Reviews—Fuel cell and ion-exchange

Recent Advances in Inorganic Ion-Exchangers in Chinese Universities

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Abstract

The recent advances in inorganic ion-exchangers in Chinese universities are briefly reviewed in the following groups: (1) clay minerals, (2) zeolites, (3) hexacyanoferrates, (4) salts of heteropoly acids, (5) oxides and hydrous oxides. The preparations, the ion exchange properties and the applications of these inorganic ion exchangers are presented and discussed. Some representative research articles in this field are introduced in detail.

1. Introduction

Historically, inorganic ion exchangers were studied at first for the practical applicability of ion exchange. The first monograph on inorganic ion-exchangers was published in 1964 by Amphlett\(^1\). Recently, the inorganic ion-exchangers have been widely investigated by Chinese universities and substantial advances made in this area, because of their increasing importance in application, particularly in the application in nuclear science and technology.

Here, I will describe recent research on five groups of inorganic ion-exchangers in Chinese universities; (1) clay minerals\(^2\), (2) zeolites\(^3\), (3) hexacyanoferrates\(^4\), (4) salts of heteropoly acids\(^4\), (5) oxides and hydrous oxides\(^4,5\).

Clay minerals are layer silicates and belong to the group of siliceous ion-exchangers. They have a variety of structural types and are primarily cation exchangers. To a lesser extent they exhibit simultaneous uptake of anions. The cation exchange capacity (CEC) of clay minerals is low. However, the CECs and ion exchange properties of clay minerals are very important for arable soils. Clay minerals have more or less rigid, two-dimensional structures. Most of the clay minerals have exchange sites only on the outer surfaces of the crystallites. In accordance with their chemical properties, clay minerals are rather resistant to heat and radiation. The solid phases that exhibit surface reactivity in soils are found to be primarily the clay fraction.

Zeolites are crystalline hydrated aluminosilicates of alkali metals and alkaline earth metals. Their structures are built up from tetrahedral SiO\(_4\) and AlO\(_4\) units crosslinked by the sharing of oxygen atoms. In contrast to the clay minerals, zeolites have porous and three-dimensional frameworks, which bear a negative charge created by partial substitution of Si (IV) by Al (III), and there are channels and/or cavities accommodating water molecules and cations. These alkali and alkaline earth metal cations can be exchanged with other cations.

Salts of heteropolyacids, such as molybdo-phosphate, tungsto-phosphate, molybdosilicate, and tungstosilicates can be used as ion-exchangers in batch separation and column separation. For heteropolyacids variation of ion-exchangeable cations are possible. Generally, NH\(_4^+\), K\(^+\), Rb\(^+\), Cs\(^+\) ions are the cations of these salts. All salts of heteropoly acids are decom-

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posed in alkaline solutions. In strongly acid solutions the cations are exchanged with hydronium ions.

Acid salts, such as silicates, phosphates, arsenates, antimonates, molybdates, tungstates and hexacyanoferrates exhibit ion exchange properties. The crystal structures of many acid salts have been determined, and most of these have been found to have layered structures. Some have fibrous structures. The cation exchange properties of all acid salts are due to the presence of hydrogen atom bound to the anionic groups, as in \( \text{HPO}_4^{2-} \), \( \text{HAsO}_4^{2-} \), \( \text{HFe}^{2+}(\text{CN})_6^{2-} \). High selectivity for \( \text{Cs}^+ \) was found for the hexacyanoferrates.

Oxides and hydrous oxides of divalent elements (Mg, Be), trivalent elements (Al, Fe, Bi), tetravalent elements (Si, Ti, Zr, Mn, Ce, Sn), pentavalent elements (Sb, Bi, Nb, Ta) and hexavalent elements (Mo, W) are sparing soluble and can be used as inorganic ion-exchangers which are amorphous or crystalline materials. All oxides and hydrous oxides may be characterized by a certain pH at which the overall charge on the surface is zero (zero point of charge or isoelectric point). This pH value depends on the nature of the cations and anions in aqueous solution and on ionic strength.\(^6\) When the pH was lower than that value, protonation and anion exchange reaction are observed, and at higher pH value deprotonation and cation exchange reaction are observed. In other words, the ion exchange properties of these ion exchangers depend on the amphoteric reaction of hydroxyl groups as the functional groups. The oxides and hydrous oxides of Si, Al, and Fe are rich in soils and sediments.

