

Inorganic and Composite Ion Exchange Materials and their Applications

(Review)

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Received: 22. 1. 2009 Revised: 12. 3. 2009 Published: 16. 3. 2009

ABSTRACT

Article describes applications of several groups of inorganic and composite ion exchange materials. Zeolites, acidic salts, hydrous oxides, metal ferrocyanides, heteropolyacids and composite organic/inorganic ion exchangers are reviewed.

Keywords: inorganic materials, composites, ion exchangers

INTRODUCTION

In science, analytical chemistry is an ancient branch, yet may be regarded as one of the youngest science with the growing global awareness in health hazards and environmental pollution, it has played a key role to unveil the causes. So the scientists all over the world are paying great attention to analytical chemistry.

Analytical Chemistry is basically concerned with the determination of chemical composition of matter. The aspects covered by modern analytical chemistry are identification of a substance, the elucidation of its structure, separation of different elements and synthesis of ion exchangers. Separation has very important applications in various fields namely medicine, agriculture and environmental analysis.

Separation is basically a pre-treatment method which, usually precedes any quantitative or qualitative analysis. Separation involves both classical and modern techniques. The examples of the classical methods are precipitation and distillation. The general methods of separation include distillation, extraction, precipitation, crystallization, dialysis, diffusion etc.

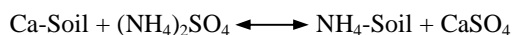
The most modern and versatile techniques used for the purpose of separations are chromatography, electrophoresis and ion exchange chromatography. Ion exchange

chromatography has emerged as a most versatile and standard analytical tool.

Ion exchange is basically a process of nature occurring throughout the ages from even before the dawn of human civilization. The phenomenon of ion exchange is not of a recent origin. The earliest of the references were found in Holy Bible, which says 'Moses' succeeded in preparing drinking water from brackish water by an ion exchange method [1]. Aristotle [2] stated that the seawater loses part of its salt content when percolated through certain sands. In 1623, Francis Bacon and Hales described a method for removing salts by filtration and desalination from sea water. In 1790, Lowritz purified sugar beet juice by passing it through charcoal.

In the beginning of 19th century, chemists were quite aware about ion exchange and were busy in new researches. Gazzari (1819) discovered that clay retained dissolved fertilizer particle. In 1826, Sprengel stated that the humus frees certain acids from soils. Fuchs (1833) pointed out that the lime frees potassium and sodium from some clay. By middle of 19th century sufficient experimental observations and information had been collected but principle of ion exchange had not yet been discovered. Thompson 1845, [3] and Way [4] in 1850 laid the foundation of ion exchange by base exchange

in soil. They observed that when soils are treated with ammonium salts, ammonium ions are taken up by the soil and an equivalent amount of calcium and magnesium ions are released. During 1850-55 the agrochemist Way demonstrated the following mechanism to be one of the ion exchange method involving the complex silicates present in the soil. As described by Way the process observed by the Thompson could be formulated:



The ion exchange process is reversible and aluminosilicates (zeolites) are responsible for the exchange in soil, established by Eichorn (1850) [5]. The first synthetic aluminum based ion exchanger was prepared by Harms and Rumpler [6] in 1903 to purify the beet syrup. According to Lamberg and Wiegner [7, 8], the materials responsible for the phenomenon were mainly clays, zeolites, gluconites and humic acids. Lamberg also obtained analcite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) by leaching the mineral leucite ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) with solution of sodium chloride and found that, this transformation could be reversed by treating analcite with a solution of potassium chloride, thereby exchanging Na^+ again by K^+ .

The first application of synthetic zeolite for collection and separation of ammonia from urine was made by Follin and Bell [9]. Gans [10] succeeded in utilizing the synthetic aluminium silicates ion exchangers for industrial purpose like softening of water and also for treating sugar solutions. Due to the limitations in the applications of neutral and synthetic silicates in various industrial applications and in an attempt to meet the demands of the industries, Adam and Holms [11] in 1935 laid the foundation of organic exchangers when they observed that the crushed phonograph records exhibit ion exchange properties. This led to investigators to develop synthetic ion exchange resins. These resins were developed and improved by the former I.G. Farben industries in Germany followed by the manufacturers in U.S.A. and U.K, which proved very effective for separations, recoveries, the ionization catalysis etc.

Although inorganic ion exchanger materials were first to be recognized, they lost their utility after the discovery of organic resins. However, revival of the interest in these materials took place in the 20th century, because of their use in the field of nuclear research. At that time there was need of some new materials

that were stable at high temperatures and in presence of intense radioactive radiations.

Kraus et al. [12, 13] at Oak Ridge national laboratory and C.B Amphlett [14, 15] in United Kingdom did the excellent work on these materials in the initial stages. The work up to 1963 has been summarized by Amphlett [16] in the classical book 'Inorganic Ion exchangers'. The later work up to 1970 has been condensed by Pekarek and Vesely [17], Clearfield [18, 19], Alberti [20, 21] and Watton [22, 23] have also worked on different aspects of synthetic inorganic ion exchangers, In India Qureshi and co-workers have prepared a large number of such inorganic material and studied their ion exchange behavior during the last 15 years. Other groups that were engaged in the field of research and whose work is significant interest are Anil K. De at Shantiniketan and Tandon at Rorkee. The few important uses of these inorganic ion exchangers are:

- Separations of metal ions
- Separations of organic compounds
- Removal of wastes and air pollutants
- Preparation of ion-selective electrodes
- Preparation of artificial kidney machines
- Preparation of fuel cells

The analytical importance of the synthetic inorganic ion exchangers is now firmly established. The review of ion exchange in analytical chemistry for the year 1970 includes the significant statement; the obvious advances in the last two years are in the area of inorganic ion exchangers. Even today this statement is almost equally true. Synthetic ion exchanger may be classified in the following categories:

- 1) Synthetic zeolites
- 2) Polybasic acid salts
- 3) Hydrous oxides
- 4) Metal ferrocyanides
- 5) Insoluble ion exchange materials
- 6) Heteropolyacids

1 SYNTHETIC ZEOLITES

Zeolites were the first inorganic materials to be used for the removal of waste effluents at large scale. Zeolites are crystalline aluminosilicate based materials and can be prepared as micro-crystalline powders, pellets or beads. The main advantages of synthetic zeolites when compared with naturally occurring zeolites are that, they can be engineered with a wide

variety of chemical properties and pore sizes, and they are stable at high temperatures but have some limitations too.

The main limitations of synthetic zeolites are:

- Relatively high cost compared to natural zeolites
- Limited chemical stability at extreme pH ranges (either high or low)
- Ion specificity is susceptible to interference from similarly sized ions

The actual processing capacities obtained with zeolites are lower than their maximum capacities since the bed is changed at the early stages of breakthrough and because the waste streams usually contain other ions that will occupy some of the exchange sites and therefore reduce the processing capacity. Synthetic silica based ion exchangers were produced for technical purpose by fusing soda, potassium carbonate, feldspar and kaolinite (Schmaltz permutite) and later from aluminum sulphate solution containing sodium silicate by precipitation with sodium hydroxide solution (Gel permutite). Since then, artificial crystalline zeolites have also been successfully synthesized.

The advantageous properties of the crystalline silicate based ion exchanger over modern synthetic resin based ion exchangers are as follows:

- Less sensitive to higher temperatures
- Stiff and uniform structure
- More selective and suitable for separation of ions on the basis of their different sizes

Some of them are now also used as molecular or ionic sieves. In India, a systematic investigation has been carried out to evaluate the performance of locally available synthetic zeolites for the removal of cesium, strontium and thorium from solution [24-26]. The zeolites after exchange with cesium, strontium or thorium, were thermally treated to fix the ions successfully in the same matrix [27].

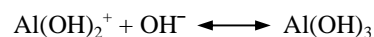
2 POLYBASIC ACIDS SALTS

Acidic salts of multivalent metals formed by mixing acidic oxides of metals belonging to IV, V and VI groups of the periodic table. Acid salts of the quadrivalent metals are most studied groups of this class. They are extremely insoluble. Their composition is non-

stoichiometric and depends on the condition under which they are precipitated. The materials which have been so far synthesized includes the phosphates, arsenates, molybdates, tungstates, antimonates, silicates, vanadates, and tellurates of zirconium, titanium, thorium, tin, cerium, chromium, iron, niobium, tantalum etc.

3 HYDROUS OXIDES

The hydrous oxides of some metal ions have also been the well-established materials for ion exchange purpose. Freshly precipitated trivalent metal oxides are very effective in this respect, e.g. hydrous ferric oxides and ferric hydroxides readily absorb alkaline earth cations according to the law of mass action [28, 29], other bivalent cations [30] being absorbed above pH 7. In this process, the alkali metals and alkaline earths are adsorbed on the surface and are readily eluted while more highly charged cations Ce(III), Y(III), Pm(III), Ru(IV) are sorbed in bulk and eluted only with difficulty [31]. The ion exchangers of this class show an amphoteric behavior depending upon the pH of the solution. The process can be described by the following equilibria [32].



