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The Potential of Zeolites to Block the Uptake of Radioactive Strontium-90 in Organisms

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Abstract

Zeolites have numerous environmental and industrial applications in which they function as molecular sieves, ion-exchangers, absorbers, catalysts, and even detergent builders. While several general reviews about zeolites are available in the literature, the sorption characteristics of the natural and synthetic zeolites, which could possibly be used in blocking the uptake of ingested radioactive 90Sr in organisms, have not been described previously.

Keywords: Modified zeolites, Absorption, Radioactive strontium-90, SEM: Scanning Electron Microscopy; AECL: Atomic Energy Canada Limited.

Introduction

Zeolites comprise a group of natural or synthetic, micro porous, hydrated aluminosilicate minerals containing alkali and alkaline metal ions. Formally, zeolites belong to a class of minerals known as “tectosilicates”. The term zeolite was first proposed in 1756 by Axel Cronstedt, a Swedish mineralogist, who observed that when stilbite, $NaCa_4 (Si_{27}Al_9) O_{72}.28H_2O$, was heated, steam was produced. He came up with the name zeolite from the Greek zeo meaning “to boil” and lithos meaning “stone”. A common description of a zeolite today, based on the definition of Armbruster and Gunter [1] is: A zeolite mineral is a crystalline substance with a structure characterized by a framework of linked tetrahedra, each consisting of four O atoms surrounding a cation. This framework contains open cavities in the form of channels and cages. These cavities are usually occupied by H_2O molecules and extra framework cations that are commonly exchangeable. The channels are large enough to allow passage of guest species. In the hydrated phases, dehydration occurs at temperatures mostly below 400 °C and is largely reversible. The framework may be interrupted by OH and F groups, which occupy an apex of a tetrahedron that is not shared with adjacent tetrahedra.

Three main types of sorbents have been identified: (1) inorganic materials (zeolites, clays and silica); (2) carbon-based adsorbents (activated carbon, graphite, carbon molecular sieves and pre-shaped carbon fibers and nanotubes); and (3) organic polymers. In the case of zeolites, over 200 different types have so far been identified [2] and about 40 of these occur naturally. Zeolites can be sub-classified into four molecular sieve groups based on their pore ring sizes: ultra-large (>14-membered rings), large (12-membered rings), medium (10-membered rings) and small (8-membered rings). Zeolites with medium and large pores are mostly used in catalysis since ready diffusion of molecules within the pores means that they can reach the catalytically active sites more easily. Zeolites with a high concentration of cation exchange sites and small pores are more suitable for sorption processes. Moreover, zeolites with precise pore shapes are useful in systems where molecular recognition is needed.

Zeolites are highly hydrophilic sorbents owing to their charged frameworks and the presence of large amounts of alkali and alkaline earth cations. Synthetic zeolites prepared without any Al^{3+} ions built into their structures, however, exhibit hydrophobic characteristics [3, 4]. Most zeolites (especially those with high Al^{3+} content) show type-I water sorption isotherms reflecting their high affinity for water at low partial pressures. Water sorption capacity is generally proportional to pore size. Large-pore aluminosilicate zeolites (Na^+ forms), such as ZSM-20, which has 12-membered rings, have the highest capacities for water absorption. Natural zeolites are found where volcanic rocks and ash layers have interacted with alkaline ground water. Zeolites are often present in marine basins. The ability of zeolites to sorb heavy metal species and radionuclides from aqueous media is especially important in environmental applications. The necessity for the removal of radioactive ^{90}Sr from aqueous systems by clay minerals and

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zeolites was quickly realized following the development of the nuclear power industry.

Structure of natural zeolites

Zeolites are comprised of three components-an aluminosilicate framework, alkali and alkaline earth cations, and water molecules of crystallization. The general formula of a zeolite may be written as $M_{x/n}[(Al_xSi_y O_{2(x+y)}].pH_2O$, where M=$Na^+$, K^+ or Li^+ and/or Ca^{2+}, Mg^{2+}, Ba^{2+} or Sr^{2+}, n is cation charge, y/x = 1-6 and p/x = 1-4. The basic building block of a zeolite is a tetrahedron with Si^{4+} or Al^{3+} ions located at the centre of the tetrahedron and four O^{2-} ions at the vertices. Substitution of Si^{4+} by Al^{3+} leads to a negative charge on the zeolite framework, which is compensated for by the presence of monovalent or divalent cations in the structure. The water molecules are in the empty spaces in the cavities in the structure or are bridged between Si^{4+} and Al^{3+} ions. The structures of zeolites therefore consist of three-dimensional frameworks of linked $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra.

The two most common commercial zeolites being used as sorbents are zeolite-A and zeolite-X. The pore sizes of these materials can be fine-tuned by the appropriate choice of cations. For example, the Na^+ form of zeolite-A has a pore size of ~4Å (hence the term 4A molecular sieve). When Na^+ is replaced by K^+, the pore size is ~3Å (3A molecular sieve). In the case of Ca^{2+}, which can replace two Na^+ or K^+ ions, the pore opening is ~5 Å. Most natural zeolites are used to selectively adsorb molecules from air or liquids [5]. It is less expensive to mine natural zeolites than to synthesize them- natural zeolites cost about 80-90% less than do synthetic zeolites. The exchangeable cations Na^+, Ca^{2+}, Mg^{2+} and K^+ are relatively safe for humans, plants and animals, which further promotes their extensive commercial use. Among the major uses of natural zeolites are pet litter, animal feed, agriculture, oil absorbents, odor control, desiccants, pesticide carriers, water purification, aquaculture, wastewater cleanup, gas absorbent and catalysts [6]. Pet litter, animal feed and agricultural applications account for more than two-thirds of worldwide sales. Zeolites containing Na^+, K^+ and Ca^{2+} are particularly useful in the removal of undesirable heavy metal ions from industrial effluents. In fact, one of the earliest applications of natural zeolites was in the removal Cs^+ and Sr^{2+} radioisotopes [7]. Natural zeolites are rarely pure and are usually contaminated by other minerals (including other zeolites), metal ions, and even quartz. Zeolites rich in Al^{3+} ions are being exploited as desiccants because of the large number of hydrophilic sites present and the resulting increased water sorption capacity.

