluble in water than the hydrate, $CaSO_42H_2O$. When water is added, the calcium sulphate is momentarily partially dissolved, but at once becomes hydrated, and crystallising out causes the mass to solidify.

The action in hydraulic limes and cements is exactly the same, but is, of course, due to other substances, usually silicates, and, to a less extent, aluminates of calcium.

The ordinary calcium silicates, $CaSiO_3$ and Ca_2SiO_4, which exist in minerals and slags, have little or no hydraulic power, as they are insoluble in water, but a more basic silicate, Ca_3SiO_5 ($3CaO, SiO_2$), seems to be formed when some silicates are heated with excess of lime, and to occur in, or be formed by the calcination of certain natural substances, and this seems to be the principal hydraulicising material in ordinary hydraulic cements.* When strongly heated it decomposes into Ca_2SiO_4 and CaO, therefore overheating may destroy the hydraulic properties of a material.

When this hydraulic silicate is treated with water it partially dissolves, and a hydrated metasilicate, $CaSiO_3xH_2O$, and calcium hydrate crystallise out, the former in microscopic needles, the latter in hexagonal plates.†

Many other substances behave similarly, but are probably of less importance. The calcium aluminates (*e.g.*, $3CaO, Al_2O_3$) take up water very rapidly, so rapidly indeed that they usually become hydrated during slaking, and they contain so much water that they effloresce in dry air. These aluminates unite with calcium silicate, forming double salts, which crystallise with a large quantity of water and expand considerably, and this may lead to the destruction of cement exposed to sea water.‡

A lime, therefore, will become hydraulic when it contains a silicate of such a character that on heating with excess of lime it will undergo decomposition, with the formation of basic-calcium silicates. This is the case with clay, but sand or silica in the free condition is not sufficiently readily acted upon.

The following hydraulic cements may be mentioned :—

1. Plaster of paris.
2. Roman cement.
3. Portland cement.
4. Slag cement.

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* See Le Chatelier. Trans. Am. Inst. Mining Engineers.

† Ibid.

‡ Ibid.

Plaster of Paris.—Gypsum, hydrated calcium sulphate, $CaSO_4 2H_2O$, is fairly abundant in the crystallised and amorphous condition. When this is gently calcined so as to expel almost, but not quite, all the water, it yields plaster of paris. The rationale of the hardening has already been explained. The paste sets very rapidly, often requiring minutes only, and soon becomes quite hard. As the paste expands on solidification, it can be used for making casts, indeed this is probably the principal purpose for what it is used. When the hydrate is heated to full redness, the water is completely expelled and a porous mass is left, which will absorb a large quantity of water, but is incapable of entering into the combination with it.

Plaster of paris may be used for most purposes for which cements are required, except that it is too expensive. It must not, however, be exposed to water or to the weather, as it is somewhat soluble in water.

Roman Cement.—This may be taken as a type of the natural cements—*i.e.*, those which are prepared by the calcination of materials which occur in nature without admixture of other substances. The true Roman cement is made from the nodules of argillaceous limestone that occur abundantly in the London clay. These contain about 40 per cent of clay, the remainder being chiefly carbonate of lime. They are of a bluish-grey colour, and are very fine grained. The nodules are calcined at a temperature only just high enough to expel the carbon-dioxide from the limestone. After calcination the mass has a brown colour, due, no doubt, to the presence of ferric oxide. Roman cement sets very quickly, probably on account of the presence of considerable quantities of calcium aluminates, but its ultimate strength is not great, and is greatly reduced by the admixture of sand.

Portland Cement.—This—the most largely used of all the cements—may be taken as the type of the artificial cements. The name has no connection with the place of manufacture, but was given because the dry cement was thought to have a resemblance to Portland stone.

It is made in various places, the raw materials being chalk or lime and clay or shale, the proportions in which they are used depending on their composition, three or four volumes of chalk in general being added to one volume of clay.

Two methods of manufacture are in use, the wet and the dry.

Wet Process.—As used on the Thames and Medway, "the chalk and clay are mixed in water to the condition of a creamy liquid, which is called 'slimy.' The fine particles in suspension are allowed to settle in large tanks, reservoirs, or becks for several weeks, and when the deposit becomes nearly solid the water is run off, the residue is dug out, sometimes pugged, dried on iron plates over cooling ovens, or over the flues from the kilns, burnt in intermittent kilns at a very high temperature, and then ground to fine powder."*

Dry Process.—This is used where chalk or other material which disintegrates with water is not available, and harder limestones and shales have to be used.

The limestone is crushed to powder, the clay is burnt and also crushed. The powdered materials are mixed in the required proportions with a little water and moulded into blocks. These are then dried in kilns, burnt to clinker, and afterwards ground to powder.

The rate at which Portland cement will set depends on the temperature at which it has been burnt. Under-burnt cements set much more rapidly, but these often contain free lime, which is very objectionable, as it may slake in the work. A properly burnt cement sets more slowly, but acquires much greater strength; whilst an overburnt cement has little hardening power.

Good Portland cement should be of a grey colour; if brown and earthy-looking, it probably contains too much clay; and if bluish-grey, too much lime.

Portland cement sets quickly, but continues to gain in

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* Rivington's "Building Construction."

strength for about two years, becoming stronger under water than in air.

Slag Cement.—Blast furnace slag is essentially a silicate of lime and alumina. It nearly always approaches to the composition of a mono-silicate ($Ca_2SiO_4 = 2CaO, SiO_2$), and therefore contains much less lime than a hydraulic cement. Even if the right amount of lime were present, the temperature at which the slag is formed is so high that the hydraulic silicate could not exist, and therefore the slag itself could not be hydraulic.

An ordinary fairly basic blast furnace slag, ground fine, mixed with enough lime to convert the silica into the hydraulic silicate and the alumina into calcium aluminate, moulded into blocks, fired at a fairly high temperature, and then ground, yields an excellent hydraulic or Portland cement.

Concrete.—This consists of stones cemented together with mortar, or better with cement. As the mortar or cement hardens it binds the whole together into a solid mass.

Concrete is largely used for foundations and also for building, especially heavy structures. In the latter case the concrete is made into blocks in suitable moulds, these blocks, when set, being used for the buildings, or frames of parallel boards may be arranged to enclose the space where the wall is to be, and the concrete is rammed into this.

Physical Tests for Cements.—As the strength of a structure depends very much on the mortar or cement used, this should be carefully specified, and tests should be made to make sure that the material used is equal to the specification.

The following points are to be noted :—

1. *Fineness.*—The cement must be uniformly and finely ground. As a rule, it should pass almost entirely through a sieve with 50 holes to the inch run.

2. *Weight.*—Portland cement weighs from 95 lb. to 130 lb. per bushel. As a rule, heavier cements set more slowly, but are stronger than the lighter ones.

Tensile Strength.—This is the most important test. The cement is cast into a briquette, allowed to set under water for a period of three to six days, and the tensile strength of the block is then determined. The strength varies very much: that used for the Metropolitan main drainage works was specified to give after seven days a strength of 350 lb. per square inch.

Shrinkage.—The amount of shrinkage is important. This is determined by casting a small block and noting how much it contracts.

Chemical Tests.—The principal constituents to be determined in the analysis of a cement are clay and free silica, these being quite useless; soluble silica, which indicates the amount of silicates present; alumina (not in clay), lime, and carbonic anhydride, and sulphates.

Chemical analysis taken alone, however, does not give very conclusive evidence as to the quality of a cement.

CHAPTER XXI.

FUEL.

THE engineer has to make a very large use of fuel for many purposes, but more particularly for steam raising, as the combustion of fuel is still the principal source of energy available under ordinary circumstances. The heat required is always obtained by the combustion of the fuel in the air. Air contains approximately—

	By volume.	By weight.
Oxygen	21	23
Nitrogen	79	77
	100	100

and of this only the oxygen is available for combustion, the nitrogen acting as a diluent, and making the action much less vigorous than it would be if the air were pure oxygen.

All the fuels in ordinary use are of organic origin, and contain the elements carbon and hydrogen, which are combustible, with small quantities of other elements. For all practical purposes, therefore, the combustion of fuel may be considered as the combination of the carbon and hydrogen of the fuel with the oxygen of the air.

Combustion of Hydrogen.—Hydrogen in the free condition is a colourless gas; in combination it exists in many fuels—solid, liquid, and gaseous. When hydrogen burns, the only product that can be formed is water, H_2O.; thus $2H+O=H_2O$. Hence water is produced whenever fuels containing hydrogen are burnt.

Combustion of Carbon.—Carbon is present in all fuels. When carbon burns in presence of a large excess of air, it is burnt to carbon-dioxide, $C+2O=CO_2$; but when the quantity of air is insufficient, carbon-monoxide, which contains only half the amount of oxygen, is formed, $C+O=CO$. Carbon-dioxide is also reduced by carbon to carbon-monoxide at a red heat, $CO_2+C=2CO$; so that if the air supply be deficient, or carbon be in excess, the carbon can only be burnt to carbon-monoxide. Carbon-dioxide is also dissociated at very high temperatures into carbon-monoxide and oxygen, which will, of course, re-combine if they remain in contact till the temperature is sufficiently reduced.

Combustion of Hydrocarbons.—When compounds containing both carbon and hydrogen are burnt in excess of air the combustion is complete—the hydrogen is burnt to water, and the carbon is burnt to carbon-dioxide; but when the supply of air is deficient combustion is incomplete, the reactions are usually very complex, and depend on the temperature and the quantity of oxygen present. The carbon is partially oxidised to carbon-dioxide, but principally to carbon-monoxide; the hydrogen is partially burnt to water, and partially may escape in the free condition; the hydrogen in the compounds of carbon and hydrogen may be partially burnt to water and lower hydrocarbons produced—*e.g.*, ethylene may yield acetylene and water,

$C_2H_4+O=C_2H_2+H_2O$—the presence of acetylene being often recognisable in cases of imperfect combustion by its unpleasant smell—and very frequently solid carbon is separated in the form of smoke.

Conditions of Complete Combustion.—For the complete combustion of any fuel two conditions are essential: (1) There must be a sufficient excess of air; and (2) that air must be brought in contact with the combustible material at a sufficiently high temperature. Excess of air alone may produce smoke by reducing the temperature below that at which combustion can take place, and a high temperature alone cannot prevent the production of smoke unless there be excess of air present at the same time. In most cases, in practice, smoke is due to cooling, not to lack of air.

Flame.—When a solid body burns, it simply glows brightly, as is the case with coke or charcoal; but when a gas burns, it produces a flame. Flame is always burning gas, and where flame is produced by the burning of a solid or liquid body, this is always first converted into gas. Thus, in a coal fire it is the gas distilled out of the coal that burns with a flame; and in an oil lamp or a candle the oil or tallow is first gasified and then burned. The structure of a flame is always much the same. In the centre is a blue, non-luminous core, consisting mainly of unburnt gas, no doubt partially decomposing by the heat radiated from outside, and outside this is the region where the gas and air are mixing, combustion taking place, and, therefore, heat being evolved, the combustion being more complete as the gas reaches the outside of the flame.

When the gas is of such a nature that its combustion produces only gases, as in the case of carbon-monoxide or hydrogen, the flame is only very feebly luminous, but bodies containing both hydrogen and carbon often burn in such a way as to cause the separation of solid particles of carbon in the flame, and these, becoming intensely hot, make the flame luminous. A luminous flame is always—potentially—a smoky flame, for this separated carbon may be cooled below its ignition point before it comes in contact with the oxygen, and, thus escaping combustion, may produce smoke. It would probably not be too much to say that all luminous hydrocarbon flames produce a certain amount of smoke. When the gas is diluted, especially with a combustible gas, before combustion, the combustion is much more complete, and a non-luminous flame may be produced, as in the ordinary Bunsen burner.

Heating by Contact and by Radiation.—The fuel is always used as a source of heat, and the heat may be transmitted to the body to be heated in two ways: (1) By direct contact; (2) by radiation. In the blast furnace, where the material being heated is in direct contact with the hot fuel, the heating is mainly by contact, but in most other cases the heat is transmitted by radiation across space. Sometimes bodies are heated by direct contact with flame, but not often. When a piece of thin wire is held in a flame it is heated by contact, and becomes intensely hot; but when a vessel of water is placed over a flame there is no contact; the vessel containing water cools the gases in contact with it below the combustion temperature, so that there is between the vessel of water and the flame a thin space, across which heat can only be transmitted by radiation.

A non-luminous flame, such as that of the Bunsen burner, has very little radiative power, gases being very poor radiators, so that when such burners are used to heat by radiation—as for heating a room by a gas fire—it is necessary to introduce metal bars or masses of fire clay or asbestos, which, becoming heated, though not hotter than the gas flame, radiate much more freely. Since carbon is a very good radiator, the luminous flame has a high radiative power, and is much better than the non-luminous flame for heating by radiation.

HEATING POWER OF FUELS.

The amount of heat which a fuel will evolve on complete combustion is fixed and definite. It is always measured in heat units, and three such units are in general use.

The British Thermal Unit (B.T.U.) generally used by engineers in this country, is the amount of heat which will raise 1 lb. of water 1 deg. Fah. (from 60 deg. to 61 deg.)

The Centigrade Unit (C.U.) is the amount of heat which will raise 1 lb. of water 1 deg. Cen. (from 15 deg. to 16 deg.)

The Calorie is the amount of heat required to raise 1 gramme or 1 kilogramme of water 1 deg. Cen. (from 4 deg. to 5 deg. Cen.), the former being called the gramme calorie, and the latter the kilogramme calorie.

The pound is so universally used as the unit of mass in this country, that only the two first-named units need be considered. As the only difference between the two is the thermometric degree used, the units will be in the same proportion as the degrees. As the Fahrenheit degree is smaller than the Centigrade degree in the proportion of 100 : 180, the units will have the same ratio, and an amount of heat expressed in the two units will always be in the proportion of 180 to 100. Thus, an amount of heat x in B.T.U. will be $\frac{5}{9}x$ in Centigrade units, and an amount y in Centigrade units will be $\frac{9}{5}y$ B.T.U. In what follows the B.T.U. will be used.

Calorific Power of Hydrogen and Carbon.—One pound of free gaseous hydrogen burning to form water will evolve about 61,500 B.T.U. This is the calorific power (C.P.) of hydrogen. One pound of solid carbon burning to form carbon-dioxide will evolve about 14,500 B.T.U., but if it be burnt only to carbon-monoxide it will evolve only 4,350 B.T.U.; therefore

C.P. of carbon to CO_2	14,500
C.P. of carbon to CO	4,350
C.P. of carbon-monoxide to CO_2......	4,370

It is evident that the loss of energy when carbon is incompletely burnt, so that it passes away as carbon-monoxide instead of as carbon-dioxide, is very large, being no less than $\frac{10150}{14500}$, or about 68 per cent of the total available heat.

Evaporative Power.—The heating power of a fuel is very often stated not as C.P., but by the amount of water which the combustion of 1 lb. of it would evaporate from water at 100 deg. Cen. (212 deg. Fah.) to steam at the same temperature. Since the latent heat of steam is 967 B.T.U., or 537 C.U., it is evident that the evaporative power will be

$$\text{E.P.} = \frac{\text{C.P. (B.T.U.)}}{967} = \frac{\text{C.P. (C.U.)}}{537}$$

For instance, in the case of carbon,

$$\text{E.P.} = \frac{14500}{967} = \frac{8080}{537} = 14{\cdot}9.$$

In the case of hydrogen, or fuels containing it, the case is not quite so simple, because the combustion of the hydrogen forms water, and as this must be evaporated, its weight must be deducted from the total quantity. Thus, in the case of hydrogen itself, since each pound forms 9 lb. of water,

$$\text{E.P.} = \frac{61500}{967} - 9 = \frac{34000}{537} - 9 = 56.$$

INFLUENCE OF CONSTITUENTS OF FUEL ON ITS HEATING POWER.

Carbon.—This is always an important heat-giving constituent, and in most fuels it is the most important.

Hydrogen.—This is usually present in smaller quantity. It gives out a large amount of heat, but usually only a portion of the hydrogen present is available. All the hydrogen present ultimately forms water, which has to be evaporated at the expense of the fuel.

Oxygen.—The effect of oxygen in a fuel on its heating power is always bad. Combustion is the union of the combustible with oxygen, but any oxygen present in the fuel is not free, but is in a state of combination, and therefore combined with elements which, if free, could combine with the oxygen of the air and burn. Thus these elements are rendered useless. It is usually assumed that the oxygen is present, combined with hydrogen in the proportions required to form water (8 : 1), so that each eight parts of oxygen will render unavailable 1 part of hydrogen. If h and o represent the percentages of hydrogen and oxygen, $h - \frac{1}{8} o$ will be the percentage of available hydrogen.

Sulphur, when present in large quantity, may be a heat-giving constituent, but in ordinary fuels it is of no importance.

Ash.—The inorganic material left when the fuel is burned has no effect on the C.P., except that it excludes a certain amount of combustible material, since the more ash the less combustible material there can be.

Water.—This is always present as moisture, and must be evaporated.

