INORGANIC SORBENTS FOR RADIOSTRONTIUM REMOVAL FROM WASTE SOLUTIONS: SELECTIVITY AND ROLE OF CALIXARENES

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ABSTRACT

The challenge in the remediation of ⁹⁰Sr-contaminated waters arises from the need to achieve very high removal efficiencies to meet discharge targets from waste effluents containing relatively high concentrations of non-radioactive cations. Low-cost natural zeolites are not selective for strontium over other divalent cations, notably such ions as calcium; and produce low ⁹⁰Sr removal performance, and large volumes of spent sorbent waste. The synthesis and use of selective, synthetic inorganic sorbents could prove to be a feasible approach for high ⁹⁰Sr removal efficiencies, and much smaller volumes of secondary solid waste generation. The essential advantages of inorganic sorbents include their stability and resistance to radiation, and the potential for producing stable waste forms such as vitrified glass or ceramics for disposal. However, the cost of strontium-specific sorbents is prohibitive for large-scale applications at present.

This paper is a review of the reported information on removal mechanisms and performance of Sr-specific inorganic sorbents. The analysis has revealed promising performance, efficiency and selectivity for strontium removal from solutions containing low and high concentrations of salts. The leading sorbents are crystalline silicotitanate and oxides of metals such as titanium. An initial assessment has also been made of the performance of calixarene-based macrocyclic compounds. These are known for their selectivity for strontium in solvent extraction processes.

From the initial strontium removal results in bench-scale tests using different solid substrates, impregnated with calixarene derivatives, only sodium-mordenite impregnated with calyx[8]arene octamide gave an overall strontium removal efficiency in the range of 90 to 95% in the presence of 3.5 ppm calcium. There was no improvement observed for strontium-removal efficiency or selectivity over calcium in the calixarene-impregnated inorganic sorbent matrix. In several tests, the overall efficiency of the sorbent was reduced by up to 50% in the presence of high concentrations of Ca (e.g., 15 ppm). Presently, the reasons for this behavior are not evident.

This paper also reports high strontium removal performance measured in column tests using crystalline silicotitanate sorbent with actual ground waters containing low and high concentrations of calcium. The spent sorbent waste volume has been estimated to be approximately one order of magnitude less than that using a natural zeolite such as chabazite. Until costs can be lowered, the presently available selective sorbents are not attractive for large volume applications. Further development in the modification of relatively low-cost sorbents, including natural zeolites and certain metal oxides such as titanium and zirconium oxides, would be advantageous.

1. INTRODUCTION

This paper addresses issues based on the use of inorganic sorbents for the removal of strontium-90 (⁹⁰Sr) from aqueous wastes (e.g., ground waters). Sixteen major radioactive isotopes of strontium exist [1.], but only ⁹⁰Sr has a half-life sufficiently long (~29 years) to warrant concern. The main health concerns for ⁹⁰Sr are related to the energetic beta particle from its daughter yttrium-90. Strontium-90 is a heat-producing isotope (decay heat: 3.137 x 10⁻¹⁴ W/Bq) that behaves chemically much like calcium, and therefore tends to concentrate in the bones and teeth. It is commonly found in many aqueous, process waste effluents and ground waters migrating from historic nuclear waste storage sites. ⁹⁰Sr is present with naturally occurring inactive strontium. The most prevalent stable isotope is ⁸⁸Sr, comprising about 83% of natural strontium. The natural strontium is present in concentrations generally orders-of-magnitudes greater than ⁹⁰Sr in many of the ground waters. Thus ⁹⁰Sr removal also implies the removal of inactive strontium. ⁹⁰Sr is usually accompanied by high concentrations of other cations such as Ca, K and Na, which further complicates its removal. The ⁹⁰Sr removal target is defined by the remediation goals set in a given jurisdiction. For example, a common objective is to meet the drinking water limit of 5 Bq ⁹⁰Sr /L in most countries or 0.34 Bq/L in the US.

Low-cost natural zeolites are non-selective for strontium over other divalent cations. The implication is that use of these materials for strontium removal generates large volumes of secondary solid wastes requiring costly management. The synthesis and use of selective, synthetic sorbents could prove to be a feasible approach for high ⁹⁰Sr removal efficiencies, and result in much smaller volumes of secondary solid waste generation.

This paper presents a review of the major solid sorbents studied previously for strontium removal from aqueous solutions. Results using simulated and actual ground waters with selected commercially available sorbents are examined. Finally, initial results of a study of calixarene(s)-impregnated inorganic substrates performed as part of a collaborative participation of the G8 Global Partnership program in progress at the Institutes of Organic Chemistry in Kiev and Single Crystals in Kharkiv within the National Academy of Sciences Ukraine are discussed. The collaborative project (STCU #4955) is managed by the Science Technology Centre Ukraine (STCU) and AECL-Chalk River Laboratories (CRL) is one of the foreign collaborators.