Types of zeolites

Seven of the 63 naturally occurring zeolites are found in quite large quantities, i.e., analcime, chabazite, clinoptilolite, erionite, mordenite, phillipsite and ferrierite. All these zeolites can be synthesized, but only mordenite and ferrierite are produced in any significant quantities.

Examples of some natural zeolites

The chemical formulae and structural types (including the space group symmetry) of some common zeolites are given in ref [8]. Some specific properties of a few natural zeolites are described below.

Analcime or analcite

Analcime is a white, gray or colourless tectosilicate consisting of sodium aluminium silicate having a cubic crystalline structure. Although it is classified as a zeolite, it is more like the feldspathoids. It occurs chiefly in the form of the mineral analcime basalt [9].

Chabazite

Chabazite is a tectosilicate mineral that is closely related to gmelinite. It is found in many different colours (colourless, white, orange, brown, pink, green or yellow) and it crystallizes in the triclinic system with a rhombohedral shape. Its hardness falls in the 3-5 Moh range [10].

Clinoptilolite

Clinoptilolite occurs as white-to-radish, monoclinic tectosilicate crystals, with a hardness of 3.5-4 Moh. Its microporous structure is resistant to extreme pressures. High temperatures are required to melt the material and it is unaffected by treatment with strong acids or alkalis. It is commonly found in basalts, andesites and rhyolites in the form of glass shards in compressed volcanic ashes known as tuffs. Clinoptilite has been used extensively in industry, e.g., in an ion-exchange system for NH^{4+} ions in an enzyme-based urea sensor. Because of its high cation-exchange capacity, it has found uses in water purification and as an additive to animal feeds. Clinoptilite tuffs have also been employed in underground nuclear weapons testing [11, 12]. In addition, Zanin et al. have used natural clinoptilolite as an adsorbent for the removal of heavy metals such as a Cu^{2+}, Cr^{3+} and Fe^{3+} ions from the wastewater in the graphic industry [13].

Erionite

Erionite is a fibrous, naturally occurring zeolite that has a hexagonal, cage-like structure. The structure forms chains of indefinite length with six (Si, Al)O_4 tetrahedra on each edge. This zeolite is found as white prismatic crystals that can absorb up to 20% of their weight in water. It has a specific gravity of 2.02-2.08 and has gas absorption, ion exchange and catalytic properties that are highly selective and dependent on the molecular sizes of the compounds being sorbed. It is no longer mined for commercial purposes, although erionite-rich blocks have sometimes been used in building houses in the western United States [14].

Mordenite

Mordenite crystallizes as white, faintly yellow or pink fibrous delicate aggregates of prismatic crystals. Its hardness and density are 5 Moh and 2.1 g.cm-3, respectively. The molecular structure consists of a framework of chains of five-membered rings of linked (Si, Al)O_4 tetrahedra. Its high Si/Al atom ratio leads to it being particularly resistant to attack by acids when compared to most other zeolites. It is used in many chemical reactions. Mordenite is one of the most abundant zeolites in deposits from volcanic lava flows, such as rhyolite, andesite and basalt. It is often associated with other zeolites, such as stilbite and heulandites, and there are deposits located in Iceland, India, Italy and the United States. It has also been observed in marine sediments in the Ural Mountains in Russia. Apart from typical applications in agriculture and the construction industry, it is used as a sorbent and in molecular sieves. Gas separation processes utilizing mordenite are well known to produce high-grade O_2 from air and there are commercial plants based on mordenite-rich tuffs that have been operating in Japan for over 50 years. Because of its fibrous nature, however, it does pose a possible health risk as do erionite and asbestos [15, 16]. Consequently, the crystalline morphology of mordenite-bearing sedimentary rocks is usually examined by scanning electron microscopy (SEM) prior to use.

Phillipsite

Phillipsite occurs as colorless or pale-yellow crystals in basalt cavities throughout the world. The prismatic crystals range in size from 2 to 400 μm and are mostly twinned [17]. The mineral is found in fine-grained pelagic sediments, such as brown clay and various oozes, and is commonly associated with clinoptilolite, palagonitic glass, smectite, iron and manganese oxides, hydroxides and barite [18]. The relative abundances of clinoptilolite and phillipsite are particularly interesting as they provide information on the crystallization process of these minerals in deep-sea sediments [17-20]. Major deposits of phillipsite occur at Aci Castello in Sicily and at Capo di Bove near Rome in Italy [21]. Other industrially important deposits of sedimentary phillipsite are found in Bulgaria, Hungary, Jordan and the United States. Phillipsite-bearing tuffs are currently being used for the removal of NH^{4+} ions and various heavy metals from water [22]. Another use of this zeolite tuff is as a dimension stone in building construction throughout the world, especially in Italy [10].

