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Ion memory in inorganic ion exchangers

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INTRODUCTION

Ion exchange is a technology that has been ever receiving growing attention in various industries for several decades. This technology is commonly used to purify solutions by removing the dissolved ions by electrostatic sorption into ion exchange materials of various physical forms. The removed ions are replaced with equivalent amounts of other ions of the same charge in the solutions. The use of ion exchange reaction allows either all ions to be removed from a solution or particular ions to be selectively separated. Therefore, both selective removal of ionic contamination and complete deionization can be distinguished. The selection between both depends mainly on the composition of the solution and the extent of decontamination required^[1].

The applications of ion exchange are numerous and cover wide ranges of industries and households. These applications mainly cover purification purposes; however, ion exchange is also widely implemented in the separation and extraction of valuable substances such as uranium and plutonium from the nuclear industry waste^[2]. Deionization (demineralization) of water and water softening are known to be the most common applications. However, the spectrum of other applications varies from large-scale extraction of metals in hydrometallurgical and metal finishing processes to recovery of precious metals^[3,4]. The applications of ion exchange are also extended to food and beverages, petrochemical and chemical, pharmaceutical, sugar and sweeteners, industrial wastewater, ground and potable water, semiconductor, production power soil remedy, and pulp and paper industry.

ION EXCHANGE MATERIALS

Ion exchange is the process through which ions in solution are transferred to a solid matrix which, in turn releases ions of a different type but of the same polarity. In other words the ions in solutions are replaced by different ions originally present in the solid^[5-13].

Ion exchange materials are a class of functional materials that display ion exchange properties owing to existence of fixed ionic sites bonded to their framework, which is held together by chemical bonds or lattice energy and can be called polyions. Oppositely charged ions move throughout the framework and can be replaced by ions of similar charge. Ion exchange materials are available in different forms and structures varying in their classifications depending on origin, physical form (morphology), immobilized functional group, and their functions. The mechanism of ion exchange is dictated by various parameters related to the ion exchange materials such as the nature and type of fixed functional groups, the physical forms, and the origin of the ion exchange material^[14].

CLASSIFICATION OF ION EXCHANGE MATERIALS

Ion exchange materials are classified into natural and synthetic materials. Naturally occurring materials

such as clays and zeolites have some ion exchange properties but often it is difficult to use them, for example, in column operation. Synthetic ion exchangers such as styrene divinely benzene copolymer and synthetic zeolites behave as selective sorbents and it must be conditioned before use in an effort to overcome their limited resistance to acids and alkalis and limited mechanical stability.

According to the general classification of ion exchangers^[15,16], resins are divided into cation-exchange resins, anion-exchange resins and amphoteric resins. Cation-exchange resins may be of the strong-acid or weak-acid types; anion-exchange resins may be of the strong-base or weak-base types. If the electric charge carriers in the molecular network of an ion exchange resin are fixed ions (functional or ionogenic group) of a single type, such as sulphonic acid groups, the ion-exchange resin is called mono functional. However, if the resin contains ionogenic groups of varies types, its called poly functional.

Synthetic organic and inorganic ion exchangers can be classified on the basis of exchangeable species (cation, anion, ampholyte and multifunctional types), fractional group (strong, weak and acid/base types), skeleton types (polymers, copolymers, and poly condensations), and the rigidity of the polymeric structure [micro porous gel, macro porous (macro reticular), isoporous].

A similar classification of inorganic ion exchange materials is practically impossible. The chemical variety of these materials, their very characteristic properties of ion exchange, and the general in homogeneity of the structure of sorbents with ion exchanging sites with various selectivity all make it very difficult to find a single classification system.

Consequently, the chemical composition of inorganic ion exchange materials can be highly diverse, they are typically single or mixed metal oxides, hydroxides and insoluble acid salts of polyvalent metals, heteropolyacid salts, and insoluble metal ferrocyanides. The wide diversity of such materials includes natural minerals (as is or modified) and synthetic substances^[17]. Finally, classification of these materials on the basis of the chemical characteristics of the ion exchanging species appears still useful, as proposed by Vesely et al.^[17];

Hydrous oxides.

- Acidic salt of multivalent metals.
- Salts of heteropolyacids.
- Insoluble ferrocyanide.
- Aliminosilicates.

The real utility of an ion exchanger depends largely on its ion exchange characteristics. Ion exchange capacity, concentration and elution behavior, pH titrations and distribution behavior are some of the properties that constitute the ion exchange characteristics of the materials.

STRUCTURE FEATURE OF ION EXCHANGE MATERIALS

Structure feature of ion exchange materials play an important role in their applications. Ion exchange materials are classified according to the arrangement and bonding of atoms into:-

Amorphous structure

In this type of structure; the atoms are arranged in a random way similar to the disorder we find in a liquid (Figure 1). In the amorphous structure there is no longrange order (LRO). The structure of glass is an example for amorphous materials.



Figure 1 : Amorphous structure

Crystalline structure

The atoms are arranged in a regular pattern, and there is as smallest volume element that by repetition in three dimensions describes the crystal. e.g. we can describe a brick wall by the shape and orientation of a single brick (Figure 2 a and b). This smallest volume



element is called a unit cell. In crystalline structure there is long-range order (LRO) in crystals - a unit repeats itself and fills the space. The dimensions of the unit cell are described by three axes: a, b, c and the angles between them alpha, beta, and gamma.



Figure 2 : Crystalline structure

As we mentioned, a solid is a material that retains both its shape and volume over time. If a solid possesses long range, regularly repeating units, it is classified as a crystalline material. Crystalline solids are only produced when the atoms, ions, or molecules have an opportunity to organize themselves into regular arrangements, or lattices. For example, crystalline minerals found in nature have been formed through many years of extreme temperature and pressure, or slow evaporation processes. Most naturally occurring crystalline solids

Inorganic CHEMISTRY An Indian Journal comprise an agglomeration of individual microcrystalline units; single crystals without significant defects are extremely rare in nature, and require special growth techniques. If there is no long-range structural order throughout the solid, the material is best described as amorphous. Quite often, these materials possess considerable short-range order over distances of 1-10 nm or so. However, the lack of long range translational order (periodicity) separates this class of materials from their crystalline counterparts. Since the majority of studies have been addressed to study crystalline solids relative to their amorphous counterparts, there is a common misconception that most solids are crystalline in nature. In fact, a solid product generated from many chemical reactions will be amorphous by default, unless special procedures are used to facilitate molecular ordering (i.e., crystal formation). Although the crystalline state is more thermodynamically-favorable than the disordered state, the formation of amorphous materials is favored in kinetically bound processes (e.g., chemical vapor deposition, sol-gel, solid precipitation, etc.).

