Further Reading

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Inorganic Ion Exchangers

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Summary

In the first part of this chapter, the origins of ion exchange in inorganic materials are discussed in relation to the structure of the exchanger. Thereafter, the various types of inorganic ion exchangers are introduced and categorized according to their ion exchange properties. Descriptions of particular materials follow, with special emphasis on some structure-specific and composition-specific ion exchange properties. The materials which are discussed include zeolites and zeolite-like materials, clays and other layered materials, zirconium phosphates, heteropolyoxometalates and hydrous oxides.

Types of Ion Exchange Sites in Inorganic Materials and their Origin

For the purposes of this chapter, ion exchange interactions will be defined as those involving the interchange of positively or negatively charged species (atomic or molecular) at an ion exchange site.

There are two types of chemical species which constitute the vast majority of ion exchange sites in inorganic materials:

1. structure-terminating, covalently bonded groups such as –OH
2. charge-compensating groups, electrostatically associated with, and not covalently bonded to, a charged moiety

Type 1 sites, illustrated in **Figure 1A**, are responsible for the ion exchange properties of materials such as hydrous oxides and single-layer clays. All oxidic materials have these sites to some degree, at the surfaces of particles or crystals or at defect sites within the structure. Ion exchange reactions involving these types of sites may be regarded as chemical reactions, which may display amphoteric nature.

Type 2 sites, illustrated in Figure 1B, are responsible for most of the ion exchange capacity of zeolites, double-layer clays and zirconium phosphates. These sites arise in structures possessing, for instance, charged layers or charged porous frameworks. The exchangeable ions are present to retain overall electroneutrality. When materials such as zeolites are concerned, a mixture of Type 1 and Type 2 sites is available, although Type 2 sites will usually greatly outnumber Type 1 sites, and the latter are often ignored. Exchange interactions involving Type 2 sites are physical in nature, as chemical bonds are neither made nor broken.

Types of Inorganic Ion Exchange Material

An important distinction between ion exchange materials is whether they exhibit capacity for cations, anions, or both. Cation exchangers, and in particular zeolites, clays and zirconium phosphates, are the most common and best understood of the ion exchangers. Anion exchangers are also important but

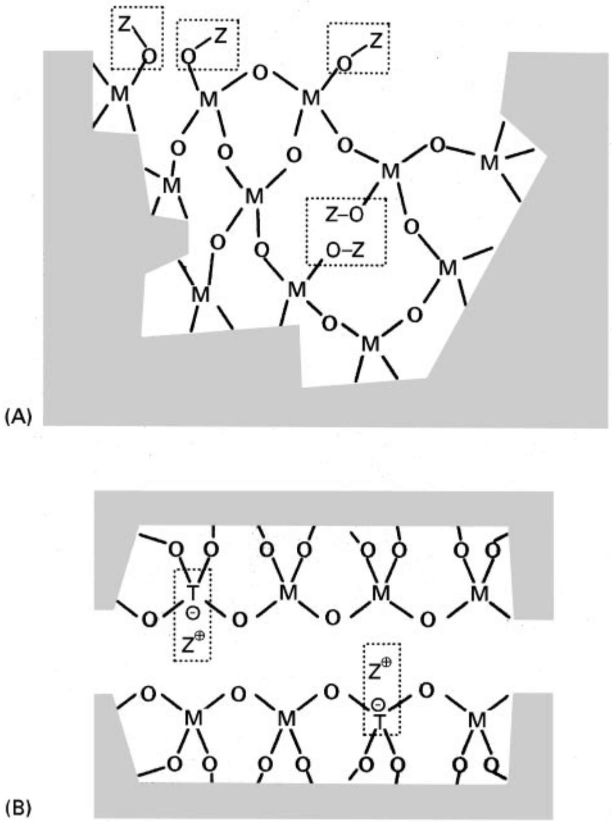


Figure 1 The two major types of ion exchange site. (A) Type 1, structure-terminating and defect groups; (B) Type 2, charge-compensating groups. M is an oxide-forming metal with oxidation state 4; T is an oxide-forming metal with oxidation state 3. The regions enclosed in dotted lines are those giving rise to ion exchange where Z^+ (or Z–O^-) is exchangeable. Shaded areas represent a continuation of the oxidic network.

the exchange of anions is often not fully reversible, thus the exchangers cannot be easily regenerated and the reactions are more difficult to treat thermodynamically. Multiply charged anions, in particular, may be held tenaciously by the exchanger. Examples of anion exchangers are certain clays such as hydroxy double salts (e.g. $[CuNi(OH)_3]Cl$) and layered double hydroxides (e.g. hydrotalcite, $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$). Amphoteric ion exchangers possess predominantly Type 1 exchange sites, e.g. hydrous oxides.

While ion exchange properties may be exhibited by both amorphous and crystalline solids, studies of the ion exchange properties of amorphous solids are often hampered by difficulties in preparing materials reproducibly and the difficulties in characterizing them fully. With crystalline materials, however, reproducible preparations can be easily verified and well-defined structural data aids in the interpretation of the results of ion exchange experiments.

Most crystalline inorganic ion exchangers are porous. This porosity may arise through the presence of void space between the layers in clay materials and layered double hydroxides, or through the intrinsic microporosity present in zeolitic materials. Many of the layered materials have the versatility to (reversibly) change their interlayer spacing and hence the size of the voids, which allows the ion exchange properties to be adjusted. The more rigid zeolite structures give rise to exchange reactions which may show extremely high selectivity to certain cations, or perform ion sieving.

Zeolites

Zeolites are microporous crystalline aluminosilicate minerals which occur naturally and may be synthesized easily in the laboratory. An introduction to the structures and properties of zeolites is given in the article by Dyer. Zeolites are used on a large scale as ion exchangers in many fields; most notable are their use as 'builders' or water softeners for laundry detergents, and their use in the decontamination of various types of waste streams. Typical applications of zeolites as ion exchangers are given in **Table 1**. Additionally, the ion exchange capability of zeolites can be used as a tool to modify their catalytic and sorptive properties. Some attention will be paid to structural parameters which influence the ion exchange properties of zeolites in the following paragraphs.