Ferrierite (FER)

Significant deposits of ferrierite minerals are located at Kamloops Lake in Canada and Leavitt Lake in California. The name ferrierite stems from that of its discoverer, the Canadian geologist/mining engineer, Walter Ferrier (1865-1950). The three main ferrierite minerals are ferrierite-Mg, ferrierite-Na and ferrierite-K, which are often associated with mordenite and clinoptilolite, and occasionally with opal, chalcedony and calcite [23]. Important applications of synthetic ferrierites include their uses as commercial filters and in ion-exchange beds. Another major use is in the acid-catalyzed isomerization of n-butene to isobutene, the starting material for the commercial production of methyl-t-butyl ether (MTBE), which is used as an anti-knock agent in gasoline.

Examples of synthetic zeolites

There are approximately 40 naturally occurring zeolites that have been identified. Because of the enormous industrial demands for these materials, it is difficult to find enough of the materials that behave consistently, and synthetic zeolites are now being extensively used [24]. The earliest work on synthetic zeolites goes back to the 1940s [25]. There are many synthetic zeolites known, some of which have no natural counterpart. When compared to natural zeolites, synthetic zeolites are purer and have more uniform pore sizes resulting in them having better ion-exchange capacities and behavioral predictability. Over 180 synthetic zeolites have now been classified, including the well-known zeolite-A,-X,-Y and ZSM-5 [26]. Gas and oil companies, such as Linde, Mobil and Exxon, have had a considerable interest in the production of large quantities of synthetic zeolite-A and-X, NaY, mordenite, zeolite-L, erionite, chabazite and clinoptilolite for gas purification and separation studies [27]. One major area of interest has been the use in the bulk separation of paraffins, xylene isomers and olefins. Zeolite-A and -X have also been employed in the detergent industry and in radioactive and industrial liquid waste treatment because of their excellent ion-exchange capacities. Nowadays, only a few of the approximately 180 known frameworks are being used to any great extent in industry [28]. Interestingly, synthetic mordenite has larger pores than does natural mordenite.

Apart from mordenite and ferrierite, the main industrial synthetic zeolites are Linde Type-A, -X and -Y (Al-rich and Si-rich), Silicates-1 and ZSM-5 (MFI) and Linde Type-B (Zeolite P). Several other synthetic zeolites are commercially available, including Beta, Linde Type-F, -L and-W, and SSZ-32, which are either aluminosilicates or pure silica analogs. Recently, Moamen et al. have reported the synthesis of a nano-sized zeolite, which they used for the removal of the Cs^+ and Sr^{2+} ions from aqueous solutions [29]. Similarly, Shilina et al. have prepared an alumosilicate zeolite-like adsorbent, which has been applied for the efficient removal of heavy metals and radionuclides from aqueous solution [30].

Aluminophosphates

Several non-aluminosilicate synthetic molecular sieves have now become available commercially including aluminophosphates ($AlPO_4$ structures), silicoaluminophosphates (SAPO family), various metal-substituted aluminophosphates (meAPO family, such as CoAPO-50AFY) and other microporous framework structures, such as crystalline silicotitanates. Over 30 types of $AlPO_4$ materials have been synthesized [2] and the AlPO frameworks are neutral. There are no other cations present in these materials, which accounts for their poor ion-exchange properties [31]. AlPO molecular sieves are expected to have weak catalytic and sorption properties because of the low concentration of surface OH groups. If P atoms in the framework are replaced by Si or metallic atoms, however, new properties should be generated [32-36]. Most AlPO materials are not hydrothermally stable, but several of them, e.g., AlPO-5, remain structurally intact after heating at high temperatures (< 600 °C) [37]. AlPOs sorb water, even at low pressures [38-39]. AlPOs can be categorized as dense or very small pore (4- and 6-membered rings of diameter ~3Å), small pore (8-membered rings of diameter ~4 Å), medium pore (10-membered rings of diameter ~6 Å), large pore (12-membered rings of diameter

~7-8 Å) and ultra-large pore (18-and 20-membered rings of diameter > 12.5 Å) materials. Because of its extremely large pores the aluminophosphate VPI-5 is of considerable interest as a selective sorbent for large organic molecules. The gas sorption properties of AlPO-5 have been focused chiefly on N_2 [40], argon [41] and light organic compounds [42-43].

Applications of natural and synthetic zeolites

As mentioned earlier, zeolites are now widely used industrially because of their thermal stability, acidity, surface hydrophobicity/hydrophilicity, ion-exchange capacity, low density, large void volume, uniform molecular-sized channels suitable for gas and vapor adsorption, and their catalytic properties. Zeolites are becoming increasingly important in several environmental applications, but especially in water purification for the removal of NH^{4+} ions, radioactive and heavy metal species, and organic substances.

Role of zeolites in catalysis

The first report of NaA zeolite being used in the separation of normal and isoalkanes appeared in the 1950s from the Linde Company. A few years later, X-and Y-zeolites were introduced as catalysts for petroleum cracking reactions. Since then, NaA, NaX and NaY have been extensively used by all the major oil companies in numerous reactions, e.g., cracking, alkylation, isomerization, shape-selective reforming, hydrogenation and dehydrogenation, and methanol-to-gasoline conversion. These highly porous materials have also found use in the detergent industry, in the removal of CO_2 from natural gas, and in the separation of xylene isomers and of O_2/N_2 from air. Recently, Woo et al. have prepared CuY zeolite catalysts and used them for the oxidative carboxylation of methanol to dimethyl carbonate [44].