Calorific Power of Fuels.—Formulæ for the calculation of the C.P. of complex fuels are usually given in text books :—

Let c, h, o stand for the percentages of carbon, hydrogen and oxygen. Then—

1. Fuels containing carbon only.

$$\text{C.P.} = \frac{c \times 14500}{100} \text{ in B.T.U.}$$

$$\text{C.P.} = \frac{c \times 8080}{100} \text{ in C.U.}$$

2. Fuels containing carbon and hydrogen.

$$\text{C.P.} = \frac{(c \times 14500) + (h \times 61500)}{100}$$

or

$$\frac{(c + 4{\cdot}265\, h) \times 14500}{100} \text{ in B.T.U.}$$

$$\text{C.P.} = \frac{(c \times 8080) + (h \times 34100)}{100}$$

or

$$\frac{(c + 4{\cdot}265\, h) \times 8080}{100} \text{ in C.U.}$$

3. **Fuels containing carbon, hydrogen, and oxygen.**

$$\text{C.P.} = \frac{c \times 14500 + (h - \frac{1}{8}o)61500}{100} \text{ in B.T.U.}$$

$$\text{C.P.} = \frac{c \times 8080 + (h - \frac{1}{8}0)34100}{100} \text{ in C.U.}$$

These equations are often used, but they are not accurate. The results vary very considerably from those obtained by direct experiment. Also they need a complete analysis of the fuel, which is very rarely to be had.

The sources of error in the formulæ are chiefly the following :—

1. Uncertainty of the C.P. of carbon when in combination, since the different varieties of the element give different figures.

2. The C.P. of hydrogen is determined for the free gas. In solid fuels, the hydrogen is not gaseous, but solid, and in that condition its C.P. must be different.

3. Compound bodies never give the same amount of heat on combustion as the elements of which they are composed would do in the free state ; the amount of heat evolved by the combustion of a compound being usually less, though sometimes it is more, than that given by the free elements, according as the compound itself was formed with the evolution or absorption of heat.

When the heating power of a fuel is required, it is far better to determine it experimentally by means of one of the calorimeters in use, rather than depend on any calculation.

Calorific Intensity.—The amount of heat which a fuel will evolve on combustion is fixed and definite, depending only on its chemical composition ; but the temperature which will be produced by its combustion—*i.e.*, the calorific intensity or pyrometric heating power—depends on many conditions, such as—(1) The rate of combustion ; (2) the amount of products of combustion which have to be heated ; and (3) the excess of air which is supplied.

Amount of Air Required for Combustion —The amount of air required to burn a fuel can be readily calculated if its composition be known.

When carbon burns, each pound of carbon requires $2\frac{2}{3}$ lb. of oxygen to form $3\frac{2}{3}$ lb. carbon-dioxide, and when hydrogen burns it requires eight times its weight of oxygen. So that if a fuel contain carbon and hydrogen only, the weight of oxygen required for its combustion will be—

$$\frac{2{\cdot}67\,c + 8\,h}{100} = {\cdot}0267\,c + {\cdot}08\,h.$$

As air contains 23 per cent of oxygen by weight, the amount of air required will be—

$$\frac{2{\cdot}67\,c + 8\,h}{100} \times \frac{100}{23}$$

$$= \frac{2{\cdot}67\,c + 8\,h}{23}$$

or

$$(0267\,c + {\cdot}08\,h) \times 4{\cdot}35$$

in either case $(h - \frac{1}{8}\,O)$ being used in place of h if the fuel contain oxygen.

A cubic foot of air may be taken as weighing (at 0 deg. Cen. and 760 mm. bar) ·0809 lb., so that the volume will be—

$$V = \frac{({\cdot}0267\,c + {\cdot}08\,h) \times 4{\cdot}35}{{\cdot}0809}$$

or

$$V = (0267\,c + {\cdot}08\,h) \times 53{\cdot}6.$$

If the temperature or pressure vary, then the necessary calculation must be made according to the usual rules for the change of volume of gases by changes of temperature and pressure.

The following formulæ calculated for air at ordinary temperatures and containing an average amount of moisture are often used :

$$W = {\cdot}12\,c + {\cdot}36\,h$$
$$V = 1{\cdot}57\,c + 4{\cdot}71\,h.$$

In practice a large excess of air must be used, so that the figures obtained must be multiplied by a factor. This will be for gas furnaces 1·5, for good grates 2, for defective grates 3 or more.

Products of Combustion.—The weight of the products of combustion will be the weight of the fuel consumed plus the air supplied; so that if W_p be the weight of the products of combustion, W_f the weight of the fuel, a the weight of the ash it contains, A the weight of the air required, and f the factor for excess, then

$$W_p = (W_f - a) + (A \times f.)$$

The volume of the products of combustion can, of course, be calculated, but in general for solid fuels it may be taken as being equal to that which the air consumed would occupy at the same temperature, but it will usually be a little more. Carbon-dioxide contains its own volume of oxygen, and the volume of the steam is twice that of the oxygen used, but there will also be the moisture from the fuel and the combined hydrogen, neither of which consume any oxygen.

Heat Carried out by the Gases.—This can be calculated by multiplying the weight of each constituent by its specific heat and the temperature of the escaping gas. The specific heat of carbon-dioxide is ·2387, that of steam ·4805, of nitrogen ·2485, and of air ·2375. For practical purposes it is quite sufficient to take the weight of the products of combustion, and multiply by ·25 and by the temperature of of the escaping gases; so that if H = the heat carried away, then

$$H = W_p \times \cdot 25 \times t,$$

t being the temperature of the escaping gases.

Whilst there are many fuels which are used locally under special conditions, there are few that are of special interest to the engineer, or with which he is likely to have to deal in his ordinary work.

The fuels in use may be conveniently classified into solid, liquid, and gaseous; and each of these may be sub-divided into two classes: (1) Those which are used in the condition in which they occur in nature; and (2) those which are subjected to some preliminary treatment, other than mere drying, before use. The former may be called natural, and the latter prepared fuels.

1. *Solid Fuels:—*	
(α) Natural:	Wood.
	Peat.
	Coal.
(β) Prepared:	Charcoal.
	Peat charcoal.
	Coke.
	Briquettes.
2. *Liquid Fuels:—*	
(α) Natural:	Natural oils.
(β) Prepared:	Distilled oils.
3. *Gaseous Fuels:—*	
(α) Natural:	Natural gas.
(β) Prepared:	Coal gas.
	Producer gas.
	Water gas.
	Oil gas.

WOOD.—Wood, though at one time the only fuel with which man was acquainted, is now very little used in the arts.

Average air-dried wood—*i.e.*, that has been allowed to dry by exposure to the air after the bark has been removed—contains a large quantity of water—often 20 per cent or more—which, of course, has to be evaporated. Even perfectly dry wood contains only about 50 per cent of carbon, about 6 per cent of hydrogen, and 41 per cent of oxygen; the amount of oxygen being so large that there is very little available hydrogen, and thus a large quantity of additional water to evaporate. The calorific power is therefore very low, that of air-dried wood being about 5,600 B.T.U., and that of perfectly dry wood about 7,000 B.T.U.

Wood is also very light and bulky, and does not pack well. On the other hand, it is not fragile, it kindles easily, burns with a long flame, and leaves only a small quantity of ash.

PEAT.—Peat is used as a domestic fuel in many parts of the country, and has been used for minor metallurgical operations. Being the partially decayed remains of plants, its composition is much like that of wood, but it has the additional disadvantages that as it burns it crumbles to small fragments, and that it may contain a large quantity of ash, from the intermixture of extraneous mineral matter. Peat when freshly cut is always very wet, and when air dried it may contain 20 per cent or more of water.

COAL.—Coal is now the universal fuel. It is the remains of plants, or certain parts of plants, which have undergone great changes. All trace of the individual plants has been lost, and the coal is a more or less compact brown or black mass. As a rule, the coal is found where the plants of which it is formed grew, and the roots of these are often found in the underlying beds of clay.

Considered merely as a fuel, coal may be defined as being "a solid, stratified mineral substance, black or brown in colour, and of such a nature that it can be economically burned in furnaces or grates."*

Effect of Heat on Coal.—When powdered coal is heated to redness in a closed vessel—*i.e.*, when it is subjected to destructive distillation—more or less volatile matter, including much combustible gas and some tarry matter, is expelled, and a residue, or coke, is left. This residue may be an incoherent powder, the particles seeming to be little changed by the heat, or the mass may soften, swell up, pass apparently into a semi-fused condition, and yield a hard, compact coke, in which every trace of the original particles of the coal has disappeared. In the first case the coal is said to be a non-caking, and in the second a caking, coal. Between these two extremes there is every possible variation, most

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* Dr. Percy.

coals occupying an intermediate position, and giving more or less compact and coherent cokes. When a coal yields a coherent coke, it is called a caking coal; the caking power being strong when the coke is dense and compact, and weak when it is soft and friable. For many purposes the value of a coal is largely influenced by its caking power.

Water in Coal.—All coal as raised from the pit contains water, and ordinary air-dried coal retains from 2 to 4 per cent. On heating to 212 deg. Fah. for about an hour, the water is completely expelled.

Sulphur in Coal.—Coal always contains sulphur, the quantity varying very much in different samples. The sulphur seems to be present in three forms: (1) As iron pyrites (FeS_2). In this form it is distributed through the coal in layers, masses, or nodules, of a brass-yellow colour with a metallic lustre, whence it is often called "coal brasses." (2) As calcium sulphate; and (3) in some form of combination with the organic matter of the coal. The distribution of the sulphur when the coal is distilled, and its influence on the value of the coal, depends much on the form in which it is present. When the coal is burnt the sulphur, as pyrites and in organic combination, burns to sulphur dioxide, and passes away with the products of combustion, whilst the calcium sulphate remains unchanged.

Other Constituents.—Coal always contains small quantities of nitrogen (up to 1·5 per cent), of phosphorus, as calcium phosphate, and of chlorine, as sodium chloride.

Ash of Coal.—When coal is completely burnt a residue of inorganic matter or ash is always left. This consists partially, but usually only to a small extent, of the true ash of the plant and partially of inorganic matter which has become intermixed; in coal free from visible shale or earthy material it may be as much as 10 per cent. When much pyrites is present the iron is left after combustion as ferric oxide, and the ash is therefore red, but this red colour is hidden if there be a large excess of white earthy material. The most important points to be considered with reference to the ash are: (1) Its amount, a large quantity of ash being always objectionable; and (2) whether it is fusible or not.

Gas in Coal—Coal as raised from the pit often contains a large quantity of absorbed gas, which is given out when the coal is exposed to the air. The gas may contain a large percentage of marsh gas (CH_4), in which case it is explosive, or it may consist principally of carbon-dioxide and nitrogen, in which case it is non-combustible. When coal gives off the former variety of gas perfect ventilation of all places where it is stored is essential, or explosive mixtures of gas and air may accumulate.

CLASSIFICATION OF COALS:—

Coals may be classified into four groups:—

1. Lignites.
2. Bituminous coals.
3. Cannel coals.
4. Anthracites.

LIGNITE.—This variety of coal is of little importance in this country, there being only one locality where it occurs, viz., Bovey Tracey, in Devonshire. Lignite is always of much more recent date than the true coal, the deposits belonging to the tertiary period, those at Bovey being probably oligocene. The coal may vary from a black, structureless, pitchy mass (pitch coal) to a brown mass showing a distinct woody structure (wood coal or brown coal).

Lignite usually contains a large quantity of water and volatile matter, and leaves from 40 to 60 per cent of coke on ignition, the caking power being very small. An analysis of a sample of Bovey coal gave:—

Carbon	66·31
Hydrogen	5·63
Oxygen	22·86
Ash	2·27

the amount of available hydrogen thus being only 2·77.

Bituminous Coal.—This class includes all the coals in ordinary use as house or furnace coals. They burn with a more or less luminous, smoky flame—like the flame of mineral bitumen, whence the name—the amount of flame varying very much, and depending on the amount of volatile matter which the coal yields on distillation, long-flame coals giving much and short-flame coals but little. The amount of coke left on distillation varies from 50 to 90 per cent, and it may be hard and coherent, or simply the apparently unaltered coal. The amount of carbon varies from about 75 to about 93 per cent, and the oxygen from 20 to only 2 or 3 per cent.

Coals are best classified according to the amount of coke which they leave on heating, but it must be remembered that no hard and fast line can be drawn between the different varieties, as they pass gradually one into the other. Five classes are usually given :—

1. *Long-flame Non-caking Coals.*—These coals somewhat resemble lignite in composition; they may be black and pitch-like, or hard and strong. They contain about 75 to 80 per cent of carbon, and on heating leave about 50 to 60 per cent of a pulverulent or only slightly coherent coke. They are black or brown in colour, and have a specific gravity of about 1·25. They contain a large quantity of oxygen, and therefore but little available hydrogen, and they contain a large quantity of nitrogen (1·4 to 1·5 per cent), and yield a considerable quantity of ammonia on distillation. The calorific power is low. On account of the large quantity of volatile matter which they yield they burn with a long, smoky flame.

These coals occur abundantly in Scotland, Derbyshire, and Staffordshire, and include most of the hard splint coals used for iron smelting in Scotland.

2. *Gas Coals.*—These are black in colour, and are usually hard and dense (specific gravity about 1·3). They contain 80 to 85 per cent of carbon, and on distillation leave 60 to 68 per cent of a coke, which, while stronger than that

yielded by coals of class 1, is yet soft and easily broken. They yield about 10,000 to 11,000 cubic feet of gas per ton.

These coals are very largely used. Some are used in the blast furnaces raw. They are good house and furnace coals, and are largely used for gas making. They burn with a very luminous smoky flame.

3. *Furnace Coals.*—These are probably the most valuable coals for furnace and general use, and include most of the best house coals. They contain 85 to 89 per cent of carbon, and leave on heating about 75 per cent of a moderately compact coke, in which all, or almost all, trace of the original particles is lost. They are usually black and shining, and are often very brittle. They burn with a bright, luminous flame, and yield a considerable amount of gas.

4. *Coking Coals.*—These coals are usually black and shiny. They cake very strongly, yielding about 75 per cent of a dense, hard coke, suitable for blast-furnace use. Owing to the small quantity of volatile matter given off, they burn with a much shorter flame than those of the classes previously mentioned. They are used for furnace and house coals, and also for making coke.

5. *Anthracitic Coals.*—These coals are bright and black, and do not soil the fingers. They are hard and compact, have a specific gravity of 1·35 to 1·4, ignite with difficulty, and burn with very little flame or smoke. On distillation they yield about 90 per cent of a powdery or very slightly coherent coke. They are largely used for firing boilers, and are often known as blind coals or smokeless steam coals.

ANTHRACITE.—This coal is hard and dense. The colour is black, and the lustre very bright, often with a beautiful iridescence (peacock coal). When heated it gives off very little gas, loses hardly anything but water, and the residue is apparently quite unchanged. It contains up to 98 per cent of carbon, only a trace of which is volatile. Anthracite is very difficult to ignite, but gives an intense local temperature, and it burns without smoke or flame. It is used for firing the boilers of warships, for furnace purposes, and occasionally for iron smelting in blast furnaces.

Anthracite represents a further stage of mineralisation than ordinary coals, and in some coalfields the bituminous coals pass gradually into anthracites.

CANNEL COALS.—These coals are different in structure, and probably also in origin, to ordinary coals. They are close and compact in texture, black or dark grey in colour, and often break with a conchoidal fracture. On distillation they yield a very large quantity of gas, and leave a coke which usually contains but little fixed carbon and a large quantity of ash. The gas which they yield has a high illuminating power, and they are almost exclusively used for gas making.

SOLID PREPARED FUELS.

CHARCOAL —The residue which is left when wood is heated to redness in a closed vessel is called charcoal. It was at one time largely used for metallurgical purposes, but is now but little used. Charcoal is not, as is often supposed, pure carbon, but always contains considerable quantities of hydrogen and oxygen, the amount depending on the temperature. The best charcoal contains about 95 per cent carbon, ·5 per cent hydrogen, 1·5 per cent oxygen, and 3 per cent ash, but most of that used is of much poorer quality.

Charcoal is black in colour, and should show distinctly the structure—*i e*, the rings of growth—of the wood. Its specific gravity is about ·2, varying somewhat according to the nature of the wood from which it is prepared. It absorbs water very readily, often retaining, even when apparently quite dry, as much as 10 per cent.

Charcoal is an excellent fuel; its calorific power is high, about 13,700 B.T.U; it ignites readily and burns without flame unless in mass, when carbon-monoxide may be produced and burn with its characteristic blue flame. It is well suited for use in small blast furnaces, but it is so fragile that it crushes easily under the weight of a high column of material. Owing to its porosity air finds ready access, and therefore it burns very readily. It is quite unsuited for domestic use, except in fireplaces with a good draught, as poisonous carbon-monoxide is very apt to be formed.

Charcoal is prepared in various ways. By the old method, which is still in use, the wood was stacked in piles, covered with an impervious layer of sods, the whole being kindled at the bottom; small quantities of air are admitted, the products of combustion and a part of the charcoal being burned, and the remainder being left. In modern works the charcoal is often made in closed kilns, the yield in this case being considerably larger.

Much of the charcoal now used is a by-product obtained by the distillation of wood in closed retorts, for the manufacture of wood spirit and pyroligneous acid.

Wood yields, when distilled in retorts, about 81 per cent by volume and 28 per cent by weight of charcoal, whilst in piles the yield is about 52 per cent and 18 per cent, the difference being mainly due to charcoal consumed.

PEAT CHARCOAL.—Many attempts have been made to prepare a fuel from peat, but though to a certain extent successful the result has never been such as to enable it to compete in price and quality against coal and coke. The most successful method is probably to pulp the peat thoroughly and remove any fragments of wood, &c., then to make the pulp into blocks, dry them—producing a peat fuel—or carbonise them, producing peat charcoal.