2. Clay minerals

\( \text{TiO}_2 \)-crosslinked rectorite was prepared in a solution containing polymeric titanium cations formed by partial hydrolysis of \( \text{TiCl}_4 \) in dilute hydrochloric acid (pH 1.71-1.78), in order to improve the thermal stability and the resistance to acid and base, and to increase the specific surface area and to expand the distance between the neighbouring layers. The \( \text{TiO}_2 \)-crosslinked-rectorite was characterized by element analysis, XRD, DTA-TG, FT-IR and SEM techniques. The cation exchange capacity (CEC) of the \( \text{TiO}_2 \)-crosslinked rectorite increased to 114 mmol/100 g from 47.9 mmol/100 g of the original rectorite. As compared with the weight % of \( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \) 31.1% and 22.7 % for the original rectorite, those for the \( \text{TiO}_2 \)-crosslinked rectorite decreased to 22.4% and 18.6%, respectively. On the contrary, the weight % of \( \text{TiO}_2 \) increased from 1.75% to 27.3%. At pH 7, the adsorabilities for \( \text{NH}_4^+ \) and \( \text{K}^+ \) increased from 37.7 and 98.0 mmol/100 g to 96.5 and 166 mmol/100 g, respectively, while that for \( \text{Cs}^+ \) had no obvious change. It was found that the ion exchange properties of this product were better than those of the orinal rectorite.\(^7,8\)

The sorptions of radiocobalt by bentonite and kaolinite were studied in order to assess the important factors which should be included in migration model of radiocobalt in soils and waters. The distribution coefficients of radiocobalt sorption on bentonite and kaolinite from aqueous solutions were determined by using the batch technique. It was found that the distribution coefficients of bentonite were obviously greater than those of kaolinite, and that they were insensitive to the loading, the initial pH, the ionic strength, and the sorption direction. Thus the sorption characters of radiocobalt on bentonite and kaolinite facilitated the mathematical modeling of radocobalt migration. In addition, the sorption kinetics and the sorption mechanisms of radiocobalt on 2:1 and 1:1 phyllosilicate were examined.\(^9\)

The distribution coefficients of 47 elements from Na to Bi on bentonite were simultaneously determined by using the radioactive multitracer technique. It was found that qualitatively for cationic elements the distribution coefficient increased with increase of the electron binding energy, whereas for oxyanion-forming elements the distribution coefficient decreased with increase of the electron binding energy.\(^10\)

A novel preparation method of montmorillonite pillared by mesoporous silica was proposed. The products were characterized by XRD, TG, FT-IR, and N\(_2\) adsorption-desorption isotherms. The average pore size was 2.17 nm, the specific surface area 821.6 m\(^2\)/g, the super-gallery height 2.75 nm. The layered structure was hold up to 800°C and this excellent thermal stability was ascribed to uniformity of pillars.\(^11\)

3. Zeolites

The natural clinoptilolite from Jinyun county in Zhejiang province was treated by 3 mol/L \( \text{NH}_4\text{NO}_3 \) solution. The thermal resistance and the nitric acid resistance of the natural clinoptilolite were investigated. The distribution coefficients of alkali metals and alkaline earth elements on the natural clinoptilolite in \( \text{NH}_4^+ \) form were determined. It was found that the distribution coefficients of alkali metals were 12 (Li), 70 (Na), 814 (K), 1039 (Rb) and 1345 (Cs) mL/g at \([\text{NH}_4^+] = 0.0028 \text{ mol/L}\) and [alkali metal] = 0.001 mol/L.\(^12\)