Role of zeolites in absorption

The amount of metal ion that can be absorbed in a zeolite is strongly dependent on the nature and concentration of the metal ion concerned, the pH and the presence of any competing ions [45]. Zeolites are particularly effective in heavy metal removal, e.g., Cu^{2+} and Pb^{2+}, and also PO_4^{3-} [46], H_2 [47], CO_2, CH_4 and N_2 [48], NOx [49], N_2 and O_2 [50], and volatile nitrosamines [51].

Appreciable social and environmental problems have surfaced recently throughout the world because of restricted landfill capacity-nobody wants any problematic materials stored in or near their homes. Polluted water and the limited access to clean water are already major crises, especially in under-developed countries. One successful solution is to use zeolites to overcome problems in water purification and soil conditioning [52, 53]. Research is mainly being concentrated on the application of fly ash-based zeolites in the removal of heavy metal and other ions [54], NH^{4+} [55], Cs^+ [56] and As^{3+} and Cr^{6+} [57]. A polyacrylonitrile/Na-Y-zeolite composite with amidoxime groups has been used for the sorption of Cu^{2+}, Cd^{2+} and Pb^{2+} metal ions [58]. In some other work, Moamen et al. have synthesized magnetic nano zeolite materials, for the sportive removal of ions from radioactive wastewater [59]. Also, Alswata et al. have reported the preparation of zeolite/zinc oxide Nano composites that are useful for the absorption of $Pb^{2+}$and As^{5+} ions from aqueous solution [60].

Table 1 lists some research articles published during 2008-2018 on the ^{90}Sr removal from aqueous solution, wastewater, and radioactive waste by adsorption. There are different types of adsorbents used, e.g., natural and synthetic zeolites, modified zeolites, nanomaterials, nan composites, inorganic materials, and biopolymers.

No.	Objective	Type of adsorbent	Reference	Year
1	Strontium(^{90}Sr) removal from seawater and evaluation of Sr adsorption performance	Zeolite-alginate foam composite	H.-J. Hong *et al.*	2018
2	For the efficient removal of strontium ions from aqueous solution	Fabrication of alginate/humic acid/Fe-aminoclay hydrogel composed of a grafted-network	S.R. Choe *et al.*	2018
3	Removal of Sr^{2+} from aqueous solutions: Kinetic, equilibrium, and thermodynamic studies	Preparation of magnetic clinoptilolite/ $CoFe_2O_4$ composites	Y. Huang *et al.*	2017
4	Removal of strontium-90 (^{90}Sr) from water samples: Kinetics and thermodynamic reactions study	MnO_2 NPs-AgX zeolite composite	M. Sadeghi *et al.*	2017
5	Removal of cesium and strontium ions from aqueous solution	Modified hydroxyapatite	S.S. Metwally *et al.*	2017
6	Strontium removal from wastewater	Ba-titanate material	C. Guévar *et al.*	2017
7	Enhanced Sr adsorption performance from seawater and evaluation of its mechanism	MnO_2-alginate beads	H.-J. Hong *et al.*	2017
8	Efficient removal of Cs^+ and Sr^{2+} from aqueous solution	Hexagonal tungsten trioxide coated Fe_3O_4	W. Mu *et al.*	2017
9	Removal of strontium from aqueous solutions and synthetic seawater	Resorcinol formaldehyde polycondensate resin	T. Nur *et al.*	2017
10	Strontium sorption from the water solutions in static conditions	Clinoptilolite and synthetic zeolite	V.V. Levenets *et al.*	2016
11	Removal of Cs^+ and Sr^{2+} from water	MWCNT reinforced Zeolite-A beads	A.K. Vipin *et al.*	2016
12	Removal of strontium(II) and cobalt(II) from acidic solution	Manganese antimonate	L. Zhang *et al.*	2016