SELITIVITY OF INORGANIC ION EXCHANGERS

Ion exchange process depends on the mechanism by which mobile ions from an external solution are exchanged in the opposite direction for an equivalent number of ions that are electrostatically bound to the functional groups contained within a solid matrix of the ion exchange material. The preference of one ionic species over another by the ion exchangers can be attributed to several causes^[16]:

- 1. The electrostatic interaction between the charged framework and the counter ions depends on the size and valence of the counter ion.
- 2. Other effective interactions between ions and their environment.
- 3. Large counter ions may be sterically excluded from the narrow pores of the ion exchanger.

All these effects depend on the nature of the counter ion and thus may lead to preferential uptake of species by the ion exchanger. The ability of the ion exchanger to distinguish between the various counter ions species is called selectivity.

The selectivity coefficients in ion exchange systems

can describe the ion exchange equilibrium and provide a means of determining what to expect when various ions are involved. However, they are not constant and vary with the operation conditions such as types and properties of the resins, concentration of the feed solution, pH of the solution, temperature, and the presence of other competing ions in the solution^[18].

When two ions have similar charge and ionic radii, the selectivity stemmed from the properties of the ion exchange material (acidity, basicity, and the degree of crosslinking) is not sufficient for performing effective separation. Therefore, an appropriate complexing agent has to be added to the aqueous phase to allow the selectivity to be attained through either the difference in the stability constants, the difference in charges, or the variation in the structures of the complexes formed. As a result, an increased selectivity can be achieved. However, the determination of selectivity coefficients is practically complicated task and is ordinarily not undertaken in the design of ion exchange processes such as waste treatment systems. In fact most of these parameters can be extracted from manufacturers' data or research literature^[19].

The rules of thumb that have to be considered for general design purposes when cationic polymeric ion exchange materials at low concentrations and normal waste processing, the selectivity typically increases with increasing charge on the exchanging cation in the order: Li+ < H+ < Na+ < K^+ < Cs^+ < Rb^+ < Ag^+ < Be^{2+} < Mg^{2+} < Cu^{2+} < Ni^{2+} < Co^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+} < Ce^{3+} < La^{3+} < Th^{4+}. Selectivity also increases with increasing the atomic number (decreasing hydrated ionic radii) of the exchanging cation in the order of Li⁺ < H⁺ < Na⁺ < K⁺ < Cs⁺ (Li⁺ is an exception, owing to its high hydration energy). For anions, a typical series of selectivity is as follows: F⁻ \cong OH⁻ < HCO₃⁻ < CH₃COO⁻ < Cl⁻ < ClO₄⁻ < Co₄²⁻ < SO₄⁻²⁻.

Inorganic ion exchangers with their much more rigid three- dimensional frameworks undergo much less shrinkage or expansion in parallel situation. These inorganic exchangers will show different properties from organic ion exchange resins by experiencing ion sieve and steric effects^[20].

Ion sieve effect

In order to replace protons in the acid form of inor-

ganic ion exchangers, the cation present in the external solution must diffuse through the windows connecting the cavities. The water molecules of the hydrated ions are exchanged frequently with bulk water molecules in the solution. When the size of the window is smaller than the diameter of the hydrated counter ions, a part or all the water of the hydrated counter ions, a part or all the water of the hydration shell must be lost to allow the cation to pass through the window. If the cations can pass the inorganic ion exchanger pores after having lost water molecules coordinated to them in solution, the distinct kinetic observed varies with the hydration energies of the varies ions. If the counter ions have larger crystal ionic radii than this opening of the window, ion sieve effect can prevail (Figure 3).



Figure 3 : Ion sieve in ion exchange material

Ion sieve effect can be used to evaluate the window size of structurally uncharacterized inorganic ion exchangers. A series of cation differing in size is tested in exchange experiments for this purpose. The vanderwaals dimension for alkyl ammonium cations available over a wide range of values^[20] has been of use to such a program. When cations are smaller than 0.6 nm in two directions, they can pass through the window of the C-SbA structure without any resistance and exchange with the cations initially present. For the cations extending less than 0.6 nm in only one direction, the cation may pass its window with some distortion. However, a cation larger than 0.6 nm in all three directions cannot pass the window, even if the cavity has enough room for the large cations. Cations such as $(CH_3)_4 N^+$ and $(C_2H_5)_4 N^+$ can only be adsorbed on the surface of the C-SbA exchanger and its window size, as a consequence can be estimated to be about 0.6 nm.

The α -zirconium phosphate has a layered structure in which each layer consists of a plane of zirconium atoms coordinated octahedrally to oxygen. The free space in the sides of the layered structure is large enough to allow a spherical ion of 0.263 nm diameters to diffuse the cavity without any obstruction and is accessible to Li⁺, Na⁺ and K⁺. However, the size of the window is smaller than the ionic spheres of Rb^+ (0.296 nm) and Cs^+ (0.338 nm) and the ion sieve effect is encountered with these ions.

Acid salts of group IV phosphate and arsenate have layered structures with interlayer distances large enough to accommodate a number of ions. The size of the opening to the cavities of the acid salts with the same layered structure is dependent upon the particular composition.

Steric effect

If there is not enough available space for ingoing large ions within the cavities in the exchangers, their exchange becomes increasingly difficult in the course of the ion exchange reaction^[21,22]. The extent of the steric effect indicated by the absolute values of the Kielland coefficient C that is calculated from the following equation:

 $\ln K_{H}^{M} = 4.606 C X_{M}^{n+} + (\ln K_{H}^{M}) X_{M}$ Where.

 K^{M}_{H} : is the corrected selectivity coefficient $\overline{X_{M}^{n+}}$: is the equivalent fractions of the exchanging M^{n+}

in the exchanger phase.

C: is the Kielland coefficient.

The absolute values of the kielland coefficient increase generally with increasing difference in the crystal ionic radii of the two exchanging cations. Incomplete exchange can also arise with large ions from lake of interstitial space even when no ion sieve effect occurs.