The synthetic mordenite in \( \text{K}^+ \) form was treated by 2 mol/L \( \text{NH}_4\text{NO}_3 \) solution. The composition was \( (\text{Na}_2\text{O})_{0.05} \)
The thermal resistance and the nitric acid resistance of the synthetic mordenite were investigated. It was found that the distribution coefficients of alkali metals and alkaline earth metals on the synthetic mordenite in NH$_4^+$ form were determined. It was found that the distribution coefficients of alkali metals were 142 (Li), 205 (Na), 6289 (K) and 29498 (Cs) mL/g at [NH$_4^+$] = 0.003 mol/L and [alkali metal] = 0.001 mol/L. The purpose of both the studies was to recover K from the brine.

The natural clinoptilolites from Jinyun county (1, Zhejiang province), Hailin county (2, Heilongjiang province), Weichang county (3, Hebei province), and Australia (4) were treated by 20 g/L NaCl solution. The ammonium exchange capacities of these natural clinoptilolites were determined and found to be 1.11 (1), 1.42 (2), 1.12 (3), and 1.05 (4) mmol/g at 25°C. The ion exchange isotherms for NH$_4^+$ on these natural clinoptilolites were determined and the sequence of these isotherms was (2) > (1) > (3) = (4). The ammonium exchange rates of these natural clinoptilolites were determined and the diffusion coefficients of ammonium ion were found to be 3.6 \times 10^{-12} (1), 7.2 \times 10^{-12} (2), 3.6 \times 10^{-12} (3), and 1.5 \times 10^{-12} m^2/s, respectively. It was found that the value of diffusion coefficients was proportional directly to the density of these clinoptilolites. The particles of the natural clinoptilolite from Jinyun county (1) were prepared from the powder by using the agglomeration, agglutination and gel techniques. It was found that the diffusion coefficients of ammonium ion in these particles were evidently greater than that in the original one and ranged from 5.1 \times 10^{-12} to 7.8 \times 10^{-12} m^2/s.

The adsorabilities of stellerite with different sizes from Chetian county (Guangxi province) for K$^+$, Na$^+$, NH$_4^+$, Ca$^{2+}$ and Mg$^{2+}$ were determined at 30°C. It was found that the sequence of adsorabilities was NH$_4^+$ > K$^+$ > Na$^+$ > Ca$^{2+}$ > Mg$^{2+}$, and that the stellerite was resistible to concentrated H$_2$SO$_4$, HNO$_3$, NaOH and HCl at 25-30°C.

### 4. Hexacyanoferrates

In 1960, selective sorption of Cs$^+$ was reported for nickel hexacyanoferrate (II) (NiFCN), and the ion exchange properties of MFCNs (M = metal) for a great number of elements (Al, Ti, Fe, Co, Ni, Cu, Zn, Sh, Mo, Ag, Cd, W, Pb and Bi) have been studied. Stabilities and exchange capacities of MFCNs depend on the nature of the compounds and the method of preparation. But, in principle, the ion exchange properties of this group are very similar. In most cases, the great difference in the distribution coefficients was found for alkali ions and the selectivity sequence is Cs$^+$ > Rb$^+$ > K$^+$ > Na$^+$, That for alkaline earth ions is Ba$^{2+}$ > Sr$^{2+}$ > Ca$^{2+}$ > Mg$^{2+}$ > Be$^{2+}$.

The chemical stability of MFCNs is limited. Although all MFCNs are relatively stable in acid media, hydrolysis is observed in neutral and alkaline solutions. As compared with the AlFCN, the hydrolysis of TiFCN begins at higher pH.

Twenty types of MFCNs were prepared. By taking account into the CEC of Cs$^+$, the mechanical property and the hydraulic property of these MFCNs, it was concluded that TiFCN is the best of these MFCNs, and the CECs of Cs$^+$ are respectively 1.54 mmol/g at [HNO$_3$] = 0.001 mol/L, 1.33 mmol/g at [HNO$_3$] = 0.5 mol/L and 1.07 mmol/g at [HNO$_3$] = 1.0 mol/L. The KTiFCN was prepared by using the sol-gel technique and the precipitation technique, and it was found that the latter was far better than the former.