13	Study of the sorption properties of strontium ions	Mesoporous manganese oxides	A.I. Ivanets *et al.*	2016
14	Strontium ion (Sr^{2+}) separation from seawater	Titanate nanotubes	J. Ryu *et al.*	2016
15	Removal of strontium (Sr) from seawater	Alginate/Fe_3O_4 composite	H.-J. Hong *et al.*	2016
16	Removal of Sr(II) from aqueous solutions	PPy@NiO nano-particles	V. Srivastava et al	2016
17	Study of strontium adsorption from aqueous system: A comparative study with and without calcination	Cation doped hydroxyapatite nanoparticles	P. Ramakrishnan *et al.*	2016
18	Removal of cobalt and strontium from aqueous solution	Birnessite	M. Ghaly et al	2016
19	Competitive adsorption of strontium and cobalt	Tin antimonate	L. Zhang et a	2016
20	Efficient static and dynamic removal of Sr(II) from aqueous solution using	Chitosan ion-imprinted polymer functionalized with dithiocarbamate	F. Liu et al	2015
21	Strontium removal from wastewater	Recycled iron oxide	Y.-J. Tu *et al.*	2015
22	Strontium(II) adsorption	Sb(III)/Sb_2O_5	L. Zhang et al	2015
23	Study of the adsorption properties for Sr(II) and Co(II) ions	Graphene oxide–magnetite	A. Tayyebi *et al.*	2015
24	Study the adsorption characteristics of strontium	Antimony silicate	L. Zhang et al	2015
25	Investigation of strontium and uranium sorption	Zirconium-antimony oxide/polyacrylonitrile (Zr-Sb oxide/PAN) composite	P. Cakir *et al.*	2014
26	Strontium adsorption	Tantalum-doped hexagonal tungsten oxide	X. Li *et al.*	2014
27	Adsorptive removal of Sr^{2+} : Kinetic and thermodynamic study	Waste iron oxide	C.-H. Liu *et al.*	2014
28	Removal of Cs^+ and Sr^{2+} from aqueous solutions	Magnetic zeolite composite	M. Iravani	2014
29	Removal of Cs^+ and Sr^{2+} from aqueous solution	Magnetic zeolite nanocomposite	H. Faghihian *et al.*	2013
30	Removal of Cs^+ and Sr^{2+} from aqueous solutions: Kinetic, equilibrium, and thermodynamic studies	PAN–zeolite nanocomposite	H. Faghihian et al	2013
31	Removal of radionuclide Sr^{2+} ions from aqueous solution	Magnetic chitosan beads	J. Wang et.al	2012
32	Removal of radioactive strontium from aqueous wastes	Synthetic sodium nonatitanate and zeolite A	A. Merceille et al	2012
33	Study of the adsorption properties Strontium	Granulated NaY zeolite nanoparticles	A. Charkhi *et al.*	2012
34	Removal of radioactive strontium from aqueous effluents: Application to the case of Fukushima	Macroporous LTA-monoliths	A. Sachse *et al.*	2012
35	Application on strontium removal from aqueous solution	Tin (IV) molybdophosphate onto mesoporous silica SBA-15	H. Aghayan *et al.*	2012
36	Study the sorption from cobalt and strontium aqueous solution	Moss *Rhytidiadelphus squarrosus*	J. Marešová *et al.*	2011
37	Removal of strontium(II) ions by from aqueous solution	Potassium tetratitanate whisker and sodium trititanate whisker	W. Guan *et al.*	2011
38	Removal of Co^{2+}, Sr^{2+} and Cs^+ from aqueous solution by	Phosphate-modified montmorillonite (PMM)	B. Ma *et al.*	2011
39	Investigation of Sr(II) sorption by experimental design	Zirconium–manganese oxide/polyacrylonitrile (Zr–Mn oxide/PAN)	S. ˙ Inan, Y. Altas	2011
40	Study the sorbing barrier for strontium in a radioactive disposal facility	Synthetic zeolite Na A–X	R.O.A. Rahman *et al.*	2010
41	Study of strontium adsorption behaviours	ZrO_2 and ZrO_2–TiO_2 microspheres	H. Tel et al	2010
42	Removal of cobalt, strontium and cesium from radioactive laundry wastewater	Ammonium molybdophosphate–polyacrylonitrile (AMP–PAN),	Y. Park et al	2010
43	Adsorption study of the Strontium and calcium ion	Molecularly imprinted hybrid gel	Q. Li et al	2010
44	Removal of strontium from aqueous solutions and kinetic and thermodynamic studies	Activated carbon	S. Chegrouche et al	2009
45	Comparison of strontium and calcium adsorption	Composite of magnetic particles derived from Fe_3O_4 and bis(trimethoxysilylpropyl)amine	X. Ye *et al.*	2008
46	Removal of Cs^+ and Sr^{2+} ions from aqueous solutions using batch and fixed bed column operations	Zeolite A	A.M. El-Kamash	2008

Table 1: Articles published on ^{90}Sr sorption onto modified zeolites, inorganic materials, Nano composites and biopolymers over the past 10 years

Role of zeolites in ion-exchange systems

Zeolites play a crucial role in the removal of NH^{4+} ions from wastewater [61]. Montegut et al. have studied the cation-exchange properties of the zeolites. They used two natural and one synthetic zeolite for their work, viz., clinoptilolite, chabazite and NaX faujasite, respectively, for the removal of NH^{4+} and K^+ ions from swine liquid manure [62]. For the thermal energy storage, P. Aprea et al. have synthesized Sr-, Zn- and Cd-exchange zeolitic materials as water vapor adsorbents [63]. R. Tekin, N. BAC has described the use of ion-exchanged zeolite X containing fragrance for antimicrobial behavior study [64]. These materials are also useful for the removal of cationic and anionic pollutants, such as Cr^{6+} and As^{5+} [65], Cu^{2+}, Pb^{2+} and Cd^{2+} [66], Fe^{3+} and Zn^{2+} [67], and Sr^{2+} [68]. Some 68current research papers have described the interaction of synthetic zeolites with Cs^+ [69], U^{6+} [70] and Sr^{2+} [68] in particular.

Some disadvantages of zeolites

The synthesis of zeolites and aluminophosphates is well developed and materials with special properties, such as high catalytic activity, good adsorption or ion exchange behavior, optical transparency and adequate guest incorporation, can be readily produced. The purity of the adsorbents is a problem that needs to be overcome. The zeolite frameworks often contain B, Al, Ga, Si and P atoms bridged by oxygen atoms. Many of these materials are insulators. Another disadvantage of zeolites is that metal uptake is often limited to a few percent. An attempt to overload the zeolites leads to collapse of the framework. This is a critical factor for catalytic applications [71].

The literature on the medical applications of natural or synthetic zeolites is much less by comparison with other applications. Natural zeolites, such as clinoptilolite or clays, are used for various medical applications, e.g., as anti-parasitary, antibiotic [72] and anticancer drugs [73]. Zeolites play an important role with respect to the acidic conditions in the stomach. The optimum pH value in the stomach lies between 3 and 4. At a pH less than 4, the crystal structures of the zeolites may be subject to hydrolysis and then destroyed releasing Na+ ions, silicic acid and aluminium salts, which may be taken up in the gastrointestinal area [74].