2. ORGANIC SORBENTS AND STRONTIUM-90 REMOVAL PERFORMANCE

2.1 Inorganic sorbents

Inorganic sorbents, also referred to as ion exchangers, are generally stable at relatively high temperatures [2.][3.] and in ionizing radiation. The most important groups of inorganic sorbents are clays, zeolites, hydrous oxides, insoluble acid salts, heteropolyacids and hexacyanoferrates.

Certain inorganic sorbents also show high selectivities for specific ions, often better than their organic analogs. The selectivity of these sorbents has been examined in terms of ion-sieve effect, steric factor, ion size preference, an entropy effect and ion memory preference [4.].

In this paper, inorganic sorbents for ⁹⁰Sr removal from aqueous solutions are considered under the following three categories of materials:

- 1. Natural inorganic materials
- 2. Synthetic inorganic compounds
- 3. Inorganic materials impregnated with organic reagents

2.1.1 <u>Natural Zeolites</u>

The removal of radionuclides from waste solutions using natural zeolites [5.] has been studied since the 1950s. Among the more than 30 different species of zeolites that occur in nature, only some natural zeolites such as analcime, chabazite, clinoptilolite, erionite, ferrierite, mordenite, and phillipsite occur in sufficient quantity and purity to be considered as viable mineral resources [6.]. Zeolites are three dimensional, microporous, crystalline solids with well-defined structures that contain aluminum, silicon and oxygen in their regular framework. The net negative charge of the framework [7.] is balanced by cations (e.g., alkali and alkaline-earth metals). These cations and water are located in the pores of the zeolite, and the cations can be readily exchanged for other cationic species. Zeolites have reversible hydration properties in addition to their cation-exchange properties [8.].

Although ion exchange is the most predominant mechanism for cation removal by natural zeolites, physical adsorption of cations cannot be ruled out. Consequently, the term, "sorption", will be used to denote these combined actions. Because of the favourable cation removal capacity and low cost of many natural zeolites, they are being used increasingly for the treatment of wastewaters containing radiostrontium and radiocesium ions [9.][10.][11.].

2.1.2 Synthetic Inorganic Compounds

A detailed review and account of such sorbents and ion-exchange behavior can be found in several publications [2.][3.][4.][11.][12.][13.][14.][15.].

Many hydrous oxides of metals are known to have suitable structures for use as cation and anion exchangers. These can be divided into particle hydrates and framework hydrates. Most of the group 3, 4, 13 and 14 metals form particle hydrates, having a bulk structure resembling one of their ceramic oxides. The surface, however, is largely covered with hydroxyl groups, and both coordinated and hydrogen bonded water molecules. The higher the pH, the greater is the uptake of cations, and conversely anion uptake increases with increasing acidity in solution. Examples are SnO₂ and ZrO₂.

Framework hydrates are formed by metals in groups 5 and 15 in their higher oxidation states. For example, Sb can form a structure referred to as polyantimonic acid $[(H_3O)_2Sb_2O_6.xH_2O]$ having an exchange capacity of 5.1 meq/g. This rigid pyrochlore structure imposes size limitations on cation selectivity. Several papers describe mixtures of hydrous oxides with compounds such as stannic molybdate, tin antimonate, zirconium molybdate and zirconium tungstate. The ion exchange behavior seems to be caused by the presence of hydroxyl groups on the surface of the gels.

There are numerous compounds that are built from frameworks that enclose tunnels, including zeolites. Examples are sodium titanium silicate, pharmacosiderites, manganese oxides, and ammonium molybdophosphate ($(NH_4)_3PMo_{12}O_{40}$, AMP). AMP does not have a tunnel structure, but behaves in many respects as if it does. Titanium silicate ($Na_2Ti_2O_3(SiO_4) \cdot 2H_2O$) was discovered through a collaboration between Sandia National Laboratory and Texas A&M University. This compound was reported to be highly selective for Cs⁺ and Sr²⁺ removal in the presence of large concentrations of sodium ions. It should be noted that since Sr²⁺ only exchanges in neutral or basic solutions, it would be exchanged as Sr(OH)⁺. The sodium titanosilicate is referred to as the crystalline silicotitanate (CST)[14.].

Behrens et al., [16.] have reported the synthesis of a semicrystalline, layered sodium nonatitanate $(Na_4Ti_9O_{20}\bullet xH_2O)$ and several pharmacosiderite materials (three dimensional tunnel-structured compounds) of the type $[M_3H(AO)_4(BO_4)_3\bullet 4-6H_2O)$, where M=H, K; A=Ti, Ge; B=Ti, Ge]. These are effective for strontium and cesium removal from US DOE waste simulants.

For actual alkaline storage tank waste applications involving the removal of Sr and Cs, a pioneering work involving synthesis and pelletization of two sorbents, a crystalline form of Na₄Ti₉O₂₀ for Sr, and synthetic mica for Cs, was initiated by USDOE through Pacific Northwest Laboratories in collaboration with Texas A&M University and Allied Signal Corp. (now UOP LLC, a Honeywell Company; [17.][18.]).