The chemical composition of KTiFCN was K$_2$TiFe(CN)$_6$ nH$_2$O ($x = 0.5-0.75$). The specific surface area, porosity, and the pore size distribution of KTiFCN were 14 m$^2$/g, 50% and $d$ (pore size) $> 1.0 \mu$m, 10.2%, 0.1 $\mu$m $< d < 1.0 \mu$m, 84.2%, $d < 0.1 \mu$m, 5.2%, respectively. The kinetics experiments indicated that the film diffusion was the rate controlling step for K-Cs exchange and the ion exchange process was regarded as a shell process reaction.

After TRU (transuranic elements), $^{99}$Tc, and $^{90}$Sr were removed by using the extraction technique with Tri-alkyl phosphine oxide and crown ether as extractants, the pilot-plant scale removal of Cs from simulated HLLW (High Level Liquid Waste) by three KTiFCN columns was studied. The composition of simulated HLLW is listed in Table 1.

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<th>Element</th>
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<tr>
<td>Na</td>
<td>13.7</td>
<td>Cs</td>
<td>1.15</td>
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<tr>
<td>Al</td>
<td>4.1</td>
<td>K</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>5.0</td>
<td>Mo</td>
<td>0.01</td>
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<tr>
<td>Ni</td>
<td>3.8</td>
<td>Mn</td>
<td>0.09</td>
</tr>
<tr>
<td>Cr</td>
<td>0.9</td>
<td>Ba</td>
<td>0.028</td>
</tr>
<tr>
<td>Sr</td>
<td>0.06</td>
<td>[H$^+$]</td>
<td>1.10 mol/L</td>
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and 0.77 mmol/g at 90% breakthrough at flow rate 2 L/h, and the Cs+ sorbed on the KTIFCN particles can be washed with 0.1 mol/L HNO₃ solution.

The shallow bed technique was employed to study the influences of Cs+ concentration in solution, temperature, and flow rate on mass-transfer performance of cesium ion exchange with KTIFCN from nitric acid solution. The conclusion is summarized as follows.

i) The effect of Cs+ ion concentration in solution was negligible from 1 x 10⁻⁴ to 6 x 10⁻² mol/L.

ii) The over-transfer-coefficient increased with an increase in temperature from 30°C to 50°C.

iii) The over-mass-transfer coefficient increased with an increase in flow rate and decreased with a increase in Cs+ concentration in the ion-exchanger.

5. Salts of heteropoly acids

The granular crystal of 12-ammonium molybdophosphate was prepared from the pyrophosphate and the molybdate in 1 mol/L HNO₃ and the chemical composition of the product was (NH₄)₃PMO₁₂O₄₀H₂O. The ion exchange capacity for Cs+ in 1 mol/L HNO₃ was 0.63 mmol/g and the distribution coefficient for Cs+ was 350 mL/g in 1 mol/L HNO₃. The dynamic exchange capacity for Cs+ was 0.55 mmol/g at 1% breakthrough from the simulated Chinese fission waste (1 mol/L HNO₃).

The hydrous titanium dioxide microsphere was synthesized by the sol-gel method and the new composite inorganic ion-exchanger was prepared by combining hydrous titanium dioxide with ammonium molybdophosphate. The ion exchange capacities and the distribution coefficients for Cs+ were 0.24 mmol/g and 55 mL/g at 1 mol/L HNO₃, 0.34 mmol/g and 111 mL/g at 0.1 mol/L HNO₃, 0.45 mmol/g and 190 mL/g at 0.01 mol/L HNO₃. This ion-exchanger was resistible to acid, heat and radiation and had excellent mechanical strength.