Zinc oxide also shows amphoteric exchange properties [33]. Mixed oxides can be prepared in which second cations of higher charge than the parent cation is introduced into the structure. The resulting net positive charge is being balanced by the presence of anions other than oxides and hydroxides. Example of such materials include Zn(OH)_2 in which Zn^{2+} is partly replaced by Al^{3+} and Al(OH)_3 containing Si^{4+} , Ti^{4+} or Zr^{4+} . The general formulae $\text{Zn}_{n-1}\text{Al}_n(\text{OH})_2\text{X}_n$ and $\text{Al}_{n-1}\text{M}_n(\text{OH})_3\text{X}_{n-1}$, where M^{4+} is a tetravalent oxide and X is a monovalent anion. Quadrivalent metal oxides are also commonly used as inorganic ion exchangers such as SnO_2 , SiO_2 , ThO_2 and ZrO_2 . Actually these materials do not possess simple oxide formula as given above unless they are ignited at a high temperature. They are found to contain varying amount of water, which is not present as water of hydration since on heating, it is lost continuously over a range of temperature. Consequently these oxides are usually described as hydrous oxides. Inoue et al. [34-36] and A.K. De et al. [37-40] have done important work on hydrous oxides.

4 METAL FERROCYANIDES

Insoluble metal ferrocyanides can also be used as inorganic ion exchangers. They are also known as scavengers for alkali metals. They are easily prepared and useful in the separation of radioactive wastes and fissionable materials [41] with less damage to radiation than their organic counter parts. Baetsley et al. [42] studied ferrocyanide molybdate and determined its structure by X-ray studies. They also used molybdenum and tungsten ferrocyanides for the separation of Cs-137 and Sr-90 from fissionable products in acidic medium.

Amine based metals ferrocyanides have also received attention. They were first introduced by Hahn and Clein [43], who prepared a cobalt amine ferrocyanide. Ferric hydroxides also have fast growing applications in the separation of metal ions and it has been used as an adsorbent for the removal of arsenic from natural water [44].

5 INSOLUBLE ION EXCHANGE MATERIALS

Various insoluble ion exchanging materials are also of interest. A large number of such compounds have been prepared. These materials have been prepared by precipitation from metal salt solution with Na₂S or H₂S. The ion exchange properties of insoluble sulphides (e.g. Ag₂S, SnS, CuS, PbS, FeS, NiS, As₂S₃, Sb₂S₃) have been investigated. The sulphides are selective towards cations forming insoluble sulphides. The exchange reaction occurs through metathetical reactions in which the metal of sulphide is displaced by appropriate ion from the solution. Quantitative sorption of Tl⁺, Ni²⁺, Co²⁺, Mn²⁺, Cu²⁺ and Pb²⁺ have been reported on ZnS, CdS and PbS [45], Uranium on PbS [46], separation of Cu²⁺ from Zn²⁺ and Cd²⁺ on SnS [47] and noble metal on CuS [48, 49]. Some of the important two component ion exchangers with their composition, ion exchange capacity and selectivity of metal ions have been reported in table 1.1.

6 HETEROPOLYACIDS

Heteropolyacid salts can be used as inorganic ion exchangers. This group of exchangers is derived from 12-heteropolyacids of general formula H_nXY₁₂O₄₀.nH₂O where X may be P, As, Si, B or Ce and Y may be one of the elements such as Mo, W or V. The heteropoly compounds especially those of 12-molybdo compounds are quite strong oxidizing agents. The exchangers of this type are stable in

moderately concentrated acid. However they dissolve in the solution of alkali.

The heteropolyacids exhibit high affinity to heavy alkali metals, thorium and silver. The size of univalent ions of these elements is suitable for their retention in the crystal lattice of heteropolyacids. Apart from the heteropolyacid salts, many other substances like mixed salts have also been synthesized and studied in detail for ion exchange properties. It has been found that double salts or mixed salts of the metal ions possess ion exchange properties different from that of simple salts. Usually they show superiority over simple salts mainly in three aspects. They are more thermally and chemically stable, secondly they are selective in nature and their ion exchange capacities are higher as compared to their simple salts. It is with this view, attention has been given to synthesize and to investigate ion exchange properties of these class of ion exchangers. Some mixed salts or double salts prepared earlier have been reported in table 1.2.

In order to characterize a new substance as an inorganic ion exchanger, its utility in various fields and its limitation, the following properties may be studied as per given order of preference.

- Ion exchange capacity
- Chemical and thermal stability
- Composition
- pH titration
- Structural studies
- Selectivity
- Analytical applications

Besides the applications, inorganic ion exchangers have some limitations:

- Relatively low exchange capacities
- Relatively low mechanical durability
- Non-controllable pore size
- Clay minerals tend to peptize (i.e. convert to a colloidal form)
- Zeolites are difficult to size mechanically
- Partial decomposition in acids or alkalis
- Limited chemical stability in many solutions
- Need for a chemical or thermal pretreatment (especially those with a very low salt content)

Table 1.1 Two-component ion exchange materials with their properties

| S. No. | Ion exchange Materials | Type | Composition | Empirical Formula | IEC (meq g ⁻¹) | Selectivity | References |
|--------|-----------------------------|-------------|---|---|----------------------------|--|------------|
| 1 | Aluminium antimonate | Amorphous | Al/Sb=4.20 | - | 1.14 | Ag ⁺ , UO ₂ ²⁺ , Ba ²⁺ | 50 |
| 2 | Aluminium oxide | Crystalline | - | - | - | - | 51 |
| 3 | Aluminium vanadate | Amorphous | - | (Al ₂ O ₃) _n .(V ₂ O ₅) _n | - | - | 52 |
| 4 | Aluminium silicate | Amorphous | - | - | - | - | 53 |
| 5 | Aluminium tripolyphosphate | Amorphous | Al/P=0.50-0.66 | - | 2.50 | - | 54 |
| 6 | Aluminium metatungstate | - | - | - | - | - | 55 |
| 7 | Antimonic acid | Amorphous | - | Sb ₂ O ₅ .4H ₂ O | 1.28 | Li ⁺ , Na ⁺ , K ⁺ , Ta ⁵⁺ | 56 |
| 8 | Antimony molbdate | - | - | - | - | - | 57 |
| 9 | Antimony phosphate | - | - | Sb(HPO ₄) ₂ .H ₂ O | - | Cd ²⁺ , Hg ²⁺ | 58 |
| 10 | Antimony silicate | Crystalline | - | Sb ₂ O ₅ (H ₂ SiO ₃) ₆ .nH ₂ O | - | Rh ⁺ | 59 |
| 11 | Antimony ferrocyanide | Amorphous | - | - | - | Sr ²⁺ | 60 |
| 12 | Antimony sulphide (Hydrous) | - | - | - | - | - | 61 |
| 13 | Bismuth tungstate | Amorphous | Bi/W=0.50 | - | 0.50 | Pb ²⁺ | 62 |
| 14 | Bismuth nitrate | Amorphous | - | - | - | - | 63 |
| 15 | Bismuth tellurate | Amorphous | Te/Bi=0.70 | Bi ₄ (H ₂ TeO ₆) ₃ .nH ₂ O | 3.20 | - | 64 |
| 16 | Bismuth silicate | Amorphous | - | - | 3.30 | - | 65 |
| 17 | Cerium vanadate | Amorphous | - | CeO ₂ .2V ₂ O ₅ .4H ₂ O | - | - | 66 |
| 18 | Cerium antimonate | Amorphous | Sb/Ce=0.30 | - | 1.23 | Hg ²⁺ , Cu ²⁺ , Tl ⁺ | 67 |
| 19 | Cerium arsenate | Crystalline | As/Ce=2.0 | Ce(HAsO ₄) ₂ .2H ₂ O | 4.30 | Li ⁺ , Na ⁺ , K ⁺ , Cs ⁺ | 68 |
| 20 | Cerium molybdate | Amorphous | Mo/Ce=2.3, 8.2 | - | 0.96 | Pb ²⁺ | 69 |
| 21 | Cerium oxide | Amorphous | H ₂ O/CeO ₂ =3.0 | - | 0.99 | Cu ²⁺ | 68 |
| 22 | Cerium oxide (Hydrous) | Crystalline | CeO ₂ /H ₂ O=2.50 | - | - | - | 70 |
| 23 | Cerium tellurite | Amorphous | - | - | - | - | 71 |
| 24 | Cerium tungstate | Amorphous | Ce/W=0.49 | - | - | Al ³⁺ , Hg ⁺ | 72 |
| 25 | Cobalt antimonate | Amorphous | Co/Sb=1.3 | - | 0.89 | Bi ³⁺ | 73 |
| 26 | Cobalt ferrocyanide | Amorphous | - | - | - | Ag ⁺ | 74 |
| 27 | Copper ferrocyanide | Amorphous | - | - | - | - | 75 |
| 28 | Copper phosphate | Amorphous | - | - | - | - | 76 |
| 29 | Chromium phosphate | Amorphous | P/Cr=0.6-1.0 | Cr ₂ O ₂ HPO ₄ Cr ₂ O ₃ (HPO ₄) ₂ | 5.90 | Li ⁺ , Na ⁺ , K ⁺ , Rb ⁺ , Cs ⁺ | 77 |
| 30 | Chromium arsenate | Amorphous | As/Cr=1.98 | Cr ₂ O ₃ (H ₃ AsO ₄) ₄ .3H ₂ O | 0.63 | Zr ⁴⁺ , Hf ⁴⁺ | 78 |
| 31 | Chromium molybdate | Amorphous | Mo/Cr=1.90 | Cr ₂ O ₃ (H ₂ MoO ₄) ₄ .8H ₂ O | 0.34 | Pb ²⁺ , Ca ²⁺ | 79 |
| 32 | Chromium tungstate | Amorphous | W/Cr=1.92 | Cr ₂ O ₃ (H ₂ WO ₄) ₄ .11H ₂ O | 0.02 | Th ⁴⁺ , Hf ⁴⁺ | 80 |
| 33 | Chromium antimonite | Amorphous | Sb/Cr=2.95 | Cr ₂ O ₃ .3Sb ₂ O ₅ .22H ₂ O | 0.42 | Co ²⁺ , Pb ²⁺ | 81 |
| 34 | Chromium tellurate | Amorphous | Te/Cr=0.20 | - | - | - | 82 |
| 35 | Chromium ferrocyanide | Amorphous | Cr/Fe=0.33 | K ₆ Cr ₂ [Fe(CN) ₆] ₃ .16H ₂ O | 2.65 | Li ⁺ , Na ⁺ , K ⁺ , Ca ²⁺ | 83 |
| 36 | Ferric phosphate | Amorphous | P/Fe=2.00 | FeH(HPO ₄) ₄ .nH ₂ O | 0.77 | Pb ²⁺ , Eu ³⁺ , Ca ³⁺ | 84 |
| 37 | Ferric arsenate | Amorphous | As/Fe=1.33 | - | 0.80 | Li ⁺ , Na ⁺ , K ⁺ | 85 |
| 38 | Ferric silicate | Amorphous | - | - | 0.20-1.60 | Zn ²⁺ , Cd ²⁺ , Cr ³⁺ , Al ³⁺ | 86 |
| 39 | Ferric antimonate | Amorphous | Sb/Fe=2.40 | - | 0.80 | Cd ²⁺ | 87 |
| 40 | Ferric tungstate | Amorphous | Fe/W=1.0 | - | 0.84 | Ce ⁴⁺ | 88 |
| 41 | Ferric ferrocyanide | Amorphous | - | - | 3.60 | Cs ⁺ | 59 |