Antacids are used to control the pH in the stomach, which is the result of changes in the HCl concentration [75]. Generally, antacids are composed of a combination of metallic compounds, such as Al and Mg hydrotalcites, which gradually hydrolyze thereby controlling the pH at an optimum value [76]. Purified natural clinoptilolite NZ from the Tasajera deposit, in Cuba, has been used as an active ingredient in the new antacid drug Neutacid, which was developed by Rodriguez-Fuentes et al. [77]. These authors reported that clinoptilolite NZ zeolite does not exhibit any harmful toxic hazards towards human beings. Furthermore, they observed that the neutralizing effect of clinoptilolite NZ is a result of proton exchange and hydrolysis of the species present in the zeolite.

Wei et al. have also employed zeolites in NO (nitric oxide) delivery materials in biological systems [78]. They have described the use of moisture-saturated zeolites for the release of NO to cure ulcers inside the stomach and/or intestines, which were caused by bacterial infection. In addition, Reeve and Fallow field have investigated microbial toxicity using HDTMA-Br modified zeolites [79].

Blocking of radioactive strontium using zeolites: An overview

Selection of a candidate for further testing

Strontium-containing materials have been known since 1790 [80]. It was only in 1948, however, that radioactive ^{90}Sr ($t_{1/2}$ = 28.79 years; soft β- emitter, 0.5460 MeV) was reported as one of the products from the neutron fission of 233U [81]. Since Sr is in the same group of the Periodic Table as is Ca, it has similar chemical properties, forming a slightly soluble carbonate and sulphate. Moreover, because it is susceptible to cation exchange reactions, ^{90}Sr is strongly sorbed into clays and various organic matters [82]. Strontium metal reacts violently with water and ignites spontaneously in air to produce SrO and Sr_3N_2. Strontium compounds are almost always present in the atmosphere in the form of a fine dust resulting from coal and oil combustion. These dust particles eventually fall back to the Earth's surface and are subsequently found in surface water and soils, and on plants. Strontium-90 is transported through soils by percolating water and it adheres to soil particles, especially sandy soils.

After uncontrolled or accidental releases of radioactive strontium, e.g., from nuclear testing events, or Chernobyl and Fukushima type incidents, the most important way of the transferring ^{90}Sr to organisms is the consumption of contaminated water, vegetation and animal products. Radioactive strontium has reportedly been detected in various plants at many contaminated nuclear sites [83-86]. Following its uptake in the plants, strontium will be passed to organisms that feed on the plants and eventually on to humans. This pathway substantially contributes to the ingested radiation dose [87]. Once ingested, Sr^{2+} is produced under the acidic conditions in the stomach (pH 3-4). The Sr^{2+} ion closely parallels Ca^{2+} and is taken up through the gastrointestinal track in humans and animals, ultimately becoming part of bone marrow tissue and blood cells. Because $^{90}Sr^{2+}$ is readily incorporated into bone, it leads to the irradiation of the surrounding tissues and the onset of bone disease. For this reason, 90Sr is now regarded as one of the most hazardous nuclear fission products. The decay product of ^{90}Sr is ^{90}Y, which is also a β- emitter further complicating the issue [88].

Owing to the Chernobyl accident, studies in Europe on blocking the uptake of ingested strontium have been concentrated on the reduction of strontium in the domestic animal products. Because of the similarity in their physical and chemical properties, strontium, including radioactive strontium and calcium are proportionally taken up in the food chain. As calcium is present as one of the major nutrients in the diet in much larger quantities than is strontium, 40 to 60 % reduction in the strontium uptake in animals has been achieved by calcium supplementation in feedstuffs. However, the statistical data have shown that this method eventually becomes inefficient when the dietary calcium intake is greater than 100 g.d-1 for dairy cows and 20 g.d-1 for dairy goats; and further increasing the calcium supplement would only reduce the absorption of other essential nutrients [89, 90]. Doubling the quantity of stable strontium in feedstuffs has proved to be ineffective in the prevention of strontium uptake as its quantity is too small [91]. Several limited tests with modified and natural zeolites administered at 0.5 g.kg-1 live weight per day showed approximately 40% reduction of strontium uptake in the gastrointestinal environment [92, 93]. The zeolites tested were stable under low pH; however, the dissociation of strontium binding under the high pH in parts of the animal gut reduced the blocking efficiency. The blocking efficiencies of the methods studied thus far are limited below 60%. There have been no studies related to humans available in literature. Given the fact that only approximately 40% radioactive strontium can be removed from animal products, such as milk, finding effective methods to blocking the ingested radioactive strontium in humans has its significance.

Finding the best sorbent for blocking of strontium-90

Efforts to remove Co, Cs and Sr radionuclides from radioactive waste are receiving continued attention, especially with respect to the waste water produced in nuclear power plants. With this aim in mind, ammonium molydophosphate-polyacrylonitrile (AMP-PAN) has been studied for competitive adsorption [94]. Also, an ion-exchange material that consists of a composite of hydrous manganese oxide and polymethylmethacrylate (PMMA) has been exploited for the removal of strontium ^{90}Sr from aqueous radioactive waste [95]. This composite should be amenable to column procedures for the removal of ^{90}Sr from low-level radioactive waste solutions [96]. This observation is important since it has been long known that inorganic cation exchange materials are preferable to organic ones because of their better thermal stabilities [97]. Unfortunately, there is no obvious relationship between the selectivity of a zeolite for Sr^{2+} and rate at which it can be adsorbed [98]. Organic materials are not well suited for the uptake of radioisotopes because of their poor radiation and thermal stabilities, and significant waste management cost. Most zeolites are unstable in acid environments, thus limiting their possible applications. The only really acid resistant zeolites are mordenite [99] and clinoptilolite [100, 101]. And the latter is well established as a ^{90}Sr adsorbent [102-105]. Sorption of strontium has been investigated under static conditions at ~20 °C using both ^{90}Sr and its stable isotope ^{88}Sr [106]. Adsorption of strontium on montmorillonite [107-109], clinoptilolite [110-112] and natural clays comprised of these two minerals has been extensively studied by many researchers [113]. Clinoptilolite is a member of the high-silicon zeolite group (SiO_2/Al_2O_3=4…10), while synthetic zeolites NaA, NaX, NaY belongs to the low-silicon zeolite group (SiO_2/Al_2O_3=2…3) [114]. Mordenite is the best choice for radioactive waste disposal because of its excellent sorption capacity for $^{137}Cs^+$, $^{90}Sr^{2+}$ and the transuranic elements [115-117].