Besides the conditions under which an ion exchange reaction is performed, a number of factors may influence the ion exchange properties of zeolites, including:

- the structure of the zeolite, particularly the diameters of the windows allowing access to the pores and cavities
- the location of the ion exchange sites; different cation environments lead to different ion exchange properties. The number of charge-balancing cations required for an electroneutral material is often less than the number of available ion exchange sites, thus partial occupancy of sites is common. Some of the possible cation positions in zeolites A and X (two of the most widely used synthetic zeolite ion exchangers) are indicated in **Figure 2**
- the composition of the zeolite framework; varying the Si : Al ratio or changing the framework substituent elements may change, for example, the density of exchange sites, the electric field strength or the hydrophobicity of the sample as a whole

Table 1 Principal applications of zeolites as ion exchangers

Application	*Type of zeolite frequently used*	*Ion exchange process*
Detergent building	A (synthetic) MAP (synthetic) X (synthetic)	Removal of Ca^{2+} and Mg^{2+} from solution
Wastewater treatment	Clinoptilolite (natural) Chabazite (natural) Mordenite (natural) Phillipsite (natural)	Uptake of NH_4^+ and heavy metals from waste streams
Nuclear waste treatment	Clinoptilolite (natural) Chabazite (natural) Phillipsite (natural) Mordenite (natural) Mordenite (synthetic) Ionsiv IE-96 (synthetic) Ionsiv A-51 (synthetic)	Uptake of $^{137}Cs^+$, $^{90}Sr^{2+}$ and other radionuclides
Animal food supplement	Various (natural)	Regulation of NH_4^+ and NH_3 levels in stomach
Animal food supplement	Various (natural)	Scavenging of radionuclides following contamination of livestock
Fertilizer	Various NH_4^+ forms (natural), often those used to remove NH_4^+ from wastewater	Slow release of NH_4^+ (and other cations)

The empirical structural formula for an aluminosilicate zeolite may be given as

$$M^{(n)}_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot wH_2O$$

where the framework is constructed from the entities within the square brackets and the water molecules and charge-balancing cations (M) occupy the interstitial space. The $x/n\,M^{n+}$ cations are present to counterbalance the x units of negative charge on the framework due to the presence of x AlO_2 groups. In many cases, ion exchange reactions in zeolites may reach completion, that is, all of the charge-balancing cations (M) initially present are capable of being replaced by the ingoing cation.

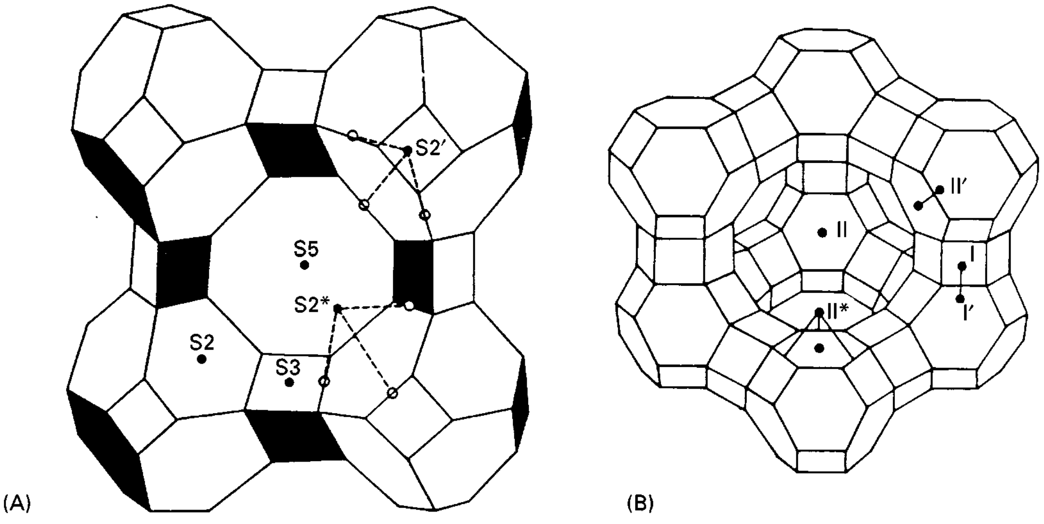


Figure 2 A representation of some of the possible positions of exchangeable cations in the structures of zeolites A (A) and X (B). Note: the two structures are not shown on the same scale. Reproduced with permission from Stucky GD and Dwyer FG (eds) (1983) *Intrazeolite Chemistry.* ACS Symposium Series, vol. 218, p. 288. Washington, DC: American Chemical Society.

Incomplete ion exchange reactions In some cases, some of the cations are constrained within the structure and are nonexchangeable. Such cations are introduced into small cavities in the structure during growth of the zeolite crystal. This situation is common with feldspars and feldspathoids, which are similar in composition to zeolites, but possess more limited porosity. Even in instances when all charge-balancing cations in the zeolite are physically exchangeable, the total theoretical exchange capacity might not be obtained practically.

There are several reasons for incomplete ion exchange; the three most important of these are given below and illustrated schematically in **Figure 3**.

1. The most obvious cause of partial or nonexistent exchange is ion-sieving, where the cation to be exchanged into the zeolite is too large, or has a hydration sphere which is too large and robust for it to have unrestricted access to the pores of the zeolite. Univalent cations will typically reach 100% exchange, except in limiting cases such as large cations combined with small-pore zeolites. Ion-sieving is more commonly observed with multiply charged cations, which tend to have larger hydration spheres on account of their higher charge densities. Zeolites which possess more than one ion exchange site (see Figure 2) may display ion-sieving properties depending on the thermodynamics of the exchange reactions occurring at the various sites. The sites which offer the greatest thermodynamic advantage are exchanged first, while the less favourable sites may not exchange at all.
2. Volumetric exclusion may occur if bulky (organic) cations are exchanged into zeolites of high charge density. Here, the volume occupied by the cations may reach that available in the pores of the crystal before complete exchange has occurred.
3. A third reason for limited exchange to be observed is when multivalent cations are exchanged into zeolites of low charge density. As the density of ion exchange sites decreases, the mean separation between adjacent sites increases, until a point is reached where multivalent cations are unable to satisfy two or more cation exchange sites because of the distance between them. **Table 2** illustrates this point by listing the maximum exchange limits observed for several multivalent cations in samples of zeolites ZSM-5 and EU-1 possessing a range of Si/Al ratios.

It is easy to visualize the limiting factors of ion exchange under equilibrium conditions; however, practical ion exchange may have also kinetic limitations. A particular example of when the desired ion exchange is kinetically limited but still capable of reaching 100% of the theoretical capacity is the softening of water.