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|----|--------------------------|------------------|--------------------------|--|-----------|---|-----|
| 42 | Germanium (IV) phosphate | Crystalline | - | Ge(HPO ₄) ₂ .H ₂ O | 7.80 | - | 89 |
| 43 | Hafnium phosphate | Crystalline | - | Hf(HPO ₄) ₂ .H ₂ O | 4.17 | - | 90 |
| 44 | Hafnium arsenate | Amorphous | - | HfAsO ₄ | - | - | 91 |
| 45 | Lead phosphate | Crystalline | - | Pb(HPO ₄) ₂ .H ₂ O | 4.79 | - | 89 |
| 46 | Lead tungstate | Amorphous | W/Pb=2.50 | - | 1.00 | Cu ²⁺ | 92 |
| 47 | Lead strontium phosphate | Amorphous | - | - | - | - | 93 |
| 48 | Lead ferrocyanide | Amorphous | - | Pb ₂ [Fe(CN) ₆] | - | Cs ⁺ , Co ²⁺ | 94 |
| 49 | Lanthanum tellurate | Amorphous | La/Te=0.66 | La ₂ (TeO ₄) ₃ | 1.61 | - | 95 |
| 50 | Lanthanum oxalate | Amorphous | - | - | - | - | 96 |
| 51 | Niobium phosphate | Amorphous | - | - | - | - | 97 |
| 52 | Niobium arsenate | Amorphous | Nb/As=1.96 | - | 1.06 | Cd ²⁺ , Mn ²⁺ , Al ³⁺ | 98 |
| 53 | Niobium vanadate | Amorphous | - | - | - | Ce ⁴⁺ , Eu ³⁺ | 99 |
| 54 | Niobium Antimonate | Semi-Crystalline | Nb/Sb=1.40 | - | 1.10 | Mg ²⁺ | 100 |
| 55 | Niobium pentaoxide | Amorphous | - | - | - | - | 101 |
| 56 | Stannic arsenate | Amorphous | Sn/As=1.84 | - | 0.79-0.94 | Pb ²⁺ , Al ³⁺ , Fe ³⁺ , Ga ³⁺ , In ³⁺ | 102 |
| 57 | Stannic phosphate | Amorphous | P/Sn=1.25 | SnO ₂ .0.62P ₂ O ₅ . nH ₂ O | 1.20-1.44 | Li ⁺ , Na ⁺ , K ⁺ , Rb ⁺ , Cs ⁺ | 103 |
| 58 | Stannic tungstate | Amorphous | Sn/W=1.30 | - | 0.58 | Ba ²⁺ , Ca ²⁺ , Sr ²⁺ , Mn ²⁺ , Ni ²⁺ , Co ²⁺ | 104 |
| 59 | Stannic antimonate | Amorphous | Sb/Sn=1.0 | SnO ₂ .Sb ₂ O ₅ .nH ₂ O | 0.75 | Co ²⁺ , Ni ²⁺ | 105 |
| 60 | Stannic oxide | Amorphous | - | SnO ₂ .xH ₂ O | 1.98 | Cu ²⁺ , Zn ²⁺ , Co ²⁺ , Fe ³⁺ , Ni ²⁺ , Mn ²⁺ | 106 |
| 61 | Stannic molybdate | Amorphous | Sn/Mo=1.0 | - | 1.00 | Pb ²⁺ | 107 |
| 62 | Stannic silicate | Amorphous | Sn/Si=4.0 | - | - | Cu ²⁺ , Pb ²⁺ , Cr ³⁺ | 108 |
| 63 | Stannic selenite | Amorphous | Sn/Se=1.33 | (SnO ₄)(OH) ₂ (SeO ₃) ₃ .6H ₂ O | 0.75 | Li ⁺ , Na ⁺ , K ⁺ , La ³⁺ | 109 |
| 64 | Stannic vanadate | Amorphous | Sn/V=1.0 | [(SnOH) ₃ V ₃ O ₉ .4H ₂ O] _n | 0.85 | Li ⁺ , Na ⁺ , K ⁺ | 110 |
| 65 | Stannic ferrocyanide | Amorphous | Sn/Fe=3.0 | [(SnO) ₃ (OH) ₃ H ₄ Fe(CN) ₆ .3H ₂ O] _n | 0.85 | Na ⁺ , K ⁺ , Ba ²⁺ | 111 |
| 66 | Tantalum pentaoxide | Amorphous | - | - | - | - | 112 |
| 67 | Tantalum phosphate | Amorphous | - | - | - | - | 113 |
| 68 | Tantalum arsenate | Amorphous | Ta/As=2.80 | - | 1.09 | Na ⁺ , K ⁺ , Ba ²⁺ | 114 |
| 69 | Tantalum antimonate | Amorphous | Ta/Sb=1.30 | - | 0.99 | NH ₄ ⁺ , Na ⁺ , K ⁺ , Vo ²⁺ | 115 |
| 70 | Tantalum selenite | Amorphous | Se/Ta=1.5 | - | 1.19 | Fe ³⁺ , Ba ²⁺ | 116 |
| 71 | Tantalum tungstate | Amorphous | - | - | 0.84 | K ⁺ | 117 |
| 72 | Thorium Phosphate | Crystalline | Th/PO ₄ =0.50 | Th(HPO ₄) ₂ .2H ₂ O | 0.77 | Ca ²⁺ , Sr ²⁺ , Ba ²⁺ | 118 |
| 73 | Thorium tungstate | Amorphous | Th/W=2.0 | Th(OH) ₂ (HWO ₄) ₂ .nH ₂ O | 0.46 | Na ⁺ , K ⁺ , Cs ⁺ , Bi ³⁺ , Hg ²⁺ , Vo ²⁺ | 119 |
| 74 | Thorium antimonate | Amorphous | Sb/Th=3.65 | - | 0.32 | Cu ²⁺ , Pb ²⁺ | 120 |
| 75 | Thorium oxide | Amorphous | - | Th(OH) _n . nH ₂ O | 2.00 | Na ⁺ , Rb ⁺ , Ca ²⁺ , Sr ²⁺ | 121 |
| 76 | Thorium arsenate | Crystalline | As/Th=1.53 | Th(HAsO ₄) ₂ .H ₂ O | 0.20 | Li ⁺ | 122 |
| 77 | Thorium molybdate | Amorphous | Th/Mo=0.5 | - | 0.75 | Pb ²⁺ , Fe ³⁺ , Zr ⁴⁺ | 123 |
| 78 | Titanium arsenate | Amorphous | - | Ti(HAsO ₄) ₂ .2.5H ₂ O TiO ₂ . 0.5 As ₂ O ₅ .nH ₂ O | 1.00 | Ba ²⁺ , Sr ²⁺ , Cd ²⁺ , Zn ²⁺ , Cu ²⁺ , Pb ²⁺ | 124 |
| 79 | Titanium antimonite | Amorphous | Sb/Ti=1.0-1.36 | - | 0.70 | Mg ²⁺ , VO ²⁺ , Zn ²⁺ and rare earths | 125 |
| 80 | Titanium tungstate | Amorphous | Ti/W=0.80 | - | 0.40-0.76 | Cs ⁺ , Ca ²⁺ , Cr ³⁺ | 126 |
| 81 | Titanium oxide | Amorphous | - | TiO(OH) ₂ .nH ₂ O | 2.00 | Rb ⁺ , Cs ⁺ , Co ²⁺ | 121 |
| 82 | Titanium molybdate | Amorphous | Mo/Ti=0.5-2.0 | - | 0.80-1.60 | Na ⁺ , K ⁺ , Ba ²⁺ , Pb ²⁺ | 127 |
| 83 | Titanium selenite | Amorphous | Ti/Se=1.39 | - | 0.78 | Cd ²⁺ | 128 |
| 84 | Titanium vanadate | Amorphous | V/Ti=4.0 | Ti ₃ (V ₃ O ₉ .1.5 H ₂ O) ₄ | 0.68 | Sr ²⁺ | 129 |
| 85 | Titanium tellurate | Amorphous | Te/Ti=2.06 | - | - | - | 82 |
| 86 | Titanium ferrocyanide | Amorphous | Fe/Ti=2.00 | - | 1.40 | Cs ⁺ | 130 |