A summary of key Sr removal performance data for synthetic inorganic sorbents in the literature is given in Table 1 (Data included in Table 1 cite references [19.] to [31.]).

2.1.3 Inorganic Materials Impregnated with Organic Reagents

Selective removal of Sr using solvent extraction reagents (e.g., crown ethers, calixarenes) has been known for decades [31.][32.]. Many of these function well in highly radioactive waste solutions. Examples are 1) a chlorinated cobalt dicarbollyde with polyethylene glycol in a polar diluents, 2) 0.15 M 4, 4',(5')-di(tert-butylcyclohexano-18-crown-6 (DtBuCH18C6) and 1.5 M tri-n-butyl phosphate in a diluent. An extraction chromatographic material specific for Sr, prepared by impregnating 1 M (DtBuCH18C6) in 1-octanol into pores of a polymeric support, has been extensively used. A macroporous, silica-based DtBuCH18C6 polymeric composite, DtOct/SiO₂-P, has shown promising results in Sr removal from acidic solutions (optimum performance for 2 M HNO₃) containing most interfering cations except Ba.

The synthesis and use of use of specific calixarenes for the removal of cations of many isotopes in nuclear waste solutions has been reported [32.]. As part of the STCU project #3863, over two dozen calixarene extractants were synthesized, characterized and tested for the separation of different cations including actinides from nuclear waste solutions. Specific calixaranes for low concentrations of Sr, Cs and selected actinides were also synthesized and tested as part of the STCU #4955 project. The synthesis goal is to functionalize the macrocyclic calixarene skeleton (readily available from products of para-substituted phenols and formaldehyde cyclocondensation) by phosphoryl-, carbonyl- or nitrogen-containing fragments in order to create pre-organized cavities for the retention of desired metal ions of corresponding size and topology.

As to the name, *calix* means the Greek vase and *arene* indicates the aryl residues in the macrocyclic array. Calixarenes are easily amenable to chemical modifications. They are synthesized easily in a simple, one-pot procedure.

(2)

Preliminary test results with actual ⁹⁰Sr-contaminated groundwater samples using calyx[8]areneamide-impregnated in different inorganic solid substrates (Na-mordenite, hydrogel of methyl silica acid and hydroxylapatite) are discussed in Section 3.

Apart from the goal of using these inorganic materials/sorbent impregnated with Sr-specific reagents for radiochemical analysis, the ultimate goal is also to explore the use of this approach of producing low-cost alternative sorbents for larger-scale waste remediation applications involving neutral and acidic waste solutions. As discussed previously in Section 2.1.2, the commercially available inorganic sorbents are suitable only for Sr removal from alkaline solutions.

2.2 Strontium-90 Removal Parameters

Several performance parameters are used to judge the ⁹⁰Sr removal performance of a sorbent. One or more of these parameters are used to qualify the suitability of a sorbent for an application. In the sorbent performance data available from the literature (Table 1), the following parameters are referenced.

1. Equilibrium Partition Coefficient, Kd

The efficiency of a sorbent is often measured by distribution or partition coefficient, K_d , defined as:

$$K_d = [(C_o - C_e)/C_e] x [V/M] (in mL/g)$$
 (1)

where,

 C_0 , C_e are initial and equilibrium activity concentrations per unit volume for ⁹⁰Sr, respectively.

V is the volume of aqueous phase (mL)

M = weight of the sorbent material (g)

2. Maximum (Theoretical) Exchange Capacity of Sorbent

The ion exchange capacity of sorbent material is a key characteristic defined as the weight of loaded (sorbed) cations per unit mass of the sorbent. The theoretical exchange capacity is the maximum uptake possible on the sorbent surface. It is dependent on the availability of exchange sites(s) in the sorbent or alternative vacancies in the frame work structure. In actual waste solutions, however, various factors such as the presence of competing cations and solution pH can significantly lower the actual capacity.

The adequacy of a particular sorbent for removing specific metals depends on the chemistry of the solution. A key parameter is needed to address the difference between a theoretical maximum efficiency and that obtained under actual test conditions in a particular application.

3. <u>Percent Removal Efficiency</u>, R (%)

 $R(\%) = [(C_o - C_t)/C_o] \times 100$

The activity concentration at a given time, t, of contact between the sorbent and the solution containing, say 90 Sr is C_t. When C_t = C_e, this denotes equilibrium activity concentration. Thus, when used in Eq. (2), provides equilibrium removal efficiency.

(5)

4. Amount of Material Sorbed on Sorbent

The amount of 90 Sr sorbed onto the sorbent material at any time, $q_t (mg/g)$ may be calculated from Eq.(3):

$$q_t = [(C_o - C_e)/C_o] \times C_s \times (V/M)$$
 (3)

The decontamination factor is defined as the ratio of the initial concentration of a certain cation in a solution to be removed (C_0) to the final concentration of that cation in solution (C_f), after using a specific treatment such as sorption.

$$DF = C_o/C_f \tag{4}$$

6. Selectivity

The selectivity coefficient is used to measure the ion exchange equilibrium. For the Sr/Ca exchange, the selectivity coefficient $k_{Sr/Ca}$ is defined as:

$$k_{Sr/Ca} = [Sr]_S [Ca]_L / [Sr]_L [Ca]_S$$

where, the subscript letters S and L refer to the equilibrium ion concentrations in the solid and liquid phases, respectively.