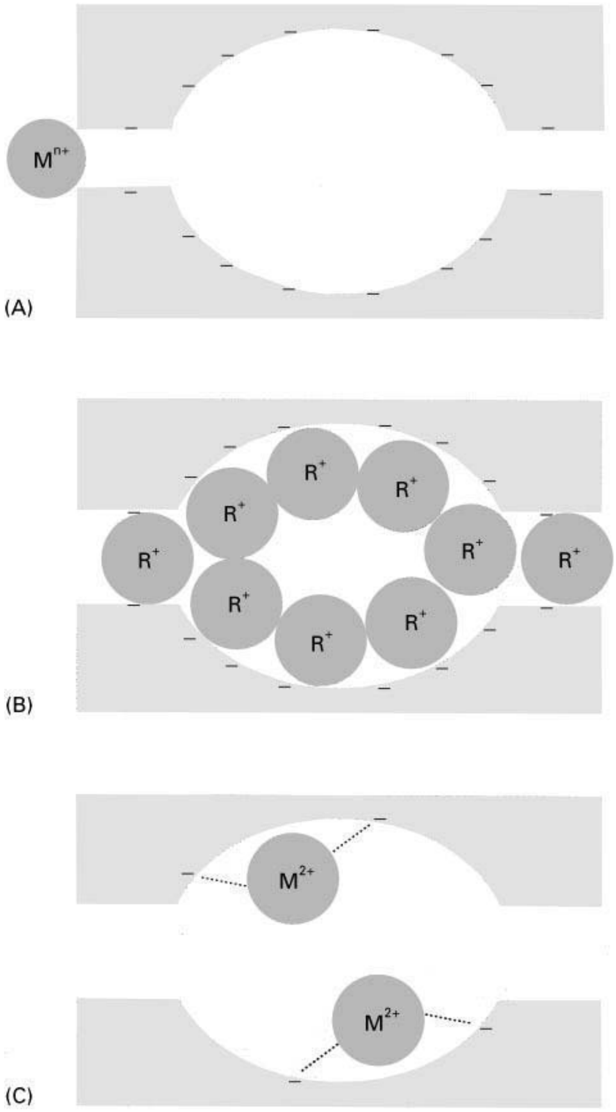


Figure 3 The principal reasons for limitations to ion exchange reactions found in zeolites. (A) Ion-sieving; (B) volume exclusion; (C) low charge density (with multivalent cations). The lightly shaded regions represent an extract of the zeolite framework. For clarity, only *ingoing* cations are shown.

Zeolites are used in vast quantities in the detergent industry as a water-softening additive for laundry detergents – up to 30% by weight of most modern washing powders is zeolite. The zeolite is added principally to remove calcium and magnesium and thus prevent their precipitation with surfactant molecules. Zeolite A is most commonly used, due to its high ion exchange capacity, which is a consequence of the framework possessing the maximum possible number of aluminium atoms (Si : Al = 1 : 1). Recently, zeolite

Table 2 Ion exchange limits (mole fraction) for various multivalent cations and temperatures in samples of zeolites ZSM-5 and EU-1 with varying numbers of aluminium atoms in the framework. In all cases, the ingoing cation replaces sodium

Zeolite type	*Al per u.c.*[a]	*Ca^{2+} (25°C)*	*Sr^{2+} (25°C)*	*Ba^{2+} (25°C)*	*La^{3+} (25°C)*	*Ca^{2+} (65°C)*	*Sr^{2+} (65°C)*	*Ba^{2+} (65°C)*	*La^{3+} (65°C)*
ZSM-5	1.1	0.28	0.31	0.36		0.50	0.51	0.52	
ZSM-5	2.0	0.31	0.36	0.56		0.54	0.64	0.76	
ZSM-5	2.4	0.36	0.48	0.67	0.39	0.50	0.67	0.77	0.48
ZSM-5	4.2	0.37	0.42	0.90		0.62	0.85	0.93	
EU-1	1.2	0.54	0.56	0.56					
EU-1	2.1	0.62	0.67	0.67		0.85	0.89	0.89	
EU-1	3.8	0.86	0.93	0.93		0.96	0.97	0.97	

[a] Number of aluminium atoms in framework per unit cell.

MAP (Maximum Aluminium P), also with Si : Al = 1 : 1, has been introduced into some detergents. Although the Mg^{2+} ion (radius 0.07 nm) is considerably smaller than the Ca^{2+} ion (radius 0.1 nm), its exchange into the zeolite is far less facile than that of Ca^{2+}, due to its large, tight hydration sphere (the radii of the hydrated Ca^{2+} and Mg^{2+} cations are estimated to be 0.42 and 0.44 nm, respectively). **Figure 4** shows the kinetics of exchange of Ca^{2+} and Mg^{2+} into Na-A zeolite. The major restriction to the hydrated Mg^{2+} cation is the 0.42 nm window in zeolite A through which it must pass to gain access to the exchange sites within the structure. In order for the ion exchanger to be effective as a water softener for detergents, it must reduce water hardness within a few minutes of beginning the wash cycle. While zeolites A and MAP perform well at removing calcium from hard water quickly, their performance towards magnesium is generally poor. Despite the kinetic limitations, Ca^{2+} and Mg^{2+} are fully exchangeable into zeolite A, although selectivity is greater for Ca^{2+} (**Figure 5**). Detergent-grade zeolites possess small crystallite sizes in order to provide acceptable kinetics of Ca^{2+} exchange.

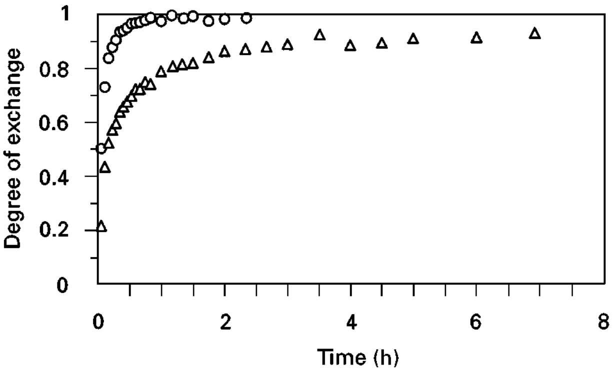


Figure 4 Kinetics of exchange of Ca^{2+} and Mg^{2+} for 2Na^{+} in zeolite A. Circles, Ca^{2+} exchange; triangles, Mg^{2+} exchange. Data were determined at 25°C, pH 10 and at a solution concentration of 0.05 mol equiv. L^{-1}.