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|-----|-------------------------|-------------|-----------------|---|------|---|----------|
| 87 | Titanium silicate | Amorphous | Ti/Si=1.0 | - | 3.62 | Li ⁺ , Na ⁺ , K ⁺ , Pb ²⁺ , Cr ³⁺ | 131 |
| 88 | Zirconium antimonate | Amorphous | - | ZrO ₂ .Sb ₂ O ₅ .nH ₂ O | - | Na ⁺ , K ⁺ , NH ₄ ⁺ , Rb ⁺ , Cs ⁺ , Li ⁺ | 132 |
| 89 | Zirconium arsenate | Amorphous | As/Zr=1.53-1.96 | ZrO ₂ .84As ₂ O ₅ .nH ₂ O | 4.30 | Na ⁺ , K ⁺ , Cs ⁺ | 133 |
| 90 | Zirconium ferrocyanide | Amorphous | Fe/Zr=0.63 | - | 0.96 | NH ₄ ⁺ , Li ⁺ , Na ⁺ , Zn ²⁺ | 134 |
| 91 | Zirconium molybdate | Amorphous | Zr/Mo= 0.5-2.0 | - | 2.18 | - | 135 |
| 92 | Zirconium oxide | Amorphous | - | ZrO ₂ .4.7H ₂ O | 1.09 | Ca ²⁺ , Ba ²⁺ | 136 |
| 93 | Zirconium pyrophosphate | Amorphous | P/Zr=2.5-2.8 | - | - | Cu ²⁺ , Ni ²⁺ , Ba ²⁺ , Ca ²⁺ , Mg ²⁺ , Fe ³⁺ | 137 |
| 94 | Zirconium hypophosphate | Amorphous | Zr/P=0.57 | - | - | Multivalent metals | 138, 139 |
| 95 | Zirconium selenite | Amorphous | Zr/Se=1.23 | - | 0.48 | Ag ⁺ , Cu ²⁺ , Au ²⁺ | 140 |
| 96 | Zirconium silicate | Amorphous | Zr/Si=0.5 | - | 3.18 | Ag ⁺ , Ca ²⁺ , Cu ²⁺ , Cr ³⁺ , Th ⁴⁺ | 141, 142 |
| 97 | Zirconium tellurate | Amorphous | - | Zr(H ₂ TeO ₆).4H ₂ O | 2.80 | | 143, 144 |
| 98 | Zirconium oxalate | Crystalline | - | Zr(OH)C ₂ O ₄ H | 2.50 | Alkali metals | 145 |
| 99 | Zirconium tungstate | Amorphous | Zr/W=1.0-0.44 | - | - | Alkali metals | 146 |
| 100 | Zirconium polyphosphate | Amorphous | - | - | - | Na ⁺ , K ⁺ , Li ⁺ , Cs ⁺ , (NH ₄ ⁺ form) Ba ²⁺ , Co ²⁺ , Cu ²⁺ , Fe ³⁺ (H ⁺ form) | 147, 148 |
| 101 | Zinc silicate | Amorphous | Si/Zn=1.25 | - | 2.00 | - | 149 |
| 102 | Zinc ferro-cyanide | Amorphous | Zn/Fe=1.98 | Zn ₂ Fe(CN) ₆ | 6.10 | - | 150 |
| 103 | Zinc phosphate | Amorphous | - | - | - | - | 151 |

Table 1.2 Three-component ion exchange materials with their properties

| S. No. | Ion exchange Materials | Type | Composition | Empirical Formula | IEC (meq g ⁻¹) | Selectivity | References |
|--------|--|-------------------|---|---|----------------------------|---|------------|
| 1 | Amine tin hexacyano ferrate | - | | - | - | - | 152 |
| 2 | Ammonium dodeca molybdoantimonate | Crystalline | | (NH ₄) ₃ (Mo ₁₂ SbO ₄₀).11H ₂ O | - | - | 153 |
| 3 | Ammonium molybdophosphate | Crystalline | | (NH ₄) ₃ PMo ₁₂ O ₄₀ | 1.57 | - | 154 |
| 4 | Ammonium tungstophosphate | Crystalline | | (NH ₄) ₃ PW ₁₂ O ₄₀ | 0.66 | - | 155 |
| 5 | Anilinium zirconium phosphate | - | | (ZrO ₂) ₂ (C ₆ H ₅ NH ₂) ₂ .HPO ₄ .3.7H ₂ O | 1.87 | Co ²⁺ , Zn ²⁺ , Cd ²⁺ , Hg ²⁺ | 156 |
| 6 | Anilinium tin phosphate | - | | - | - | - | 157 |
| 7 | Chromium arsenophosphate | Amorphous | Cr:As:P=2:1:1 | [Cr ₂ O ₃ .H ₃ AsO ₄ .H ₃ PO ₄].nH ₂ O | - | K ⁺ | 158 |
| 8 | Cesium zirconium phosphate | - | | - | - | - | 159 |
| 9 | Chromium arsenosilicate | Amorphous | | 2 Cr ₂ O ₃ .2.5 As ₂ O ₅ . 3 SiO ₂ .nH ₂ O | - | K ⁺ | 160 |
| 10 | Cerium phosphosilicate | Amorphous | Ce:Si:P=2:5:4 | (CeO ₂) ₂ (SiO ₂) ₃ (H ₃ PO ₄) ₄ .nH ₂ O | - | - | 161 |
| 11 | Dipotassium tri-zinc hexa cyano ferrate | - | | - | - | - | 162 |
| 12 | Nickel aluminosilicate | Amorphous | | - | - | - | 163 |
| 13 | Stannic arsenoborate | Amorphous | | - | 0.99 | - | 164 |
| 14 | Stannic arsenosilicate | - | | - | - | - | 165 |
| 15 | Stannic boratomolybdate | Amorphous | Sn:B:Mo=1:1:1 | - | 1.12 | Zr ⁴⁺ , Th ⁴⁺ | 164 |
| 16 | Stannic boratophosphate | Amorphous | | - | 1.10 | - | 166 |
| 17 | Stannic boratosulphate | Amorphous | | - | 0.55 | - | 164 |
| 18 | Stannic boratotungstate | Amorphous | | - | 1.15 | - | 164 |
| 19 | Stannic iodophosphate | - | | - | - | - | 167 |
| 20 | Stannic molybdophosphate | - | Sn:Mo:P=1:0.33:2 | - | - | - | 168 |
| 21 | Tin(IV) arsenosilicate | - | | - | - | Amino acid | 169 |
| 22 | Tin(IV) vanadopyro-phosphate | Micro-crystalline | | - | 3.17 | - | 170 |
| 23 | Tin(IV) tungstovanado-phosphate | - | | - | - | - | 171 |
| 24 | Tin(IV) tungstoselenate | Crystalline | Sn/Se/W=7:1:18 | - | 1.43 | Ba ²⁺ | 172 |
| 25 | Titanium tungstophosphate | - | | - | - | - | 173 |
| 26 | Titanium phosphate ammonium tungstophosphate | - | | - | - | - | 174 |
| 27 | Titanium tungstoarsenate | - | | - | - | - | 175 |
| 28 | Titanium arsenosilicate | - | | - | - | Pb ²⁺ | 176 |
| 29 | Titanium vanadophosphate | - | | - | - | - | 177 |
| 30 | Titanium tungstovanado-phosphate | - | | - | - | Amines | 178 |
| 31 | Titanium phosphosilicate | Amorphous | | - | - | Zr ⁴⁺ , Nb ⁵⁺ , Cs ⁺ | 179 |
| 32 | Titanium aluminium silicate | - | | - | - | Pb ²⁺ | 180 |
| 33 | Titanium molydophosphate | - | | - | - | - | 181 |
| 34 | Titanium phosphate ammonium phosphomolybdate | - | | - | - | - | 182 |
| 35 | Titanium (IV) tungstosilicate | Crystalline | | - | 0.44 | - | 183 |
| 36 | Zirconium hydrogen arsenate hydrogen phosphate | Amorphous | | Zr(HAsO ₄)(HPO ₄).H ₂ O | - | - | 184 |
| 37 | Zirconium iodooxalate | Amorphous | Zr:IO ₃ :C ₂ O ₄ H=2:1:3 | (ZrO) ₂ (IO ₃)(HC ₂ O ₄) ₃ .nH ₂ O | - | - | 185 |