In low-level waste solutions, as in ground waters, the activity concentration of 90 Sr is typically on the order of 100 to 1,000 Bq/L. This corresponds to a chemical concentration of 19.3-193 parts-per-billion. The concentration of Ca is always much higher than that of Sr (>>1 ppm).

2.3 Commercial Sorbents for Sr Removal from Waste Solutions

In addition to natural zeolites, three inorganic sorbents are commercially available with some degree of selectivity for Sr^{2+} . These are 1) the CST (marketed by UOP LLC, A Honeywell Company, USA); 2) a sodium titanate under the commercial name Sr-Treat (marketed previously by Selion Corporation (now by Fortum, Finland); and 3) a layered, semi-crystalline compound, sodium nonatitanate (Na₄TiO₉O₂₀) (available previously from Allied-Signal in pelletized form, and now from UOP LLC, USA). All of these sorbents work well in basic solutions. The sodium nonatitanate is known to be effective for Sr removal from highly basic tank waste solutions. The structure of this compound and its selectivity over alkaline earth metals are not well understood. An Oak Ridge National Laboratory study has reported [18.] a study of Sr removal from waste waters containing alkaline earth metals including Ca and Mg. It was also reported that approximately 40% of the sodium nonatitanate pellets disintegrated to a fine powder in batch studies involving 7 days of mixing. The price of these compounds is in the range of \$1,000-2,000 per kg.

Table 1 presents a summary of Sr removal performance data for the major inorganic sorbents from the literature. Key observations in Table 1 are 1) most synthetic inorganic sorbents give high Sr removal performance (e.g., K_d values on the order of 10^4-10^5 mg/L) for alkaline solutions when the interfering ions are low or absent; 2) the K_d value decreases (by a factor of 10^2-10^3) in the presence of interfering ions including Na, Ca and Mg; 3) the commercially available sorbents, CST and SrTreat, show favorable removal performance in slightly alkaline to highly basic solutions (these sorbents exhibit high selectivity for Sr over Na, but selectivity is impacted as the concentration of other cations (e.g., Ca) increases); and 4) only a few synthetic sorbents such as the tin antimonates and potassium metal sulphides work favourably in acidic solutions.

3. EXPERIENCE WITH STRONTIUM REMOVAL AT CRL FROM DILUTE WASTE SOLUTIONS

Selected results for Sr removal from dilute solutions (simulated and actual ground waters) using selected natural zeolites, Sr-Treat and CST are presented in Tables 2-4 and Figures 1-3. Laboratory-scale batch and continuous-column mode tests have been performed with selected ground waters and inorganic sorbents to assess the effectiveness of ⁹⁰Sr removal with respect to removal efficiency and selectivity. The concentration of ⁸⁵Sr in the water samples was determined by gamma spectrometry. ⁹⁰Sr concentration was determined by liquid scintillation counting (LSC). The removal of other non-radioactive species (Ca, Mg, K, Na) was examined by either inductively coupled plasma atomic emission spectroscopy (ICP AES) or atomic absorption spectroscopy (AA).

3.1 Batch Sr Removal Results with Natural Zeolites

For tests with natural zeolites, a 50 mL aliquot of the feed solution (pH~6-7), which contained ⁸⁵Sr and calcium was shaken with 0.05 g of zeolite at room temperature (\sim 23°C) for a predetermined conditioning time. The supernatant was then separated from the zeolite mass by filtering the suspension through a Whatman #3 (6-µm pore diameter) filter paper. The filtrate and the original feed solution were analyzed for contaminants [33.].

In general, as shown in Figure 1, the radiostrontium removal efficiencies by different natural zeolites reached approximately 90% or higher within one hour of conditioning with a solution containing low concentrations of calcium (e.g., 10 mg/L Ca). As expected, the similarity in physical-chemical properties of strontium and calcium resulted in significant reduction of strontium removal efficiency when the calcium concentration was increased, for example, to 100 mg/L. It should be noted that the strontium concentrations used in the tests were one to two orders of magnitude lower than the calcium concentration of zeobrite (Ca-clinoptilolite), all other zeolites tested in our study produced relatively high strontium removals (84 to 98%). Sodium-chabazite (TSM-310) had the highest strontium removal whereas zeobrite had the lowest strontium removal performance (~75%). Overall, sodium-chabazite (TSM-310) gave the best Sr removal performance for the range of Ca concentration (10 to 100 mg/L) tested.