Materials closely related to zeolites

Semicrystalline zeolites Some interest has been shown in the ion exchange properties of zeolite precursors, which are obtained by quenching a zeolite synthesis mixture before it has fully crystallized. In these semicrystalline materials, some larger windows and pores are present than in the crystalline counterpart because the structure has not fully formed. This leads to ion exchange selectivities which are different from the crystalline material. Also, their ion exchange capacities are lower than the corresponding crystalline zeolites. The materials typically show weak zeolite X-ray diffraction patterns, and are

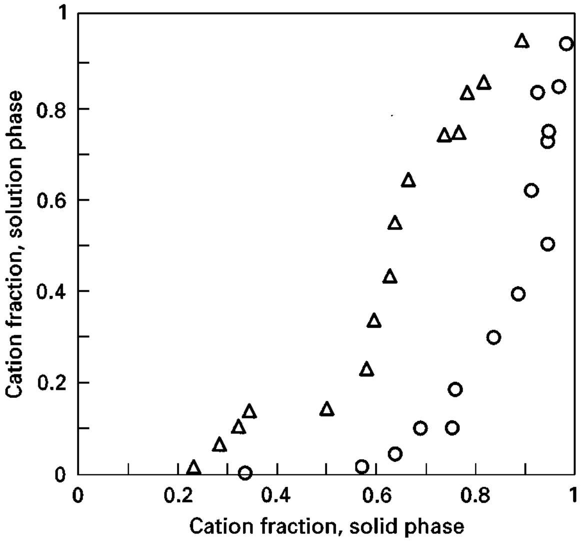


Figure 5 Isotherms for Ca^{2+}/2Na^{+} and Mg^{2+}/2Na^{+} exchange in zeolite A. Circles, Ca^{2+} exchange; triangles, Mg^{2+} exchange. Data were determined at 25°C, pH 10 and at a solution concentration of 0.05 mol equiv. L^{-1}.

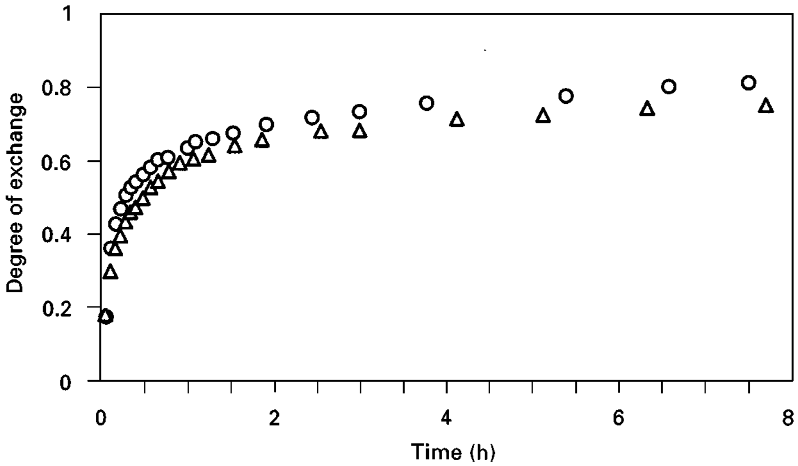


Figure 6 Kinetics of exchange of Ca^{2+} and Mg^{2+} for $2Na^+$ in the semicrystalline precursor to zeolite A. Circles, Ca^{2+} exchange; triangles, Mg^{2+} exchange. Data were determined at 25°C, pH 10 and at a solution concentration of 0.05 mol equiv. L^{-1}.

thus not totally amorphous, but possess some short-to-medium range order. Semicrystalline precursors to zeolites have been investigated as potential water softeners with enhanced magnesium performance for detergent use. The materials show slightly limited capacities for both calcium and magnesium, but the selectivity ratio of Mg : Ca is higher than that in the fully crystalline counterpart. In the kinetics of exchange, one sees the influence of the population of larger windows and pores. The rate of Mg^{2+} exchange approaches that of Ca^{2+} exchange, since the openness of the semicrystalline structure presents less limitation to the diffusion of large hydrated cations (see **Figure 6** and compare with Figure 4). Despite the improvement in Mg^{2+} exchange properties relative to Ca^{2+}, the performance of such zeolite precursors is probably too poor for detergent applications.

Materials with nonaluminosilicate frameworks Zeolite-like structures composed partially or wholly of oxides other than those of Al and Si such as silicoaluminophosphates (SAPOs), metal aluminophosphates (MeAPOs), stannosilicates, zincosilicates, titanosilicates and beryllophosphates are expected to possess ion exchange properties, although few data exist in the literature. Of these materials, the titanosilicates have received the most attention. Recently, the titanosilicate TAM-5 has been developed; this exhibits high selectivity for Cs^+ in the presence of high concentrations of other alkali cations and over a pH range from below 1 to above 14. Also, high selectivity of this material for Sr^{2+} in basic media has been observed. These high selectivities, and its stability to solutions covering this pH range, has led to commercialization of the material by UOP as Ionsiv IE-910 (powder) and Ionsiv IE-911 (granules) for use in nuclear waste treatment.

Particularly interesting ion exchange properties are shown by materials possessing high electric field strengths, which may arise with frameworks composed of oxides of elements with valencies differing from each other by more than one unit. An example is the beryllophosphate $Na_8[(BeO_2)_8(PO_2)_8] \cdot 5H_2O$, which has the same structure as the aluminosilicate zeolite gismondine (or synthetic zeolite P). Beryllium and phosphorus are strictly alternating in the structure and have valencies of $+2$ and $+5$ respectively, giving rise to a framework with alternating -2 and $+1$ nominal charges (on Be and P), as opposed to -1 and 0 for Al and Si in the aluminosilicate analogue. Due to the high electric field gradient, hard cations tend to be favoured over soft ones. Thus, magnesium is favoured kinetically over calcium; the diffusion coefficient for exchange of Mg^{2+} into $Na_8[(BeO_2)_8(PO_2)_8] \cdot 5H_2O$ is more than three times higher than that of Ca^{2+} under the same conditions (**Figure** 7), which is a reversal of the situation seen in the aluminosilicate zeolites (compare Figures 7 and 4). The relatively slow kinetics of exchange may be attributed to the small window size of the beryllophosphate material (the beryllophosphate unit cell is smaller than the aluminosilicate one). Univalent cations also exhibit unusual exchange characteristics with $Na_8[(BeO_2)_8(PO_2)_8] \cdot 5H_2O$, due in part to the relatively short Be–O and P–O bonds and the rigidity of the structure. High resistance is experienced by ingoing cations and large hysteresis loops are seen in, for instance, the exchange of K^+ for Na^+, while the same reactions in the aluminosilicate analogue do not exhibit hysteresis (compare