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| | | | | | | | |
|----|--|------------------|--|--|------|---|----------|
| 38 | Zirconium alumino pyrophosphate | - | | - | - | - | 186 |
| 39 | Zirconium arsenophosphate | Amorphous | Zr:As:P=2:1:1 | (ZrO ₂)(H ₃ AsO ₄)(H ₃ PO ₄).nH ₂ O | - | Rb ⁺ , Ag ⁺ , Tl ⁺ | 187, 188 |
| 40 | Zirconium arsenosilicate | Crystalline | | - | - | Hg ²⁺ | 189 |
| 41 | Zirconium phosphoantimonate | - | | - | - | - | 190 |
| 42 | Zirconium phosphoborate | - | Zr:P:B=1:1:1 | - | - | - | 191 |
| 43 | Zirconium phthalophosphate | - | | - | - | - | 192 |
| 44 | Zirconium vanadophosphate | - | | - | - | Li ⁺ , Na ⁺ , NH ₄ ⁺ | 134 |
| 45 | Zirconium sulphosalicylate | Semi-crystalline | | - | - | - | 193, 194 |
| 46 | Zirconium phosphosilicate | Amorphous | | - | 2.2 | Cs ⁺ | 195, 196 |
| 47 | Zirconium molybdophosphate | - | | ZrH ₂ MoO ₂ .xH ₂ O | 1.6 | - | 197 |
| 48 | Zirconium(IV) selenophosphate | - | | (ZrO) ₅ (OH) ₄ (HSeO ₃) ₂ (H ₂ PO ₄).2H ₂ O | - | - | 198 |
| 49 | Zirconium(IV) iodomolybdate | - | | - | - | Hg ²⁺ | 199 |
| 50 | Zirconium(IV) iodophosphate | - | | - | 1.78 | - | 200 |
| 51 | Zirconium titanium phosphate | Crystalline | Zr/Ti=3.25 | Zr _x Ti _{1-x} (HPO ₄) ₂ .H ₂ O | 6.87 | - | 201-206 |
| 52 | Zirconium molybdovanadate | - | Zr:V:Mo=1.68:1:0.08 8 | | - | Li ⁺ , Na ⁺ | 207 |
| 53 | Zirconium tungstoarsenate | Amorphous | | - | - | UO ₂ ²⁺ , Cs ⁺ , Tl ⁺ | 208 |
| 54 | Zirconium(IV) tungstophosphate | - | Zr:W:P= 18.8%:25.4%:4.3% | | 1.00 | Pb ²⁺ | 209, 210 |
| 55 | Zirconium cerium phosphate | - | | - | - | - | 211 |
| 56 | Zirconium(IV) 4-amino 3-hydroxy naphthalene sulphonate | - | | - | - | Hg ²⁺ | 212 |
| 57 | Zirconium bis (monoocetyl) phosphate | Crystalline | | - | - | - | 213 |
| 58 | Zirconium(IV) iodovanadate | Amorphous | Zr/IO ₃ /VO ₃ =2:1:3 | (ZrO ₂)(IO ₃)(V ₅ O ₉) | 4.20 | Electron exchanger | 214 |
| 59 | Zirconium(IV) tungsto-molybdate | Amorphous | | (ZrO)(OH) ₂ (H ₂ WO ₄) ₄ (H ₂ MoO ₄) ₃ . 8H ₂ O | 2.40 | | 215 |
| 60 | Acryl amide zirconium phosphate | Crystalline | | - | 2.26 | - | 216 |

COMPOSITES

The main advantages of synthetic organic ion exchange resins are their high capacity, wide applicability, wide versatility and low cost relative to some synthetic inorganic materials. But they also have some limitations.

The main limitations are their limited radiation and thermal stabilities. At a total absorbed radiation dose of 10^9 to 10^{10} rads most organic resins will exhibit a severe reduction in their ion exchange capacity (a 10 to 100% capacity loss), due to physical degradation at both the molecular and macroscopic level. The conversion of inorganic ion exchange materials has been taking place into composite ion exchange materials is the latest development in this discipline.

Sol-gel derived composite materials have found numerous applications in the areas of chemistry, biochemistry, engineering, and material science [217]. The 'organic-inorganic' hybrid materials prepared via the sol-gel technique have attracted significant attention in the literature [218]. The combination of organic and inorganic precursors yields hybrid materials that have mechanical properties not present in the pure materials. Organic-inorganic composite ion exchange materials show the improvement in its granulometric properties that makes them more suitable for the application in column operations. The binding of organic polymer also introduces the better mechanical properties in the end product, i.e. composite ion exchange materials.

More recently, some organic-inorganic composite ion exchange materials have been developed. Khan et al. have reported polypyrrole-Th(IV) phosphate [219], polyaniline-Sn(IV) arsenophosphate [220] and polystyrene-Zr(IV) tungstophosphate [221] used for the selective separation of Pb^{2+} , Cd^{2+} , Hg^{2+} respectively, and ion exchange kinetics of M^{2+} - H^+ exchange and adsorption of pesticide [222] have also carried out on these materials. Beena Pandit et al. have synthesized such type of ion exchange materials, i.e. o-chlorophenol Zr(IV) tungstate and p-chlorophenol Zr(IV) tungstate [223]. Styrene supported Zr(IV) phosphate hybrid material [224], and fibrous ion exchange materials such as polymethyl methacrylate, polyacrylonitrile, styrene and pectin based Ce(IV) phosphate, Th(IV) phosphate and Zr(IV) phosphate [225] have been reported by Varshney et al. have numerous analytical applications. These materials can be used as ion exchanger membranes and electrodes.

Polyacrylonitrile fibers and zeolite composites have also been reported in literature. Polyaniline-Zr(IV) tungstophosphate has been synthesized by Gupta et al. [226], which was used for the selective separation of La^{3+} and UO_2^{2+} . Chanda et al. reported polyacrylic acid coated SiO_2 as a new ion exchange material. A polymeric/inorganic hybrid sorbent has also been used for arsenic removal [227].

Ion exchangers find applications in a wide variety of industrial, domestic, governmental and laboratory operations. The composite ion exchangers show some better granulometric properties that facilitates its stability in column operations especially for separation, filtration and preconcentration of ionic species. The column operation suitability makes it more convenient in regeneration of exhausted beds also. These hybrid ion exchangers have good ion exchange capacity, high stability, reproducibility and selectivity for heavy metal ions indicating its useful environmental applications. In general these materials have their applications in the following disciplines:

- Water softening [228, 229]
- Separation and preconcentration of metal ions [230]
- Nuclear separations [231]
- Catalysis [232]
- Redox system [233]
- Electrodialysis [234]
- Hydrometallurgy [235]
- Effluent treatment [236]
- Ion exchange fibers [237-239]
- Ion-selective electrodes [219, 240]

Acknowledgement

The author (Dr. Mu. Naushad) is highly thankful to The Dean (Dr. Manoj K. Pandey), Manager (S. Vishwanathan) and HOD (Dr. Ranjana Dubey), SRM-IST, SRM University for providing all necessary facilities.

References

- [1] The second book of Moses, Exodus, Chapt.15, verse 25.
- [2] B.A. Aristotle, works, 7 (about 330, B.C.), 933 b.
- [3] H.S. Thompson, *J. Roy. Agr. Soc. Eng.* **11**(1850) 68
- [4] J.T. Way, *Agr. Soc. Eng.* **11** (1850) 313
- [5] E. Eichorn, *Ann. Phys. Chem.* **105** (1850) 126
- [6] A. Rimpler, Intern. Congr. f. angew. Chem., Berlin (1903) 59
- [7] J. Lamberg, *Z. Dent. Geol. Gos.* **22** (1870) 355
- [8] G. Wiegner, *J. Land Wirisch* **60** (1912) 111
- [9] O. Folin, R. Bell, *J. Biol. Chem.* **29** (1917) 329

