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Historical Development

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Development of Ion Exchange Concept, Materials and Methods

The main stages in the development of ion exchange are shown in **Table 1** and **2**. Ion exchange gradually became an important separation method in water treatment, waste water purification, analytical chemistry, medicine, the food industry and many other areas of application.

The first systematic studies of ion exchange occurring in natural inorganic materials were performed during the period 1850–80, clays, sands and zeolites became objects of investigation and it was shown that soil treated with ammonium salts absorbs these ions, releasing an equivalent amount of calcium ions. Later, some natural materials found application for purification of water as well as for other purposes. At that time, the evidence for existence of ions in solution had not yet been elucidated and the concept of a double electric layer had not yet been proposed. Despite this the stoichiometry of ion exchange and its connection with aluminosilicates present in the soil were established. It was demonstrated that the degree of exchange increased up to a limiting value with the increase of concentration of salt solution, while the influence of temperature on ion exchange was shown to be less significant.

At the beginning of the twentieth century complementary investigations in the areas of synthesis and application of ion exchangers took place. Industrial production of synthetic amorphous aluminosilicate ion exchange materials was started. These materials (permutites) were used for water softening and in the treatment of sugar syrups. In the first artificial sodium aluminosilicates a substitution of sodium to calcium occurred, but the ion exchanger could be regenerated in a column by treatment with saturated sodium chloride solution.

Ion exchange materials can also be obtained by oxidation and sulfonation of coals. Some types of charcoal, soft and hard brown coals, are suitable for this purpose. They can be converted into cation exchangers after treatment with fuming sulfuric acid. As a result, sulfonic and carboxylic groups (resulting from oxidation) are introduced into the coal structure, playing the role of fixed ions. Furthermore, the coal is transformed to a gel due to polycondensation reactions. The total exchange capacity of such materials is about 1.5 meq g^{-1}.

Organic Ion Exchange Materials

Later, the ion exchange properties of some organic materials were discovered, which led to the creation

Table 1 Principal practical achievements in the field of ion exchange

Year	*Milestone*
1850–52	Discovery of ion exchange phenomenon in soil (Thompson, Way and Roy)
1903	The first synthetic inorganic ion exchanger (Harms, Rümpler, Gans)
1935	The first ion exchange resin possessing high capacity (Adams and Holmes)
1944	Development of ion exchange resin synthesis by means of copolymerization (d'Alelio)
1947	Synthesis of zeolites (Barrer)
1950	Synthesis of ion exchange membranes (Wyllie, Sollner)
1958	Synthesis of inorganic ion exchanger based on zirconium phosphate (Amphlett)
1964	Synthesis of the first crystalline zirconium phosphate of α-type structure (Clearfield and Stynes)
1975–79	Development of ion chromatography (Small, Gjerde)
1980–present	New layered materials of α- and γ-types, organic ion exchangers; improvement of ion exchange chromatography method

Table 2 Important theoretical advances, elucidating the essence of ion exchange

Year	*Milestone*
1879	Helmholtz theory of electrical double layer
1911	Donnan theory of membrane equilibria
1950s	Statistical ion exchange models of Gregor, Kachalsky, Harris and Rice
1958	First edition of Helferrich's monograph devoted to ion exchange was published
1940s (2nd half)–1960s	Theories of ion exchange dynamics are developed
1960s (2nd half)–present	Theoretical models and description of new crystalline layered materials possessing ion exchange properties
1980–present	Theoretical background of ion exchange chromatography

of an ion exchange resin by Adams and Holmes. These new materials were characterized by their high capacity (5–10 meq g^{-1}) relative to inorganic ion exchangers. Resins were obtained by polycondensation of phenols or amines with formaldehyde, and their large-scale production began. Owing to their high degree of cross-linking the polymers had negligible solubility. The resins were hydrophilic due to the presence of ionic groups as an inseparable part of the polymer matrix: for example, for anion exchange resins amino groups inside the matrix were balanced by an equivalent quantity of anions. For cation exchangers phenolic, sulfoxylic, carboxylic or phosphonato or phosphinato groups were present inside the matrix, balanced by an equivalent quantity of cations.