Various materials are currently being used for the adsorption of radioactive waste, but especially $90Sr^{2+}$, including natural and synthetic zeolites [118], phytosorbent moss [119], multi-walled carbon nanotube (MWCNTs)/iron oxide magnetic composites [120], activated carbon [121], composites of magnetic particles [122], clinoptilolite [123] and kaolinite [124]. Mordenite-type zeolites with a high silica/alumina ratio are preferred for high temperature use and when acidic conditions are involved. Na-mordenite readily adsorbs water, CO_2, SO_2, cyclohexane and p-xylene and cumene, while larger hydrocarbons are physically excluded from them. With H-mordenite, the pore sizes are larger, and o-xylene can be adsorbed [125]. Furthermore, it has been shown that mordenite is more efficient for Cs^+ removal than is zeolite-A4, while the reverse is true for Sr^{2+} and Ba^{2+} removal [126]. Alkali hydrothermal treatment of mordenite results in different types of zeolites, e.g., phillipsite, hydroxysodalite and analcime [127]. The actual zeolite phase formed depends on both the NaOH concentration and the temperature [128-130].

Mordenite and clinoptilolite are useful in removing SO_2 from industrial gas streams [131]. Because of its widespread occurrence and high selectivity for ^{137}Cs and ^{90}Sr, however, clinoptilolite has been the focus of most attention [132]. Clinoptilolite deposits vary widely with the most common cations being Na^+, Ca^{2+} and Mg^{2+} and the ion-exchange properties depend markedly on the type, number and location of these cations [133]. Na-clinoptilolite is the best suited for SO_2 adsorption [134]. Strontium selectivity apparently decreases with a decrease in silica content.

Modification of zeolites by fluoride ion

Modified zeolites are known to exhibit more adsorption capacity for heavy metals than do natural zeolites [135-138]. The most common mineralizer for zeolites is the hydroxide ion OH^-. Replacement of OH^- by F^- as the mineralizer leads to the production of zeolites in acidic media at pH ~5 because of the formation of SiF_6^{2-} [139]. Zeolite syntheses in hydroxide media occur at high pH values (usually >11), while in fluoride media the pH is comparatively low (7-9) [140]. Less supersaturation occurs in fluoride media, which leads to controlled crystal growth and eventually more crystals [141-145]. Somewhat surprisingly, however, rapid crystallization in fluoride media (on a time-scale of hours) yields materials with no defects, while slow crystallization in hydroxide media (on a time-scale of weeks) produces materials containing many defects [141]. There has been relatively little research published on fluoride-silica-alumina zeolite minerals as catalysts, most probably because these materials are already highly active (as compared with Al_2O_3) for acid-catalyzed reactions [146]. Fluoridation greatly increases the activity of siliceous medium-pore zeolites, such as ZSM-5 [147].

Zeolite fluoridation is normally performed in either the gas phase using F_2 or CHF_3 or in aqueous HF or NH_4F solution

[147-150], or by reaction of the zeolite with molten AlF3 [151,152]. A summary of the acidic and catalytic properties of ZSM-5, HY and mordenite zeolites modified by fluoride are available in the literature [153]. Modification of zeolites with fluoride is useful for controlling the acidity of zeolites [154-159]. Le Van Mao et al. [159] have reported the effect of temperature on fluorine-doped ZSM-5 zeolite and showed that there is formation of new Bronsted (B) acid sites in the parent zeolite but without any change in crystal structure. Similarly, Wang et al., [160] have investigated the stability behavior of fluorinated nano-sized HZSM-5 zeolite using different calcination temperatures. These authors concluded that fluorinated HZSM-5 zeolite shows a greater stability in the methylation of biphenyl with methanol.

The starting gel for the synthesis of β-zeolite via the fluoride route is a dense, almost solid material, probably because of the low solubility of the zeolite material at neutral pH [161]. A new route for the synthesis of silica-rich zeolites using F^- instead of OH^- mineralizing species has been developed whereby a neutral or slightly acidic medium (pH 3-10) is employed [162]. The best possible fluoride ion sources are HF, simple fluoride salts or other compounds that yield F^- in aqueous solution (e.g., NH_4HF_2, NH_4F, BF_3, etc.). The sources of the so-called "T elements" (B, AI, Fe, Ga) in zeolites are usually oxides, hydroxides or alkoxides. Organic structure stabilizing species, e.g., amino compounds, such as tetrapropylammonium salts (Pr_4NBr) or amines (Pr_3N) are first neutralized by HF. The crystallization temperature is in the 80-200 °C range and the heating time is often a few days [163]. Fluoride may also be combined with the source of a framework element, e.g., in $(NH_4)_2SiF_6$ or $AlF_3.H_2O$. In the case of aluminium-rich starting gels, however, the sparingly soluble salts NH_4AlF_4 and $(NH_4)_3AlF_6$ may be present- fortunately, these can be removed by washing with an aqueous alkaline dimethylamine solution.