- [10] R. Gans, *Jahrb. preuss. geol. Landesanstalt* **26** (1905) 179
- [11] B.A. Adams, E.L. Holmes, *J. Chem. Soc. Ind.*, **54T** (1935) 1
- [12] K.A. Kraus, H.O. Phillips, *J. Amer. Chem. Soc.* **78** (1956) 644
- [13] K.A. Kraus, H.O. Phillips, T.A. Carlson, J.S. Johnson, Proceeding of second international conference on peaceful uses of Atomic Energy, Geneva, 1958, Paper No.15/P/1832, United Nations, 28, 3 (1958).
- [14] C.B. Amphlett, Proceeding on peaceful uses of Atomic Energy, Geneva, 1958, paper No.15/P/171, United Nations (1958).
- [15] C.B. Amphlett, L.A. Mcdonald, *Proc. Chem. Soc.* (1962) 276
- [16] C.B. Amphlett, Inorganic ion exchangers, Elsevier Publishing Co., Amsterdam, (1964).
- [17] V. Vesely, V. Pekarek, *Talanta* **19** (1972) 219
- [18] A. Clearfield, J.A. Styne, *J. Inorg. Nucl. Chem.* **26** (1972) 117
- [19] A. Clearfield, A.M. Laudis, A.S. Medina, J.M. Troup, *J. Inorg. Nucl. Chem.* **35** (1973) 1099
- [20] G. Alberti, S. Allulli, *J. Chrom.* **32** (1968) 379
- [21] G. Alberti, U. Costantino, *J. Chrom.* **50** (1970) 484
- [22] H.F. Walton, *Anal. Chem.* **42** (1972) 86
- [23] H.F. Walton, *Anal. Chem.* **48** (1976) 52
- [24] Sinha, Panicker, P.K. Amalraj, R.V. Krishnasamy, *Waste Management* **15** (1995) 149
- [25] Sinha, P.K. Panicker, P.K. Amalraj, R.V. Krishnasamy, *Radiochem. Acta* **73** (1996) 157
- [26] Sinha, P.K. Panicker, P.K. Amalraj, R.V. Krishnasamy, *Radiochim. Acta* **65** (1994) 125
- [27] Sinha, P.K. Krishnasamy, *J. Nucl. Sci. Technol.* **33** (1996) 333
- [28] J.D. Kurbatov, J.L. Kulp, E. Mack, *J. Amer. Chem. Soc.* **67** (1945) 1923
- [29] M.H. Kuratov, G.B. Wood, J.D. Kurbatov, *J. Chem. Phys.* **19** (1951) 258
- [30] W.D. Tucker *et al.*, Brook haven. Natl. Lab, Report BNL-3749 (1958).
- [31] S.A. Voznesenku, G.A. Sereda, P.F. Polgikh, L.I. Basakov, Report of soviet scientists to Second International Conf. Peaceful Uses of Atomic Energy, 189 (1958).
- [32] B.P. Nikol'skii, *Zh. Fiz. Khim.* **5** (1934) 266
- [33] S.N. Tewari, *Kolloid-Zeitschrift* **149** (1956) 65
- [34] Y. Inoue, H. Yamazaki, *Bull. Chem. Soc. Jpn.* **53**(4) (1980) 811
- [35] Y. Inoue, M. Tsuji, *Bull. Chem. Soc. Jpn.* **51**(2) (1978) 479
- [36] Y. Inoue, M. Tsuji, *Bull. Chem. Soc. Jpn.* **51**(3) (1978) 749
- [37] A.K. De, S.K. Das, *J. Ind. Chem. Soc.* **53**(10) (1976) 1063
- [38] A.K. De, N.D. Chawdhury, *Chromatographia* **11**(10) (1978) 586
- [39] A.K. De, S.K. Das, *Sep. Sci. Technol.* **13**(5) (1978) 465
- [40] A.K. De, S.K. Das, P. Charabarty, *J. Inorg. Nucl. Chem.* **43**(8) (1981) 1909
- [41] S. Kuamura, H. Kuraku, K. Kurotaki, *Anal. Chim. Acta* **49** (1970) 317
- [42] L.H. Baetsle, D. Huys, D. van Deyck, *J. Inorg. Nucl. Chem.* **27** (1965) 2385
- [43] R.B. Hahn, H.C. Klein, *Anal. Chem.* **40** (1968) 1135
- [44] W. Drehaus, M. Jekel, U. Hildebrandt, *J. Water Services Res. & Tech.-Aqua* **47**(1) (1998) 30
- [45] Z. Goerlich, *Zes. Nauk. Univ. Jagiel. Nauk.Chem.* **7** (1962) 5
- [46] Yu. P. Novikov *et al.*, *Radiokhimiya* **19** (1977) 660
- [47] Yu. P. Novikov *et al.*, *Radiokhimiya* **19** (1977) 653
- [48] M. Qureshi, J.P. Rawat, A.P. Gupta, *Ind. J. Technol.* **15** (1977) 80
- [49] S. Aleksandrov, *God. Sofii. Univ. Khim. Fak.* **68** (1977) 291
- [50] J.P. Rawat, J.P. Singh, *Chromatographia* **10** (1977) 205
- [51] T.E. Erikson, S.O. Engman, *Acta Chem. Scand.* **26** (1972) 3333
- [52] J.A. Bittles, U.S. Patent, 3, 499, 537 (1970).
- [53] L.E. Williams, R.K. Mays, U.S. Appl., 11, 522 (1974).
- [54] E. Kobayashi, T. Goto, *Kogyo Kagaku Zasshi* **73** (1970) 692
- [55] Q. Long, Z. Xue, F. Zhuanli Sheging Gongakai Shuomingshu CN 85, 101, 1981, 29 Apr. (1987), Appl. 01, Apr. 6 (1985).
- [56] M. Abe, T. Ito, *Bull. Chem. Soc. Jpn.* **41** (1968) 33 & **42** (1969) 2683
- [57] C. Janardhan, S.M.K. Nair, *Analyst* (London) **115** (1990) 85
- [58] K.G. Varshney, S.M. Maheshwari, *Ecotox. Environ. Safety.* **18** (1989) 1
- [59] K.G. Varshney, U. Sharma, S. Rani, A. Premdas, *Sep. Sci. Technol.* **17** (1982) 1527
- [60] R. Boeckl, K.H. Leiser, *Radio. Chim. Acta.* **20** (1973) 51
- [61] A.P. Gupta, M. Qureshi, Y. Sunanda, *Ind. J. Chem.* **22A**(8) (1983) 721
- [62] J.P. Rawat, K.P.S. Muktawat, *Chromatographia* **11** (1978) 513
- [63] P.S. Anand, D.R. Baxi, *Ind. J. Tech.* **16** (1978) 198
- [64] M.K. Rahman, A.M.S. Haq, B.A. Maroof, *J. Chromatogr.* **67**(2) (1972) 389
- [65] V. Ghoulipour, S.W. Husain, *Analytical Sciences* **16** (2000) 1079
- [66] J.S. Gill, S.N. Tandon, *Talanta* **19** (1972) 1355
- [67] G. Alberti, U. Costantino, E. Toracca, F. Digregorio, *J. Inorg. Nucl. Chem.* **31** (1969) 3195
- [68] S.K. Srivastava, R.P. Singh, S. Agrawal, S. Kumar, *J. Radioanal. Chem.* **40** (1977) 7
- [69] A.K. De, S.K. Das, *Sep. Sci.* **11** (1976) 183
- [70] K.H. Koning, E. Meyn, *J. Inorg. Nucl. Chem.* **29** (1967) 1153
- [71] J.S. Gill, S.N. Tandon, *Talanta* **20** (1973) 585
- [72] T. Akiyama, I. Tomita, *J. Inorg. Nucl. Chem.* **35** (1973) 2871
- [73] W.E. Prout, E.R. Russel, H.J. Groh, *J. Inorg. Nucl. Chem.* **27** (1965) 473
- [74] M. Walid, W. Sokyo, B. Katsser, *Talanta* **20** (1973) 405
- [75] M.T.O. Valentini, S. Malomi, V. Maxia, *J. Inorg. Nucl. Chem.* **34** (1972) 1427
- [76] E.V. Kazakar, I.F. Karpura, *Ser. Fiz. Khim.* **2** (1966) 139
- [77] T. Akiyama, I. Tomita, *J. Inorg. Nucl. Chem.* **35** (1973) 2871
- [78] J. Mathewand, S.N. Tandon, *Chromatographia* **9** (1976) 235
- [79] G.T. Desai, D.R. Baxi, *Ind. J. Technol.* **16** (1978) 201