The selectivity sequence depends very much on the effect of steric factors as the retention proceeds. For the alkali metal ions / H⁺ system on the crystalline antimonic acid, the selectivity sequences are a function of X_{M} . The order of increase is; $Li^{+} < K^{+} < Cs^{+} < Rb^{+} <$ Na^{+} for $X_{M} = 0.0 - 0.1$, $Li^{+} < Cs^{+} < K^{+} < Rb^{+} < Na^{+}$ for $X_{M} = 0.1-0.32$, and $Li^{+} < Cs^{+} < Rb^{+} < K^{+} < Na^{+}$ for $X_{M} = 0.32 - 1.0$. The selectivity coefficient for Na⁺ is attributed to highly negative values of (ΔH°) and minimal contributions of (ΔS°) at trace level concentrations of sodium ion^[21,22].

DIFFERENT TECHNIQUES FOR SYNTHE-SIS OF INORGANIC ION EXCHANGERS WITH ION MEMORIES

In-situ precipitation technique

In this technique cations or anions were in-situ precipitated in the structure of ion exchange materials during the preparation of ion exchange materials process. This process allows to the cations or ions to be hold in the texture of the ion exchange materials and occupies some places in the texture. These places and its numbers depend on the size and the charge of the in-situ precipitated cations or anions and the nature of the solid formed (amorphous or crystalline). These in-situ cations or anions in the ion exchange materials can undergoes to some elution processes using different eluants to eliminate these cations or anions from the texture, cavities and pores of the ion exchange materials leaving empty places. These places can reload again with the same cations or anions (ion memory).

In-situ precipitation of some radionuclides such as ¹³⁴Cs, ⁶⁰Co, ⁸⁵Sr and ^{152,154}Eu with cerium (IV) antimonate (CeSb) and tin (IV) antimonate (SnSb) was carried out by Abou-mesalam^[23]. The data obtained (TABLE 1) showed the higher values of decontamination factor (DF) and volume reduction factor (VRF) for ¹³⁴Cs, ⁶⁰Co, ⁸⁵Sr and ^{152,154}Eu with cerium (IV) antimonate than tin (IV) antimonate.

TABLE 1 : Chemical in-situ precipitation of ¹³⁴Cs, ⁶⁰Co, ⁸⁵Sr and ^{152,154}Eu with cerium (IV) antimonate and tin (IV) antimonate

Ion Exchanger	In-Situ Cations	Uptake, %	DF	VRF
	^{134}Cs	81.14	DF 5.3 6.08 9.18 3.59 2.56 4.15 8.19 6.53	4.2
C . 01	⁶⁰ Co	83.5	6.08	5.0
Cesb	⁸⁵ Sr	87.79	9.18	5.2
	^{152,154} Eu	72.18	5.3 6.08 9.18 3.59 2.56 4.15 8.19 6.53	4.5
	^{134}Cs	60.87	2.56	3.57
Such	⁶⁰ Co	75.81	DF 5.3 6.08 9.18 3.59 2.56 4.15 8.19 6.53	3.80
51150	⁸⁵ Sr	87.79		5.00
	^{152,154} Eu	89.79	6.53	5.60

Also, in-situ precipitation of some radionuclides such as ²²Na, ¹³⁴Cs, ⁶⁰Co and ^{152,154}Eu with titanium (IV) antimonate (TiSb) was carried out by Abou-mesalam^[24]. The data obtained showed selectivity sequence ¹³⁴Cs >²²Na>^{152,154}Eu>⁶⁰Co. Removal and leach rates of

these cations from the titanium antimonite (Tisb) in different media was reported.

Doping technique

Doping technique is the process of adding some metals to inorganic ion exchange materials to improve their characterization, structures and application.

In the field of ion exchange materials, some dopants were doped in the inorganic ion exchange materials to obtain a new material with a new characterization. The new ion exchange materials that obtained from the doping process can undergoes to some physical treatment (such as thermal treatment) and chemical treatments to eliminates these dopants from the texture, cavities and pores of the ion exchange materials leaving empty places. These places can reload again with the same cations or anions (ion memory).

New mixed materials with cation substitution are of interest since they show improved ion exchange properties and selectivity for particular metal ions in comparison to their single salt counter parts. This behavior may attribute to; cation substitution alters the properties, composition and dimensions of the structure. It has been reported that the affinity of antimony silicate towards Cs^+ can be improved by doping with Ti(IV), Nb(V), Mo(VI) or W(VI) in different molar ratios and it was found that Cs+ selectivity in acid increased with a ternary Sb-Si-W system^[25]. Preparation and characterization of sodium iron titanate^[26] and its application in heavy metal removal from waste waters has also been reported. The interest in using inorganic ion exchangers with rare earth ions is due to the ability of these ions, for example, increasing the acid sites in the structure of catalysts improve the adsorption characters^[27]. In 2010, Ali studied the doping effect of rare earth ions on the sorption properties of the crystalline sodium titanate^[28]. Sodium titanate in a needle like crystals was obtained from the fusion of TiO_2 with sodium carbonate in 2:1 molar ratio as a more stable material in aquatic environment. A series of the rare earth doped-sodium titanates were synthesized. It was reported that rare-earth doped-sodium titanate series showed responsible affinity towards Ce, Nb and Sm ions in their solution mixture with insignificant selectivity trend which reflect the high stability of rare earth-NaTi matrices.

In the field of semiconductor industry the process

was carried out by adding some desirable atoms in the semi conductor. These atoms or metals are known as dopants. After addition of these dopants some of the properties of the conductors can be changed according to our need.



Thin film deposition technique

This process is the ability to deposit thin films of material. In this text we assume a thin film to have a thickness anywhere between a few nanometers to about 100 micrometer. Deposition technology can be classified in two groups:

- 1 Depositions that happen because of a chemical reaction:
 - Chemical Vapor Deposition (CVD)
 - Electro deposition
 - Thermal oxidation

These processes exploit the creation of solid materials directly from chemical reactions in gas and/or liquid compositions or with the substrate material. The solid material is usually not the only product formed by the reaction. By products can include gases, liquids and



even other solids.