A discovery by d'Alelio had great industrial significance. He invented a method of synthesis of ion exchangers based on styrene–divinylbenzene copolymers. This invention was anticipated by Staudinger's synthesis of reticular polystyrene. The first cation exchanger of this type was obtained in 1944, followed in 1948 by an equivalent anion exchanger. These resins possess high chemical and mechanical stability; their distinguishable feature is a certain degree of control over the synthetic process. Moreover, such materials were characterized by high exchange capacity and working exchange rate. Different fixed ions can be introduced into the styrene–divinylbenzene matrix, offering a possibility to obtain resins with different cross-linking numbers and swelling behaviour. All these properties make this kind of synthetic resin of major practical significance (**Table 3**).

In the area of water treatment ion exchange techniques occupy a leading position worldwide and due to their increasing importance they are under continuous development. In 1951 Reents was the first to apply a mixed layer of anion and cation exchangers for the ultra-purification of water.

Emergence of cross-linked polymer electrolyte–ion exchange resins has allowed a new approach to the solution of problems of analytical and preparative chemistry: purification and separation of compounds possessing similar chemical properties. However, water treatment and waste water purification remain the main areas of application of ion exchange resins. Here exchangers capable of being universal absorbents for a wide variety of ions are mainly needed. Parallel to investigations aimed at enhancing sorption

Table 3 Main fields of application of ion exchange resins

Resin type	*Matrix type*	*Type of fixed groups*	*Application fields*
Strongly acidic cation exchange resins	Gel Macroreticular	Sulfonic	Water treatment; separation of rare earth elements; separation of amino acids, etc.
Weakly acidic cation exchange resins		Carboxylic	Decarbonizing of industrial water, water softening and deionization
	Gel Macroreticular		Purification of antibiotics, copper and nickel recovery
Strongly basic anion exchange resins	Gel Macroreticular	Quaternary ammonium	Different water conditioning processes; elimination of organic compounds with high molecular weight (macroreticular)
Weakly basic anion exchange resins	Gel Macroreticular	Tertiary amine or polyamine	Industrial water treatment; decolorization of sugar syrups (macroreticular)

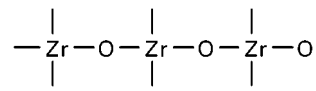
capacity, improving the exchange kinetics, thermal stability, mechanical properties and chemical resistance, there has been a considerable development of selective ion exchangers. This requirement arose in the 1950s in connection with both the analytical problem of direct selective determination of elements in a complex mixture and the problem of extraction of metals from technological solutions during complex ore processing. The selectivity of ion exchangers is determined by two factors. The first consists of an exact correlation between the dimension of the sorbent's pores and the radius of the hydrated ion to be absorbed. The second factor is related to the formation of a coordination bond supplementary to an ionic one between the ion and the functional groups within the matrix.

Besides development of polymeric acids and bases of different strengths, ion exchangers containing functional groups able to form chelate complexes with specific ions have also been obtained. This class of ion exchangers is characterized by high ion exchange constants and high selectivity owing to donor–acceptor interaction between adsorbent and adsorbate. In 1940, Skogseid made a macromolecular ion exchanger selective towards potassium, containing moieties analogous to dipicrylamine. Iron, uranium and rare-earth elements readily form complexes with oxygen-containing ligands. Several early transition metals like cobalt, nickel and copper give rise to stable amino complexes. Thus, anion exchangers containing amino groups (preferably those of primary amines) are selective for the latter group of elements, while exchangers containing phenolic groups are suitable for iron. Resins with carboxylic and phosphonic groups are suitable for uranium and rare-earth metals.