COKE.—Coke is the residue left on distilling coal, only such coals being used commercially as yield a hard, coherent coke; that is, those belonging to classes 3 and 4.

Two classes of coke are made.

1. *Soft Coke*, or, as it is often called, smithy char, is soft, kindles readily, but will not stand great pressure. It contains considerable quantities of oxygen and hydrogen, and is made at a lower temperature than hard coke.

2. *Hard Coke.*—This is the variety used for the foundry and the blast furnace. It is hard, dense, and strong, contains only very small quantities of oxygen and hydrogen, and should not lose anything but water on ignition. That made in the beehive ovens has a dark grey colour, a metallic lustre, and breaks into columnar fragments; that made in most recovery ovens is dull and lustreless, black instead of grey, and breaks into rhomboidal fragments. For most—if not all—purposes one form of hard coke is as good as the other.

Coke usually contains a large quantity of ash, though since coal washing has become general this is much lower than before; 5 or 6 per cent may be taken as the average ash in good coke, though it may rise to 10 per cent, or even more.

Coke always contains sulphur, but the idea that it is specially bad in this respect is a mistaken one. Coke always contains less sulphur than the coal from which it was made. A coal, for instance, containing 1·47 per cent of sulphur yielded a coke containing only 1·22 per cent. Coal gas made by distilling coal, therefore, always contains sulphur. Coke always retains a portion of the nitrogen of the coal.

Coke is very porous and absorbs water readily, so that it may contain a considerable amount while still appearing quite dry. It is an excellent fuel; it has a high calorific power, and the red-hot coke is a good radiator. It is largely used in the blast furnace, the foundry cupola, and similar furnaces, and it is well suited for domestic use, the one objection being that it is very difficult to ignite.

Manufacture of Coke.—Coke was at one time made in heaps, but it is now almost always made in ovens.

The common form—the beehive—is a circular chamber about 11 ft. in diameter and 2 ft. 6 in. high to the springing of the dome, covered with a brick dome, giving it somewhat the appearance of a large beehive—whence the name. Fig. 16 is a section of such an oven.

The oven being hot, about 7 tons of powdered coal is put in ; the heat is sufficient to start combustion ; the admission of air is carefully regulated so as to burn the products of distillation, but as little as possible of the coke itself. The coking is complete in four or five days, after which the air is excluded, the whole left at rest for a day, when the coke is drawn and quenched with water, and the oven is re-charged.

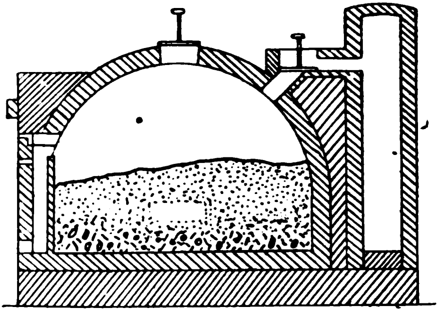


FIG. 16.—Beehive Coke Oven.

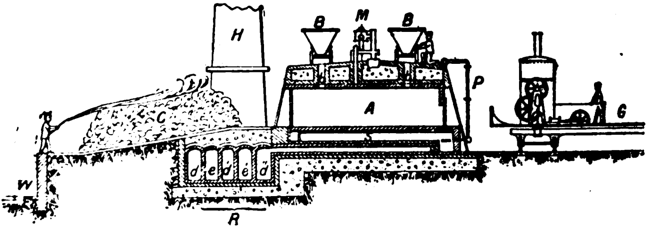


FIG. 17.—Simon-Carve Oven.

About 10 per cent of the coke is consumed, so that the yield is always low.

In modern ovens the coal is heated in fire-brick chambers or retorts, which are heated externally by the combustion of the gas from the retorts or ovens themselves. The gases are passed from the ovens through condensing apparatus, by which the tar and ammonia they contain are recovered, and they are then burnt outside the retorts containing the coal. Fig. 17 shows the general arrangement of the Simon-Carve oven, which is the most largely used in this country.

BRIQUETTES. — Powdered coal is unsuitable for use in ordinary furnaces, but it can readily be made into briquettes or fuel blocks. The coal is powdered and washed to remove mineral matter as far as possible, the powder is mixed with pitch, the mixture heated to the softening point of the pitch (over 170 deg. Fah.), either by the external application of heat or by blowing in steam. The mixture is then forced out of the machine and moulded into blocks under considerable pressure.

The briquettes are very convenient for household use, but as a rule they are too fragile to bear transport without serious loss As the blocks absorb water, they are sometimes water-proofed by dipping in molten pitch or otherwise.

POWDERED FUELS.—Many attempts have been made to burn powdered fuel, but so far not with conspicuous success. The fuel is supplied in the form of a spray, much in the same way as liquid fuels are used.

LIQUID FUEL.

NATURAL OILS are of little importance to the engineer in this country, as they are not obtainable.

DISTILLED OILS.—The oils which are available as fuels are those prepared by the distillation of the natural oils, shale, or blast-furnace tar. The lighter oils are used for lighting and other purposes, and the heavier oils are available for use as fuels. These oils consist entirely of hydrocarbons, and have a high calorific power (19,000 or 20,000 B.T.U.). They do not ignite readily, and are always burnt by means of a jet, in which the oil is blown into a fine spray by means of a current of steam, the fine oil spray burning much in the same manner as a gas.

How far oil can be used in place of coal is largely a matter of cost which at present does not seem to be in favour of the oil, though the conveniences and the saving of labour may in many cases outweigh the additional cost. The fact that oil can be used directly in an oil engine is also in its favour.

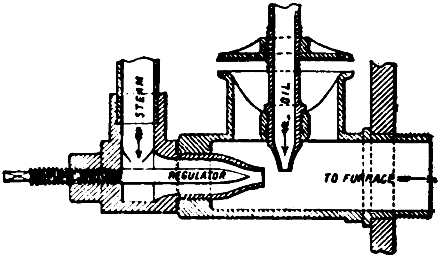


FIG. 18.—Aydon's injector.

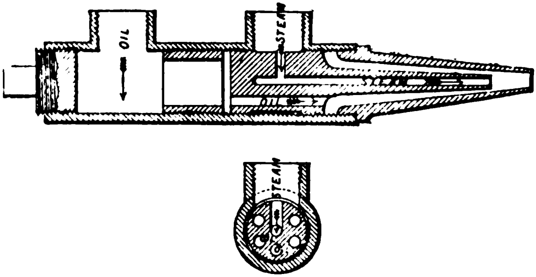


FIG. 19.—Aydon's injector (another form).

The following table gives the composition of a few oils :—

Oil.	Sp. gr. 32° F.	Composition.				C.P. B.T.U.
		C.	H.	O.	S.	
Pennsylvania heavy crude oil	·886	84·9	13·7	1·4	..	20,736
Circassian light crude oil ...	·884	86·3	13·6	·1	..	22,027
Caucasian heavy crude oil ...	·938	86·6	12·3	1·1	..	20,850
Petroleum, refined	·928	87·1	11·7	1·2	..	19,832
Good English coal, mean of 98 samples	1·380	80·0	5·0	8·0	1·25	14,112

GASEOUS FUEL.

Gaseous fuel offers so many advantages that it is rapidly coming into use wherever suitable gas can be obtained at a sufficiently cheap rate.

The chief advantages of gas are :—

1. That the supply of gas and air being both under control, the required temperature can be maintained with perfect regularity, there being no alternations of high temperature with cooling by the admission of air and addition of fuel, as is always the case with fires fed with solid fuel in the ordinary way.

2. Perfect combustion can be maintained with a very slight excess of air over that theoretically required, and no smoke is produced.

3. The ease with which the gas can be generated at a convenient place and conveyed in pipes to the furnaces, the trouble and expense of carting solid fuel being done away with.

4. Much higher temperatures can be attained than is possible with solid fuel, owing to the use of regenerators.

5. Fuels which would be quite unsuitable for use in ordinary furnaces can be used for conversion into gas.

6. The gas can be used for the direct production of energy in the gas engine, steam boilers being thus dispensed with.

On the other hand, since many gases burn with a non-luminous flame, these are not well suited for heating by radiation.

NATURAL GAS.—This gas occurs in abundance in a few localities only ; and in these it is extensively used. Natural gas consists of about 70 per cent of marsh gas, CH_4, of about 20 per cent of hydrogen, and small quantities of other gases.

ARTIFICIAL GAS.

Many forms of gas are used for heating and lighting—

1. Coal gas.
2. Producer gas.
3. Mond gas.
4. Water gas.
5. Oil gas.

Coal Gas.—Coal gas is prepared by the distillation of coal. It is mainly used for lighting purposes, being too expensive for use as a fuel, except in certain minor operations. Gas coals yield from 8,000 to 12,000 cubic feet of gas per ton, and the cost of the gas varies from 2s. to 8s. per 1,000 cubic feet. The luminosity of the flame is an advantage for some purposes. The gas has a calorific power of about 11,000 B.T.U., and it gives about 350,000 B.T.U. for each 1,000 cubic feet consumed.

Producer Gas.—When coal is distilled only a small portion of the material is converted into gas, by far the larger portion being left as coke, and if a cheap gas is to be produced the whole of the fuel must be gasified.

When air is blown over red-hot carbon, the carbon being in excess, carbon-monoxide is produced $C+O=CO$, and as this is combustible the whole of the fuel is converted into combustible gas. As air contains by volume 21 per cent of oxygen and 79 per cent of nitrogen, and as the carbon-monoxide occupies twice the volume of the oxygen which it contains, it follows that 100 volumes of air containing 21 volumes of oxygen will yield 121 volumes of gas containing 42 volumes of carbon-monoxide, so that the percentage composition of this simple producer gas will be—

Carbon-monoxide	34·7
Nitrogen	65·3

Its calorific power will be 1,493 B.T.U., and 1,000 cubic feet will give 118,192 B.T.U. As 1 lb. of carbon in burning to carbon-dioxide will evolve 14,500 B.T.U., and to carbon-monoxide 4,350 B.T.U., the latter amount will be evolved in the producer, and thus will be lost for use, whilst the heat available by the combustion of the gas will be 14,500 − 4,350 = 10,194, so that the heat used up in the production of the gas will be $\frac{4{,}350}{14{,}500}$, or about 30 per cent of that which the fuel could evolve on complete combustion. Whether the manufacture of such a gas will be economical will depend on circumstances, but the loss of energy can be diminished and the quality of the gas improved in various ways.

Use of Steam.—When steam is blown over red-hot coke, it is decomposed, $H_2O + C = 2H + CO$, the resulting gas therefore containing equal volumes of hydrogen and carbon-monoxide. Such a gas, however, cannot be prepared without an extraneous supply of heat, as the reaction absorbs a large amount of heat. The reaction consists of two parts, the union of 12 grammes of carbon with oxygen to form carbon-monoxide, and the separation of 2 grammes of hydrogen from oxygen in the decomposition of the water. The former reaction will evolve 12 × 4,350 = 52,200 B.T.U., whilst the latter will absorb 2 × 61,500 = 123,000 B.T.U., so that heat would be rapidly absorbed and the coke would soon cool below the point at which the reaction would be possible.

By use of a mixture of air and steam, so that the formation of carbon-monoxide by direct combustion and the decomposition of steam go on side by side, the heat evolved by the former may be made to balance the heat absorbed by latter reaction. A considerable excess of air must be used so as to make up for unavoidable losses of heat. In practice four or five times as much carbon is consumed by air as by steam. Assuming it to be four times, then

48 grammes of C burnt by O would give 89·6 litres CO
12 grammes of $\left\{\begin{array}{l}\text{C burnt by steam would give 22·4 litres CO}\\ \text{22·4 litres H}\end{array}\right.$

so that the gas would now contain

Nitrogen from air		168·6	= 55·6 per cent.
Carbon-monoxide from air	89·6	112·0	= 37·0
Carbon-monoxide from steam	22·4		
Hydrogen..........................	22·4	22·4	= 7·4
		303·0	100·

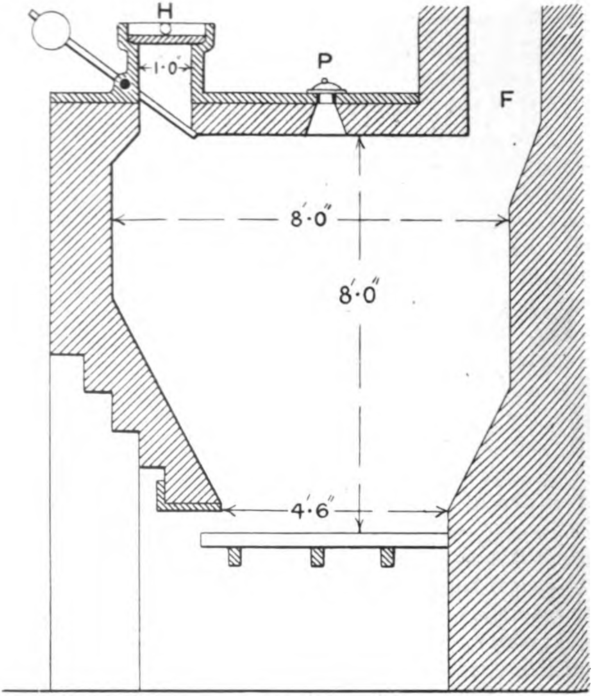


FIG. 20.—Siemens producer.

which is obviously a much better gas than that obtained without the use of steam. At the same time the loss of heat in the producer is much less.

5 lb. of carbon burnt to CO_2 would give 14,500 × 5 = 72,500

5 lb. of carbon burnt to CO would give 4,350 × 5 ... = 21,750
$\frac{1}{6}$ lb. of hydrogen separated from water = − 61,500 × $\frac{1}{6}$
= − 10,250

11,550

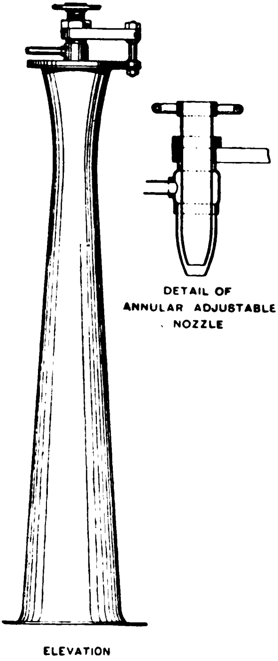


Fig. 21.—Steam jet blower.

so that the heat which is lost in the producer is 11,550 units, or

$$\frac{11550}{72500} = 15{\cdot}8 \text{ per cent},$$

which is far less than that when no steam is used.

The action of the steam must be clearly understood. It does not enable the fuel to give more heat, but it reduces the evolution of heat in the producer where it is not needed, and thus allows more to be given by combustion in the furnace where it is needed. At the same time it makes the gas richer by diminishing the amount of nitrogen and increasing the percentage of hydrogen.

If too large a quantity of steam be used, the temperature is so far reduced that carbon-dioxide is produced instead of carbon-monoxide, thus diminishing the heating power of the gas, and at the same time steam may pass through undecomposed, and as steam has a high specific heat it carries away a large quantity of heat.

Carbon-dioxide in Gas.—The presence of carbon-dioxide in gas is highly deleterious. In the first place it reduces the amount of carbon-monoxide, and as it is incombustible increases the percentage of non-combustible gas, and at the same time, the formation of carbon-dioxide is attended with a large evolution of heat, and as this heat is evolved in the producer it will be lost. So much is this the case that the value of a producer gas is often judged by its freedom from carbon-dioxide. The less there is present the better, and it should never rise above 2 or 3 per cent.

Coal in the Producer.—When coal is used in place of coke in the gas producer the coal is distilled, and the gas mixing with the producer gas still further enriches it by the addition of the coal gas.

GAS PRODUCERS.

A. Producers worked by a natural draught.
B. Producers worked with an artificial draught.
    1. Bar bottom.
    2. Solid bottom.
    3. Water bottom.

A. *Open Producers.*—The early form of producer, as introduced by Siemens, was open. The fuel rested on firebars, and air entered between these, as in an ordinary fireplace. As the producer could not, except in rare cases, be placed much below the level of the furnace, the draught would have been quite insufficient to carry the gas forward. This difficulty was overcome by the use of an overhead cooling tube. The gas ascended direct from the producer to this tube, which was placed 14 ft. or more above the producer level, and then, after traversing a considerable length of tube, descended to the furnace. The colder gas in the descending tube being heavier than the lighter gas in the ascending one, set up a syphon action by which draught was produced.

The disadvantages of open producers are (1) that the air current is necessarily slow, owing to the slight differences of pressure by which it is produced, and (2) for the same reason only a thin layer of fuel can be used, and only a small quantity of steam can be sent in. The gas made is therefore poor in quality, and only about 13 lb. of coal per square foot of grate area per hour can be gasified.

B. *Closed Producers.*—In these the ashpit is closed and the steam and air are supplied under pressure, thus more rapid combustion can be obtained, greater thickness of fuel can be used, and a larger quantity of steam can be sent in.

AIR AND STEAM SUPPLY.—As the air and steam have to be supplied together, a steam jet is almost invariably used to force the air into the producer. The usual form consists simply of a steam jet, which blows into a larger tube. The friction of the steam draws the air with it, and the two together pass on to the producer. In many modern jets a hollow jet is used instead of a solid one, it being thus possible to supply a larger quantity of air for a given amount of steam, and the size of the jet is made adjustable, so that the relative amounts of air and steam can be varied as required.