In Chemical Vapor Deposition (CVD) process, the substrate is placed inside a reactor to which a number of gases are supplied. The fundamental principle of the process is that a chemical reaction takes place between the source gases. The product of that reaction is a solid material with condenses on all surfaces inside the reactor.

- 2 Depositions that happen because of a physical reaction:
 - Physical Vapor Deposition (PVD)
 - Casting

Physical Vapor Deposition (PVD) covers a number of deposition technologies in which material is released from a source and transferred to the substrate. The two most important technologies are evaporation and sputtering.

Common for all these processes are that the material deposited is physically moved on to the substrate. In other words, there is no chemical reaction which forms the material on the substrate. This is not completely correct for casting processes, though it is more convenient to think of them that way.

Ion implantation technique

Ion implantation is a low-temperature technique for the introduction of impurities (dopants) into semiconductors and offers more flexibility than diffusion. For example, in transistors, ion implantation can be used to accurately adjust the threshold voltage. In ion implantation, dopant atoms are volatilized, ionized, accelerated, separated by the mass-to-charge ratios, and directed at a target that is typically a silicon substrate. The atoms enter the crystal lattice, collide with the host atoms, lose energy, and finally come to rest at some depth within the solid. The average penetration depth is determined by the dopant, substrate materials, and acceleration energy. Ion implantation energies range from several hundred to several million electron volts, resulting in ion distributions with average depths from < 10 nm to 10 μ . Doses range from 10¹¹ atoms/cm² for threshold adjustment to 10¹⁸ atoms/cm² for buried dielectric formation.

ION MEMORY TECHNOLOGY

Memory dfinition

Generally, memory means:

- Te remember of events, things, places and any things play an important role in human life.
- Slf-'s ability to retain past experience and restored
- Force when people kept things in mind and re-revived when appropriate.

Ion memory in inorganic ion exchangers

Ion memory in inorganic ion exchangers refers to the construction of material by keeping ionic bonding for exchangeable ions in framework of coordination ion memory after exchanging particular ion with other ion to maintain fundamentally original structures.

Ion memory effect

The retention of high selectivity for a particular cation after exchanging with other cations has been sought by endowing the crystalline structure of the inorganic ion exchanger with a fixed and well-defined structure. Examples in the literature which exhibit this characteristic and endow the ion-exchange memory sought, as a result, have been reported.

For example, Vol'khin et al.^[29] have prepared manganese oxide in spinal type, by exchanging proton for lithium ions in manganese oxide containing lithium ions. Similar results were obtained with the λ -type MnO₂^[30,31]. These oxides showed an extremely high selectivity for Li⁺ ions. Cryptomelane type manganese dioxide prepared from potassium permanganate and manganous sulphate showed an extremely high selectivity for K⁺ ions^[32]. The crystal structure was observed to remain essentially unchanged after exchanging Li⁺ or K⁺ ions in these oxides with H⁺. These results suggested that material can be constructed by keeping ionic bonding for exchangeable ions in framework of coordination ion memory after exchanging particular ion with other ion to maintain fundamentally original structures.

Lithium ion memory in inorganic ion exchangers

A new crystalline antimonic acid $HSbO_3O$. $0.12H_2O$ has been prepared from $LiSbO_3^{[33]}$ by the Li^+/H^+ ion exchange reaction affected with concentrated nitric acid solution. The $LiSbO_3$ was obtained by heating $LiSb(OH)_6$ at 900°C. The $LiSb(OH)_6$ was prepared by the addition of LiOH solution to a Sb(v) chloride solution at 60°C. The x-ray diffraction pattern (XRD) of $HSbO_3O$. $0.12H_2O$ has been attributed to monoclinic cell configuration. This monoclinic cell of $HSbO_3)M$ -SbA) has essentially the same arrangement as the $LiSbO_3$ where the oxygen atoms form a distorted hexagonal close backing configuration with antimony and lithium occupying some of the octahedral holes. The $LiSbO_3$ is also obtained by heating a mixture of Sb_2O_3 and Li_2CO_3 .

The pH response of M-SbA to neutralization with standard base is apparently that of a strong monobasic acid for the alkali metal ion/H⁺ system^[33]. The order of metal ion uptake is $K^+ < Rb^+ < Cs^+ < Na^+ << Li^+$ throughout the pH range studied. The M-SbA exhibits a capacities of Na⁺ and Cs⁺ at pH = 1.6 are higher than those for K^+ or Rb^+ at pH = 3. The XRD patterns of the products exchanged with Na⁺ and Cs⁺ at low pH show the presence of a mixture of cubic and monoclinic antimonic acids. No phase transformation is observed at pH > 5, however, a large ion-exchange capacity of 4.3 meq./g is obtained at pH = 11. Thermodynamically based parameters have been resolved for the Li⁺/H⁺ exchange with M-SbA by applying the simplified Gaines-Thomas equation through use of the pH data compiled during neutralization of the theoretical capacity of 5.7 meq./g assigned to it. The equilibrium constant for the Li⁺/H⁺ exchange at 25°C was determined to be 7.09x10⁻³ leading to a ΔG_{2980} value of 12.25 KJ/mole. The ΔG_{2980} value decreases with increase of temperature, indicating that the reaction is favored by increase of temperature. This indicates an entropy-producing process prevails in the Li⁺/H⁺ exchange system. In conclusion, the studies indicate that lithium ion exchange occurs predominantly with protons immobilized in Sb-OH⁺. Similar conclusions are reached from the results obtained with Li⁺/H⁺ systems in contact with cubic niobic acid^[34] and cubic tantalic acid^[35]. An extremely high selectivity for lithium ions in these ion-memorybased exchangers is due to the sizable electrostatic force between the sites and the lithium ions whose hydration shell has been removed by the exchangers. M-SbA can be applied for the selective removal of lithium ions from seawater and hydrothermal water^[36].

The ion-exchanger LiAlTiO₄ of spinal type was prepared by the common precipitation/hydrothermal crystallization method, and was acid-modified. Its ion-exchange properties for alkali ions such as saturation capacity of exchange, distribution coefficient and pH titration curve were determined. LiAlTiO, was characterized by the X-ray diffraction method. The acid treatment of LiAlTiO, caused Li⁺ extraction ratio to change from 28% to 72%, while the dissolution of Al is less than 6.8%. This inorganic ion-exchanger (LiAlTiO₄-700) has a higher saturation capacity of exchange for Li than for other alkali ions, the saturation capacity of exchange for Li⁺ reaches 4.29 mmol/g (30.03 mg/g);LiAlTiO₄-700(H) has a higher selectivity of ion exchange for Li⁺ than for other alkali ions. These results show LiAlTiO₄-700(H) has better memory and selectivity of ion exchange and higher capacity of ion exchange for Li^+ . It is a kind of prospective ionic sieve for $Li^{+[37]}$.