The cation-exchange performance of a zeolite depends on the size and charge of the exchanged cations and the structure of the zeolite. Most of the zeolites have channels whose dimensions, because of strong (Si,Al)-O-Si bonds in three dimensions, are unchanged by ion-exchange. In most cases, the cations are situated along with water molecules in these interconnected channels, which provide paths for the cations to diffuse freely throughout the structure. Studies (e.g., [34.]) have shown that the diffusion of a particular cation is dependent on its size, relative to the smallest free diameter of the channel, and on its charge.

It appears that the strontium removal behaviour of the zeolites may be related to the elemental composition of the zeolites, although this alone may not offer a complete explanation of the observed performance. For a zeolite with relatively high Si/Al ratio, the negative charge on the framework and the coulombic interaction energy would be reduced. Thus, the repulsion-dispersion interaction between the diffusing cation and the ring of oxygen atoms making up the channels is not negligible. This will result in a less favourable environment for the cation-ion exchange (e.g., low cation exchange capacity).

Table 1: Inorganic Sorbents for Strontium Removal from Solutions

Inorganic Sorbent	Scale of Production	Sr Removal Performance	Selectivity	Sr Removal Mechanism	Ref
Sodium (nano) Titanate (Na ₄ Ti ₉ O ₂₀ . xH ₂ O)	Commercial	The Sr exchange capacity from pure SrCl ₂ solution is 4.4 - 5.3 meq/g (theoretical) at pH 5.5-12.8. The K _d values are 52, 5,000, 56,000 mL/g at pH 2, 4 and 6, respectively. The capacity increases with increasing pH where it reaches a maximum at pH 11.	The sorbent is effective in the presence of 4 M Na ⁺ (K _d 3100 mL/g). Interfering cations are Ba > Sr = Ca > Mg. There is no selectivity over Ca ²⁺ (K _{Sr/Ca} = 1).	Removes Sr by ion exchanging with Na. Na ₄ Ti ₉ O ₂₀ + 2 Sr ²⁺ \rightarrow Sr ₂ Ti ₉ O ₂₀ + 4 Na ⁺	[19.]
Sodium Titanium Oxide (Sr-Treat)	Commercial	Average decontamination factor (DF) is 7,400 for solutions 0.4 g/L salt (Na, Ca, Mg, and Fe) at pH 9.8. The optimum pH range for its use is ten and above. Decontamination factors higher than 10,000 were obtained which decreased by more than two order of magnitude in solutions containing 2 mM Ca (at > 400 treated bed volume). Maximum capacity observed at pH >10.	High sodium (5 M) has no impact on Sr loading ($K_d \sim 10^4 \text{ mL/g}$). Calcium negatively impacts Sr ²⁺ removal (K_d decreased from 15,000 mL/g to 4,000 mL/g as Ca increased from 1.4 mM to 14 mM). The sorbent has no selectivity between Sr ²⁺ and Ca ²⁺ . K_d for Sr decreased by NH ₄ ⁺ and Mg ²⁺ but K ⁺ and Li ⁺ have no effect on Sr uptake.	Removes Sr by exchange with cations such as Na and hydronium ions.	[21.]

Inorganic Sorbent	Scale of Production	Sr Removal Performance	Selectivity	Sr Removal Mechanism	Ref
Tin Antimonate "SnSb(P)"; P represents Pyrochlore Sn:Sb 1:3.8 and "SnSb(MOX)" MOX denotes Mixed Oxides Sn:Sb= 1:1.2	Laboratory scale	SnSb(P) shows excellent Sr removal from acidic solutions (pH 3.5) with DFs of 2,500 up to 16,000 bed volume (BV), but decreased to a DF of 300 as number of treated BV was increased to 25,000.	Selectivity tests are not reported for SnSb(P). However, the presence of competing ions (Ca) is expected to dramatically decrease the DF value. SnSb (MOX) gave DFs > 5,000 from solutions containing Ca ²⁺ (1.5 ppm) and Na+ (100 ppm) at pH 6.7. With Ca ²⁺ at 15 ppm gave DFs > 2,500. The selectivity for ions at pH <3 is Co ²⁺ > Ni ²⁺ > Sr ²⁺ > Ca ²⁺ > Mg ²⁺ > Cs ⁺ > K ⁺ > Na ⁺ .	No mechanism reported. Amorphous tin antimonates with 67% Sn showed superior exchange properties.	[22.]
Potassium Multi- sulfides (KMS-1); K _{2x} Mn _x Sn _{3-x} S ₆ (x=0.5-0.95)	Laboratory scale	This sorbent is efficient with K_d as high as 2.49 x 10 ⁴ mL/g for Sr. A removal efficiency of 96.3 % occurs for pure Sr solutions. The sorbent works effectively in entire pH range (0.4-14).	The K _d decreased to 1.8 x 10^4 mL/g in the presence of (Na =1.1 mM; Ca = 0.28 x 10^{-1} mM; Mg = 1.5 x 10^{-1} mM; Cs = 6.9 x 10^{-2} mM) at pH 11. The sorbent is effective in presence of 5 M Na ⁺ (K _d = 5.84 x 10^3 ml/g). The order of selectivity is Sr ²⁺ > Ca ²⁺ > Mg ²⁺ > Cs ²⁺ >> Na ⁺	Polycrystalline KMS-1 replaces K ⁺ with Sr ²⁺ ions, also supported by X-ray diffraction measurements	[23.]