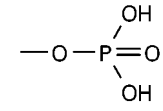
However, some researchers consider the ion exchange procedure of water treatment a kind of 'ecological boomerang', bearing in mind the fact that wastewater after ion exchange still contains many mineral compounds. Regeneration solutions contain them in quantities greater by an order of magnitude than the level of contaminants to be extracted. Ion exchange membranes avoid this disadvantage. The increase of mass of compounds in wastewater with respect to the quantity of extracted substances does not take place during membrane purification, providing a significant advantage for this method, when compared to distillation or sorption on ion exchangers. In 1950, the first samples of heterogeneous membranes were obtained by Wyllie and Patnode based on commercial ion exchangers reinforced by inert polymer fibres in order to provide high mechanical stability. In 1952, Manecke and Sollner reported the first homogeneous membrane, and in 1957 Gregor made the first inter-polymer membranes, where the ion-exchange and binder components are linked to each other by chemical bonds. Ultra-pure water cannot be obtained by the sole use of ion exchange membranes: nowadays one has to assemble a combination of separation methods such as filtration, microfiltration, ultrafiltration, reverse osmosis, electrodialysis with ion exchange membranes and a mono-layer of granulated ion exchange resin, and electrodialysis with ion exchange membranes filling the inter-membrane space with a mixed layer of granulated ion exchange resins.

Inorganic Ion Exchangers and Application of Inorganic Layered Materials

A reawakening of interest in inorganic ion exchangers was connected with the search for materials which can withstand high temperature, ionizing radiation and some aggressive chemicals. In 1943, Russel *et al.* discovered that insoluble zirconium phosphate is suitable for the separation of uranium and plutonium from nuclear fission products. Thus, a new class of inorganic ion exchangers was synthesized on the basis of group 4 elements, mainly of titanium and zirconium. Various kinds of functional groups can be attached to the polymer chains consisting of Ti or Zr atoms bonded to oxygen, producing different types of ion exchangers. It is a well-known fact that zirconium readily forms chains:



in solution. The behaviour of titanium is analogous. The most intense polymerization occurs in a range of pH values close to that of the hydroxide sedimentation. A polymer containing zirconyl groups together with residues of acid is obtained by addition of salt or acid to a zirconium (or titanium) salt solution. If the acid is polyprotic, then one obtains a cation exchanger containing an exchange site like:



The first material of this kind was zirconium phosphate obtained by Amphlett in 1958. It possessed a capacity of 1 meq g^{-1} at pH 3, and 5 meq g^{-1} at pH 11. Amorphous inorganic sorbents had a great advantage over organic resins owing to their ease of preparation.

In 1947 Barrer realized a synthesis of zeolite for the first time. He became a founder of zeolite chemistry, studying synthesis, structure, sorption and ion exchange properties of this new class of materials.

In 1964, Clearfield and Stynes synthesized the first crystalline zirconium phosphate and established its layered α-type structure α-$Zr(HPO_4)_2 \cdot H_2O$, usually referred to in the literature as α-ZrP. In 1968, the same authors reported the first γ-type zirconium phosphate, referred to as γ-ZrP. Since 1975, some organic derivatives of the latter modification have been synthesized by Yamanaka *et al*. Further development of this class of inorganic ion exchanger by Alberti *et al*. (1978) resulted in M(IV) phosphonates and organic phosphates with a layered structure of zirconium bis-monohydrogen phosphate (α-ZrP). Some years after the first inorgano-organic sorbent was reported, Dines and Griffith described the synthesis of diphosphonates of general formula $M(IV)(O_3P–R–PO_3)$. A series of covalently pillared diphosphonates with a regular interlayer microporosity was subsequently obtained. As far as γ-ZrP $(ZrPO_4(H_2PO_4) \cdot H_2O)$ is concerned, a wide variety of layered and pillared M(IV) phosphonates were obtained in the period 1987–1990, since their structure depends on the starting material and on the nature of the O_2PRR' group that replaced $O_2P(OH)_2$.