Han Wen ai was report a summary for its study on inorganic ion-memory material selectivity^[38]. Author was synthesizing potassium tungsten which has memory effect on K⁺ when they are mixed and heated. Sulphuric acid solution of potassium permanganate and sulphuric acid solution of manganese sulphuric synthesize hydrated manganese oxide which has memory effect on K⁺ after precipitating, acid washing and water washing under 60!. MSbA and spinal LiMn₂O₄ have evident ionmemory effect and raised many important questions existing in the study.

Mitsuo Abe et al.^[39] were studied synthesis and ion exchange properties of lithium ion selective inorganic ion exchanger by applying ion memory effect. A new crystalline antimonic acid HSbO₃O.12H₂O was prepared by Li⁺/H⁺ ion exchange reaction with concentrated nitric acid solution from LiSbO₃. The LiSbO₃ was obtained by heating LiSb(OH)₆ at 900°C. The Li

Sb(OH)₆ was prepared by the addition of LiOH solution to Sb(V) chloride solution at 60°C. The X-ray diffraction pattern(XRD) of HSbO₃O.12H₂O was indexed to a monoclinic cell with a=8.676 Å, b=4.752 Å, c=5.263 Å and β =90.75°. The pH titration curves of monoclinic antimonic acid (M-SbA) showed apparently monobasic acid for the systems of alkali metal ions /H⁺. The uptake order of the metal ions are K⁺ < Rb⁺ < Cs⁺ < Na⁺ < Li⁺ throughout the pH range studied. The low uptakes of K⁺, Rb⁺, Na⁺ and Cs⁺ at high pH might be due to steric or ion sieve effects for large unhydrated cations on M-SbA. Thermodynamic data were derived for Li⁺/H⁺exchange on M-SbA from pH titration curve.

Anatoly I. Bortun et al. was study the selectivivity of titanium phosphate for cesium ions by ion memory effect^[40]. Two synthetic methods for the preparation of spherically granulated titanium phosphates (TiP), as cesium selective exchangers, have been carried out. The first method uses the "ion memory" effect for the formation of specific adsorption sites in the matrix of TiP, whereas the second method results in the preparation of granular titanium phosphate - ammonium molybdophosphate (TiP-AMP) composites by a gel technique. The efficiency of the new materials has been studied in complex systems. The cesium distribution coefficients for some of the sorbents prepared are higher than 40,000 mL/g. It was found that, due to high exchange capacity, regenerability and high selectivity for cesium, TiP materials with "ion memory" effect can be used for radiocesium recovery from ground and surface waters, whereas granular composite TiP-AMP exchangers are useful for the treatment of cesium containing acid nuclear wastes with a high content of background electrolytes.

Ion memory in silicates as inorganic ion exchangers

In our laboratories and the literature^[41-48] the evaluation of the ion exchange properties of various synthetic inorganic ion exchange materials indicated that, most of inorganic ion exchangers loss its capacities or great extent of its capacities when treated at high temperature. So, Abou-Mesalam et al.^[48] attempt to overcome of these problems by thermal treatment of the exchangers in the loaded form at high temperature to construct the material by keeping ionic bonding for ex-

Inorganic CHEMISTRY An Indian Journal changeable ions in framework of coordination bonding. If this is done, then the product will show high selectivity just as to be retained in ion memory after exchanging particular ion with other ion to maintain fundamentally original structures.

Perform of silicate as inorganic ion exchanger with selectivity studies

Magnesium silicate (MS) and magnesium alumino silicate (MAS) ion exchange materials were prepared as reported earlier^[49] by equimolar solutions (0.25 M) and volumetric ratio equal to unity. The skeletal structure of both materials was elucidated using different tools, IR, XRD, XRF, DTA and TGA analyses. The structures of MS and MAS were found to MgSi_{5.59}O_{12.18}. 5.93 H₂O and MgAl_{2.32}Si_{5.2}O_{14.88}. 18.23H₂O, respectively.

TABLE 2 : Capacity of original magnesium silicate (OMS), Original magnesium alumino silicate (OMAS), Treated magnesium silicate (TMS) and Treated Magnesium alumino silicate (TMAS) for Cs⁺, Co²⁺ and Eu³⁺ ions at 25±1 °C

T	F	Capacity, meq./g		
ion exchanger	Form of ion exchanger	\mathbf{Cs}^{+}	Co ²⁺	Eu ³⁺
Magneso- silicate	OMS	0.55	1.14	1.39
(MS)	TMS	0.029	0.041	0.048
Magnesium alumino-silicate (MAS)	OMAS	0.77	1.06	1.09
	TMAS	0.03	0.04	0.045

The loading of MS and MAS ion exchange materials by Cs⁺, Co²⁺ and Eu³⁺ ions were carried out at 0.1 M for Cs, Co and 0.01 M Eu nitrate solutions and batch factor (V/m ratio) 200 ml/g. The capacity of these solids for the corresponding ions were calculated and tabulated in TABLE 2. The data in TABLE 2 showed that MS has a higher capacity for Co²⁺ and Eu³⁺ ions and lower capacity for Cs⁺ ion compared to MAS and the overall capacity sequence is $Eu^{3+} > Co^{2+} > Cs^+$. This sequence may be attributed to the increase of electrostatic interaction of multivalent cation compared to the monovalent ones^[49,50]. When the solids thermally treated at 850 °C the capacity are decreased from 0.55 to $0.029 \text{ meg/g for } Cs^+ \text{ ion, } 1.14 \text{ to } 0.041 \text{ meg/g for } Co^{2+}$ ion and 1.39 to 0.048 meq/g for Eu³⁺ ion on MS. Similar behaviour was observed for the capacity of TMAS ion exchanger. This decrease in capacity may be related to the loss of water molecules that act as exchangeable active site and/or an increase in crystallinity during thermal treatment at 850 °C.