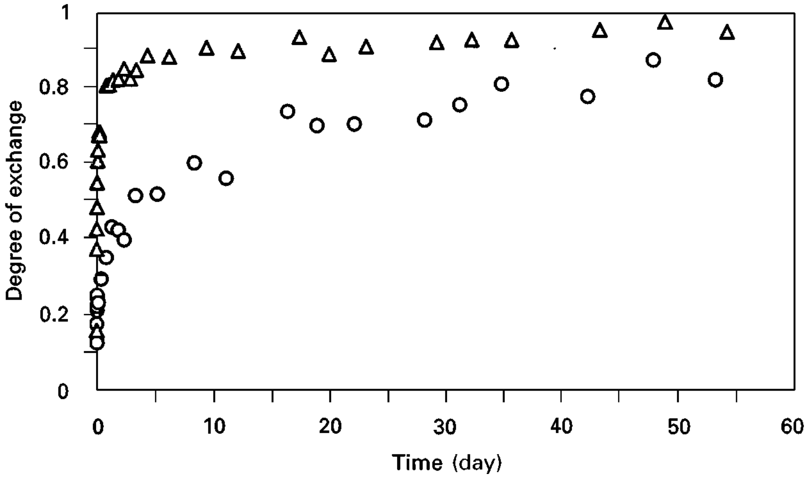


Figure 7 Kinetics of exchange of Ca^{2+} and Mg^{2+} for $2Na^+$ in $Na_8[(BeO_2)_8(PO_2)_8] \cdot 5H_2O$. Circles, Ca^{2+} exchange; triangles, Mg^{2+} exchange. Data were determined at 25°C, pH 10 and at a solution concentration of 0.05 mol equiv. L^{-1}. Interdiffusion coefficients (D): $D_{(Ca)} = 2.0 \times 10^{-18}\ m^2\ s^{-1}$; $D_{(Mg)} = 6.5 \times 10^{-18}\ m^2\ s^{-1}$. (Reproduced with permission from Coker EN and Rees LVC (1992) Ion exchange in beryllophosphate G. Part 2. Ion exchange kinetics. *Journal of the Chemical Society, Faraday Transactions* 88: 273–276.)

Figures 8 and 9). Hysteresis occurs when the two end-members of exchange (in this case, the pure K and Na forms) are mutually immiscible, and form separate phases which can usually be differentiated by X-ray diffraction. The two phases will be present simultaneously over a range of cation compositions (in intermediate Na/K forms), depending on the degree of immiscibility of the two end-members.

Solid-state ion exchange in zeolites The exchange of cations from one solid to another, probably mediated by the presence of small quantities of water, is referred to as solid-state ion exchange. This is a technique which is useful for the preparation of catalysts, that is, the introduction of cations which are only sparingly soluble, or which processess hydration spheres which are too large to allow easy diffusion into the

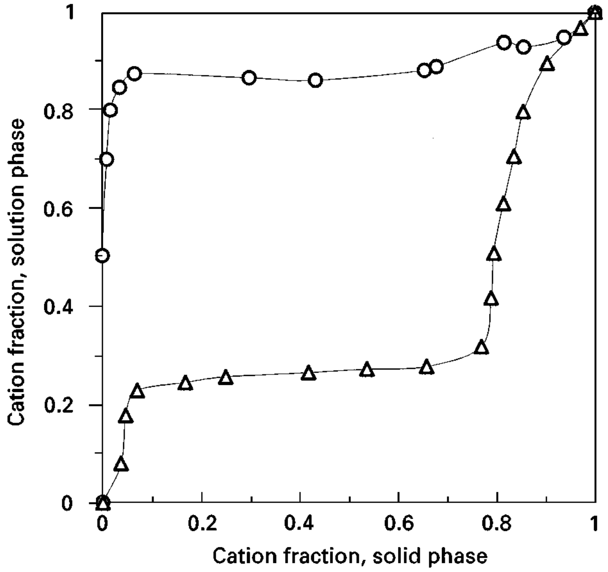


Figure 8 Isotherm for K^+/Na^+ exchange in $Na_8[(BeO_2)_8(PO_2)_8] \cdot 5H_2O$. Circles, forward exchange; triangles, reverse exchange. Data were determined at 25°C, pH 10 and at a solution concentration of 0.05 mol L^{-1}. (Reproduced with permission from Coker EN and Rees LVC (1992) Ion exchange in beryllophosphate G. Part 1. Ion exchange equilibria. *Journal of the Chemical Society, Faraday Transactions* 88: 263–272.)

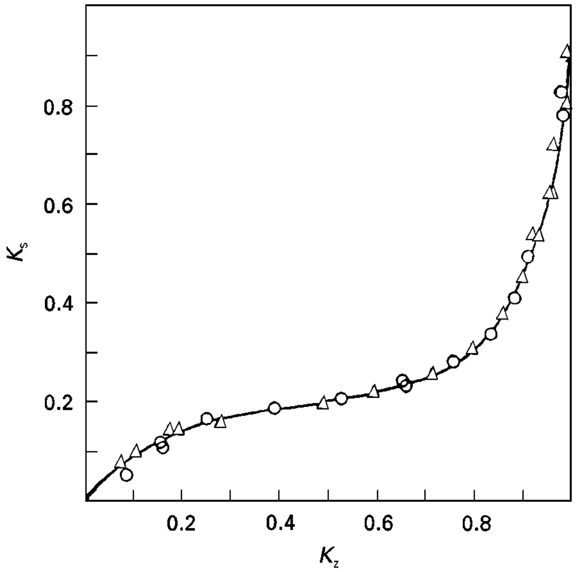


Figure 9 Isotherm for K^+/Na^+ exchange in zeolite P. Circles, forward exchange; triangles, reverse exchange; K_s, cation fraction in solution; K_z, cation fraction in the solid. Data were determined at 25°C and at a solution concentration of 0.1 mol L^{-1}. (Reproduced with permission from Barrer RM and Munday BM (1971) Cation exchange reactions of zeolite NaP. *Journal of the Chemical Society A* 2909–2914.)

cavities of the zeolite from solution. The technique may involve thermal treatment (at temperatures up to 500°C) of an intimate mixture of the zeolite and the salt containing the cation to be exchanged (or another zeolite) although, in some instances, exchange has been observed to occur under ambient conditions. Another advantage of the solid-state approach to preparing catalysts is the avoidance of generating large quantities of waste exchange solution.