Inorganic Sorbent	Scale of Production	Sr Removal Performance	Selectivity	Sr Removal Mechanism	Ref
Crystalline Silicotitanate (CST)	Commercial scale	K_d Sr was 6 x10 ⁵ mL/g, this value decreased to 2x10 ² mL/g in presence of competing cations (Na= 400 ppm, K= 18 ppm, Ca = 20 ppm). The sorbent removes Sr from neutral and alkaline solutions with maximum Sr observed at pH 14). The sorbent capacity is 1050 meq/kg with a K _d value for Sr of 6x10 ³ mL/g for solutions containing Ca (45 ppm), K (1.2 ppm) and Na (18 ppm) at pH 7-8.	Effective for Sr removal in high salt waste solution, the presence of high sodium ion does not significantly suppress the Sr ²⁺ loading, however K ⁺ has a significantly negative impact for Sr ²⁺ removals, increasing K ⁺ from 1.2 - 18 ppm caused the K _d for Sr ²⁺ to decrease from $6x10^5$ to $2x10^2$ mL/g. Order of selectivity: Cs ⁺ > Sr ²⁺ > K ⁺ > Na ⁺ > Ca ²⁺ > Mg ²⁺ .	Detailed ion exchange mechanism is not known. There is evidence to suggest that diffusion of non hydrated Na out of the sorbent lattice occurs and is replaced Sr in the spaces situated in the CST lattice.	[24.]
Antimony Silicates doped with tungsten (WSbSi6)/ W:Si:Sb = 1:1:0.4 Also, WSbSi4 and WSbSi2	Laboratory scale	High Sr uptake with K _d of 40,000 mL/g in 0.1 M HNO ₃ solution (without interfering cations). The sorbent removes Sr efficiently from acidic solutions 0.1 M HNO ₃ (pH 1) and up to pH 6.	High concentrations of sodium do not affect Sr^{2+} uptake. From K _d Sr of 40,000 mL/g at 0.1 M Na ⁺ , the presence of Ca ²⁺ (0.01 M) as calcium nitrate reduced K _d for Sr ²⁺ to 1000 mL/g. The undoped sorbent removed Sr more efficiently in the presence of Ca (K _d = 4,300 mL/g at pH 7.4). At alkaline pH Sr(OH) ⁺ speciation plays a favourable role.	The addition of Si influences the ion exchange properties of the sorbent by creating vacancies in the structure.	[25.]

Inorganic Sorbent	Scale of Production	Sr Removal Performance	Selectivity	Sr Removal Mechanism	Ref
Crystalline Synthetic Tunnel Manganese Oxides- Cryptomelane- Type-Manganese Oxide (potassium) CRY-1(K) &Todorokit-Type- Manganese Oxide (magnesium) TOD- 1(Mg).	Laboratory scale	$K_d Sr > 10^6 mL/g was$ obtained for both CRY-1 and TOD-1(Mg). Large K_d values $(10^4-10^5 mL/g)$ for Sr for solutions containing 0.001- 0.1 M Na or K at pH = 7. Below pH 10 the K_d for Sr decreased linearly on a logarithmic scale where the K_d was 3,500 mL/g at pH 8, 2,000 at pH 7, 1,000 mL/g at pH 6, and reached a low value of <1 mg/L below pH 4.2. The sorbent did not remove Sr from acidic waste solutions pH <2.	Increasing Na or K concentration from $0.03 - 0.3$ M resulted in corresponding decrease in K_d of 100- 10 mL/g. Calcium selectivity was $K_{Sr/Ca} \approx 10$ at pH 7.3-8.0. In the presence of 0.1 M NaNO ₃ , K_d for TOD-1(Mg) decreased to 11,100 mL/g and for CRY-1 the decrease was drastic (to 149 mL/g).	Strontium uptake takes place by sorption into the tunnel structure of the sorbents. For example, TOD-1(Mg) tunnel size is 4.6 Å with Mg in the tunnel. The compatibility of the size of the hydrated ion to be situated in the tunneled vacancy determines the removal efficiency for that ion. Ion exchange is the dominant mechanism for Sr removal for trace levels in solutions.	[26.]
Zeolites (synthetic — IE-96, and its modified version TIE-96); Natural zeolite — clinoptilolite; composite)	Commercial /Laboratory scale Commercial scale	The K_d Sr for modified zeolite TIE-96 and IE-96 was as high as 26,000 and 21,000 mL/g respectively. Clinoptilolite gave a lower K_d Sr value of 6,000 mL/g, in (17 ppm Ca, 40 ppm initial Sr and total salt content 1 g/L). K_d Sr for natural zeolites (clinoptilolite) was 6000 mL/g, the K_d was reduced to 680 mL/g in presence of 5 g/L total salt content.	All Zeolite-type materials showed a dramatic decrease in strontium uptake as calcium concentration and/or as total salt content increases, the K_d Sr for TIE- 96 and IE-96 decreased to 1,440 and 1,360 as Ca content increased to 85 ppm and total salt content was 5 g/L.	Strontium is removed by sorption into fixed size cavities situated in the regular frame work structure of the zeolite material, the selectivity is dependent on the diameter of the cavities in the zeolite structure.	[27.]