Design of ion memory in silicate as inorganic ion exchangers

The loaded samples of magnesium silicate (MS) and magnesium alumino silicate (MAS) were thermal treated at 850 °C in furnace and the products were characterized by surface area, IR, XRD studies.

Surface area values of OMS, OMAS, TMS, TMAS, ETMS and ETMAS solids were measured using the standard volumetric method by nitrogen gas adsorption at 77 K and application of the BET- equation. The values of the surface area obtained were represented in TABLE 3 and showed a higher surface area value for MS compared to MAS. This may be related to the presence of aluminum in MAS leads to decrease of some pores present in MS and perhaps cancel of these pores.

TABLE 3 : Surface area values of original magnesium silicate (OMS), original magnesium alumino silicate (OMAS), treated magnesium silicate (TMS), treated magnesium alumino silicate (TMAS), exchanged treated magnesium silicate (ETMS) and exchanged treated magnesium alumino silicate (ETMAS) ion exchangers

Form of ion exchanger	Surface area, m ² /g
OMS	178.47
TMS	225.51
Cs-TMS	68.59
Co-TMS	88.22
Eu-TMS	52.02
OMAS	83.46
TMAS	160.58
Cs-TMAS	31.51
Co-TMAS	42.0
Eu-TMAS	22.71

Thermal treatment of OMS, OMAS, EMS and EMAS ion exchangers heated at 850°C indicated that the treatment of OMS and OMAS solids leads to increase of the surface area values to high extent. This increase may be attributed to the loss of water molecules that occupy most of the reactive pores present in the exchangers. Also, at high temperature (850°C) ion exchanger may be undergo to some shrinkage in the lattice structure and create a new channel with a new surface area that leads to an increase in the total

surface area values. During the exchange of Cs^+ , Co^{2+} and Eu^{3+} ions on MS and MAS solids one would expect the replacement of exchangeable ions (H⁺ of H-O-H) with Cs^+ , Co^{2+} and Eu^{3+} ions. The surface area values of the ETMS and ETMAS ion exchangers are decreased compared to OMS, OMAS, TMS and TMAS ion exchange materials (TABLE 3) and the order has the following sequence;

TMS (225.51 m²/g) > Co-TMS (88.22 m²/g) > Cs-TMS (68.59 m²/g) > Eu-TMS (52.02 m²/g),

and

$$\label{eq:tmass} \begin{split} TMAS~(160.58~m^2/g) > Co-TMAS~(42.0~m^2/g) > Cs-TMAS~\\ (31.51~m^2/g) > Eu-TMAS~(22.71~m^2/g). \end{split}$$

This sequence can be explained on the basis of replacement of exchangeable ions by cation, during the exchange process the smaller ions (H⁺, H-O-H) are replaced by ions of different radius (Eu³⁺ > Cs⁺ > Co²⁺) and the surface area are reduced from 225.51 m²/g to 52.02, 68.59 and 88.22 m²/g for Eu-TMS, Cs-TMS and Co-TMS, respectively. In case of ETMAS the surface area values are decreased from 160.58 m²/g to 22.71, 31.51 and 42 m²/g for Eu-TMAS, Cs-TMAS and Co-TMAS, respectively.

IR studies of OMS, TMS, ETMS and OMAS, TMAS, ETMAS were carried out and the spectra obtained were represented in Figures. (4 and 5), respectively. The spectra in figures (1 and 2) represent the decrease of the strong and broad peaks in the range 3600 - 2800 and 1643 cm⁻¹ that assigned to free water and H-OH bending and interstitial water molecules^[49] when the OMS, OMAS, EMS and EMAS thermally treated at 850°C. Also, the degree of intensity decreasing is parallel to the capacity measurements, where the peak intensity related to H₂O becomes very low in case of exchange Eu- ion exchanger and lower than exchanged Co- and Cs- ion exchangers. The peaks at 860-1175 and 550-450 cm⁻¹ that related to silicate (Si-O) groups^[49] becomes more sharp and have high intensity by thermal treatment of the ion exchanger. The spectra of the treated exchange Co- ion exchangers show two small peaks at 673 and 570 cm⁻¹ that may be related to the adsorption of Co²⁺ ion on MS and MAS. These peaks were appeared but shifted to lower frequency where the adsorption of atom or molecules on the surface of the ion exchanger perturbs the motion of atom or a group, causing a shift in some group vibration

frequency^[49], such a shift is evidence that the deformation frequency at 2800 cm⁻¹ on the hydrogen ion form is affected by chemically adsorbed ions. A small peaks at 944 cm⁻¹ in spectra of treated exchange Co- and Eu- ion exchangers are appeared (Figures. 4 and 5)



Figure 4 : IR spectra of OMS, Cs-TMS, Co-TMS and Eu-TMS



Figure 5 : IR spectra of OMAS, TMAS, Cs-TMAS, Co-TMAS and Eu-TMAS



Figure 6 : XRD patterns of OMS, TMS, Cs-TMS, Co-TMS and Eu-TMS

that may be due to M-M bond formation^[49]. XRD patterns of OMS, TMS, ETMS and OMAS,



TMAS, ETMAS are represented in Figures. (6 and 7), respectively. The patterns of all treated and all treated exchange ion exchangers revealed exactly the same diffractometer as the OMS and OMAS. Therefore no possible structure change caused in the treated and treated exchange of some cations with the exchangers and we failed to arrive to any defined conclusion except that both exchangers still exhibit amorphous character after treatment for the original and exchanged magnesium and magnesium alumino- silicates. Also, this result indicated the high stability of both exchangers to



Figure 7 : XRD patterns of OMAS, TMAS, Cs-TMAS, Co-TMAS and Eu-TMAS

TABLE 4 : Desorption of Cs⁺, Co²⁺ and Eu³⁺ ions from ETMS ion exchanger by different concentrations of HNO₃ at 25±1 $^{\circ}C$

Form of ion exchanger	Effluent	Vol. of effluent, ml	% Recovery	% Overall recovery	
Cs-TMS	0.01 M HNO3	40	46.94	54.08	
	0.1 M HNO ₃	25	7.14		
Co-TMS	0.01 M HNO ₃	40	15.3	23.29	
	0.1 M HNO ₃	25	7.99		
Eu-TMS	0.01 M HNO ₃	40	29.86	69.12	
	0.1 M HNO ₃	30	39.26		

high temperature.