Clays and Other Layered Materials

Clays are one of the most abundant materials present on the earth's surface. They constitute a large component of soil, while many ceramic and building materials as well as industrial adsorbents and catalysts contain clay. Soils owe their ability to sustain plant life largely to clays which have the ability to exchange ions with their surroundings. Clays are typically composed of sheets of linked SiO_4 tetrahedra, which are connected to $Al(OH)_6$ octahedra. If one sheet of silica interacts with a plane of $Al(OH)_6$, then a two-tier sheet ($Al_2Si_2O_5(OH)_4$) typical of kaolinite is obtained. If the octahedral plane is sandwiched between two silica sheets, then a three-tier sheet is obtained ($Al_2Si_4O_{10}(OH)_2$), as found in the smectite and mica clays. The sheets are bonded to one another via covalent bonds between the silica and alumina sheets to yield a layer. It is how these layers stack together (via electrostatic and van der Waals forces only) which give clays many of their interesting properties, and gives a large degree of flexibility to the structures. Clay-like materials may be composed of oxides of elements other than silicon and aluminium.

The three principal types of clay – single-layer, nonexpandable double-layer and expandable double-layer – have been introduced by Dyer. Clays may be either cationic (exhibiting cation exchange properties) or anionic (anion exchangers). The former type is more common, accounting for the majority of naturally occurring clays; typical examples are montmorillonite and bentonite. Anionic clays, such as hydrotalcite, occur rarely in nature, but may be synthesized in the laboratory. Layered materials composed of neutral layers also exist, although they possess little or no intrinsic ion exchange capability. **Table 3** lists some common types of layered material possessing cationic, anionic and neutral layers.

Pillared clays Expandable cationic clays may be converted into pillared clays by exchanging some or all of their charge-balancing cations with bulky inorganic species such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ or $[Zr_4(OH)_{14}(H_2O)_{10}]^{2+}$ and then calcining the composites to dehydrate and dehydroxylate the pillaring species, leaving hydroxy/oxide pillars. An interesting pillaring process is that involving ion exchange with a cationic 'templating' agent (cetyltrimethylammonium), followed by the synthesis of a mesoporous silica phase around the template cations. The resultant materials, in which the clay layers are propped apart by the mesoporous silica, possess surface areas up to 800 $m^2\,g^{-1}$ and interlayer spacings of 3.3–3.9 nm.

For layered materials with anion exchange properties, like layered double hydroxides, species such as $[V_{10}O_{28}]^{6-}$ and $[H_2W_{12}O_{40}]^{6-}$ may be exchanged with anions residing between the layers to increase the interlayer spacing.

Table 3 Examples of layered materials

Layer charge	*Example*
Neutral (no intrinsic ion exchange capability)[a]	TaS_2 MoO_3
Positive (anion exchange properties)	Layered double hydroxides: $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[X^{n}_{x/n}]^{x-}\cdot zH_2O$ Hydroxy double salts: $[M^{II}_{(1-x)}M^{II'}_{(1+x)}(OH)_{3(1-y)}]^{(1+3y)+}[X^{n}_{(1+3y)/n}]^{(1+3y)-}\cdot zH_2O$ ($X^{n-} = Cl^{-}, NO_3^{-}, SO_4^{2-}, CO_3^{2-}, H_5C_2O^{-}$, etc.)
Negative (cation exchange properties)	Smectite clays (low charge density) Micas M^{IV}H-phosphates (high charge density, e.g. α-ZrP, γ-ZrP) Layered titanates Silicic acids

[a] Neutral layered materials may undergo a type of ion exchange reaction via redox intercalation, whereby a neutral species is intercalated, followed by a transfer of electrons between the layer and the guest species. Thus both the layer and the intercalated species become charged.

While pillared clays usually offer advantages over normal clays in terms of their higher surface areas, higher sorptive capacities and greater ion exchange capacities, these properties begin to be diminished when the density of pillars becomes too great and the interlayer space becomes filled with pillars. Pillared clays are seldom employed as ion exchangers; their main applications lie in the fields of catalysis and adsorption.

Metal Phosphates

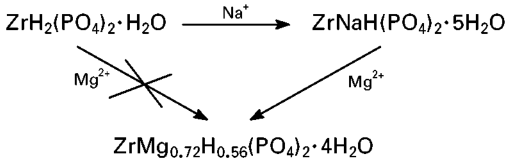
The most important and widespread of the metal phosphates is α-zirconium phosphate ($Zr(HPO_4)_2 \cdot H_2O$, or α-ZrP), which has an expandable layer structure. Each layer possesses a central plane of octahedral Zr atoms linked to two outer sheets of monohydrogen phosphate groups. The hydrogen form has an interlayer spacing of 0.76 nm, corresponding to a void space with diameter 0.26 nm. Although the calculated surface area of α-ZrP approaches 1000 $m^2\,g^{-1}$, in the unexpanded H form the surface area available to N_2 is only 5 $m^2\,g^{-1}$.

Another crystalline form of zirconium phosphate γ-ZrP ($Zr(PO_4)(H_2PO_4) \cdot 2H_2O$), is formed by a central zirconium phosphate sheet in which the PO_4 groups are linked solely to octahedral Zr atoms; this sheet is linked to dihydrogen phosphate groups to yield the γ-ZrP structure. The complex interlinking results in a more rigid framework in which only *c*. 50% of the theoretical ion exchange capacity is normally obtained.

Swelling of zirconium phosphates The interlayer cavities in α-ZrP of 0.26 nm are accessible to only small and poorly hydrated cations. A certain degree of expansion of the interlayer distance may occur concomitantly with these exchanges. Larger or more strongly hydrated ions do not readily exchange with α-ZrP. However, since the layers are held together principally by electrostatic forces, the distance between them can be increased to allow access of larger ions according to the following mechanism.

The acid form of an α-ZrP possesses H^+ cations which stabilize the negative charge on the $Zr(PO_4)_2$ units. A number of these protons may be neutralized by addition of hydroxide ions via the solution phase. This causes negative charge to build up on the layers, causing electrostatic repulsion and forcing the layers apart. Once the material has swelled, access to the exchange sites by larger and more strongly hydrated cations is possible. This view may be slightly oversimplified, since migrating OH^- ions would naturally be accompanied by cations (to preserve electroneutrality in both the solid and solution phases). It is more likely that the above two-step process actually occurs as a one-step process driven by the neutralization reaction.

'Catalytic' exchanges in α-ZrP The interlayer spacing of α-ZrP may be too small to allow large cations access (a situation anomalous to ion-sieving in zeolites). For instance, the Mg^{2+} ion will not exchange with the protons in α-ZrP directly. However, in the presence of sodium, some magnesium exchange does occur. The process is shown conceptually below.