Inorganic Sorbent	Scale of Production	Sr Removal Performance	Sr Removal Performance Selectivity		Ref
In Situ Mixed Iron Oxides (IS-MIO) [mixture of Fe(II)/ Fe(III) oxides and hydroxides]	Laboratory scale	Effective in high salt content (5.6 M Na) solution (pH 14) with a DF = 1,000 in 1 h which increased to 1,800 in 4 h.	Impact of other interfering cations was not reported.	Sr removal mechanism could be either by adsorption on the surface of the material or co- precipitation.	[28.]
Hydrous Zirconium Oxide (HZO)	Laboratory scale	The ion exchange capacity was 3.5 meq/g in solutions containing 0.1 M Na and 10 ppm Sr. The removal efficiency was > 90% after 1 h at 30°C, and 98% at 35°C.	Na, Ca and Ba negatively impacted Sr removal. The K _d for Sr decreased from $10^{4.5}$ to $10^{2.5}$ with increase in Na ⁺ concentration ([Na ⁺] = $10^{-1.2}$ to $10^{0.2}$). K _d decreased from 1,154 mL/g to 50 mL/g as Ca or Ba concentration was increased from zero to 492 mg/L.	Sr sorption occurs by ion exchange: $2Na_s^+ + Sr_a^{+2} \rightarrow Sr^{+2}_s + 2Na_a^+$ Where the subscripts, 'a' is aqueous phase and 's' is sorbent phase. The sorbent can act as cationic or anionic exchanger depending on the net charge on the oxide surface.	[29.] [30.]

As expected, based on the lowest Si/Al ratio values among the zeolites tested (Table 2), chabazite (TSM-310, ZS500H) performed the best for strontium removal in the presence of high concentrations of competing calcium ions (100 mg Ca/L). Of the two chabazites tested, the Na-chabazite (TSM-310) revealed slightly higher removal efficiencies for strontium (97-98%) than Ca-chabazite (ZS500H, 88-95%) over the range of competing calcium ion concentrations (10 and 50 mg Ca/L). The higher strontium removal by Na-chabazite may be because sodium ions are more easily displaced than calcium ions in the zeolite by strontium ions. Although the diameters of Na⁺ (1.90 Å) and of Ca²⁺ (1.98 Å) are similar, the self-diffusion coefficient of Ca²⁺ was found to be lower [34.]. These Ca²⁺ ions are locked in sites that are barred for energetic reasons to the divalent ions. However, at 100 mg Ca/L the two chabazites removed (within experimental error), approximately 93% of the strontium.

With chabazite, the channels have a free diameter of 3.9 Å, and are thus much larger than the diffusing ions (e.g., the diameter of a calcium ion is 1.98 Å and the diameter of a strontium ion is 2.26 Å). The coulombic interaction is the main control mechanism. For mordenite, because it has a more complicated channel structure, the minimum free diameter of the channel is approximately 2.8 Å. Diffusion of the large ions is limited by the relatively small free diameter. This implies that chabazite has more pore space or capacity to retain cations and certain compounds. High sodium, and low calcium and potassium values are indicative of the relative ease of exchange of strontium (with a diameter of 2.26 Å). Calcium and potassium in the zeolites have been found to be more difficult to exchange with the free cations than sodium because of relatively low diffusion rates and large ionic dimensions. An analysis of the chemical composition expressed as ratios of dominant species (Table 2) suggests that TSM-310 has the lowest values for mole ratios of Si/Al (= 3.1) and Ca/Mg (= 0.3), and the highest value for Na/K (= 11.3). Calcium-chabazite (ZS500H) has the next best favourable properties (Si/Al = 3.6; Na/K=3.8), but the Ca/Mg ratio is slightly higher (=2.4) than Na-clinoptilolite (Ca/Mg = 1.9). The relatively poor performance of other zeolites tested at high concentrations of competing calcium ions may also be due to relatively high values for Si/Al and Ca/Mg, and low values for Na/K.

The clinoptilolites performed similarly to Chabazite for strontium removal, but only at low Ca concentrations. The relatively superior performance of the TSM-140 Na-clinoptilolite as compared with the other clinoptilolites in the presence of the competing calcium ion can be rationalized in terms of the low values of Si/Al and Ca/Mg, and high value of Na/K in the case of TSM-140 Na-clinoptilolite (Table 2).