BAR-BOTTOM PRODUCERS.—As a type of this class of producer, the Thwaite simplex may be taken. The fuel rests on bars, the air being blown into the closed ashpit beneath them. The air is warmed by passing through a jacket round the body of the producer.

With bar-bottom producers a high rate of combustion cannot be attained. The bars require constant attention, and there is always the possibility of loss by unconsumed fuel falling through the bars.

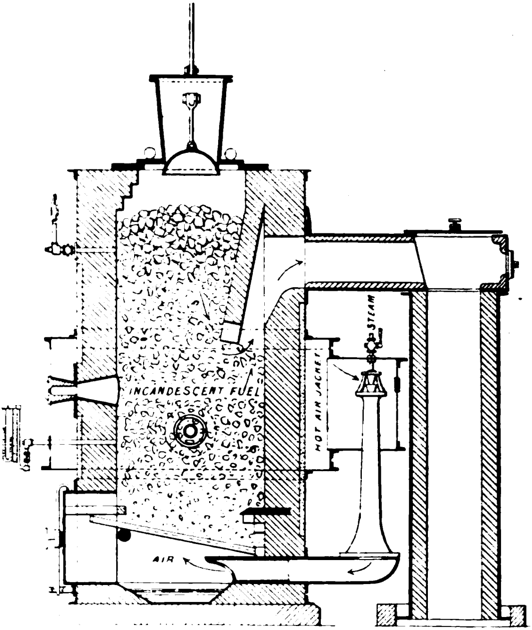


Fig. 22.—Thwaite simplex producer.

Solid-bottom Producers.—Of these the Wilson producer is the best known and most largely used. The fuel rests on the solid bottom of the producer, across which passes a ridge of brickwork, with a passage through the middle communicating by means of openings with the body of the producer. The steam and air are sent into this passage, and pass through the openings into the fuel, thus producing combustion. These producers are usually about 8 ft. internal diameter, but they have been successfully built up to 12 ft., and the fuel consumption can be brought up to about 40 lb. of coke per square foot of bottom area per hour, though in ordinary cases it is from 25 lb. to 30 lb.

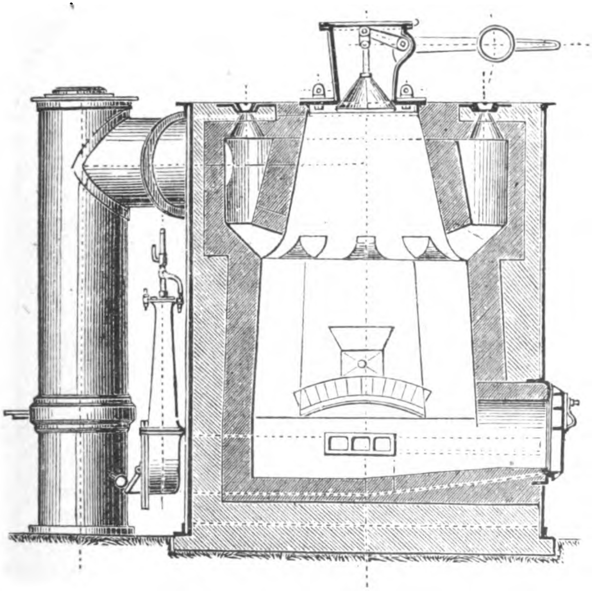


FIG. 23.—Wilson gas producer.

The producer has to be stopped periodically for the removal of ashes. A narrow door in the side is opened, and iron bars are put through and rest on the brick ridge. The cleaning doors are opened and the ashes are raked out, the fuel above being supported by the bars. When the cleaning is complete the bars are withdrawn, the charge sinks, and the blast is turned on.

Mr. Wilson has also designed a producer based on similar lines, but in which the ashes are continuously removed by means of an Archimedean screw without stopping the producer.

WATER-BOTTOM PRODUCERS.—In these the ashes fall into a trough of water at the bottom of the producer, from which they can be withdrawn from time to time, the escape of gas being prevented by a water seal of sufficient depth. As an example, the new form of Dawson producer may be taken.

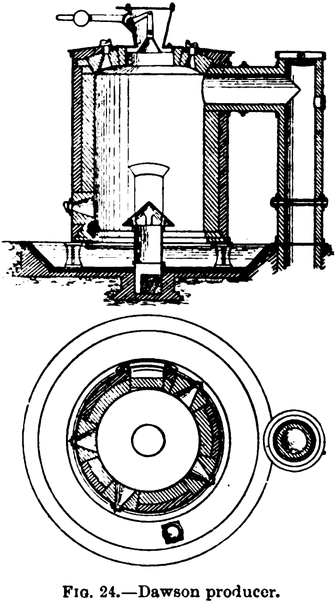


FIG. 24.—Dawson producer.

The shell rests upon short columns in a trough of water, the air being supplied well up into the mass of fuel by means of a central air pipe. The casing of the shell dips down into the water so as to form a water seal, and prevent the escape of the gas.

The advantages of the water-bottom producer are that the ashes are well cooled, all the heat being utilised in converting water into steam, and that the ashes can be drawn without stopping.

DESTRUCTION OF TAR.—When coal is used in a gas producer, a large quantity of tarry matter is always produced. This is very troublesome ; it partly condenses in the mains, and is very objectionable if carried forward into the regenerators.

It may be got rid of in two ways :—

1. The gas may be compelled, before leaving the producer, to pass down through a considerable thickness of hot coke. In this way the tar is broken up into carbon, which remains, and gas, which passes away. One objection to this method is that the gas leaves the producer at a very high temperature, and thus carries away a large quantity of heat.
2. The gas may be cooled and washed, the tar and ammonia being recovered. The tar which is recovered is of value, and the amount of ammonia may be anything up to about 23 lb. or 24 lb. of ammonium sulphate for each ton of coal consumed.

WASHED GAS.—The washed gas is quite well suited for most purposes for which gas is required. Owing to the removal of the tar it burns with a less luminous flame than the unwashed gas, and there must be a loss of heating power owing to the removal of the combustible tar. There is, however, no data as to the actual loss of heating power.

On the other hand, the washed gas is clean and free from dust, and as it is cool it carries with it but little moisture. On the whole washed gas is better for most purposes than the green or unwashed gas.

CONDITIONS OF EFFICIENCY OF A GAS PRODUCER.—The efficiency of a producer is the ratio of the heat available by the combustion of the gas to that which could be obtained by the combustion of the solid fuel. As will be seen from the figures already given in the simple producer, this will be about 70 per cent, whilst in a good steam-blown producer it may rise to 85 per cent or more.

In order to obtain the greatest efficiency, the greatest possible amount of steam must be used, but the temperature must be kept high enough to prevent the formation of carbon-dioxide, and the layer of fuel must be sufficiently thick to cool the gases as completely as possible. These conditions are not all met with in any ordinary producer. The layer of fuel is usually far too thin to allow of perfect cooling, and very often too much steam is used, so that the gas contains carbon-dioxide, and often uncondensed steam.

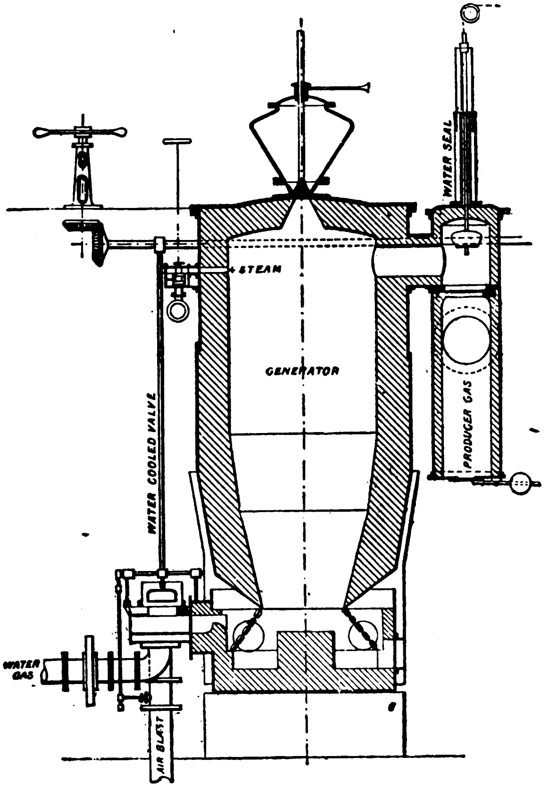
If the producer is to be efficient, therefore, the sources of loss of heat must be guarded against as completely as possible. These are—

1. Loss by radiation.
2. Loss by heat carried out in the gas. The hotter the gas and the more steam it contains, the greater will this be.
3. Loss by heat carried out in the ashes. This should be very little, and in the case of water-bottom producers almost nil.
4. Loss by unconsumed fuel. This should be nil, except in the case of bar-bottom producers.

MOND GAS.—Mr. Mond obtains a gas somewhat different from ordinary gas by using a very large excess of steam, as much as 2½ tons of steam being blown in for each ton of coal consumed. As a result, the temperature in the producer is low, and a large quantity of carbon-dioxide is produced, but this is to some extent compensated for by the large amount of hydrogen in the gas. The calorific power of the gas is about 2,570 B.T.U., and 1,000 cubic feet give about 168,900 B.T.U., and the efficiency of the producer is said to be about 80 per cent.

Owing to the large quantity of nascent hydrogen, a very large quantity of ammonia is produced, as much as 90 lb. of sulphate having been obtained for each ton of coal consumed.

The plant is very costly, owing to the condensation of the large quantity of steam, the production of which also is expensive. This is, however, compensated for by the large amount of ammonia recovered.



Water gas plant.

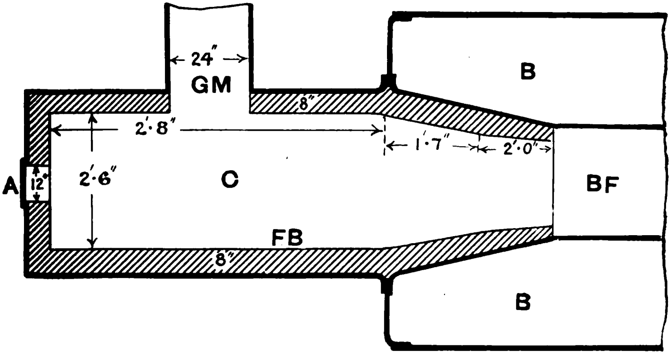
WATER GAS.—As already explained, when steam is blown over red-hot coke it is decomposed, and a gas consisting of equal volumes of carbon-dioxide and hydrogen is obtained, $C+H_2O=CO+2H$. This would be an excellent gas for heating purposes, but as the reaction is attended with a large absorption of heat, it can only go on if heat be supplied from outside, or by combustion inside, the apparatus, while the gas is not being made. The latter, or intermittent method, is that which is always used.

A closed-bottom producer fed with coke is used, and air, without steam, is sent in in the usual way. The coke burns and the temperature rises. When the coke is hot enough the air supply is stopped, and steam is sent downwards through the hot mass. The steam is decomposed, and water gas ($CO+2H$) is produced. The decomposition of the steam rapidly cools the coke, and after a short time the steam is turned off, and air is again sent through. In ordinary working, the time occupied in heating up is about 10 minutes, and the gas making about 4 minutes. The reason for the long time required for heating up is that the carbon can only be burnt to carbon-monoxide; the evolution of heat is therefore small, and combustible gas (CO and N) escapes. If the carbon could be burnt to carbon-dioxide, so as to obtain all the heat it is capable of evolving, the heating up stage could be shortened very considerably, and the manufacture of water gas might become practicable on the large scale. This has recently been done by Delwick-Fleischer. By burning the carbon to carbon-dioxide in the producer, they obtain a much larger evolution of heat, so that the blowing-up stage lasts about 1¾ minutes, and the gas making 8 or 10 minutes only, 18 per cent of the fuel value being lost in making the gas, and 82 per cent being obtainable by its combustion.

The principal peculiarity of the producer seems to be that air is supplied in large quantities, and at different levels, so as to ensure complete combustion.

By this process water gas will become a practicable fuel, and owing to its high calorific power it may be used in many cases without the use of regenerators.

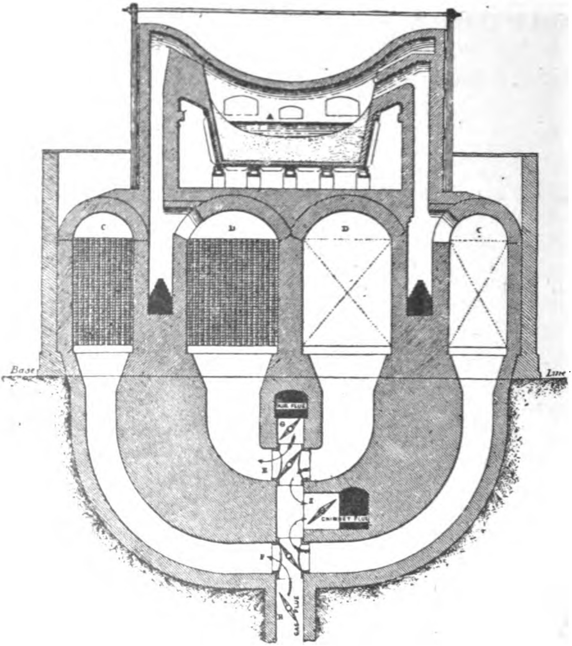
Burning Gas.—When the gas is to be used for firing steam boilers, regenerators are not used. The gas producer should be as near the boiler as possible, so that the gas may not cool much, and may carry forward nearly all the tarry matter to increase the luminosity of the flame. A very tall producer is no advantage, as it is not necessary to cool the gas, but it should be deep enough to ensure the absence of carbon-dioxide. Ordinary washed producer gas, being non-luminous, is not well suited for boiler firing. As the boiler furnace itself never becomes very hot, the gas should be ignited in a firebrick combustion chamber, which will become sufficiently heated to ignite the gas should it become accidently extinguished.



Gas burner for Lancashire boiler.

GM—gas main.
FB—firebrick lining.
BF—boiler flue.
C—combustion chamber.
B—boiler.
A—air hole.

Regenerative Furnaces.—Producer gas could never have come into successful use had it not been for the introduction of the regenerative furnace by Siemens. The principle of this is very simple. The furnace is provided with four chambers filled with a chequer work of firebrick, so arranged that the direction of the air gas and products of combustion can be changed. The products of combustion, which in the case of an ordinary steel furnace will be very hot, are passed through two of the firebrick regenerators. When these are hot the direction of the current is reversed, the air is sent through one of the hot chambers and the gas



Sections of Siemens steel melting furnace, with valves.

through the other, the products of combustion being sent through the second pair. There will thus be two regenerators always heating the air and gas, and two others always being heated by the products of combustion. By reversing every hour or so a very high temperature can be maintained, and the gas and air become very hot before they are burned.

The gas supplied to the regenerators should be free from tarry matters, as these will be decomposed by the hot brickwork, carbon being deposited, and when the valves are reversed, the products of combustion carrying excess of air will burn this carbon, thus increasing the temperature, heating the escaping gases unduly, and perhaps slagging the the bricks.

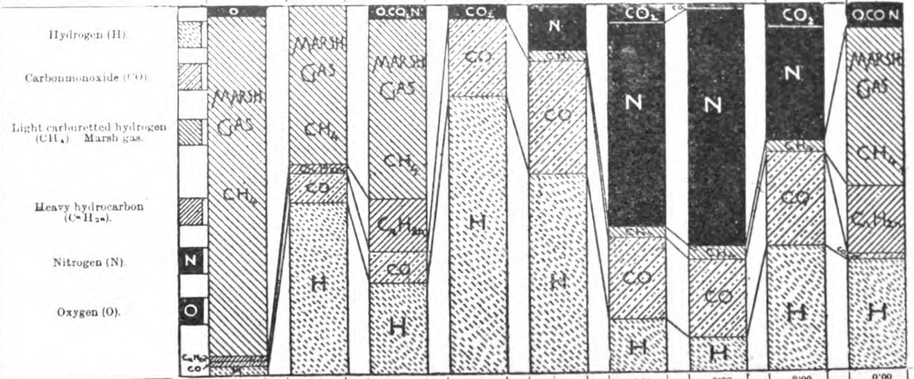
In a more recent form of furnace two regenerators only are used, viz., those for the air; the products of combustion are divided, one-half passes through the regenerator, the other half is passed into the gas producer, from which the hot gas passes at once to the furnace. The carbon-dioxide and steam in the products of combustion are decomposed, and the sensible heat of the products of combustion raises the contents of the producer to a very high temperature.

The regenerative system is not applicable to boiler fires, as the temperature of the escaping gases will not be higher than that of the incoming gas. The waste heat of the products of combustion can be utilised in this case by economisers in which the gas is made to heat the feed water for the boiler.

EXAMPLES OF THE COMPOSITION OF GASES.