6. Oxides of Si, Al, Fe, Mn, and Ti

The adsorption and the desorption of radio cesium from aqueous solutions containing NaNO₃ or CaCl₂ as a background electrolyte on Al₂O₃ were studied over a wide range of background electrolyte concentration and solution pH by using the batch technique. The wall of the glass test tubes had a great effect on the adsorption and desorption data, and the adsorption/desorption hysteresis was negligible by using the same aqueous solutions for both the adsorption and the desorption in the polyethylene test tubes. The dependences of the distribution coefficient on the pH and the background electrolyte concentration were discussed. The adsorption of Cs+ on Al₂O₃ was very rapid and the adsorption/desorption hysteresis was negligible, and from these experimental results and the dependences of distribution coefficients on the pH and background electrolyte concentration, it was unambiguously concluded that the ion exchanger is the prevailing adsorption mechanism of Cs+ on Al₂O₃.

The effects of pH, ionic strength and dissolved fulvic acid on the adsorption of Eu(III) and Yb(III) on Al₂O₃ were investigated by using the batch technique and radionuclides ¹⁵²⁺¹⁵⁴Eu and ¹⁶⁹Yb. The adsorption of Eu(III) and Yb(III) onto a bare alumina surface was dependent on the pH, but independent of the ionic strength. The adsorption mechanism of hydrolyzable rare earth elements appeared not to be pure ion exchange. The existence of free >SOH groups on the surface was an essential requirement of the adsorption process, and the steep rise in distribution coefficient was caused by the increase in free >SOH concentration. In the presence of fulvic acid, the surface of alumina was coated by fulvic acid and the coating of fulvic acid had a great effect on the surface properties of alumina. The effect of fulvic acid was dependent on pH and concentration of fulvic acid, the adsorption of Eu(III) or Yb(III) was observed to be either enhanced or decreased at different pH ranges as compared with fulvic acid free systems.

The effects of pH, ionic strength and dissolved humic substance on sorption and desorption of Co(II) on alumina under aerobic conditions were investigated by using the batch and column techniques and radionuclides ⁶⁰Co. The sorption of Co(II) onto a bare alumina surface was strongly dependent on pH but independent of ionic strength. In order to compare the experimental results of alumina with those of silica, whose chemical properties differ distinctly from those of alumina, the effects of pH, ionic strength and dissolved humic substance on sorption of Co(II) by silica were investigated too. The distinctly different sorption characteristics were observed between alumina and silica. The sorption mechanism of hydrolysable Co(II) on the alumina was not pure ion exchange. The strong chemical bonds were formed between the bare alumina and Co(II), and a transition from the two-dimensional adsorption to the surface induced precipitation of Co(II) on the bare alumina surface took place.

The distribution coefficients of 47 elements on an alumina, 36 elements on a silica and 32 elements on a natural hematite were determined by using the radioactive multitracer technique. In general the sequences of distribution coefficients of alkali elements on these oxides were Cs+ > Rb+ > K+ > Na+, the sequences of distribution
coefficients of alkaline earth elements on these oxides were \( \text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} \), and the values of distribution coefficients of lanthanides on these oxides against the atomic number exhibited as a "W" figure approximately.

The adsorption of Am(III) (total concentration, \(10^{-9}\) mol/L) on alumina, silica, and hematite was studied by using the batch technique. The effects of pH, ionic strength, and humic substance on the adsorption of Am(III) on alumina and silica were investigated, and the adsorption isotherms of Am(III) on alumina and silica at different pH values were determined. In contrast to the Am(III) adsorption on alumina and silica, the adsorbability of Am(III) on hematite was found to be tremendously high. The sequence of adsorabilities of Am(III) on the basis of mass was Fe₂O₃ > Al₂O₃ > SiO₂. Under aerobic condition (\(E_0 > 300\) mV) in the atmosphere at relatively lower concentration, Am(III) exists as positively charged species \(\text{Am}^{3+}\), \(\text{Am(OH)}^{2+}\), \(\text{Am(OH)}_2^{+}\), \(\text{Am(CO}_3\)\(^2-\) and negatively charged species \(\text{Am(CO}_3\)\(^2-\) and these species are in equilibrium with each other in aqueous solution and these equilibria are shifted with changing pH, besides the ion exchange reaction. Therefore many surface reactions are responsible for overall adsorption of Am(III) on a surface, and the adsorption process is affected by numerous factors.\(^{30}\)