Ion Exchange Chromatography

High performance in the separation of organic substances by liquid chromatography had already been achieved by the 1970s, while techniques of chromatographic separation of inorganic ions were developed to a lesser extent. In 1971, the first papers dealing with automatic spectrophotometric detection of metal ions separated by ion exchange chromatography on cation exchange resins appeared. Similarly, anions were separated on anion exchange resins. Conductometric detection was established by Small *et al*. in 1975 and Gjerde *et al*. in 1979. Finally it is necessary to mention ion exclusion chromatography applied to separate sugars and carbonic acids with an ion exchange column, but without any ion exchange interaction.

Development of Theoretical Background in the Field of Ion Exchange

Helmholtz developed the theory of the double electric layer in 1879, and this had a fundamental significance for the explanation of many phenomena related to ion exchange. According to his classic theory, the double layer consists of two electric layers, analogous to the plates of an electric capacitor. The concept was later modified, as it had been proven that a double layer is formed at the interface between a solid phase and a solution. It consists of an immobile inner layer and a diffuse outer layer. Charge separation in this type of a system is of the order of molecular dimensions. As a result, the solid phase surface acquires an electric charge (positive or negative), while the counterions are distributed along the interface. These ions form a virtual outer plate of the diffuse layer. In fact, there is no interface but a dynamic equilibrium exists between the ions in the diffuse layer and those of the environment (the bulk solution). The existing equilibrium is disturbed upon changes in either pH or concentration of ions in the bulk solution. In this case new ions enter the diffuse layer, substituting ones already there and establishing a new ion exchange equilibrium.

The influence of valence, hydration and ion dimensions on the degree of ion exchange transformations has been established and ion selectivity series were composed by Wiegner for ion retention on aluminosilicate sorbents:

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

$$Na^+ < Mg^{2+} < Al^{3+} < Th^{4+}$$

Mattson demonstrated in 1927 that aluminosilicates enriched in silica gave an increase in cation exchange capacity. Jaeger demonstrated that at higher concentrations, as well as in mixed organo-aqueous solutions, the values of the exchange potentials of ions with the same valence could be quite close, with possible inversion of the selectivity series.

Selectivity, i.e. preferable absorption of one of the counterions, is an important property of ion exchangers. Hence, the ion exchanger becomes enriched in counterions which possess small dimensions in the solvated state or which are able to enter into specific interactions with the fixed ions or with the matrix. The isotherm of ion exchange is a graphical representation of the dependence of an equivalent fraction of the counterion A in the ion exchanger, versus its equivalent fraction in solution.

In 1939 Nikolskii demonstrated that the law of mass action could be applied successfully to ion exchange:

$$(y_1^{1/Z_1})/(y_2^{1/Z_2}) = K(a_1^{1/Z_1})/(a_2^{1/Z_2})$$

where y_1 and y_2 are the quantities of ions absorbed by the resin (meq); Z_1 and Z_2 are charges of these ions in solution; a_1 and a_2 are activities of the above ions in the solution and K is the ion exchange constant.

In 1935 Kielland introduced activity coefficients for the ion exchanger phase in order to estimate deviations of ion exchange equilibria from a simple form of the law of mass action. The most clear thermodynamic approach to these equilibria was provided by Gaines and Thomas in 1953, which was not connected to model concepts.

A physical model of ion exchange processes has been gradually formed together with the accumulation of empirical data. For example, the theory of membrane equilibria created by Donnan in 1911 promoted a breakthrough after its application to ion exchange processes. The essence of Donnan theory can be briefly described as follows. An electrolyte RNa is supposed to be on one side of a membrane, and an NaCl solution on the other side. Since the membrane is not permeable for R^- ions, only sodium and chloride ion redistribution will take place in the system. However, in the above case the diffusion process is unable to equalize concentrations of all ions from both sides of the membrane. For ion exchange equilibria, an interface between liquid and solid phases is considered as a membrane, while a colloidal particle bearing the exchangeable ion is assumed to be a non-diffusing ion.