	Natural gas.	Coal gas.	Producer gas (open).	Producer gas.	Blast furnace gas (coke).	Blast furnace gas (coal)	Mond gas.	Water gas.	Water gas (Delwick-Fleischer).
Hydrogen	20·62	51·8	..	11·55	2·74	3·68	27·2	49·17	50·80
Methane (CH_2) &c.	72·18	31·8	4·40	1·45	·20	3·62	1·8	·31	·82
Ethylene (C_2H_2) &c.	4·3	5·2	..	..	..	..	·4	..	·05
Carbon-monoxide	1·0	·1	25 60	26·89	28·61	27·50	11·00	43·75	39·65
Carbon-dioxide	·8	..	4·30	4·00	11·39	6·15	17·10	2·71	4·65
Nitrogen	..	2·1	65·70	56·11	57·06	59·27	42·5	4·00	3·83
Per cent combustible	99·2	97 9	30·0	39·89	31·55	34·70	40·4	93·29	91·52

Diagram and Tables, showing various Constituents of Combustible Gases. Prepared by B. H. THWAITE



Reference Indications.	Natural Gas.	Ordinary Towns Gas.		Enriched Water Gas.	Water Gas.	Steam-jet Producer or Carbonic Oxide Gas.	Natural Draught-producer Gas.	Thwaite's Semi-water Gas.	Oil Gas.
		Common Coal.	Cannel Coal.						
Carbondioxide and oxygen } Incombustible.	1·30	0·00	2·07	2·29	12·00	4·00	0·00	8·00	0·00
Nitrogen, N.	0·00	0·00	0·00	0·00	0·00	56·78	63·40	28·40	5·06
Light carburetted hydrogen (CH₄),	95·20	41·53	51·20	0·00	1·62	2·22	2·20	1·92	17·02
Heavy hydrocarbon (C_nH_{2n}),	0·50	3·05	13·06	0·00	0·00	0·00	0·00	0·00	46·17
Carbonmonoxide (CO),	1·00	7·82	7·85	20·04	31·86	23·00	24·20	27·42	0·14
Hydrogen (H),	2·00	47·60	25·82	77·03	54·52	14·00	10·20	34·26	31·61
	100·00	100·00	100·00	99·36	100·00	100·00	100·00	100·00	100·00

CHAPTER XXII.

WATER.

WHILST water is used in the arts for many purposes, the only one with which the engineer is much concerned is its use in boilers for steam raising.

Pure water is colourless, or almost colourless. At ordinary temperatures it is a liquid; when cooled it contracts till the temperature is reduced to 39 deg. Fah., after which it expands; so that water at 32 deg. has almost the same density as that at 50 deg. Fah. It therefore reaches a point of maximum density at about 39 deg. Fah., and water at that temperature, being heavier, will sink in that either slightly hotter or colder; for this reason the water at the bottom of deep lakes never freezes, but remains at a fairly uniform temperature of about 39 deg. Fah. When water freezes into ice it expands by about $\frac{1}{11}$ of its volume, and in so doing exerts an enormous force. It will therefore fracture any vessel in which it may be contained. The expansion of freezing water in porous materials such as stone or brick is a powerful aid to disintegration.

Water boils at 212 deg. Fah. at the normal pressure, but the boiling point, unlike the freezing point, is much modified by changes in pressure, being raised by increase and lowered by decrease of pressure; so that the temperature of the water in a steam boiler is always higher than that of boiling water outside, and is at the boiling point corresponding to the pressure which exists in the boiler.

The table on page 287 gives some examples of the relationship existing between pressure and boiling point. It will be noted that the pressure increases much more rapidly than the temperature.

The waters which occur in nature are never pure, but always contain more or less impurities, and thus arise the different kinds of water with which the engineer has to deal.

Temperature in deg. Fah.	Pressure in atmospheres.	In pounds (approximate).
212	1	15
236	1·5	22·5
250	2	30
276	3	45
296	4	60
308	5	75
320	6	100
359	10	150
458	20	300
487	40	600

IMPURITIES IN WATER.—The impurities in water may be either in suspension or in solution, and the latter may be gaseous, liquid, or solid.

Suspended Matter.—Matter in mechanical suspension usually gives the water a muddy appearance. Being solid, it can be removed by filtration, or it will settle if the water be left at rest for a sufficiently long time; but if, as is often the case, it be very finely divided, the settling may be very slow, so slow indeed as to render the removal of suspended impurities in this way impracticable. For drinking purposes water is always filtered, so that it may be clear.

Gases in Solution.—All gases are more or less soluble in water, and as the water is in contact with the air, the gases of the atmosphere will dissolve in it to the extent of about 25 parts in 1,000 by volume. As some of these gases are much more soluble in water than others, the proportions in which they exist in water will be very different from that in which they are present in the air. Oxygen is much more soluble than nitrogen, so that air dissolved in water contains about 33 per cent of oxygen by volume. Carbon-dioxide is much more soluble than either, and therefore water may contain a considerable quantity of it—about 2 per cent of the dissolved gas. Other gases, such as ammonia, may be present in small quantity, though in ordinary cases ammonia is probably present in the form of salts, formed by its combination with acids.

Solids in Solution.—Water has been called the universal solvent, since all substances are more or less soluble in it, and as most natural waters have been in contact with rocks or soil, they are always contaminated with various solid matters in solution.

The most important substances found in solution in ordinary waters are calcium carbonate, calcium sulphate, calcium chloride, and the corresponding magnesium salts, salts of sodium, and organic matter, with smaller quantities of other substances, such as silica, iron salts, and alkaline salts. Calcium carbonate is insoluble in pure water, but it dissolves readily in water containing carbon-dioxide, a soluble bicarbonate being formed, thus, $CaCO_3+H_2O+CO_2=CaH_2(CO_3)_2$; and since all natural waters contain carbon-dioxide in solution, if they come in contact with carbonate of lime, by flowing over or through rocks containing limestone, they will dissolve some of it.

The bicarbonate is an unstable body, and is decomposed by boiling the solution, carbon-dioxide being evolved and the calcium carbonate precipitated ; thus $CaH_2(CO_3)_2=Ca\,CO_3+H_2O+CO_2$. Similarly, by the addition of any substance which will combine with the excess of carbon-dioxide, the carbonate is precipitated; for instance, if lime water be used, $CaH_2(CO_3)_2+Ca(OH)_2=2CaCO_3+2H_2O$, the lime both from the bicarbonate and the lime water being thrown down; and if sodium hydrate (caustic soda) be used, $CaH_2(CO_3)_2+Na\,HO=CaCO_3+NaHCO_3+H_2O$, the carbonate of lime being precipitated and the sodium bicarbonate remaining in solution.

With magnesium carbonate the reactions are similar, monocarbonates of lime and magnesia being formed. Thus

$MgH_2(CO_3)_2 + Ca(OH)_2 = CaCO_3 + MgCO_3 + 2H_2O$. The carbonate of magnesium also frequently undergoes further decomposition, the hydrate $Mg(OH)_2$ being separated and precipitated, a reaction of some importance in connection with the formation of scale. Carbonate of iron is occasionally present in solution as a bicarbonate; it is, however, rapidly decomposed by the oxygen of the air, ferric hydrate $Fe_2(OH)_6$ being precipitated, and it is rarely present in large enough quantity to be of any practical importance.

Next to the carbonates, the sulphates are of most importance. The sulphates of soda and potash are very soluble, so are sulphate of magnesia and sulphate of iron, but these are rarely present in any considerable quantity. Sulphate of iron would be decomposed by the air contained in the water, the hydrate or basic salts being precipitated. Calcium sulphate (sulphate of lime) is of much more importance. It occurs fairly abundantly in the crust of the earth, as the hydrate, gypsum, $CaSO_4$, $2H_2O$. This is only sparingly soluble in water, a gallon of water at 68 deg Fah. dissolving 141 grains of calcium sulphate. The solubility varies with the temperature, and at about 120 deg. Fah. reaches its maximum, and falls as the temperature rises further, as shown by the following figures:—

At deg. Fah.	Grains per gallon.
32	120
68	141
122	147
158	142
212	12·7
240	10·5
250	9

Above 250 practically insoluble.

Calcium sulphate can be precipitated from its solutions by the addition of sodium carbonate, which throws down the insoluble calcium carbonate and leaves sodium sulphate in solution, $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$.

Chlorides are occasionally present, sodium chloride very frequently, in small quantities, and in sea water in large quantities, and more rarely magnesium chloride. Magnesium chloride is often present, and is decomposed by water at high temperatures, hydrochloric and magnesium hydrate being formed, $MgCl_2 + 2H_2O = Mg(OH)_2 + 2HCl$. Solid organic matter is also frequently held in solution, and this often has an acid reaction.

HARDNESS OF WATER.—When soap is mixed in with pure water it dissolves, forming a lather. With hard water, on the other hand, no lather is formed, but an insoluble sticky precipitate separates when soap is added to the water. This hardness is always due to the presence of salts of calcium or magnesium in solution, and the hardness of the water, therefore, as measured by the quantity of soap required to make a permanent lather, is a measure of the quantity of these salts present.

The destruction of the soap is due to a chemical change. Soap is the sodium salt of certain fatty acids; *e.g.*, stearic ($NaC_{18}H_{35}O_2$, sodium stearate). Calcium and magnesium stearates are insoluble, so that when soap is added to a solution of such salts a double exchange takes place, and the insoluble salt or soap is formed; thus $2NaC_{18}H_{35}O_2 + CaSO_4 = Ca(C_{18}H_{35}O_2)_2 + Na_2SO_4$, and thrown down as a precipitate.

It is obvious that the water can be softened by the removal of the salts which decompose the soap. When the salts are carbonates held in solution by carbon-dioxide, this can be done by boiling. Hardness due to these is therefore called "temporary hardness"; on the other hand, hardness due to the sulphates or chlorides cannot be so removed, and is called "permanent hardness."

The hardness is usually estimated by adding a standard solution of soap to a measured quantity of the water, with constant shaking till a permanent lather is produced. This gives the total hardness. A sample of the water which has been well boiled is then treated, and thus the permanent hardness is obtained. The difference is the temporary hardness.

The hardness is usually measured in degrees, 1 deg. of hardness being that (by whatever salt produced) which would be given by 1 grain of calcium carbonate per gallon; 1 deg. of hardness will represent 1 grain of calcium carbonate, 1·36 grains of calcium sulphate, or ·84 grains of magnesium carbonate.

SOFTENING WATERS.—The methods by which water can be softened have already been indicated. Permanent hardness is always removed by the use of sodium carbonate, and most of the methods for the removal of the temporary hardness are based on Clarke's process, which consists in the addition of exactly the right amount of lime water to precipitate all the calcium carbonate, the modern improvements being mainly on the methods of separating and removing the precipitated calcium carbonate so as to leave the water clear.

NATURAL WATERS.

Rain Water.—This, if collected in an open space, is the purest natural water. It contains only a trace of solid matter derived from dust in the air, and small quantities of ammonium salts. When collected in towns it often contains small quantities of sulphuric and sulphurous acids, and when collected from roofs, etc., is often very dirty.

River Water.—This is the water most largely used for technical purposes. Its dissolved impurities vary very much according to the rocks over which it has flowed. It very often carries a large amount of suspended matter, the amount varying with the season. It may contain organic matter, derived from the soil with which it has been in contact, or, in the neighbourhood of towns, from sewage pollution or manufacturing refuse. If it has flowed over limestone rocks, it will probably be very hard; but if it has only flowed over hard igneous or metamorphic rocks, it may contain but little mineral matter in solution.

Surface Well Water.—Shallow wells are, of course, fed by surface drainage, and are likely to vary much with the amount of rainfall. The water is usually clear, the soil having acted as a filter, not very hard, unless the soil contains a considerable quantity of calcium carbonate, but they are often highly charged with organic matter, and nitrates, &c., derived from the oxidation of organic matter.

Deep Well Waters and Spring Waters.—These waters, having passed through a considerable thickness of rock, are usually bright and sparkling. Solution has had ample time to go on, so that they are often highly charged with dissolved mineral matter, and are often very hard, but contain but little organic matter. When the mineral constituents are present in large quantity, and different to those contained in ordinary water—for instance, as magnesium sulphate, ferrous carbonate, or sulphuretted hydrogen—it is often called mineral water, and the spring is a mineral spring. Mineral springs often have a temperature much above that of the atmosphere.

Sea Water.—The water of the sea is highly charged with soluble salts, sodium chloride (common salt) and magnesium chloride being the most important.

BOILER WATERS.

The principal purpose for which the engineer needs water is for feeding boilers, and for this purpose many natural waters are quite unfit. There are two dangers, which may be produced by the use of unsuitable waters, to be guarded against. They are: (1) Pitting and corrosion, (2) the deposition of scale.

Corrosion.—Corrosion may be irregular, in which case it is marked by the formation of pits in the plate, corrosion around bolt heads or along seams; or it may be general, in which case the whole plate is more or less regularly eaten away.

Corrosion is very frequently due to the use of a water containing acid, as even the weak organic acids from decomposing vegetable matter have a marked action. These are often present, and in rarer cases other acids, such as sulphuric acid, produced by the decomposition of pyrites, may also be present. Acid waters should always be neutralised before use.

The cause of corrosion, when not due to acid water, is often very obscure. It has been suggested that it may be due to the action of the oxygen liberated from the water on heating. As already remarked, natural water always contains a considerable quantity of air in solution. When the water enters the boiler this is expelled, but, as is well known, bubbles of gas expelled from solution in liquids often do not rise freely, but tend to accumulate on any roughnesses on the surface with which they come in contact, and thus the oxygen and the carbon-dioxide together might produce a rusting action. It has been noticed that the pitting is most common in the neighbourhood of projections, such as bolt heads or seams, and in parts of the boiler where there is least circulation. Once rusting has started, the little patches of hydrate will afford good foothold for more bubbles.

On the other hand, it has been suggested that corrosion may be due to electric action set up between the iron and the impurities present, when the former, being the electro-positive element, is attacked. To overcome this it has been suggested to suspend in the boiler a piece of zinc or other metal more electro-positive than iron, so that it may be attacked and the iron left. In order that such a method may be successful it is essential—(1) that the zinc be in metallic connection with the boiler; (2) that the zinc be pure, as if it contains lead this may be deposited in flocks as the zinc dissolves, and set up the very action it is intended to prevent; and (3) the water must be a sufficiently good conductor. As pure water is a very poor conductor, it will generally be necessary to dissolve common salt or other soluble salt in it.

It must be remembered that some salts which are neutral in ordinary solutions break up into hydrates and acids at the temperatureand pressure in the boiler. This is the case with magnesium salts, both the chloride and the nitrate, which are therefore very destructive to boilers, and even when present in small quantity may lead to corrosion. The waters which produce corrosion are usually not those which produce scale; indeed, a thin layer of scale sometimes acts as a preventive to corrosion.

FORMATION OF SCALE.

The deposition of solid matter in the form of scale is one of the great troubles of the boiler manager. Obviously some water containing more or less solid matter in solution is constantly being evaporated. The salts in solution will—unless means be taken to prevent it—accumulate until they crystallise out, so that the separation of solids would become inevitable. This is prevented in the case of salts which need considerable evaporation by systematic blowing off. Only those constituents which are thrown down before the solution becomes unduly concentrated, and which cake in a hard scale on the boiler plates, need therefore be considered as scale formers.

The material may either be deposited on the boiler in a hard coherent scale, or it may be thrown down as a loose incoherent mud, which afterwards becomes consolidated; and it must be remembered that, as a rule, the quicker the precipitation the more incoherent will the precipitate be.

The formation of a hard scale is attended with considerable danger. The scale being a poor conductor of heat, the plate beneath may become very hot, even red hot, and then may give way under the pressure, or the scale, owing to unequal contraction, may break up, and the water coming against the hot plate may cause fracture. Even if this does not take place, flakes of separated scale may cause a considerable interference with the circulation.

Suspended Matter.—When turbid water containing matter in suspension is run into a boiler, this will accumulate as the water is boiled away. Probably only very fine material will be in suspension, as the coarser matter will have been deposited outside, and this is not likely to separate while the water is in vigorous circulation, unless the quantity be very large, and when it does settle it will be in the form of sludge, which can be blown out; but if the boiler be stopped, it will gradually subside. If, now, the fires be made up again, it may not unlikely become more or less caked, especially if, as will probably be the case, it contains a good deal of clay; and if there be organic matter, this may char, and help to bind the whole together. Once a more or less non-conducting layer has been formed, it will become harder, and thus may form a hard layer of scale.

SOLIDS IN SOLUTION.—These are very much more troublesome, and the composition and character of the scale depends almost entirely on the nature of the precipitate formed.

Calcium Carbonate.—When water containing calcium carbonate goes into the boiler, the carbon-dioxide is at once expelled, and most of the calcium carbonate comes down rapidly in the form of an incoherent precipitate, which forms a sludge that can be easily blown out, though a small quantity may remain in solution, and come down slowly enough to form an adherent scale. "Many of the carbonate of lime scales are produced by emptying the boiler whilst the plates and brickwork are hot, and the soft sludge is thus baked on to the plates."* Magnesium carbonate behaves similarly, but may be further decomposed into hydrate. This is specially objectionable when calcium sulphate is also present, as it cements the whole into a hard, compact scale.

Calcium Sulphate.—This, as already pointed out, is slowly deposited at high temperatures, and it forms a compact scale; and when magnesium hydrate is deposited at the same time, the scale is hard and difficult to remove. Calcium sulphate is the basis of most of the boiler scales, as is shown by the analyses by H. Silvester, on page 297.

An impurity which is often very troublesome, but which does not properly belong to the water, is oil, carried over by the steam, condensed, and returned to the boiler. This oil

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* H. Silvester. Proceedings S. Staff. Inst., 1891-92.

at first floats on the water, forming a scum. As the particles of solid matter separated from the water are carried upwards by the circulation of the water, they come in contact with the particles of oil scum, and are entangled, till the mass becomes heavier than the water, and sinks, and, coming in contact with the shell, sticks firmly. Being a very bad conductor, the plate beneath becomes hot, the oil chars, and cements the whole to a solid mass of scale. The nature of the scale will vary with the nature and amount of the oil and the temperature to which it has been heated; it may be porous and charred, or it may be soft and india-rubber-like. Should patches of oil become deposited on a portion of the boiler by the lowering of the water, other matters are sure to become attached to it, and form a patch of scale.