The ion memory in silicate was studied by desorption of samples ETMS and ETMAS. The results obtained for the desorption of three sorbed cations Cs^+ , Co^{2+} and Eu^{3+} from MS and MAS are represented in TABLES (4 and 5), respectively. TABLE 4 shows that the desorption extent of Cs^+ , Co^{2+} and Eu^{3+} ions from ETMS in 0.01 M HNO₃ is higher than those obtained by 0.1 M HNO₃. This indicated that these sorbed ions are physically or weakly bonded with the exchanger and the other extent are trapped in pores

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and channel in the ETMS, so when higher concentration of HNO₃ used the small extent trapped are recovery. On the other hand, desorption of the above mentioned cations from magnesium alumino- silicate show small desorption extent by 0.01 M HNO₃ (TABLE 5) and the major extent are recovery by 0.1 M HNO₃. This may be attributed to the strong adsorption of these cations on MAS as represented from IR spectra (Figure 2). TABLES (4 and 5) also indicated that the overall recovery percent of these cations from MAS is higher than those obtained from MS ion exchanger.

TABLE 5 : Desorption of Cs⁺, Co²⁺ and Eu³⁺ ions from ETMAS ion exchanger by different concentrations of HNO₃ at 25 ± 1 °C.

Form of ion exchanger	Effluent	Vol. of effluent, ml	% Recovery	% Overall recovery	
Cs-TMAS	0.01 M HNO ₃	40	29.0	88	
	0.1 M HNO ₃	40	59.0		
Co-TMAS	0.01 M HNO ₃	40	8.72	21.84	
	0.1 M HNO ₃	35	13.12		
Eu-TMAS	0.01 M HNO ₃	40	25.52	94.16	
	0.1 M HNO ₃	60	68.64		

Magnesium silicate (MS) and magnesium alumino silicate (MAS) ion exchangers produced from the desorption studies were taken to study the ion memory of these exchangers to the previous exchangeable ions (Cs⁺, Co²⁺ and Eu³⁺) in framework of MS and MAS.

Selectivity modification in silicate as inorganic ion exchangers by ion memory

The capacity and selectivity of the eluted ETMS and ETMAS for Cs^+ , Co^{2+} and Eu^{3+} ions were studied and the results tabulated in TABLE 6. The data in TABLE 6 showed that the selectivity of MS and MAS for Cs^+ , Co^{2+} and Eu^{3+} ions are modified in the direction of the exchanged form of the ion exchangers and the selectivity sequence seems to be;

 $\begin{array}{l} Cs^{*} \ (0.33 \ meq/g) > Co^{2+} \ (0.31 \ meq/g) > Eu^{3+} \\ (0.087 \ meq/g) \ for \ eluted \ Cs- \ MS, \ Co^{2+} \ (1.09 \ meq/g) > \\ Cs^{*} \ (0.55 \ meq/g) > Eu^{3+} \ (0.139 \ meq/g) \ for \ eluted \ Co- \\ MS, \ Cs^{+} \ (0.59 \ meq/g) > Co^{2+} \ (0.48 \ meq/g) > Eu^{3+} \\ (0.153 \ meq/g) \ for \ eluted \ Cs- \ MAS \ and \ Co^{2+} \ (0.75 \ meq/g) > \\ Cs^{+} \ (0.23 \ meq/g) > Eu^{3+} \ (0.066 \ meq/g) \ for \ eluted \ Co- \\ MAS. \end{array}$

TABLE 6 : Capacity of eluted ETMS and ETMAS ion exchangers for $Cs^{\scriptscriptstyle +}, Co^{\scriptscriptstyle 2+}$ and $Eu^{\scriptscriptstyle 3+}$ ions at 25±1 oC

Form of ion ouchoncor	Capacity, meq./g			
Form of ion exchanger	Cs^+	Co ²⁺	Eu ³⁺	
Eluted Cs-TMS	0.33	0.31	0.087	
Eluted Co-TMS	0.55	1.09	0.139	
Eluted Eu-TMS	0.075	B.D.L.	B.D.L.	
Eluted Cs-TMAS	0.59	0.48	0.153	
Eluted Co-TMAS	0.23	0.75	0.066	
Eluted Eu-TMAS	0.33	B.D.L.	0.07	

B.D.L.: Below detection limit

These results suggest that the materials can be constructed by keeping cavity for exchangeable ions in the framework of coordination bonding; the product will show high selectivity for the exchangeable ions just as to be retained in ion memory after exchanging particular ion with other ion to maintain fundamentally original structures. For the eluted treated Eu- solids, the capacity values for the studied cations is very low and have not definite selectivity that may be attributed to the higher cavity created by thermal treatment of the solid and this cavity may undergoes some shrinkage and divided into large number of small cavity that make satiric hindrance and leads to very low capacity values for the studied cations.

By comparison the data in TABLES (2 and 6) we found that MS and MAS ion exchangers are loss ~ 94-96 % from its original capacities when thermally treated at 850°C (TABLE 2), on the other hands, the eluted EMS and EMAS thermally treated at the same high temperature have capacity values relatively smaller than its original values. This means that we can overcome the problem of the loss of capacity of the ion exchangers at high temperature by thermally treatment of the exchanged magnesium and magnesium alumino-silicates.

SHAPE MEMORY EFFECT

Shape memory effect, first discovered in binary alloys of Cu–Zn alloys and Cu–Sn alloys in 1938^[51], was not widely applied until the discovery in Ni–Ti alloys in 1963^[52]. In addition to the shape memory effect giving the material the ability to return to a predetermined shape when heated, NiTi shape memory alloys (SMAs) are capable of displaying pseudo elasticity giving the mate-

rial the ability to transform between phases upon loading and unloading and recover to its original zero strain shape after significant deformation. With the properties such as repeatability, wear resistance, corrosion resistance and biocompatibility, NiTi is the most commercially successful shape memory alloy^[53-55]. The shape memory effect of NiTi is related to a martensitic transformation between the high-temperature austenite phase and the low-temperature martensite phase. Unlike fully annealed near-equiatomic Ni-Ti alloys which transform from austenite to martensite directly, post-aged nearequiatomic Ni-Ti alloys normally transform in two steps showing two peaks on the differential scanning calorimetry (DSC) curve in the cooling direction. The first DSC peak correlates with the transformation from the austenite in a cubic structure (B2) to the R-phase in a rhombohedral structure; the second DSC peak correlates with the transformation from the R-phase to the martensite in a monoclinic structure (B190)^[56]. Dlouhy et al.[57] proposed a new explanation based on their insitu TEM observation that the second DSC peak in the cooling direction may include two transformations: Rphase to B190 in the grain boundary regions with precipitates, and B2 directly to B190 in the precipitatefree grain interiors. Multi-step (three or more steps) transformation could occur in appropriately aged nearequi atomic Ni-Ti alloys. The explanations for the conditions of multi-step transformation are still debated^{[57-} ^{60]}, but it is clear that Ti11Ni14 precipitates enhance the R-phase formation which is favorable for the shape memory effect^[61].