In the early 1950s, Gregor proposed an osmotic theory of exchange. According to this model, the matrix of ion exchange resin is expanded upon swelling, and thus applies pressure to the liquid inside the pores. In such a case the equilibrium is determined by a difference in the osmotic pressure between the external solution and that of the liquid inside the pores together with the elastic forces of the matrix. However, Gregor's model does not consider the formation of ion pairs, and hence does not explain selective adsorption; moreover, its accuracy is not sufficient to describe exchange in dilute solutions, which are typical for ion exchange processes.

Some years later another model of ion exchange appeared, built on a molecular background rather than the macroscopic Gregor model. The model of Kachalsky (mid-1950s) presumes that the energy of electrostatic interaction which imparts changes in free energy of the system is uniformly distributed over the polymer chain between the ionogenic groups. The model describes the resin as a linear polyelectrolyte and provides an accurate description of ion exchangers with a small number of cross-linking bonds.

A similar approach was used in the model developed by Harris and Rice at about the same time. It also uses a molecular level approach and the concept of linear polyelectrolytes, but the authors concentrated on interactions of neighbouring functional groups both in the same and in the adjacent polymer chains, taking into account the regular distribution of fixed ions in the ion exchange resin phase. Another distinctive feature of this model is that it considers ion pair formation between the fixed ions and counterions.

Pepper has studied swelling of different absolutely dry resins in water and demonstrated that the total volume of the system undergoes shrinkage at the first step and then remains unaltered. Thus initially, the primary hydration shell is formed which consists of the so-called 'fixed' water, possessing specific properties. The water absorbed afterwards is called 'free' water and behaves like ordinary loosely bound water. The degree of swelling depends on the structure and cross-linking of the particular resin. Inorganic ion exchangers usually have a rigid crystal structure and their swelling is insignificant; layered ion exchangers undergo intralaminar swelling.

Ion exchange interactions occur at different rates in heterogeneous media; therefore studies dealing with ion exchange kinetics are of great importance. In 1947, Boyd and co-workers showed that the exchange rate is determined either by the diffusion rate inside the resin bed (gel diffusion) or by the diffusion in the layer of liquid surrounding the bed (film diffusion). When the rates of gel and film diffusions are comparable, both components determine the exchange rate. Determination of the mechanism and the limiting stage of the ion exchange process presents a rather difficult problem, because the kinetics simultaneously depend on a number of parameters, such as the concentration of adsorbate in solution, the nature of the ionic species, the type and granular composition of the ion exchanger and the relative migration rate of the interacting phases. The limiting stage of ion exchange can be approximately estimated as follows:

for gel diffusion:

$$(c\bar{D}\delta)/(cDr_0)\cdot(5 + 2K_{A/B}) \ll 1$$

for film diffusion:

$$(c\bar{D}\delta)/(cDr_0)\cdot(5 + 2K_{A/B}) \gg 1$$

and in case of mixed diffusion:

$$(c\bar{D}\delta)/(cDr_0)\cdot(5 + 2K_{A/B}) \approx 1$$

where $\bar{c} = z_i\bar{c}_i$, $c = \sum z_j c_j$ are total concentrations of exchanging ions in the solid and liquid phases

respectively; $\bar{D}$ and D are ionic diffusion coefficients in the solid and liquid phases, respectively; δ is the thickness of the diffusion interlayer; r_0 is the radius of the ion exchanger bed; and $K_{A/B} = \bar{c}_A c_B / c_A \bar{c}_B$ is the separation coefficient for both sorts of counterions in the equilibrium state: the counterion A is present initially inside the bed, while the counterion B is initially in solution.