	A carbonate scale.	Very hard scale.	Sulphate scale.	From marine boiler using salt water (Prof. Lewes).
Calcium carbonate..........	77·85	2·49	4·45	46·06
Calcium sulphate	3·68	74·28	77·80	..
Magnesium hydrate........	2·56	18·00	11·15	4·16
Sodium chloride............	·45	..	..	38·66
Silica	7·66	1·83	2·14	1·09
Oxides of iron and alumina.	2·96	1·27	1·35	·65
Organic matter	3·64	2·12	3·11	..
Moisture	3·20	..	..	9·38

PREVENTION OF SCALE.

To prevent the formation of scale from the ordinary scale formers several methods are in use. In general they are of two kinds :—

1. Purification of the water before it enters the boiler.
2. Treatment with reagents in the boiler.

The first is certainly the best, and is largely coming into use for large plants, many water-softening installations having recently been erected; and it should be used wherever the water needs purification.

When a chemical is added to the boiler, it should always be added in solution, *never* in the solid form, and should, if possible, be supplied continuously with the feed.

An enormous number of scale preventers have been suggested, and they are based on three principles :—

1. Precipitating the salts in such a form that they do not form scale, but a sludge which can be blown out. This is brought about by rapid precipitation by the formation of insoluble salts by chemical reagents. Among the best known of these agents are lime water, carbonate of soda, caustic soda, silicate of soda (which throws down lime and magnesia as silicates), and tannate of soda, which throws down the lime as tannate. Many mixtures of these are used in various proportions, and in place of tannic acid materials such as oak bark, which contain it, are sometimes used.

The following analyses by Tatlock, given by Silvester in the paper already referred to, will indicate the nature of some of these compositions :—

Caustic soda	12·30	11·44
Sodium chloride	1·24	1·22
Sodium sulphate	·68	·72
Calcium carbonate	·48	·40
Tannin	6·65	6·36
Organic matter	19·60	18·99
Water	59·05	60·87
	100·00	100·00

Sodium fluoride is suggested by Prof. Lewes as being an efficient precipitant for lime and magnesium salts, the precipitate having no tendency to harden.

2. Those which by mechanical action prevent the precipitate forming a scale. These are such substances as potatoes, dextrine starch, &c., which form slimy masses with the precipitates, and thus prevent them hardening.

3. Substances which increase the solubility of the incrusting salts, and thus prevent their precipitation; the most used are gelatine and sugar.

Whenever chemicals of any kind are used, care must be taken that they are suitable for the water being used, and, especially in the case of alkaline salts, that they are not used in excess.

The removal of scale once formed is almost impossible by chemical means, the scale-forming materials being mostly too insoluble, though some of them are slightly attacked by alkaline salts, which, therefore, may "rot" the scale, and cause it to break up, and come away in flakes, but such action is always slow and uncertain. In nothing is the advantage of prevention over cure better seen than in connection with boiler scale. In no branch of engineering is there more quackery than in this, and no engineer should add anything to his boilers for the prevention of incrustation without knowing exactly what he is using.

Oil *must* be kept out of the boiler, and where condensed water is used this can only be done by the use of suitable oil separators, of which there are many on the market. Probably oil is the greatest source of danger in boilers fed with water condensed from steam.

WATER ANALYSIS.—It is not necessary that the engineer should be able to make an analysis of a sample of water, but it is essential that he should understand the real meaning of the figures usually given.

An analysis of water is usually stated in grains per gallon (parts in 70,000), or in parts in the 100,000 or 1,000,000; which method is used is of little importance, but the first is that most general in this country.

To convert parts per 1,000,000 into grains per gallon × ·07.

Suppose we take two salts—say magnesium sulphate

($MgSO_4$) and sodium chloride ($NaCl$)—and dissolve them in water; it does not follow that they will remain in their original forms in solution; indeed, it is certain that they will not. The two salts will react upon one another, and a redistribution of the radicals will take place. For example, suppose the weights dissolved were 1·20 grammes of magnesium sulphate (containing ·24 grammes of magnesium and ·96 grammes of the radical SO_4) and 1·170 grammes of sodium chloride (containing ·46 grammes of sodium and ·73 grammes of chlorine). These constituents will undergo a re-arrangement, and these will be in solution not two salts, but four, viz., magnesium sulphate, sodium sulphate, sodium chloride, and magnesium chloride, the relative proportions varying with circumstances.

Suppose now it be required to make an analysis of such a solution, four separate determinations will be necessary, viz.:—

1. The sodium will be determined probably by converting it all into sulphate, and weighing this salt, from which the Na can be calculated, = ·46 grammes Na.

2. The magnesium can be determined by precipitating as ammonium-magnesium phosphate, and weighing as pyrophosphate, whence the Mg can be calculated, = ·24 grammes of Mg.

3. The chlorine can be determined by precipitation as silver chloride, whence the Cl can be calculated, = ·73 grammes of Cl.

4. The sulphuric acid radical SO_4—*i.e.*, that part of the sulphate which is left when the metal is removed, or when the hydrogen is removed from the acid—will be estimated as barium sulphate ($BaSO_4$), whence the SO_4 can be determined, = in this case ·96 grammes of SO_4.

The analysis has therefore given:—

Sodium = ·46 grammes, Chlorine ·73 grammes.
Magnesium = ·24 „ Sulphuric acid radical ·96 grammes.

But it gives no idea as to how these were combined, whether there was 1·17 grammes of sodium chloride and 1·20 grammes of magnesium sulphate, or 1·42 parts of sodium sulphate and ·97 parts of magnesium chloride; indeed, in this case, as remarked above, neither would be correct, as all four salts will be present, and the analysis gives no data for determining in what proportions.

It is customary in stating the results of a water analysis to allocate the various metals found to the various acid radicals in a way depending on individual taste, and, therefore, two analysts, making an accurate analysis of the same water, might state the results in such a way that they appeared quite different. That this might be so will be quite clear from what has been stated above; but the following two statements, derived from the same analytical figures, will illustrate this point further :—

The results actually obtained from an analysis were :—

Magnesium	·240
Calcium	·040
Sodium	·966
Potassium	·780
Sulphuric acid (SO_4)	1·056
Chlorine	·803
Carbonic acid (CO_3)	·600
Nitric acid (NO_3)	1·240
	5·725

Or, stated in a form very often used :—

Magnesia (MgO)	·400
Lime (CaO)	·056
Soda (Na_2O)	1·302
Potash (K_2O)	·940
Sulphuric acid (SO_3)	·880
Carbonic acid (CO_2)	·440
Nitric acid (N_2O_5)	1·080
Chlorine	·803
	5·901

It will be seen that the total here is too high. The reason for this is that the chlorine is in combination with some of the metals displacing its equivalent of oxygen. If we deduct the oxygen equivalent of the chlorine, we have—

$$5{\cdot}901 - {\cdot}176 = 5{\cdot}725.$$

From these data the two results given below are calculated:

(1)

Magnesium sulphate	1·200
Calcium "	·136
Sodium chloride	1·309
" carbonate	1·060
Potassium nitrate	2·020
	5·725

(2)

Magnesium chloride	·970
Calcium chloride	·113
Sodium sulphate	1·562
" nitrate	1·600
Potassium carbonate	1·380
	5·725

In order that analyses of waters may be compared, it is essential therefore that the figures should be reduced to the simple form, so as to eliminate the influence of any theory the analyst may have as to the way in which the various constituents are combined.

The analyses on page 303 will serve as examples of the composition of various kinds of waters. It will, of course, be understood that they are examples only; and in order to ascertain the fitness of any given water for any purpose, an analysis must be made—full or partial, according to the information required.

Fresenius gives the following rule for combining the constituents obtained in an analysis of a water, so as to bring

	Parts in 1,000,000.									
	1	2	3	4	5	6	7	8	9	10
Total solids	310·3	408·4	116·1	76	1437	80	991·5	15478	38400	240483·3
Calcium..............	76	82·1	18·1	8·1	170·4	9·7	18·8	493·6	576·8	9000
Magnesium	4·7	..	4·7	1·8	39·7	..	9·1	198·7	1198·1	19883·4
Sodium	8·7	14·3	2·9	6·4	96·4	7·4	265·3	490·4	11719·7	47968
Potassium	3·9	1·7	..	2·3	109·4	..	99	479·7	668·2	6385·1
Aluminium and iron..	10·9	..	..	..	..	..	..	..	..	..
Carbonic acid (CO_3) ..	105·3	69·4	31·3	trace	..	..	197·1	104·8	..	..
Sulphuric acid (SO_4)..	39·5	32·2	7·9	13·3	220	2·8	180·5	18·2	3029·8	479
Chlorine	12·1	63·6	8·3	12·8	129·2	7·9	174·2	9187·4	20839·7	156442
Bromine	..	..	..	..	..	..	..	..	387·8	2176·7
Silicia	6·3	1·8	3·0	12·3	12·4	19·0	13·1	4·4	3·4	..
Organic matter	43·9	100·0	26·1	16	..	..	13	..	..	..
Sulphur hardness	..	..	..	..	..	..	..	87·7	..	617·3
Total	20°	..	..	2 8°	..	..	..	..	..	..

1. Thames, at Kew.
2. Thames, at London Bridge.
3. Clyde, above Glasgow.
4. Spring, Witley, Surrey.
5. Spring, at Highgate.
6. Ben Rhydding, Yorks.
7. Artesian well, London.
8 Harrogate spring.
9. Sea.
10. Dead Sea.

it to the conventional form : "The chlorine is combined first with sodium, and if there is excess (which rarely occurs) this is combined with calcium. The sulphuric acid is combined first with lime. The nitric acid is combined first with ammonia, and the remainder (if any) with soda, if the latter has not been used up for the chlorine, otherwise with magnesia. The silicic acid is put down in the free state, the remainder of the lime and magnesia as carbonates."

CHAPTER XXIII.

LUBRICANTS.

Friction.—When one surface is made to slide over another there is always considerable resistance to motion, this resistance being called friction. Friction is mainly due to the roughness of the surfaces, and the interlocking of the projecting portions. It is impossible to prepare perfectly smooth surfaces, and thus friction always accompanies motion of one body on another. There is another cause of resistance to motion that may come into play under certain conditions—that is, molecular attraction or cohesion. When the molecules of a body are brought into very close proximity molecular attraction takes place, and in the case of bodies the molecules of which are easily moved, such as lead, or iron at a welding temperature, perfect union may take place. In order that the surfaces may unite, they must be at a temperature such that the molecules are mobile, the pressure must be enough to bring them into sufficiently close proximity, and the surfaces must be perfectly clean. These conditions rarely hold in the cases in practice where one body has to slide over another.

The friction between surfaces is measured by the force which is required to slide the one over the other, measured in terms of the force with which the surfaces are pressed together, or what comes to the same thing, the unit is the force which would be required to slide a unit weight of the one body over a horizontal surface of the other. This is called the coefficient of friction, and is indicated by the sign μ. If one body were placed on a plane surface of the other, and the plane were tilted till motion took place, the angle at which the plane would be inclined would be such that its tangent would be $= \mu$. The laws of friction have been investigated by various observers. The following laws are given by Morin:

1. The friction between two bodies is directly proportional to the pressure—*i.e.*, the coefficient is constant for all pressures.

This only holds until the pressure is sufficient to cause serious breaking up of the softer surface, so that in practice it is only true of hard surfaces under moderate pressures.

2. The coefficient and amount of friction—pressure being the same—is independent of the areas in contact.

This is only approximately true, and fails altogether in the case of easily abraded bodies.

3. The coefficient of friction is independent of velocity, although static friction or friction at rest is greater than friction in motion.

This is not strictly true; friction at low speeds seems to be almost the same as static friction, but that at high speeds is considerably less.

The following will serve as examples of the value of μ:—

Brass on brass	·175
Brass on steel	·139
Brass on cast iron	·141
Brass on wrought iron	·135
Steel on steel	·146
Steel on cast iron	·151
Steel on wrought iron	·188
Cast iron on cast iron	·163
Wrought iron on wrought iron	·160
Wrought iron on tin	·181

It will thus be seen that where two metal surfaces are in motion in contact, there must be considerable absorption of energy, and the surfaces therefore become very hot. To avoid this the dry metals are never allowed to run in contact, but are separated by a layer of some lubricant.

LUBRICANTS.—These may be either solid or liquid. They form a layer between the moving surfaces, so that these do not touch, and therefore the friction depends much more on the nature of the lubricant than on that of the surfaces.

When two well-oiled surfaces are made to slide one over the other, a layer of oil adheres firmly to each surface, and the motion takes place, not by the sliding of either surface on the oil, but by the shearing of the mass of oil, and thus the sliding of one layer of it on another. The same is the case with solid or semi-solid lubricants.

The value of a lubricant depends largely on its viscosity. A very fluid liquid, such as water, having very little viscosity, would be squeezed out at very moderate pressure. It is, of course, essential that the lubricant, if a liquid, should wet the surface of the metal.

Thurston gives the following as being the characteristics of a good lubricant.*

1. Enough "body," or combined capillarity and viscosity to keep the surfaces between which it is interposed from coming in contact under maximum pressure.

2. The greatest fluidity consistent with the preceding requirements—*i.e.*, the least fluid friction allowable.

3. The lowest possible coefficient of friction under the conditions of actual use—*i.e.*, the sum of the two components, solid and fluid friction, should be at a minimum.

4. A maximum capacity for receiving, transmitting, storing, and carrying away heat.

5. Freedom from tendency to decompose or to change in composition by gumming or otherwise on exposure to the air, or while in use.

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* "Materials of Engineering," vol. i., p. 224.

6. Entire absence of acid or other properties liable to produce injury of material or metals with which they may be brought in contact.

7. A high temperature of vaporisation, and of decomposition, and a low temperature of solidification.

8. Special adaptation to the conditions as to speed and pressure of rolling surfaces, under which the unguent is to be used.

9. It must be free from grit and all solid matter.

Viscosity.—All liquids have more or less viscosity—that is, there is some resistance to the free motion of the molecules one over another, or there is some internal or fluid friction. If water be set in motion it comes to rest in time, while a more viscous fluid, such as treacle or a heavy oil, will come to rest very much more quickly, but at the same time the mass will flow under the smallest force, and is therefore a true liquid, whilst a plastic, solid body, such as a fat, will not flow until the pressure reaches a certain minimum value, but in either case, when used as lubricants, the resistance is to the separation of the portions of the mass by shear.

The viscosity of an oil may be measured in various ways. The readiest, though not the most accurate, are (1) to fill a burette, and note the number of seconds it takes to empty from one mark to another; and (2) to note the rate at which air bubbles rise through the oil. There are many viscometers in use, for description of which the student must refer to some work on lubricants.

Capillarity, or surface tension, is the force with which the surface of the liquid resists being broken. This is due to molecular attractions, and is very important in preventing the liquid being entirely forced out from between two surfaces. The "body," as it is called, is principally due to these two properties.

Fluidity.—The greater the viscosity, the less the fluidity. Such bodies as pitch and sealing wax have a very high vicosity, but very little fluidity. The greater the viscosity, the greater the power required to slide the molecules one over the other, whilst the greater the fluidity the more readily will they move. It is obvious, therefore, that the two properties are antagonistic, and a substance must be selected for a lubricant in which the viscosity is only just as great as is required.

Heating.—The expenditure of energy in friction always develops heat, and therefore the lubricant will always become more or less warm as work goes on. This may considerably modify its properties, increasing the fluidity and decreasing the viscosity. The better conductor of heat the lubricant is, the more quickly will the heat be carried away; and the higher the specific heat, the more heat will be required to produce a rise of temperature. It is obvious, therefore, that high conductivity and high specific heat will always be advantageous.

Freezing Point and Boiling Point.—If a lubricant has a very low boiling or vaporising point the heat generated may be sufficient to convert it into vapour, and thus leave the surfaces unprotected, and if it be decomposed at a moderate temperature it may leave a residue which would increase the friction. Materials which are very volatile or are easily decomposed are therefore unsuitable for lubrication. On the other hand, if it solidifies at too high a temperature the expenditure of energy may be unduly increased in cold weather.

Oxidation.—Many oils, on exposure to the air, undergo chemical changes which quite unfit them for use as lubricants. The drying oils, for instance, absorb oxygen and pass into the solid condition. Many oils, on long exposure to the air, are partially oxidised with the formation of gummy bodies, which would be most objectionable. Some oils, on the other hand, on exposure to the air, oxidise with the formation of acids, which may attack the metal with which they are in contact, and thus lead to corrosion.

Acidity.—Many oils have an acid reaction. It may be due to free fatty acid, naturally existing in the oil, or produced by decomposition of other organic bodies, or it may be mineral acid which has been used in the preparation of the oil and not properly removed. Any form of acid is objectionable, as it may lead to corrosion.

Classification of Lubricants.—Lubricants may be classified into—

1. Mineral oils.
2. Fixed oils and fats.
3. Thickened oils.
4. Resin oil.
5. Greases.
6. Mineral lubricants.

1. *Mineral Oils.*—These are derived from two sources—the natural oils of the United States, Russia, and a few other localities, and the oil made by the distillation of shale The crude oils—in either case—are very dark in colour, and are subjected to distillation to separate the more volatile constituents, which are used for various purposes, mainly for lighting oils, and the residue, if the distillation has not been pushed too far, or the heavier distillates, are used for lubricating purposes.