The sorption of Np(V) (total concentration \(10^{-5}\) mol/L) on alumina and silica was studied by a batch technique under aerobic conditions at 25°C. The effects of pH, ionic strength, humic substance, and added carbonate on the sorption onto alumina and silica were investigated. The sorption isotherms of Np(V) on alumina and the relationships between the equilibrium concentrations after sorption and the initial concentrations before sorption in the presence and absence of humic substance and added carbonate in solution were determined. The sorption of Np(V) on alumina under aerobic conditions was obviously stronger than that on silica, and the negative sorption onto silica occurred. Under aerobic conditions (\(E_0 > 300\) mV) in the atmosphere at relatively higher Np(V) concentration, because Np(V) exists as positively charged species NpO₂⁺, neutral species NpO₂OH, negatively charged species NpO₂(OH)\(^2-\), NpO₂CO₃\(^-\), NpO₂(CO₃)\(^2-\) and colloids, and these species are in equilibrium with each other in aqueous solution and these equilibria are shifted with changing pH and adding carbonate, besides the ion exchange reaction. As many surface reactions are responsible for the overall sorption of Np(V) on surface, the sorption of Np(V) is very complicated and the factors affecting the sorption process are numerous.\(^{31}\)

Manganese acetate was complexed with citric acid, oxalic acid and 8-hydroxyquinoline in solid state. The complex precursors were thermally decomposed and then treated with acid to yield nanoparticle-MnO₂. The particle size of samples were about 20–30 nm and their shapes were found to be spherical from TEM images.\(^{32}\)

The nanometer TiO₂–SiO₂ composite oxide, which had a high surface area and better thermal stability, was prepared by the sol-gel method. The effects of feed composition and calcination temperature on the specific surface area, thermal stability and acidity of the composite oxide were examined. Compared with pure TiO₂, the addition of SiO₂ obviously improved the thermal stability and crystallinity of the composite oxide.\(^{33}\)

### 7. Concluding remarks

Chemists in Chinese universities have paid considerable attention to inorganic ion-exchangers during the past decade. The following properties of inorganic ion-exchangers are required for separation and purification processes:

- a) the ion exchange capacity must be high, because a considerable amount of ions are to be separated and purified;
- b) the ion exchange rate must be high;
- c) the selectivity for different ions should be high;
- d) the shape of an inorganic ion-exchanger should be spherical and the distribution of the particle diameters as small as possible;
- e) the inorganic ion-exchanger must be stable enough to withstand washing with acids or alkaline solutions;
- f) the exchanger should be mechanically stable, this is, neither deformed nor compressed by pressure;
- g) the heat resistance and the radiation resistance should be high;
- h) the exchanger should not shrink or swell with a change in pH or salt concentration;
- i) the cost should not be high and the exchanger should be able to withstand repeated use.

The property g) is especially important for nuclear science and technology, while the properties a), d), h) and i) are important for a continuous use or a large-scale separation. It is well known that the ion exchange properties depend not only on the composition and crystal structure, but also on the method and condition of preparation, that most inorganic ion-exchangers are amorphous precipitates which are unsuitable for use in column, and that the inorganic ion-exchangers usually have rigid structures and high densities. The ion exchange rate is slow as compared with the organic ion exchange resins. Therefore, actually it is
not easy to produce an inorganic ion-exchanger that fulfills all these requirements. Since the selectivity of inorganic ion-exchanger is attributed generally to the ion sieve effect, steric factor, ion size preference, the entropy effect and ion memory preference, even in the simplest cases, understanding of the factors and mechanisms underlying ion exchange selectivity have not been perfect yet. Additionally and unfortunately, there are many factors that make valid comparison between data from different laboratories difficult.

References
16) N. C. Chen, C. J. Hu, W. B. Ruan and T. S. Cui, ibid, 18, 80 (2002).