An equivalent exchange takes place under the following condition:

$$z_R \bar{c}_R = \sum_i^n z_{Ai} \bar{c}_{Ai}$$

where $\bar{c}_R$ is the concentration of fixed groups inside the bed, $\bar{c}_{Ai}$ is the concentration of i-th counterion. This is only an approximation, applicable to ion exchangers of high capacity treated with relatively dilute aqueous solutions. In all other cases, the ion exchanger absorbs a significantly higher quantity of ions than is needed for equivalence, i.e. a super-equivalent exchange occurs. An excess of counterions penetrates into the exchanger bed accompanied by a quantity of co-ions, necessary to compensate the electric charge of the former, in order to preserve a condition of electroneutrality of the bed:

$$z_R \bar{c}_R + \sum_{j=1}^{n} z_{Xj} c_{Xj} = \sum_{i=1}^{m} z_{Ai} \bar{c}_{Ai}$$

The higher the concentration of external solution, the greater is the contribution of super-equivalent exchange. Even for zeolites and highly cross-linked resins it becomes apparent at concentrations of external solution of about 0.1 N and higher. For scarcely reticulated, macroporous, highly swelling or weakly charged ion exchange resins the super-equivalent exchange has a much more pronounced effect and it becomes distinguishable at considerably lower concentrations.

A sorption without ion exchange is usually named Donnan absorption of electrolyte, because the thermodynamic description of the process is principally the same both for the system 'ion exchanger–solution' and for systems with a real semipermeable membrane as an interface separating phases in Donnan theory. However, the latter postulates that the dissociation in both phases is complete. Another situation is observed when the exchange occurs between the bed and weakly dissociated electrolyte or when ionogenic groups on the former are weakly dissociated. In that case, one deals with sorption of fragments of undissociated molecules and ion pairs and the exchange cannot be described in terms of Donnan theory. The concept of 'super-equivalent exchange' includes the exchange of ions, absorption of electrolyte molecules without ion exchange, and other processes which could be characterized as between the above two cases.

Recent Progress in Ion Exchange

In recent years extensive research has been carried out on new crystalline inorganic and inorgano-organic layered compounds which possess ion exchange properties. Each layer in their structure can be considered as a planar macromolecule, while the substance as a whole is assumed to be a molecular crystal formed by these planar macromolecules. A reversible process of intercalation between the layers occurs due to interactions of guest species with active sites on the surface of the layer (lamella). However, the layers are unable to move spontaneously in a direction perpendicular to the plane. This is due to a certain rigidity of layers that plays an important role in intercalation reaction mechanism and energetics. Like other ion exchange materials, the charged layered solids may be strong, medium or weak cationic (or anionic).

The exchange of protons of α-ZrP phase for Li^+, Na^+ and Ca^{2+} occurs rapidly in acidic solutions, while H^+ exchange for larger or strongly hydrated cations like NH_4^+, Rb^+, Cs^+, Ba^{2+}, Mg^{2+}, Cu^{2+} and Cr^{3+} is quite slow at room temperature due to the high activation energies of interlayer expansion. Exchange can be facilitated in materials with large interlayer distances like α-$Zr(HPO_4)(NaPO_4) \cdot 5H_2O$ ($d = 11.8$ Å) or in intercalation compounds with ethanol or alkylamines. The compounds that can be protonated are preferably used as guest species. For example, an amino derivative of cyclodextrin has been used for intercalation, increasing the interplanar distance in α-ZrP up to $d = 35.6$ Å. These distances for other guest species are; 14.2 Å for ethanol, 20.4 Å with benzimidazole, 22.8 Å with 1-hexylamine and 23.1 Å with lysine. The layered compounds under discussion can swell upon introduction of water or other solvents into the interlayer space. Sometimes the process leads to delamination, i.e. destruction of the crystal into separate lamellae. Withdrawal of the solvent results in reaggregation of the lamellae in thin films or membranes. Inorgano-organic derivatives, phosphonates of layered α-structure, can be obtained by introducing the corresponding acid H_2O_3PR (where R = $-CH_3$, $-C_6H_5$, $-O(CH_2)_nCH_3$ etc.) into the reaction, instead of H_3PO_4. It is also possible to synthesize those compounds by substitution of existing OH groups in the α-ZrP structure by R or OR. Another interesting group of compounds is