The oils vary in boiling point from about 170 deg. to 320 deg. Cen., in colour from pale yellow to nearly black, and in specific gravity from ·85, or so, up to ·92. A wide range of properties can therefore be obtained. The oils have a high boiling point and do not solidify readily, though solid paraffin and similar bodies may separate at low temperatures.

The mineral oils are mainly composed of hydrocarbons. They do not oxidise, and therefore do not become acid or gummy in use, and undergo little chemical change. They do not saponify when mixed with alkalies, and they can be detected by this and by the "bloom" which is usually visible. Vaseline is a solid product of the distillation of mineral oils.

2. *The Fixed Oils and Fats.*—These oils are both of vegetable and animal origin, the former being derived mainly from the seeds of fruit. They are usually yellow in colour, do not show a bloom, often have a characteristic

odour, and, whilst they vary very much, the properties of the oil obtained from the same source are fairly uniform. They may be either solid (fats) or liquid (oils), and are not volatile without decomposition.

They differ entirely in chemical character from the mineral oils, being organic salts or glycerides of certain fatty acids. These salts are decomposed by caustic soda or potash, forming soda, or potash salts or soaps, with the separation of glycerine. Thus in the case of olein and palmatin :—

$$C_3H_5(C_{18}H_{33}O_2)_3 + 3NaHO = C_3H_5(OH)_3$$

Olein. Sodium hydrate. Glycerine.

$$3NaC_{18}H_{33}O_2$$

Sodium oleate.

$$C_3H_5(C_{16}H_{31}O_2)_3 + 3NaHo = C_3H_5(OH)_3$$

Palmatin.

$$+ 3NaC_{16}H_{31}O_2.$$

Sodium palmate.

Hence they are said to be saponifiable, and can be separated from the mineral oils by the action of sodium hydrate When such fats are treated with superheated steam, water under pressure, or sulphuric acid, a similar decomposition takes place, the free acid and glycerine being produced. These fatty acids are mostly solid bodies. The fixed oils and fats are all more or less oxidisable on exposure to the air. Some of them, as for instance linseed oil, pass into an elastic solid mass on oxidation, and are called drying oils. The oils with strong drying power are, of course, quite unsuitable for use as lubricants, but most of the oils undergo the change to some extent, and thus tend to become thick on exposure to the air. As this oxidation evolves heat, vegetable oils, when spread over large surfaces, as in the case of oily rags, are liable to spontaneous ignition.

VEGETABLE OILS. *Colza* (*rape*) *Oil* is obtained from the seeds of several varieties of brassica, which are extensively cultivated for the purpose. The extracted oil contains various albuminous impurities, which are apt to decay and lead to acidity of the oil by the breaking up of the glyceride. It is purified in various ways, usually by agitation with sulphuric acid, drawing off the oil from the separated impurities, and washing to remove acid.

The acid refining tends to increase the acidity of the oil, not only because traces of acid may be left, but also by setting up decomposition of the glycerides.

Colza oil is brown or yellow in colour, has a specific gravity of about ·914, and consists almost entirely of glycerides of stearic and other acids.

It solidifies at about 0 deg. Cen., or a little below, and oxidises considerably on exposure to the air.

Olive Oil.—This is obtained from the olive, the fruit of *Olea Europæa Sativa*, which is largely cultivated on the Mediterranean. The fruit is pressed, the finest or virgin oil being obtained by hand pressure, inferior qualities afterwards by machinery with the aid of heat, the last traces being obtained by heating the pressed mass with a solvent. It is too expensive for use as a lubricant, though it is probably one of the best oils for the purpose. The commoner varieties, obtained by the later crushings, are sometimes used. It should be clear yellow in colour, but may be greenish or brown. It decomposes readily, becoming acid, especially in the crude state. Being an expensive oil, it is very frequently mixed with cheaper oils. It consists largely of olein, with some palmatin.

Castor Oil.—This oil is prepared from the seeds of the castor oil plant, which is extensively cultivated. That used in medicine is extracted by pressure without heat, but the coarse oil used for lubrication is extracted with the aid of heat, and is afterwards refined by boiling with water. Castor oil differs in composition from most oils, and is the glyceride of two isomeric acids, ricinoleic and triricinoleic acids, which belong to a different series to those which exist in most fats. It is soluble in alcohol (in which most oils are insoluble), and does not mix with petroleum, spirit, and mineral oils, unless other oils are present also.

Palm Oil.—This is a solid fat, obtained from the fruit of the oil palms. It melts at about 80 deg. to 97 deg. Cen. It often contains large quantities of free fatty acid, and is therefore not well suited for lubrication.

Cotton Seed Oil.—The seeds are pressed, and the cake is heated and again pressed. The oil is then refined. It has a spirit gravity of ·920 to ·923, and solidifies at a little above 0 deg. It is sometimes used for lubrication, and for adulterating other oils, but has distinct drying properties.

Blown Oils.—When air is blown through oils having some drying properties, oxidation takes place, and the oils are more or less thickened. The oil is warmed, and air is blown through until the required viscosity is obtained. They are usually used in admixture with mineral oils.

Rosin Oil is obtained by distilling rosin in iron stills. It is dark brown in colour, and shows a distinct fluorescence, which is destroyed by exposing the oil to air and light, or by treatment with certain oxidising agencies.

ANIMAL FATS—The animal oils and fats most largely used for lubrication are tallow and tallow oil, lard and lard oil, neatsfoot oil, sperm oil, whale oil, &c.

Tallow.—Tallow is the fat of various animals, purified from the organic tissue. The fats are melted either in open or in closed vessels under pressure, whereby the fat is separated from the organic tissue. Tallow is usually made from either mutton or beef fat. It is a mixture of stearine, palmatin, and olein, and, since the two former are solids and the latter liquid, it is thinner and softer the larger the proportion of olein, the amount being usually about 46 per cent. Tallow is often acid, owing to the separation of free acid, mainly oleic, during the purification.

Tallow Oil.—If tallow be subjected to pressure a liquid portion is squeezed out. This is tallow oil, and the residue is tallow stearine The oil consists principally of olein.

Lard and Lard Oil are similar to tallow and tallow oil, except that the source is the pig, instead of the ox or the sheep. Their composition is also very similar.

Neatsfoot Oil.—This oil is prepared by boiling the feet of oxen with water. It is now but little used as a lubricant.

Whale Oil.—This is obtained from the blubber of the Greenland whale.

Sperm Oil.—This is one of the most valuable oils. It is pale yellow in colour, is very liquid, and as it has a low viscosity, is best suited for light machinery. It is different in chemical character from most of the fats, not being a glyceride, but an ester of a mono-hydric fatty acid, the nature of the alcohol and acid present being unknown. The crude oil contains a large quantity of spermaceti, which is separated by cooling and filtration. The bottlenose oil obtained from another variety of whale is very similar.

GREASES.—These are thicker than oils, and are made by mixing solid fats or soaps with oils. Aluminium oleate or soap, made by saponifying an oil rich in oleic acid with caustic soda, and mixing with a solution of alum, is often used as a thickener. Lead soap is sometimes used. Rosin oil unites with slaked lime to form a grease.

The following may be taken as examples of greases suitable for railway wagons :—

Tallow	20
Palm oil	12
Colza oil	1·5
Soda crystals	5·0
Water	61·5
	100·0

or,

Tallow	23·3
Palm oil or mineral oil	7·8
Dry soap	16·3
Water	52·6
	100·0*

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* Archbutt-Deeley Lubricants, page 123-127.

SOLID MINERAL LUBRICANTS.—These are only sparingly used in cases of heavy pressure. The most important are graphite, which is used either alone or mixed with oils; talc (soapstone), used in powder or mixed with fat, and various mixtures such as fibre-graphite, which consists of a prepared mixture of wood fibre and graphite.

BEST LUBRICANTS FOR DIFFERENT PURPOSES.†

Low temperatures, as in rock drills driven by compressed air	Light mineral lubricating oils.
Very great pressures, slow speed	Graphite and other solid lubricants.
Heavy pressures, slow speed	Lard, tallow, and other greases.
Heavy pressures, high speed	Sperm oil, castor oil, and heavy mineral oil.
Light pressures, high speed	Sperm, refined petroleum, olive, rape, and cotton seed oils.
Ordinary machinery	Lard oil, tallow oil, heavy mineral oil, and the heavier vegetable oils.
Steam cylinders	Heavy mineral oils, lard, tallow.
Watches and other delicate mechanism	Clarified sperm, neatsfoot, porpoise, olive, and light mineral lubricating oils.

Testing Lubricants.—The examination of lubricants consists of two parts.

1. The identification of the lubricant, or the constituents of which it is composed, or if it is stated to be a definite "oil," detection of impurities and adulterants. This examination can only be properly carried out in a well-equipped chemical laboratory, and is often somewhat complex, as the characters of the individual oils are largely obscured by admixture.

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† Kent, "Mechanical Engineer" Pocket-book.

Mineral oils can often be detected by the fluorescence which they show. This is readily seen by spreading a little of the oil on a piece of glass over black cloth or paper, but the absence of this "bloom" does not prove the absence of mineral oils. They can also be recognised by not being saponified when mixed with caustic soda. Unsaponifiable matter may, however, consist of other substances than mineral oils.

2. The testing of the lubricant as to its suitability for a given purpose. This is as a rule of more importance to the engineer than the mere identification of the individual constituents. The characters to be tested are usually—

(*a*) Viscosity. Various forms of apparatus have been designed for this purpose. As there are no convenient units in which this property can be expressed, it is usually given as compared with some standard oil, such as pure rape or olive oil.

With solid lubricants, in place of viscosity the consistence has to be determined. This may be measured by the time a pointed rod of given weight takes to sink a given depth into a mass of the grease contained in a suitable vessel. Temperature is, of course, an important factor in the consistence of a grease.

(*b*) Specific gravity, which is determined in the usual way.

(*c*) Flashing point—*i.e.*, the temperature at which the material gives off an inflammable vapour. This is important in certain cases.

(*d*) Volatility, the temperature at which the lubricant boils, and the rate at which it will volatilise at lower temperatures.

(*e*) The solidifying point of liquid lubricants. This may be of importance in some cases, especially with such oils as solidify, or from which a solid constituent separates at temperatures to which it may be exposed in practice.

(*f*) In the case of solid greases, the melting point is of importance.

(*g*) The amount of free acid, and also the nature of the acid to which acidity is due. As a rule, not more than a trace of acid should be present, and most good oils do not show even that.

8. The oxidation or gumming of the oil. This may be judged by putting a little of the oil in a concave glass, such as a watch glass, and leaving it exposed to the air for 24 hours or so.

Many instruments have been devised for the testing of lubricants, and some of these are of great practical value. The results obtained by any of them are only comparative, and so many conditions lead to variations in the results obtainable that they are only trustworthy as auxiliary to a complete examination of the material, and a practical test of a lubricant to be of real value must be carried out approximately under the same conditions of speed, pressure, and temperature as those under which it is to used.

CHAPTER XXIV.

PAINTS AND VARNISHES.

Paints and varnishes are largely used for covering surfaces both for protective and ornamental purposes. A paint is opaque, so that it completely hides or covers the underlying material, whilst a varnish is transparent and protects the surface without hiding it.

A paint consists essentially of two parts. A body or opaque material which "covers" the surface and a vehicle by which the body is made up into a suitable consistence for application, and which by its drying retains it on the surface. In addition to these various other substances may be added for various purposes, such as "solvents" to make the paint more liquid, and therefore more easily applied; driers, to hasten the hardening; and pigment, to impart a colour, when this is not done by the base.

Paints may roughly be classed into two groups, oil paints and water paints or distempers, the former only being generally called paint.

The Vehicle.—The vehicle for oil painting is almost invariably linseed oil. This is one of the best of the drying oils—that is, oils which on exposure to the air absorb oxygen and pass into a transparent resin-like mass. Other oils are occasionally used, but they are all much inferior in drying power to linseed oil.

Linseed oil is obtained by pressing the seed of *linum usitatissimum.* The best—cold drawn—oil is pressed cold but the ordinary oil is expressed at about 200 deg. Fah. It is dark yellow in colour and dries readily. The drying power of the oil is greatly increased by "boiling" either alone or with agents called driers, such as litharge, sugar of lead, or zinc sulphate. Such boiled oils are much thicker than the raw oil, flow less freely, and therefore frequently need the admixture of solvents, but they dry much more rapidly than the raw oil. The solvent used is usually turpentine (spirit of turpentine), commonly called turps. This volatilises readily on heating, leaving only a small residue, but on slow volatilisation in the air it oxidises, leaving a resinous residue. It therefore acts mainly as diluent. At the same time it imparts a very unpleasant odour to the paint; when this odour is objectionable, the paint may be "thinned" with methylated spirit in which a little shellac has been dissolved.

Good boiled oil should dry in about 24 hours, provided the layer be thin, but the raw oil takes much longer.

Enamel paints, which dry with a bright enamel-like surface, are made with a vehicle consisting mainly of a solution of some resinous matter in petroleum spirit with the addition of a comparatively small quantity of oil.

For water colours, or colouring as it is usually called, the vehicle is water and size or gelatine. This dries, forming an adherent film, which is, however, attacked by water. Many attempts have been made to prepare washable or insoluble distempers by the addition of alum or other substance which renders the gelatine insoluble.

Driers.—These are substances which increase the rate of oxidation, and therefore the drying, of the oil. The most used are litharge, acetate of lead (sugar of lead), oxide of manganese, sulphate of zinc (for zinc bases), or some other solutions which have the same effect. They are ground up with oil, and added to the paint just before use. The action of these substances is not well understood; but in some way they facilitate the oxidation of the oil. Terebenine is sometimes used as a substitute for driers "in the proportion of 1 oz. to 1 lb. of paint. Alone it will dry in about half an hour."

Base.—For ordinary oil painting the base is almost always white lead. This is a basic carbonate of lead, and as produced by the Dutch process is a dense white amorphous powder. White lead is made also by other processes, some of which are said to yield a material equal to that made by the Dutch process, but most of them give the carbonate in a crystalline form deficient in covering power. White lead is very largely mixed with other white pigments, such as sulphate of barium, carbonate of barium, carbonate of lime, &c., and the mixtures are known by various trade names.

White lead is dense, has a good body, and is the most largely used of all the bases. Indeed, many engineers seem to think that only white lead paints are any use. White lead, however, is quite unsuited for situations where it is exposed to fumes containing sulphur, as in towns, or in rooms lighted by gas, as it speedily darkens, owing to the formation of black lead-sulphide.

For protective painting red lead (Pb_3O_4) is largely used. This is a bright red powder made by heating molten lead in air to convert it into litharge (PbO), and then gently heating the litharge in air till it acquires the required colour. It is largely used for painting ironwork, and as a priming coat in painting wood.

Zinc Bases.—Where lead cannot be used, and a white base is required, zinc compounds are often used, as these are not blackened by sulphur compounds. They do not, however, mix so readily with oil, nor have they the same body as white lead. Oxide of zinc (ZnO) is most largely used, but zinc sulphide (ZnS) and the oxy-sulphide (Zn_2OS) are also good. The last named is the base of Griffiths' patent white, which is an excellent white paint for all purposes.

Iron Oxide Base.—Where a paint is only required for protection, especially for the protection of iron, and therefore where colour is of no moment, ferric oxide is an excellent base—the best that can be used. It may be either a ground natural oxide, or that which is artificially prepared by calcining ferrous sulphate. The colour varies from brown to red, according to the material used. In general, the finer the oxide the better fitted is it to serve as a base for protective paint. The oxide must be in the form of an impalpable powder. Black oxide of iron and titanite (oxide of iron and titanium) or titaniferous iron ore, when not crystalline, also form good bases for painting. These paints go by various names according to the taste of the maker.

Silicate Base.—Pure levigated silica forms the base of certain silicate paints. They stand well, and are said to have great covering power.

Distemper Bases.—For water colouring the base is always whiteing, carbonate of lime, though no doubt other materials might also be used.

Pigments.—All the bases except red lead and oxide of iron are white. The colours of paint are obtained by the addition of pigments. These are usually metallic salts, though of late years aniline dyes have been largely used in colour making. The latter are, however, highly objectionable, as they fade rapidly on exposure to light. Many metallic pigments are also changed by the action of light, air, sulphur fumes, &c.

Paints.—When a paint is intended as a protective coating, it is essential that suitable materials should be used. Oil alone would not do, as the resinous layer which it would leave on drying would crack, and thus allow air and moisture to penetrate. The object of the base is, therefore, not only to make the paint opaque, but also to make it more impervious to air and moisture. The particles of the base—themselves non-porous—are united by the film left by the oil, and it is essential, therefore, that the base should be of such a nature as to bind well with the dried oil. There is very great difference in behaviour between the different bases, depending both on their chemical and physical nature. As a rule the base must be in an extremely fine uniform powder, and it should be amorphous, not crystalline. The best base from this standpoint seems to be pure oxide of iron, but this is only available for shades of red, brown, or black, and next stands good white lead. Oxide of iron paints are, however, often not by any means pure, as is shown by the following analyses :—*

	1	2	3	4	5
Oil and volatile matter	13·35	30·67	..	26·30	16·23
Ferric oxide................	4·83	27·13	18·5	51·16	75·46
Barium sulphate	57·95	..	..	..	..
Calcium carbonate..........	18·77	..	..	..	..
Calcium sulphate	4·17	..	..	..	..
Alumina	·67	..	..	..	3·10
Siliceous matter............	..	42·20	..	25·51	5·13
	99·74	100·00	..	99·97	99·87

On trial it was found that No. 5 was much better, and No. 1 much worse, than ordinary red lead paint for protecting iron from rust.