- [80] M.Qureshi, K.G. Varshney, N. Fatima, *J. Chromatogr.* **169** (1979) 365
- [81] M. Qureshi, R. Kumar, H.S. Rathore, *Talanta* **19** (1972) 1377
- [82] L. Szirtes, L. Zsinka, *J. Chrom.* **102** (1974) 105
- [83] W.U. Malik, S.K. Srivastava, V.M. Bandari, S. Kumar, *J. Inorg. Nucl. Chem.* **38** (1976) 343
- [84] J.P. Rawat, P.S. Thind, *Canad. J. Chem.* **54** (1976) 1892
- [85] V. Kourin, J. Rais, B. Millon, *J. Inorg. Nucl. Chem.* **26** (1964) 1111
- [86] J.P. Rawat, T. Khatoon, H. Shankar, *Ann. Di. Chimica* **68** (1978) 913
- [87] J.P. Rawat, J.P. Singh, *Canad. J. Chem.* **54** (1976) 2534
- [88] C. Janardhan, S.M.K. Nair, C.P. Savariar, *Ind. J. Chem.* **28A** (1989) 693
- [89] V.A. Winkler, E. Thilo, *Z. Anorg. Allg. Chem.* **346** (1965) 92
- [90] V.N. Krylov, K.P. Larina, *Zh. Fiz. Khim.* **52** (1978) 2040
- [91] A. Clearfield, J.R. Thomas, *J. Inorg. Nucl. Chem. Lett.* **5** (1969) 775
- [92] V.N. Krylov, K.P. Larina, *Zh. Fiz. Khim.* **54**(10) (1980) 2498
- [93] M. Fedoroff, L. Dabove, *C.R. Acad. Sci. C.* **275** (1979) 1189
- [94] J.P. Rawat, S.Q. Mujtaba, R.A. Khan, *Acta Chem. Ind.* **5** (1979) 108
- [95] P.S.Thind, T.K. Bindal, *J. Liq. Chromatogr.* **3** (1980) 573
- [96] G.C. Gonzalez, R.A.G. Carvalho, *J. Chromatogr.* **136** (1977) 176
- [97] H.O. Phillips, K.A. Kraus, *U.S. Atomic Energy Comm.* **81** (1962) 3320
- [98] M. Qureshi, A.P. Gupta, J.S. Thakur, V.P. Singh, *Sep. Sci. Technol.* **15** (1980) 1255
- [99] V.V. Volkhin, T.N. Tatlieva, M.V. Zill, *Berman Izv. Akad Nauk. USSR, Neorg. Mater.* **12** (1976) 1634
- [100] J.P. Gupta, D.V. Nowell, M. Qureshi, A.P. Gupta, *J. Inorg. Nucl. Chem.* **40** (1978) 454
- [101] Y.V. Egorov, Y.I. Sukharev, N.N. Pstovalov, *Izobert, Prom Obraztry. Tovarnye. Znaki*, **22** (1966) 46
- [102] M. Qureshi, R. Kumar, H.S. Rathore, *J. Chem. Soc. A* (1970) 272
- [103] Y. Inoue, *J. Inorg. Nucl. Chem.* **26** (1964) 2241
- [104] M. Qureshi, K.G. Varshney, *J. Inorg. Nucl. Chem.* **30** (1968) 3081
- [105] M. Qureshi, V. Kumar, N. Zehra, *J. Chromatogr.* **67** (1972) 351
- [106] N. Jattreziac-Renault, *J. Inorg. Nucl. Chem.* **40** (1978) 539
- [107] M. Qureshi, J.P. Rawat, *J. Inorg. Nucl. Chem.* **30** (1968) 1083
- [108] J.D. Donaldson, M.J. Fuller, *J. Inorg. Nucl. Chem.* **30** (1968) 1083
- [109] M. Qureshi, S.A. Nabi, *Talanta* **19** (1972) 1033
- [110] M. Qureshi, S.A. Nabi, N. Zehra, *Can. J. Chem.* **55** (1977) 1667
- [111] M. Qureshi, K.G. Varshney, A.H. Israili, *J. Chromatogr.* **59** (1971) 141
- [112] M. Abe, T. Ito, *Nippon Kagaku Zasshi* **86** (1965) 1259
- [113] K.A. Kraus, H.O. Phillips, Oak Ridge Report, ORNL-50, 2983 (1960).
- [114] J.P. Rawat, S.O. Mujtaba, *Canad. J. Chem.* **53** (1975) 2685
- [115] M. Qureshi, J.P. Gupta, V. Sharma, *Anal. Chem.* **45** (1973) 1901
- [116] J.P. Rawat, K.P.S. Muktawat, *J. Liq. Chrom.* **4** (1981) 85
- [117] M. Qureshi, J.S. Thakur, H.S. Rathore, P.M. Qureshi, *React. Func. Polym.* **1** (1983) 101
- [118] G. Alberti, U. Costantino, *J. Chrom.* **50** (1970) 482
- [119] M. Qureshi, S.A. Nabi, *J. Chem. Soc. A* (1971) 139
- [120] A.K. De, S.K. Das, *Chromatographia* **1** (1978) 50
- [121] C. Heitner-wrguin, A.I. Mun, *J. Inorg. Nucl.Chem.* **28** (1966) 2379
- [122] G. Alberti, M.A. Massucci, *J. Inorg. Nucl. Chem.* **32** (1970) 719
- [123] M. Qureshi, W. Hussain, *J. Chem. Soc. A* (1970) 1204
- [124] W. Grace, British Patent, 1, 181089 (1970).
- [125] M. Qureshi, V. Kumar, *J. Chem. Soc. A* (1970) 1488
- [126] M. Qureshi, J.P. Gupta, *J. Chem. Soc. A* (1969) 1755
- [127] M. Qureshi, H.S. Rathore, *J. Chem. Soc. A* (1969) 2515
- [128] M. Qureshi, R. Kumar, H.S. Rathore, *Anal. Chem.* **44** (1972) 1081
- [129] M. Qureshi, K.G. Varshney, S.K. Kabiruddin, *Canad. J. Chem.* **50** (1972) 2071
- [130] K.H. Lieser, J. Bastian, A.B.H. Hecker, W. Hild, *J. Inorg. Nucl. Chem.* **29** (1967) 815
- [131] C. Heitner, Wirguin, A. Albu-Yaron, Belg, Patent, 10, 668 (1965).
- [132] S.N. Tandon, J. Mathew, *J. Radioanal. Chem.* **27** (1975) 315
- [133] A. Clearfield, G.D. Smith, B.H. Hammond, *J. Inorg. Nucl. Chem.* **30** (1968) 277
- [134] J.S. Gill, S.N. Tandon, *J. Radioanal. Chem.* **13** (1973) 391
- [135] A. Clearfield, R.H. Blessing, *J. Inorg. Nucl. Chem.* **34** (1972) 2643
- [136] A.L. Ruvarac, M.I. Tratanj, *J. Inorg. Nucl. Chem.* **34** (1972) 3893
- [137] D. Cvjeticanin, N. Milic, *Bull. Boris Kidrich. Inc. Nucl. Sci.* **15** (1964) 73
- [138] K.H. Koning, K. Demel, *J. Chrom.* **39** (1969) 101
- [139] K.H. Koning, F. Hoyer, *Atompramis* **11** (1965) 275
- [140] M.J. Nunes, D.A.Costa, M.A.S. Jeronimo, *J. Chromatogr.* **5** (1968) 546
- [141] K.V. Lad, D.R. Baxi, *Ind. J. Tech.* **10** (1972) 224
- [142] T.P. Tang, P. Sun, K.Y. Chan, *Hua-Hsuch* (1965) 33
- [143] M.K. Rahman, A.M.S. Haq, *J. Chrom.* **53** (1970) 613
- [144] L. Zsinka, L. Szirtes, Proc. Second Hungarian conference Ion exch., Balatenzepalk, 2, 627 (1969).
- [145] L.O. Mederios, *J. Inorg. Nucl. Chem.* **28** (1966) 599
- [146] N.U. Osipora, E.S. Biochinova, *Zh. Prikl. Khim* (Leningrad) **41** (1969) 2186
- [147] E.S. Biochinova, E. Vkharitopnova, *Zh. Prikl. Khim* (Leningrad) **40** (1967) 1833
- [148] E.S. Biochinova, E. Vkharitopnova, *Zh. Prikl. Khim* (Leningrad) **38** (1965) 674
- [149] M.V. Goloshehapov, S.K. Khodzhibaev, *Izv. Voroneh. Gos. Pedagos. Inst.* **5** (1966) 55
- [150] M. Qureshi, K.G. Varshney, F. Khan, *J. Chromatog.* **65** (1972) 547
- [151] N. Mishio, A. Kamoshida, S. Kodoya, T. Ishihara, *J. Atomic Energy. Soc. Jpn.* **6** (1964) 2
- [152] K.G. Varshney, S. Naheed, *J. Inorg. Nucl. Chem.* **39** (1977) 2075