β-zeolites with a wide range of Si/Al ratios can be prepared in the presence of tetraethyl ammonium hydroxide (Et_4NOH) and F- ions at near neutral pH [164]. The resulting zeolites have more hydrophobic sites because of fewer framework defects [165]. Finally, the synthesis of β-zeolite (Si/Al = 12.5) using NH_4F as the fluoride source in basic media under microwave irradiation has recently been reported [166]. High-silica zeolites synthesized in fluoride media have substantially fewer defects as compared to those obtained by the hydroxide synthetic route [167,168]. The thermal stability of β-zeolite, synthesized using NH_4F, has been examined and it is higher than that of β-zeolite synthesized in the absence of NH_4F, because of the fewer defects sites [169].

Water-soluble amines and quaternary ammonium cations are often employed as so-called "structure directing agents" (SDAs) in zeolite chemistry [170]. Replacement of hydrogen atoms by fluorine atoms for some SDAs has a profound influence on the crystallization of both pure silica and aluminophosphate zeolite materials [171,172]. Eilertsen et al. have reported the synthesis of CHA zeolite in fluoride media and they used N, N, N-1-trimethyladamantammonium hydroxide as a SDA [173]. Organofluorides are suitable for zeolite syntheses since the C-F bond is stable under hydrothermal conditions provided that the pH and temperature are not too high [174]. Calcination in air removes the organic and fluorine components [175] opening the microporous voids in the zeolites, which remain highly crystalline. These same authors have also reported that it is possible to synthesize β- and ITQ-4 zeolites containing a wide range of Si/Al ratios (10-∞ for β and 20-∞ for ITQ-4) by properly adjusting the water content [176].

Degree of crystallinity, ion-exchange capacity and selectivity

Amorphous and crystalline impurities are inevitably present in commercially available natural zeolites and these are not considered as intrinsic constituents. Synthetic zeolites can be produced with negligible impurities. The degree of crystallinity can be determined from measurements of the relative intensities of the peaks in powder X-ray diffraction spectra when the reference and sample have a similar history of preparation and composition [177]. The ion-exchange capacities of zeolites and inorganic sorbents change significantly after thermal, hydrothermal and chemical treatments, and have a correlation with th8e degrees of crystallinity of the treated samples relative to their untreated precursors [178, 179]. The degree of crystallinity of a zeolite material is reduced following dealumination processes, such as acid extraction and hydrothermal treatment [180, 181]. The concentrated-acid treatment of clinoptilolite and mordenite materials with high Si/Al ratios, which are otherwise stable in mild acidic solution, leads to the partial breakdown of the frameworks and produces more Si-OH functional groups. Framework Al^{3+} ions associated with extra framework alkaline cations are more vulnerable to attack by acids as the alkaline cations are more easily replaced by hydronium ions [182]. Although the zeolite framework does undergo rearrangement during dealumination, more defects are created due to the loss of framework Al^{3+} ions and the associated extra framework cations. The ion-exchange capacities decrease with the decreasing degree of crystallinity of the treated materials. This situation is also found with zeolites after hydrothermal treatment for dealumination [183]. For zeolites with negligible framework Al^{3+} ions, there will be more stable ion-exchange processes in acid media without the extraction of framework Al^{3+} ions. Introducing fluoride to replace oxygen attached to aluminium will also hopefully lower the vulnerability of aluminium in typical acid media (e.g., HNO_3 or HCl solutions).

Non-crystalline materials having a broad distribution of pore sizes and amorphous structures that allow ready access of cations of various sizes have shown poor ion-exchange selectivity [184]. If a zeolite loses part of its crystallinity in acid media, its selective sorption performance is expected to be weakened.

Conclusions

Zeolites having many cation exchange sites and small pores are suitable for sorption processes because of the molecular sieving effect. Most commercial uses of natural zeolites are based on their ability to selectively adsorb molecules from air or liquids. The cost of the natural zeolites is usually substantially lower than is that of the cheapest synthetic zeolites. Owing to the impurity and contamination in natural zeolites, however, it has become important to synthesize large amounts of zeolites. Strontium-90 selectivity appears to decrease systematically with an increase in the Al/Si ratio, i.e., with decreasing silica content. Synthetic mordenite has large pores, whereas natural mordenite has small pores. AlPO molecular sieves will have only weak catalytic and sorption properties owing to the low concentration of surface OH groups. There appears to be no relationship between strontium selectivity of a zeolite and the rate at which it will remove strontium. Finally, because of their lower cost, high silica content and good cation exchange properties, both clinoptilolite and mordenite can be used to remove Sr^{2+} in the environment. Fluoride ion acts as a good solubilizing agent with associated thermal stability. Fluorine modification is a useful method to control the acidity of a zeolite. Fluoride may be combined with the source of the framework element, such as $(NH_4)_2SiF_6$ or $AlF_3.H_2O$, and be released on hydrolysis. For the synthesis of high-silica zeolites, fluoride media have resulted in substantial decreases in defects as compared to zeolites obtained by the hydrolysis route. By using the fluoride route, high-silica zeolites can be synthesized, even at acidic pH. Calcination in air leads to the removal of fluorine and organics. Thus, it is important to synthesize fluorine-modified zeolites at low temperatures and acidic pHs if one wants them to have good thermal stability, reasonable solubility, as well as less defect sides. It is therefore suggested that fluoride-containing clinoptilolite and mordenite zeolites will be the best choice for sorbents required to block the uptake of ingested ^{90}Sr in organisms and we plan to investigate this possibility in the future.

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