It is obvious that for paints exposed to the weather all carbonates should be absent, since they are all (even lead carbonate) dissolved by water containing carbon-dioxide.

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* Industries, May 19, 1893.

VARNISHES.

Where only a transparent protective coating is required a varnish is used, though when applied to metal work it is often called a lacquer. The varnish may be colourless when it is required to show the colour of the underlying material, or coloured where any additional colour is required.

Varnishes consist always of gums or resins dissolved in oil, spirit, water, or other volatile liquid. The resins used are principally common resin or colophony, either brown or white (used only for common varnishes), copal, mastic, gum dammar, sandarack, dragon's blood (a red resin used for colouring varnishes), and lac. Lac is perhaps the most largely used; it comes into the market in several forms, of which shell lac, in which it is in thin flakes, is the best known and purest, and in white amorphous masses (bleached lac). The solvents used are principally linseed, and more rarely other oils, turpentine, methylated spirit, benzol, petroleum spirit, and water.

Oil Varnishes.—These are usually made from the harder resins, such as copal. The gum is melted, the oil added, and the mixture is boiled for some time, and usually mixed with turpentine, driers being added to facilitate hardening. Such varnishes are very hard and durable, the "dried" oil helping to form the varnish layer. Copal varnishes improve by keeping.

Turpentine Varnishes, made by dissolving the gums in turpentine, are made from the softer gums, such as dammar and common resin dissolved in turpentine. They dry quickly, but are not as durable as oil varnishes.

Spirit Varnishes.—These are made of soft gums, such as lac and sandarac dissolved in methylated spirit. The spirit volatilises very quickly leaving a layer of the gum. As this is not bound together by the oxidised film as in oil varnishes, it is much more likely to flake off. Such varnishes are, however, hard and brilliant, but owing to the rapidity with which they dry are more difficult to apply.

Water Varnishes are made by dissolving lac in a solution of ammonia, borax, potash, or soda. They are not very durable, and are usually dark coloured.

Applying Varnish.—The surface to which the varnish is to be applied must be non-absorptive; if not naturally suitable it must be prepared by well sizing with a gelatine size. Great care must be taken to avoid dust. The varnish should be applied in thin layers, each being allowed to dry before the next is applied. By experience the varnishes best suited for most purposes have been ascertained, and recipes will be found in several published works.

CHAPTER XXV.

MINOR MATERIALS.

POLISHING MATERIALS.—The surface of a metal article usually requires finishing in some way before the article is ready for use. A casting, for instance, is always more or less rough, and a forging may have its surface contaminated by adherent scale.

Scale and similar impurities are often removed by pickling or dipping in dilute sulphuric or other acid. The oxide is partially dissolved and is partially separated by the action of the acid on the underlying metal. The article is then washed to remove acid, and sometimes receives an additional alkaline wash.

Various materials are used for polishing, depending on the metal being treated and the nature of the surface required. The work is usually commenced with a file, by which the metal is rapidly removed, but the surface is always left more or less rough, and showing the distinct file marks, which have to be removed by subsequent operations.

The essential conditions on which a good abrasive depends are hardly known, and certainly there is no ready means of testing them.

Undoubtedly hardness is one of the essential characters of a polishing agent, but there is no ready means of measuring hardness, and the effective hardness as far as polishing is concerned seems to be something different to hardness as measured by the mineralogist. In polishing, the polishing material, either free and loose, or embedded in some fixing material, is rapidly moved over the surface to be polished, and the abrading or polishing power seems to depend on the mineralogical hardness, the way in which the particles are fixed, and on their shape, so that the only real test of abrading value is an actual experiment. As polishing is almost entirely a mechanical process, the various materials will only need brief description.

Emery.—This is one of the best known polishing materials, and is largely used for the first rough polishing of metals. Emery is an impure alumina.

Alumina occurs abundantly in nature in various forms of combination, but pure it is comparatively rare. It is known mineralogically as corundum, and in its purest form occurs in colourless transparent crystals; when coloured blue it is the sapphire, and when red the ruby. An impure pale-coloured variety, consisting of alumina with intermixed silica, is often called corundum, and under that name is used as a polishing material, but it is generally inferior to emery.

Emery is a dark, nearly black variety, consisting of a mechanical aggregation of alumina in a crystalline or granular condition with iron oxide, principally in the form of magnetite and a little silica.

The abrading power does not seem to be proportional to the amount of alumina present, and the oxide of iron does not render it soft unless in large excess. As the iron is present as magnetic oxide, it is attracted by the magnet, but it is so intimately mixed with the alumina that it cannot usually be separated, however finely the material be powdered. Pure corundum has a mineralogical hardness of

9, standing next to the diamond. Emery is softer, but at the same time seems to have more abrading power.

Emery is used in the form of powder in various ways. It is ground and sieved through wire sieves, yielding the three grades—coarse, fine, and flour, and from the last named very much finer forms are obtained by shaking up with water, pouring off the water holding the fine material in suspension, and then letting it settle, yielding levigated emery.

Emery may be used as a powder loose, but more usually it is fixed by strong glue to paper (emery paper), or cloth (emery cloth), or made into solid blocks, such as emery wheels or sticks. For this purpose the powdered emery is mixed and heated with some cementing material such as shellac (which becomes hard on cooling), pressed into suitable forms in moulds, and let cool. Such wheels can be fitted on spindles and driven rapidly, and they are powerful abrading tools.

Emery is largely used for polishing steel tools.

Carborundum.—This material was invented by Mr. E. G. Acheson. It has recently been introduced commercially, and promises to become a very important agent for polishing purposes. It is excessively hard, almost as hard as the diamond, but the crystals are very brittle. It is a compound of carbon and silicon, having the formula SiC, and is prepared by subjecting a mixture of silica and carbon to the intense heat of the electric arc, when decomposition takes place thus, $SiO_2 + 3C = 2CO + SiC$. The carborundum is left in the furnace as "a porous cinder-like mass composed of groups of small glittering crystals of yellowish green, bluish green, or blue colour, surrounded by more or less coherent masses of partly altered carbon." "The separation of the carborundum from the other constituents of the mass is first effected as completely as may be by hand. The selected material is washed with water, then treated with acid to remove soluble impurities (iron, alumina, lime, &c.), again washed, then dried and crushed. By this means the individual crystals are separated, and the purified material is then separated into convenient sizes of different degrees of fineness by a process of flotation in a current of water, the several grades being thus automatically collected in separate receptacles."*

Carborundum is used for polishing gems and many other purposes.

Rouge.—This is largely used for giving a fine polish, especially for small articles. It is essentially ferric oxide, and it may be either the natural oxide or one artificially prepared, but generally the latter. It is prepared by heating ferrous sulphate or ferric hydrate to redness, so as to expel volatile constituents. The colour and molecular condition of the product depend very much on the temperature at which it is formed, the lower the temperature the softer it is, and the higher the harder. Jewellers' rouge is therefore made at a low temperature; and *crocus*, used for polishing iron, is made at a higher temperature. Rouge may be used either dry or wet, and is very often used on a rapidly-revolving wheel made of a series of discs of flannel put together. Most polishing pastes contain rouge.

Putty Powder.—This is oxide of tin (SnO_2). It may be prepared by roasting tin with free access of air, grinding the resulting oxide and separating the different fineneses, by washing, or by creating tin with nitric acid, when insoluble metastannic acid is formed, filtering and gently heating to expel water. The best quality is made by the latter process.

Silica.—Silica, SiO_2, in its various forms, is largely used as an abrasive. In the crystalline form as quartz its hardness is 6. Infusorial or dialomaceous earth, often called tripoli or fossil flower, which consists essentially of the siliceous skeletons of low forms of vegetable life, and which contains 80 per cent or more of silica, is often used for fine polishing. Sandstone, used for making grindstones and similar articles, consists of particles of crystalline or rounded silica, cemented together with amorphous silica.

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* Report of Committee of Franklin Institute. Journal of the Institute, vol. cxxxvii., page 403.

Artificial polishing stones may be made by cementing very fine white sand with shellac or similar material. Fine silica may be obtained by crushing and levigation, but the finest is prepared by throwing down silicic acid from a solution of a soluble silicate by means of acid, and igniting the residue.

Burnishing.—In burnishing, the surface is polished by rubbing with a very smooth "burnisher" of some very hard material. Agate and hard steel are the materials principally used. Comparatively soft surfaces burnish best, as the smoothing is produced not by rubbing off the inequalities, but by pressing them down.

GLUE.—Glue is very largely used as an adhesive for uniting surfaces of wood and other materials. It is an impure gelatine. Gelatine is an amorphous brittle transparent substance, quite inodorous, neutral to test paper, and which does not undergo any alteration in dry air. It contains 50 per cent carbon, 6·6 per cent hydrogen, 18·3 per cent nitrogen, and 25·1 per cent oxygen,† with small quantities of other constituents, which may or may not be essential.

Glue varies much in colour, but the purest varieties are pale yellow and translucent. It is insoluble in cold water, but dissolves in hot water, forming a solution which solidifies on cooling. It is on this property that the great value of glue depends, the solidified jelly uniting the surfaces to which it is applied very strongly.

Glue is prepared from bones or other organic refuse. The bones are digested with acid till they become soft and transparent. They are then transferred to vats and treated with high-pressure steam, the liquefied matter being run off from time to time into settling tanks, which are kept hot to keep the whole liquid. The fat which rises is skimmed off, and is used for various purposes; the gelatinous residue is treated with sulphurous acid to bleach it—if pale glue

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† Thorpe's Dictionary.

is required—filtered, and boiled down till a sample on cooling has the required consistency. The mass is then distributed to zinc moulds about 6 ft. long, 1 ft. wide, and 2 ft. deep. When the glue is set the mass is cut into squares. These are cut up into cakes the required size by a wire cutting machine, and the cakes are put upon a netting to dry, and when dry are ready for the market. The residue in the extractors is dried, and is used for making bone manure. The dry glue cakes contain from 10 per cent to 18 per cent of water, and up to 5 per cent of ash.

Glue should be thoroughly soaked in cold water till it has absorbed as much as it will before melting. It is much injured by repeated melting, or by being kept long at 100 deg. Cen. or over, as under these circumstances it gradually loses its power of forming a jelly.

Liquid Glue.—Many attempts have been made to prepare a liquid glue—*i.e.*, one which can be kept in the liquid condition, and will not need heating before use, and several such are on the market. Some acids will dissolve glue, still leaving it its power of drying. One recipe is to take 2 lb. of best glue, dissolve it in 1 quart of water, and add 7 oz. of nitric acid. Such compounds are, on account of their acid character, unsuited for many purposes.

Elastic Glue is a mixture of glue and glycerine.

Marine Glue, which will resist water, is not a glue at all, but is a solution of indiarubber and shellac in naphtha, chloroform, or similar substance, of such consistency that it will solidify when cold.

VEGETABLE FIBRES.—These are largely used in the form of cotton, hemp, and other similar fibres, for making ropes, paper, and other materials.

These vegetable fibres consist almost entirely of cellulose, which is the residual material of all vegetable tissue when extractive and other matters have been removed. The composition of cellulose as given by chemical analysis is $C_6H_{10}O_5$, though the molecular weight is no doubt a multiple of this. Cellulose always contains mineral matter, which is left as an ash when it is burnt.

The vegetable fibres are more or less regular tubes of cellulose.

Cellulose is a very stable body, and is unacted on by most substances, but it is attacked by certain reagents. It is dissolved by an ammoniacal solution of copper hydrate, free from mineral salts, and from this solution it is precipitated by acids as a white flocculent precipitate. It is acted on by strong solutions of caustic alkalies, and by strong sulphuric acid, and if the mass after treating with strong sulphuric acid be diluted and boiled for some time, the cellulose is converted into glucose or fruit sugar.

Cotton is the soft filaments enclosing the seeds of certain plants. They only need to be separated, straightened out, and separated from the seeds before use. Cotton fibre is almost pure cellulose.

Hemp.—This consists of fibres derived from several varieties of plants. The fibres are round. The stems are bruised, fermented in water to break up the connecting tissue which holds the fibres together, and these are then scutched and combed out.

Hemp is well suited for the manufacture of cordage canvas and similar coarse materials, the fibres being strong.

Flax.—This is the fibre of the flax plant. The fibres exist in an intermediate bast layer between the core and the external layers. The fibres are separated by fermentation in water (retting), exposure to the air, and then breaking up and combing by means of suitable machinery. The fibres are "cylindrical tubes, not continuous as in the case of cotton, but broken up by septs or knots at irregular distances." They are $\frac{1}{1100}$ in. to $\frac{1}{1800}$ in. in diameter.

Jute.—This fibre is obtained from two plants cultivated chiefly in India. It forms the bast layer, and is obtained by similar processes to those used for hemp and flax. The fibres are polygonal in section, and "are much thickened." The fibres are short compared with those of hemp and flax, and this renders the yarn into which they are spun weaker. They are also more readily attacked by air and moisture, and jute is therefore only used for articles when great strength and durability are not required. The jute fibre does not seem to be pure cellulose, but a liguocellulose, $C_{12}H_{18}O_9$, which is decomposed by water, especially sea water, and by acids.

Cord.—The fibres of the various materials are twisted together or spun into yarn, and these yarn fibres are twisted up into strands, which are again twisted to form cord or rope of any required size. Owing to the inertness of the celluloses, cordage is very durable, but it may be protected from the action of moisture by being coated with a layer of tar. This, however, reduces the strength of the rope by about 25 per cent.

PAPER.—Paper is used for various purposes. It has recently been suggested that it might be twisted into ropes, and such ropes have been found to be strong and durable. Paper is made from any cellulose fibre, the best being made from linen rags, but almost all fibres, except perhaps jute, can be used, the shortness of the jute fibre preventing the production of a good felt. Pure cellulose material, such as cotton or linen rags, requires no boiling with alkali. Other fibres, such as straw, esparto grass, wood, &c., are boiled with strong caustic soda, and undergo various processes, according to the kind of paper required. If white paper is being made, the pulp is bleached. The pulp is beaten by machinery to ensure complete disintegration; mineral matter of some kind is mixed in, colouring matter added if necessary, and the pulp spread by hand or machine into a mould of wire cloth, after which it is dried and sized.

The paper is therefore a felted mass of vegetable fibres, its strength depending on the interlacing of these fibres, and therefore on their length, and its properties evidently depending on the nature of the fibres and of the added mineral matter.

Parchment Paper is made by treating unsized paper with strong sulphuric acid. The acid attacks the fibres superficially, converting them into amyloid, the fibres swell up, and the paper becomes tough and translucent.

Willesden Paper.—This is largely used as a water-proof covering. The paper is dipped in an ammoniacal solution of copper oxide, which attacks and partially dissolves the fibres of cellulose. The paper is then dried, and as the water evaporates a green varnish-like compound of copper and cellulose is left, which fills up the spaces between the fibres, and binds them together, and which resists water. Calico, cordage, or any cellulose material may be thus treated.

LEATHER is occasionally used for valves, belts, and other purposes.

The skins of animals contain a large quantity of gelatinous matter, which when treated with tannin is converted into a tough material known as leather. The processes of tanning involve several distinct stages of preparation of the skins and after treatment. The tanning material almost always used is oak bark, which contains 8 to 12 per cent of tannin, though other materials will answer. The nature of the leather obtained depends on the nature of the skins and on the treatment they have undergone.

Good belt leather has a tenacity of about 650 lb. per inch of width, and about 300 lb. may be allowed in practice.

INDIARUBBER AND GUTTAPERCHA.—Indiarubber is the coagulated juice of several species of plants which grow in tropical climates, the best, known as "Para," coming from Brazil. Indiarubber is not of definite chemical composition, but is a mixture of several different bodies. The indiarubber used in the arts is almost always vulcanised—that is, incorporated with sulphur up to 20 or 30 per cent. By this means a substance is obtained very different to the original rubber, far less readily influenced by temperature, which can be moulded into required forms or spread on fabrics, and which retains its pliability. Since indiarubber is attacked by most oils and volatile spirits, it cannot be used in places where it is likely to come in contact with these.

Indiarubber is also oxidised under some conditions; it then loses its plasticity and becomes brittle.

Indiarubber valves are made of well-vulcanised rubber. Indiarubber belts are made by coating cotton canvas with vulcanised rubber. "These belts are considerably stronger than leather belts, are usually truer and run more smoothly, and are perfectly impervious to water. They have a higher coefficient of friction, but if overloaded are apt to be rapidly and seriously injured."*

Ebonite.—When indiarubber is mixed with about 40 per cent of sulphur it yields the hard material known as *ebonite.*

Gutta Percha is the hardened sap of certain trees found in the Malay Peninsula. It is white, brown, or yellow in colour, it can be easily moulded at a moderate temperature. "In solubility it resembles rubber, as well as in nearly all other properties except elasticity." It is an excellent insulator, and is largely used for that purpose in electric engineering. Its specific gravity is ·98 to 1·00.

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* Thurston's "Materials of Engineering." vol. i., page 292.

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