The hydrated Mg^{2+} ion is too bulky to reach the exchange sites between the layers of the acid form, while the smaller hydrated Na^+ ion is not. The partial exchange of Na^+ for H^+ causes a swelling of the interlayer spacing to a point which allows the hydrated Mg^{2+} to exchange.

Heteropolyoxometalates

Heteropolyoxometalates, or heteropolyacids (HPAs) and their salts are materials which are finding widespread applications as acidic and/or redox catalysts. The most common examples are those with the Keggin structure, composed of a central hetero species, typically PO_4^{3-} or SiO_4^{4-}, surrounded by 12 transition metal oxide octahedra, typically MoO_6 or WO_6, as depicted in **Figure 10**. The octahedra and central hetero species are linked via shared oxygens to yield materials with the formula $[XM_{12}O_{40}]^{n-}$ where $X = P$ ($n = 3$) or Si ($n = 4$) and $M =$ Mo or W. Many other structure types are known, with up to 40 transition metal octahedra per molecule. The negative charge is balanced by protons in an HPA and by certain cations in HPA salts. The charge-balancing cations are in many cases partially or wholly exchangeable, and physical properties such as solubility, surface area and porosity may vary widely depending on the nature of the cation (**Table 4**).

Heteropolyoxometalates are principally used as catalysts. Due to the high solubility of many of the cationic forms of heteropolyoxometalates in aqueous media, their application as ion exchangers has been limited. Apart from ammonium phosphomolybdate and ammonium phosphotungstate which possess low solubility and have been used to scavenge radioactive caesium, and $[NaP_5W_{30}O_{110}]^{14-}$, which has been shown to have high selectivity for lanthanide and certain multivalent ions, comparatively few data are

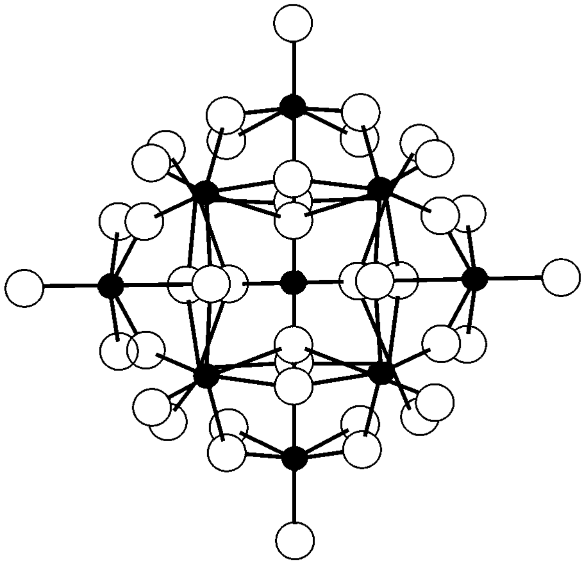


Figure 10 The structure of $[XM_{12}O_{40}]^{n-}$ where X (P or Si) is located at the centre and is surrounded by 12 metal oxide octahedra. (Reproduced with permission from Klemperer WG and Wall CG (1998) Polyoxoanion chemistry moves towards the future: from solids and solutions to surfaces. *Chemical Reviews* 98: 297–306.)

available concerning the ion exchange properties of the HPAs.

Hydrous Oxides

Hydrous oxides are amorphous metal oxides, on the surface of which exist hydroxyl groups which are present as a necessity to terminate the structure (see Figure 1A). The general formula for a hydrous oxide is $[M^{(n)}O_{(n-x)/2}(OH)_x \cdot wH_2O]_m$, where the central cation, M, is n-valent (n is typically $\geqslant 3$). Most of the metals in the periodic table are able to form hydrous oxides which exhibit ion exchange properties. However, for the material to be applied as an ion exchanger, it must be stable under the conditions used for exchange. In particular, solubility can be a deciding factor in the utility of hydrous oxides; stability to pHs extending from strongly alkaline to strongly acidic may be necessary. Those hydrous oxides comprised of large, low valent cations or small, multivalent cations tend to be soluble, while those intermediate between the two extremes are stable. Typical examples of acid- and alkali-stable hydrous oxides are those of Al^{III}, Ga^{III}, In^{III}, Si^{IV}, Sn^{IV}, Ti^{IV}, Th^{IV}, Zr^{IV}, Nb^{V}, Bi^{V}, Mo^{VI} and W^{VI}. Many of the materials are amphoteric, that is, they can act as either cation or anion exchangers depending on, principally, the pH of the electrolyte solution and the basicity of the metal forming the hydrous oxide (the strength of the metal–oxygen bond relative to the oxygen–hydrogen bond).

The change of a commercial alumina from cation exchanger to anion exchanger with varying pH is shown in the chapter by Dyer (Figure 8). The amphoteric nature of hydrous oxides may be illustrated schematically thus:

$$\text{Cation exchange} \quad M\text{–O–H} \rightarrow M\text{–O}^- + H^+$$

$$\text{Anion exchange} \quad M\text{–O–H} \rightarrow M^+ + {}^-\text{O–H}$$

Table 4 Changes in surface properties of phosphomolybdates and phosphotungstates upon ion exchange

Approximate composition of HPA salt[a]	*Surface area by N_2BET* ($m^2\ g^{-1}$)[b]	*Pore volume* $\times 10^3$ ($cm^3\ g^{-1}$)	*Mean pore radius* (*nm*)
HPMo, NaPMo, $(MeNH_3)$PMo	Essentially nonporous		
(NH_4)PMo	193	52	1.3
KPMo	40	15	0.9
CsPMo	145	6	1.4
HPW, NaPW, AgPW, $(MeNH_3)$PW, (Me_4N)PW	Essentially nonporous		
(NH_4)PW	128	50	1.0
KPW	90	31	0.9
CsPW	163	34	1.4
HSiW, NaSiW, KSiW	Essentially nonporous		
(NH_4)SiW	117	40	1.0
CsSiW	150	52	1.0
RbSiW	116	40	1.0

[a] PMo, PW and SiW represent $(PMo_{12}O_{40})^{3-}$, $(PW_{12}O_{40})^{3-}$ and $(SiW_{12}O_{40})^{4-}$ respectively. The charge-balancing cation indicated is assumed to be fully exchanged into the HPA, although some variation of composition is inevitable. Note that the surface properties will vary slightly depending upon the preparation and exact composition of the HPA.

[b] Surface area determined using the Brunauer, Emmett and Teller isotherm approach.