- [153] R.P. Singh, R.P. Khatri, J. Dubois, S.S. Gaur, M. Abe, *J. Chem. Soc., Dalton Trans.* (1990) 947
- [154] R. Van, J. Smith, W. Robb, J.J. Jacobs, *Nucleonics* **17**(g) (1969) 116
- [155] Yu Xintian, Sun Zhaoxiang, *Chim. J. React. Polym.* **7**(1) (1998) 25
- [156] D.K. Singh, P. Mehrota, *Bull. Chem. Soc. Jpn.* **63** (1990) 3647
- [157] D.K. Singh, A. Darbari, *Bull. Chem. Soc. Jpn.* **61** (1988) 1369
- [158] K.G. Varshney, A.A. Khan, *J. Inorg. Nucl. Chem.* **41** (1979) 241
- [159] A. Dyer, A.M. Yosuf, *J. Inorg. Nucl. Chem.* (1979) **41** 1479
- [160] K.G. Varshney, A.A. Khan, M.S. Siddiqui, *Colloids Surf.* **36** (1989) 405
- [161] K.G. Varshney, A. Premdas, *J. Liq. Chromatogr.* **4** (1981) 245
- [162] T.N. Dave, V.K. Induse Khar, *J. Chem. Technol. Biotechnol.* **36** (1986) 31
- [163] N.Z. Rajje, D.R. Stojakovic, *Croat. Chem. Acta.* **60** (1987) 735
- [164] S.A. Nabi, Z.M. Siddiqui, W.U. Farooqui, *Bull. Chem. Soc. Jpn.* **55** (1982) 503
- [165] K.G. Varshney, U. Sharma, S. Rani, *Ind. J. Technol.* **22** (1984) 99
- [166] S.A. Nabi, Z.M. Siddiqui, W.U. Farooqui, *Bull. Chem. Soc. Jpn.* **55** (1982) 2642
- [167] S.A. Nabi, W.A. Siddiqui, *J. Liq. Chromatogr.* **8**(6) (1985) 1159
- [168] M. Qureshi, N.A. Shakeel, S.N.A. Rizvi, A.P. Gupta, *J. Ind. Chem. Soc.* **64** (1987) 15
- [169] Y. Su, M.L. Balmer, B.C. Bunker, *Mater. Res. Soc. Symp. Proc.* **465** (1997) 457
- [170] M.G. Marageh, S.W. Hussain, A.R. Khanchi, *J. Radioanal. Nucl. Chem.* **241** (1999) 139
- [171] K.G. Varshney, A.A. Khan, *J. Inorg. Nucl. Chem.* **41** (1979) 241
- [172] S.A. Nabi, Z.M. Siddiqui, *Bull. Chem. Soc. Jpn.* **58** (1985) 724
- [173] X. Yu, Z. Sun, Chin, *J. React. Funct. Polym.* **7** (1998) 25
- [174] J.P. Rawat, M.A. Khan, *Ann. Chem.* **69** (1979) 525
- [175] K.G. Varshney, K. Agrawal, S. Agrawal, V. Saxena, A.R. Khan, *Coll. Surf.* **29** (1988) 175
- [176] J.N. Singh, S.N. Tandon, G.S. Gill, *Ind. J. Chem. A* **20A** (1981) 1110
- [177] W.A. Siddiqui, S.T. Ahmad, *Chem. Anal. (Warsaw)* **42** (1997) 377
- [178] S.J. Naqvi, D. Huys, L.H. Baetsle, *J. Inorg. Nucl. Chem.* **33** (1971) 23
- [179] S. Kuznicki, R.J. Madon, S. Gerald, K.A. Thrush, *Eur. Pat. Appl. E.P.* 405, 978, 28 (1989).
- [180] Z. Sun, S. Tao, *Li Zi Jiao Huan Yu Xifu* **6** (1990) 431
- [181] X. Yu, Z. Sun, *Beijing Shifan Daxue Xuebao Ziranxueban* **32** (1996) 243
- [182] X. Xintian, Z. Sun, X. Sun, *Li Zi Jiao Huan Yu Xifu* **13** (1997) 239
- [183] Z.M. Siddiqui, D. Pathania, *J. Chromatogr. A* **987** (2003) 147
- [184] L.M. Berardelli, A. Laginestra, M.A. Massucci, K.G. Varshney, *J. Chem. Soc. Dalton Trans.* **9** (1985) 1737
- [185] P.V. Singh, J.P. Rawat, N. Rahman, *Ind. J. of Chemistry* **41A** (2002) 1616
- [186] T. Nishi, I. Fugiwara, *Kyoto Daigaku Kogaku Kenkyusho Iho* **39** (1971) 23
- [187] N.J. Singh, S.N. Tandon, *J. Radioanal. Chem.* **49** (1979) 195
- [188] K.G. Varshney, A. Premdas, *Sep. Sci. Technol.* **18**(1) (1983) 59
- [189] K.G. Varshney, S. Agrawal, K. Varshney, *Sep. Sci. Technol.* **18**(11) (1983) 59
- [190] A.K. Mishra, R.P.S. Rajput, *J. Planar Chromatogr.* **3** (1990) 83
- [191] P.S. Thind, S.K. Mittal, S. Gujral, *Synth. React. Inorg. Met. Org. Chem.* **18** (1988) 593
- [192] E.S. Boichinova, G.N. Strelnikova, *Zh. Prikl. Khim. (Leningrad)* **40** (1967) 1443
- [193] E.S. Boichinova, R.B. Chetverina, *Zh. Prikl. Khim. (Leningrad)* **41** (1968) 2656
- [194] S.A. Nabi, A. Islam, N. Rahman, *Ann. Chim. Sci. Mat.* **2**(7) (1997) 463
- [195] D. Naumann, *Kerenergie* **6** (1963) 173
- [196] K. V. Barsukova, G.N. Radionova, *Radio Kimiya* **14** (1972) 225
- [197] B. Buna, U. Chudasama, *Bull. Mater. Sci.* **19** (1996) 405
- [198] S.Z. Qureshi, N. Rahman, *Bull. Chem. Soc. Jpn.* **60** (1989) 2627
- [199] S.Z. Qureshi, N. Rahman, *Ind. J. Chem. Sec. A* **28A** (1989) 349
- [200] S.A. Nabi, R.A.K. Rao, W.A. Siddiqui, *J. Liq. Chromatogr.* **6**(4) (1983) 777
- [201] Y. Yazawa, T. Eguchi, K. Takaguchi, I. Tomita, *Bull. Chem. Soc. Jpn.* **53** (1979) 2923
- [202] S.K. Shakshooki, N. Naqvi, J. Kowalczyk, S. Khalil, M. Rais, F. Tarish, *Reac. Funct. Polym. Ion exch. Sorbent* **7** (1988) 221
- [203] S.K. Shakshooki, L. Szites, O. Azzabi, N. Naqvi, J. Kowalczyk, *J. Radioanal. Nucl. Chem.* **121** (1988) 175
- [204] S.K. Shakshooki, L. Szites, A. Dehair, Y. Elmismary, S. Haranga, N. Benfaid, A. Benhameed, A-Maiouf, *J. Radioanal. Nucl. Chem.* **121** (1988) 185
- [205] S.K. Shakshooki, L. Szites, Y.V. Yakovlev, *J. Radioanal. Nucl. Chem.* **145** (1988) 281
- [206] R. G. Safina, N.E. Denisova, E.S. Biochinova, *Zh. Prikl. Khim.* **46** (1973) 2432
- [207] A.K. Jain, S. Agrawal, R.P. Singh, *J. Radiochem.* **54** (1979) 171
- [208] A.P. Gupta, P.K. Varshney, K. Pradeep, *Synth. React. Inorg. Met-Org. Chem.* **28** (1998) 105
- [209] S.K. Mittal, P. Singh, *J. New Mat. Electrochem. System* **4** (2001) 221
- [210] T. Nishi, I. Fujihara, *Kyoto Daigaku Kagabu Kenkyusho Iho* **39** (1971) 23
- [211] S.Z. Qureshi, G. Asif, M.R. Khayar, *Ann. Chim.* **24** (1999) 545
- [212] Z. Sun, X-Lui, *Beijing Shifan Daxue Xuebao Ziranxueban* **32** (1996) 102
- [213] J.P. Rawat, R.A. Khan, *Ind. J. Chem. A* **19** (1980) 925
- [214] P.V. Singh, J.P. Rawat, N. Rahman, *Talanta* **59** (2003) 443
- [215] S.A. Nabi, Mu. Naushad, Inamuddin, *J. Hazard. Mater.* **142** (2007) 404

- [216] K.G. Varshney, V. Jain, N. Tayal, *Ind. J. Chem. Technol.* **10** (2003) 186
- [217] M.M. Collinson, *Crit. Rev. Anal. Chem.* **29** (1999) 289
- [218] G. Philipp H. Schmidt, *J. Non-Cryst. Solids* **63** (1984) 283
- [219] A.A. Khan, Inamuddin, M.M. Alam, *Mater. Res. Bull.* **40** (2005) 289
- [220] A.A. Khan, Ram Niwas, K.G. Vershney, *Coll. Sur. (A)* **150** (1999) 7
- [221] A.A. Khan, Ram Niwas, K.G. Vershney, *Ind. J. Chem.* **37A** (1998) 469
- [222] A.A. Khan, R. Niwas, M.M. Alam, *Indian J. Chem. Technol.* **9** (2002) 256
- [223] B. Pandit and U. Chudasma; *Bull. Mater. Sci.* **24**(3) (2001) 265
- [224] K.G. Varshney, A.H. Pandith; *Chem. Environ. Res.* **5** (1996) 1
- [225] K.G. Varshney, P. Gupta, A. Agrawal; 22nd National Conference in Chemistry '03, Indian Council of Chemists, I.I.T., Roorkee, (2003).
- [226] Saiqa Ikram; "Ph.D Thesis", D.C.E., Delhi (India), p. 84 (2000).
- [227] M.J.Demarco, a.k.Sengupta, J.E. Greenleaf, *Water Res.* **37**(1) (2003) 164
- [228] R. Gans, *Jahrb. Preuss. Geol. Landesanstalt* (Berlin), **26** (1905) 179 & **27** (1906) 63
- [229] S.D. Strauss, *Power* **128** (1984) 18
- [230] J.D. Mulik, E. Sawicki, *Environ. Sci. Technol.* **13** (1975) 804
- [231] J.E. Miller, N.E. Brown, J.L. Krumkans, D.E. Trudell, R.G. Anthony, C.V. Philip, W.W. Schulz, N.J. Lombardo, (Eds.), Plenum, New York, p. 269, 1998.
- [232] A. Clearfield, D.S. Thakur, *Appl. Catal.* **26** (1986) 1
- [233] A. LaGinestra, C. Ferragina, M.A. Massucci, P. Patrono, R. DiRocco, A.A.G. Tomoilson, *Gazz. Chim. Ital.* **113** (1983) 357
- [234] K.H. Meyer, W. Strauss, *Helv. Chim. Acta* **23** (1940) 795
- [235] A.B. Mindler, C. Paulson, National Meeting of the American Institute of Mining and Metallurgical Engineers, Los Angeles, Calif, 1953.
- [236] B.A. Bolto, L. Pawlowaski, *Effluent Water Treat. J.* **23**(6) (1983) 55, 157, 208, 233, 317, 371
- [237] P. Bajaj, D.K. Paliwal, *Indian J. Fibre Text. Res.* **16** (1991) 89
- [238] M.H. Kotze, F.L.D. Cloete, *Ion Exch. Adv., Proc. IEX '92*, (1992) 366
- [239] P. Bajaj, M. Goyal, R.V. Chavan, *J. Appl. Polym. Sci.* **51** (1994) 423
- [240] A.A. Khan, M.M. Alam, *React. Funct. Polym.* **55** (2003) 277