Luis Alberto et al.^[62] studied Nanoparticles from Cu-Zn-Al shape memory alloys physically synthesized by ion milling deposition; an ion milling equipment was used to elaborate nanoparticles from Cu-Zn-Al alloys with shape memory effect. Two different compositions were used, target A: 75.22Cu-17.12Zn-7.66Al at % with an Ms of -9 °C and target B: 76.18Cu-15.84Zn-7.98Al with an Ms of 20 °C. Nanoparticles were characterized by High Resolution Transmission Electron Microscopy, Electron Diffraction and Energy Dispersive X-ray Spectroscopy. The obtained nanoparticles showed a small dispersion, with a size range of 3.2-3.5 nm. Their crystal structure is in good agreement with the bulk martensitic structure of the targets. In this sense, results on morphology, composition and crystal structure have indicated that it is possible to produce nanoparticles of CuZnAl shape memory alloys with martensitic structure in a single process using Ion Milling.

He H et al.^[63] found that The selective adsorption of phosphate ions was investigated on CO₃²⁻, Cl⁻, and NO₃⁻-type ZnAl layered double hydroxides (LDHs) and the calcined CO₃²⁻-type LDH at 200, 400, 600 and 800°C, respectively. The calcined LDHs and NO₃ -type LDH showed high selectivity toward phosphate ions, while the Cl-type LDH shows selectivity toward both SO₄²⁻ and phosphate ions. The NO₃⁻-type LDH selectively adsorbed phosphate ions mainly through ion exchange. The calcined samples possibly proceed through ligand complexation or electrostatic attraction between phosphate ions and hydrated ZnO formed after calcination, although the structural memory effect was observed for the samples calcined below 600°C with the formation of CO₃²⁻-type LDH. Adsorption/desorption behaviors indicated that the calcined samples had good stability and reusability.

APPLICATION OF ION MEMORY TECHNOLOGY

Recently, Application of ion memory technique in the field of inorganic ion exchangers is very important especially in the recovery of valuable metals in industry such as silver, gold, nuclear technology such as platinum and medicine such as production of antibiotics, ultrapure water for dilution of medicine.

Host frameworks with the ability to store guest ions are very important in a wide range of applications including electrode materials for Li-ion batteries^[64]. In this report, we demonstrate that the ion storage ability of the cyanide-bridged coordination polymer (Prussian blue analogue, PBA) can be enhanced by suppressing vacancy formation. K-ions in the vacancy-suppressed PBA framework $K_{1.72}$ Mn[Mn(CN)₆]_{0.93}· $\Delta_{0.07}$ ·0.65H₂O (Δ : a [Mn(CN)₆]⁴⁻ defect) were electrochemically extracted. The open circuit voltages (OCVs) during Kion extraction exhibited two specific plateaus at 3.0 and 3.7 V vs. Li/Li⁺. Ex situ X-ray diffraction and IR spectroscopy revealed drastic structural and electronic changes during K-ion extraction. Furthermore, after Kion extraction, the vacancy-suppressed PBA framework

was applied to the cathode material for a Li-ion battery. The charge/discharge experiments revealed that the framework can accommodate a large amount of Li-ions.

Scientists at the Japan Synchrotron Radiation Research Institute (JASRI; Tetsuhisa Shirakawa, Presi-



dent) and University of Tsukuba (Nobuhiro Yamada, President) have, for the first time in the world, succeeded in observing a reversible symmetry switch of the host framework of a cyanide complex by the exchange of guest alkali metal cations^[65]. The use of such a symmetry switch enables the switching of the color and nonlinear optical properties of a specimen. In conventional research and development, a host substance is considered to merely serve as a container for guest ions and molecules. However, we can make materials express new functions by exploiting the mutual interaction between host and guest substances. By applying a symmetry switch to memory devices, we expect to pave the way to developing new types of memory device, for example, a device that memorizes information depending on the type and number of ions. The cyanide complex used is a functional material with a small environmental impact because it is composed of only materials abundant on Earth, such as nitrogen, carbon, iron, and cobalt. In addition, the cyanide complex is lightweight and soft, and is therefore highly feasible as a next-generation memory material.

In the framework of a cyanide complex, small cavities with a width of 5×10^{-7} mm are regularly arranged. Guest alkali metal cations can move in and out of these cavities. In this research^[64], at least 30 types of compound were synthesized by combining the host framework of the cyanide complex and the guest alkali metal cations, and their structures were systematically analyzed in detail using high-brilliance X-rays at SPring-8, thus leading to the discovery of a symmetry switch. The achievements of this research were realized by Professor Yutaka Moritomo of University of Tsukuba, who is also a visiting scientist at JASRI; Tomoyuki Matsuda, a researcher at University of Tsukuba, and Jungeun Kim, an associate senior scientist at JASRI. The results of this research were published online in Journal of the American Chemical Society.

Memory effects are well known to users of nickelcadmium and nickel-metal-hydride batteries[66]. If these batteries are recharged repeatedly after being only partially discharged, they gradually lose usable capacity owing to a reduced working voltage. Lithium-ion batteries, in contrast, are considered to have no memory effect. Here we report a memory effect in LiFePO one of the materials used for the positive electrode in Li-ion batteries—that appears already after only one cycle of partial charge and discharge. We characterize this memory effect of LiFePO4 and explain its connection to the particle-by-particle charge/discharge model. This effect is important for most battery uses, as the slight voltage change it causes can lead to substantial miscalculations in estimating the state of charge of batteries.

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