Cation exchange typically takes place in alkaline solution, while anion exchange is preferred in acidic solution. Dissociation of *M*–O–H near to its isoelectric point allows both exchange mechanisms to operate simultaneously.

Silica, the most common and extensively studied of the hydrous oxides, is a weakly acidic cation exchanger. The physical properties of silica, particularly the porosity and surface area, vary widely depending upon the method of preparation. Generally, multivalent cations interact more strongly with the silica surface than do univalent ones, while in all cases the interactions are relatively weak and ion exchange is facile. Silica possesses between 0.5 and 0.8 hydroxyl groups per nm^2 on its surface.

Miscellaneous Materials

A number of specific materials have been discussed in this chapter. There are, however, numerous inorganic materials possessing ion exchange properties which have not been mentioned. In this section, a few of those materials which exhibit interesting ion exchange properties are introduced briefly. The list is far from complete, but serves to illustrate the diversity of ion exchange materials.

- Hydroxyapatites may undergo limited ion exchange reactions. While the calcium form ($Ca_{10}(PO_4)_6(OH)_2$) is the most common (it is a major component of teeth and bones), pure exchange end-members of Sr^{2+}, Cd^{2+} and Pb^{2+} are known, while various cations may form intermediate mixed-cation phases. The Sr^{2+} end-member, due to a slight lattice expansion, possesses superior ion exchange properties compared to Ca-hydroxyapatite. Of the Sr-hydroxyapatites, that with a (non-stoichiometric) Sr/P ratio of 1.73 has the highest ion exchange capacity of those measured. It is interesting that the presence of HCl may assist the ion exchange reaction by formation of a chlorapatite phase. This may be an example of simultaneous anion and cation exchange.
- Copper hexacyanoferrates, $Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$ and related compounds show quite promising exchange properties for Cs^+, and have been investigated as agents for nuclear waste treatment. On passing caesium-containing waste through a column of $Cu_2^{II}Fe^{II}(CN)_6 \cdot xH_2O$ at room temperature, decontamination factors (ratios of pre-column to post-column Cs^+ concentrations) of 10^3 can be achieved.
- Lithium manganate containing mixed-valence manganese ions exhibits unusual ion exchange properties, in that it undergoes combined ion exchange and redox reactions. Upon acid treatment of $LiMn^{III}Mn^{IV}O_4$, the Mn^{III} is oxidized to Mn^{IV} and Li is displaced from the structure thus:

$$4\,LiMn^{III}Mn^{IV}O_4 + 8\,H^+ \rightarrow 3\,Mn_2^{IV}O_4 + 4\,Li^+ + 2\,Mn^{2+} + 4\,H_2O$$

  The resulting spinel structure (γ-MnO_2) is highly selective for Li, and will readily re-insert Li^+ to regain the Li-manganate spinel:

$$Mn_2^{IV}O_4 + (n)LiOH \rightarrow Li_{(n)}Mn_{(n)}^{III}Mn_{(2-n)}^{IV}O_4 + (n/2)H_2O + (n/4)O_2$$

  This type of exchange reaction is often referred to as the ion memory effect.
- Iodide ions may be efficiently exchanged for nitrate ion using $BiPbO_2NO_3$ in solutions of $pH \geqslant 13$. Under such conditions, the theoretical exchange capacity of 2 mmoL g^{-1} is approached.

Conclusions

As with any commercial venture, improvements to large scale ion exchange processes will always be sought. With the advances made in structural characterization and synthetic methods, it is becoming increasingly possible to tailor the ion exchange properties of materials to specific needs. Thus, the strive for water-softening zeolites for detergents with greater capacity, selectivity and rate of exchange for Ca^{2+} and Mg^{2+}, or for exchangers with better stability over wide pH ranges coupled with high selectivity for certain ions present in waste streams will be ever-present. Recent advances have made some significant steps in these particular directions:

- The field of nuclear waste clean-up has spawned a number of interesting materials; inorganic exchangers are now available which have good structural stability in waste streams and exhibit high selectivities for Cs^+ and Sr^{2+} in the presence of large excesses of other ions over wide pH ranges.
- Zeolites continue to be used in vast quantities as water softeners in detergents. A significant recent development has been the introduction of a new detergent zeolite MAP, which offers improved performance over zeolite A.

Interesting ion exchange properties are exhibited by framework materials possessing high electric field gradients, such as the beryllophosphates. However, this particular area is deserving of more extensive exploration.

The prediction of ion exchange behaviour for a particular material is possible given data for exchange reactions in that material under different conditions. However, the prediction of ion exchange properties on the basis of the structure of the exchanger alone may become more readily possible through the use of computer modelling.

The study of ion exchange behaviour under the influence of microwave radiation is an area which preliminary research has suggested may be interesting.

See also: **II/Ion Exchange:** Historical Development; Novel Layered Materials: Non-Phosphates; Organic Ion Exchangers; Theory of Ion Exchange.

Further Reading

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Multispecies Ion Exchange Equilibria

See **II / ION EXCHANGE / Surface Complexation Theory: Multispecies Ion Exchange Equilibria**

Non-Phosphates: Novel Layered Materials

See **II / ION EXCHANGE / Novel Layered Materials: Non-Phosphates**

Novel Layered Materials: Phosphates

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It has long been known that many polyvalent cations can be precipitated as amorphous phosphates from dilute solutions and these salts are useful in gravimetric analysis. More recently it has been recognized that many of these precipitates contain exchangeable acid protons and behave as inorganic ion exchangers. Phosphates of tetravalent metals such as Zr(IV), Ti(IV) and Sn(IV) have been found to possess high ion-exchange capacity and good stability in acid and oxidizing solutions and when exposed to high temperatures and ionizing radiation. Because of these properties, their potential uses for the purification of nuclear reactor cooling water or for the treatment of radioactive waste were investigated during the late 1950s and early 1960s, especially in nuclear centres. The ion-exchange properties of amorphous zirconium, titanium and tin phosphates were reviewed by Amphlett in 1964. However, the beginning of the chemistry of layered phosphates may be dated back to 1964, when Clearfield and Stynes refluxed zirconium phosphate gel in phosphoric acid solutions in an attempt to produce a material which was more resistant to hydrolytic attack than the original gel. The microcrystals obtained were found to possess a layered structure, called the α-type, and with the composition $Zr(HPO_4)_2 \cdot H_2O$. This compound was indeed more resistant to hydrolytic attack than the amorphous analogue. It possesses two exchangeable protons per formula weight and is an excellent intercalating agent of protophilic species and a pure solid-state protonic conductor. Moreover, it is possible to correlate the observed properties with the structural