covalently pillared zirconium diphosphonates of general formula $M^{IV}(O_3P–R–PO_3)$. If the R group is small, then a low degree of interlayer microporosity is observed, while for pillared compounds containing fragments of 3,3(5,5)-tetramethylbiphenyldiphosphonic acid the value of interlayer porosity is raised to 375 $m^2 g^{-1}$ (an average pore size of 5 Å). Inorgano-organic derivatives have also been obtained for γ-ZrP by substitution of the interlayer $O_2P(OH)_2$ groups for O_2PRR'. Pillared phases of γ-ZrP with, for example, biphenylphosphonate groups have a volume of micropores of 320 $m^2 g^{-1}$ and an average size of 5.8 Å.

A limited number of inorganic anion exchangers is known. Layered double hydroxides (or hydrotalcite-like anionic clays) can exchange a large number of inorganic and organic anions, while layered $ZrPO_4Cl$ can selectively replace chloride anions with other monodentate anionic ligands.

Currently, ion exchange is of extreme importance for processing of irradiated nuclear fuel and treatment of spent fuel elements of nuclear power stations, where it is often combined with other techniques, e.g. extraction. The processes of sorption play an important role in deactivation of nuclear industry wastes and in purification of cooling water from nuclear reactors. Different kinds of ion exchangers are widely used for the clean-up of the world's worst nuclear accident at Chernobyl. For example, Strelko *et al*. are carrying out both research and application of highly selective inorganic granulated ion exchangers for elimination of radioactive isotopes from drinking water, milk, etc. Ion exchange is extensively used in medicine for haemosorption (or haemoperfusion) – the method of blood purification from toxic compounds by direct contact of the sorbent with the patient's blood. This method was applied for the first time by Muirhead and Reid in 1948; they directed the blood flow through a mixture of cation and anion exchangers taken in a ratio of 9 : 1. Haemosorption can be applied alone or in combinations with haemodialysis (when the toxins are distributed between two liquid phases, separated by a semipermeable membrane). The ion exchangers are used to regenerate dialysate from the artificial kidney apparatus. Further improvement of the haemosorption method is connected with the necessity to resolve problems of selective blood purification, as well as the problem of better sorbent compatibility with biological fluids. Another possible medical application of ion exchangers consists of the creation of drugs and pharmaceuticals with prolonged activity, offering the possibility to release an active component inside the patient's body over time and maintaining its necessary concentration.

A nontraditional application of ion exchangers in nonpolar organic media is the ultra-purification of organometallic compounds used as precursors in chemical vapour deposition. These precursors are widely utilized for synthesizing materials possessing valuable properties for micro-, opto- and acousto-electronics, and protective and optical coatings. The organometallics in question react readily with atmospheric oxygen and moisture, while at the same the requirements on their purity are quite rigorous (less then 1×10^{-3}% of the sum of contaminants). The above requirements can be met by treatment with a sorbent composition containing inorganic ion exchangers based on titanium and zirconium phosphates, thus replacing energy-intensive and expensive traditional methods (sublimation or distillation).

Future Developments

Undoubtedly, the future development of ion exchange as a method of separation will be directed towards ecological and biotechnological problems. The development of society parallel to scientific and technical progress will promote greater regard for natural resources. Hence, particular attention will be drawn to the application of renewable technologies and closed technological cycles including ion exchange stages or applying ion exchange materials mainly in the area of water treatment and wastewater purification, as well as in several other fields. Certainly, the use of ion exchangers in medicine will increase.

New, advanced ion exchange materials possessing desirable properties will be obtained by targeted synthesis; computer modelling and simulations as well as molecular design will be increasingly applied.

The specificity and selectivity of ion exchange will grow; i.e., the most suitable materials from the viewpoint of their origin, matrix type, the type of ionogenic groups etc. will increasingly be applied for specific cases.

The phenomenon of ion exchange discovered a century and a half ago, as well as processes established on the basis of it, are still in a process of dynamic development. The potential of ion exchange both in practical applications and from the elaboration of theoretical concepts related to ion exchange is not yet complete.

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

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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