3.2 Sorbent Column Continuous-Flow Test Results

Based on the bench-scale results, two natural zeolites (Na-chabazite (TSM-310) and Naclinoptilolite (TSM-140)) and two commercially available synthetic Sr removal sorbents were chosen for comparison. For the test work, two types of groundwater with compositions summarized in Table 3 have been used [35.].



Figure 1: Sr-85 Removal Efficiencies for Different Zeolites

Table 2:	Key Elements Controlling the Effectiveness of Strontium Removal in
	Selected Zeolites

	Si/Al	Ca/Mg	Na/K	Fe + Na
	(mole ratio)	(mole ratio)	(mole ratio)	(wt. %)
TSM-310 (Na-chabazite)	3.1	0.3	11.3	6.5
ZS500H (Ca-chabazite)	3.6	2.4	3.8	4.5
TSM-140 (Na-clinoptilolite)	5.4	1.9	2.7	3.2
Clinoptilolite (K-clinoptilolite)	6.0	3.7	0.4	2.2
Zeobrite (Ca-clinoptilolite)	4.6	3.1	0.8	1.2
Zeobrite 100 (Ca/K-clinoptilolite)	4.8	2.5	0.5	1.0
Mordenite (Ca-mordenite)	4.7	7.7	1.0	0.3

Species	Concentrations		
	SW Stream	CP Stream	
	(avg.)	(avg.)	
Strontium (mg/L)	0.2	0.01	
Strontium-90 (Bq/L)	1700	1500	
Calcium (mg/L)	25	2	
Iron (mg/L)	0.01	0.05	
Magnesium (mg/L)	10	0.7	
Sodium (mg/L)	100	12	
Potassium (mg/L)	4	0.9	
Condcutivity (µS/cm)	800	60	
pН	6.5	6.0	

Table 3: Groundwater Characteristics of the South Swamp (SW) and Chemical Pit (CP) Streams^a

^a Although the concentrations for these species will vary over a wide range with time, the values reported are from collected samples that have been combined for testing. Thus, they represent time-averaged compositions.

Laboratory-scale experiments were performed using one centimetre diameter glass columns packed with either natural zeolites (clinoptolite, SteelHead Specialty Minerals TSM 140; chabazite, TSM 310) or synthetic media (UOP, IONSIV IE-911, (CST); Selion OY (now Fortum, Finnland), SrTreat, a sodium titanate). The media were slurried into the columns to an average bed height of 10 cm (8 mL bed volume, BV). Several volumes of distilled water were flushed through the columns prior to the beginning of each test in an attempt to remove fines and avoid column plugging. Using a peristatic pump, water collected from the contaminated stream was passed through the packed column at a constant flow of 4 mL/min or 0.5 BV/min (a flow rate was selected, which provided suitable residence time for exchange/ removal of the contaminant, not to damage zeolite and cause column plugging). Effluent from the column was collected at regular intervals using a fraction collector.

3.2.1 Natural Zeolite

Contaminant removal performance data for the various sorbents tested were determined by following the ⁹⁰Sr breakthrough trends. ⁹⁰Sr breakthrough results with ion exchange column tests using the SW stream revealed that between the two natural zeolites tested, chabazite performed better, as expected from the bench-scale results. As illustrated in Figure 2, an arbitrary ⁹⁰Sr breakthrough concentration of less than 50 Bq/L was maintained for nearly 450 BV while ⁹⁰Sr discharge concentration for the clinoptilolite column exceeded the 50 Bq/L after fewer than 120 BV had circulated through the column. In contrast, experience with operating either clinoptolite or chabazite column with the CP stream, several thousand BVs (2000 to 4000 BV) could be processed before exceeding ⁹⁰Sr breakthroughs of 5 to 60 Bq/L. The difference in ⁹⁰Sr removal efficiencies for the two streams can be attributed to the higher conductivity and calcium content of the SW water and the natural zeolite's low selectivity for strontium over these species. While natural zeolite was more than adequate for ⁹⁰Sr removal from CP waters, clearly if operated with

the SW water, large volumes of spent zeolite material would be produced to meet the same discharge criteria.



Figure 2: Sr-90 Breakthrough Curves Using Natural Zeolite Sorbents for SW Water

3.2.2 Synthetic Sorbents

⁹⁰Sr breakthrough results from laboratory-scale column tests performed on the SW stream using the selective synthetic sorbents are shown in Figure 3. The CST material, known for its selectivity for ⁹⁰Sr over competing calcium, demonstrated a greatly increased removal performance over zeolite materials. After an initial high background ⁹⁰Sr concentration probably caused by fine particle leakage due to incomplete column flushing, ⁹⁰Sr discharge concentrations of less than 50 Bq/L could be maintained for up to 3.500 bed volumes of CST. This would indicate that CST would have an approximate performance advantage of a factor of 7.5 over chabazite sorption. Using SrTreat, under similar conditions, an initial ⁹⁰Sr breakthrough of nearly 30 Bg/L was observed after 300 BV had passed through the column, and this reached a level above 120 Bq/L after 450 BV. As SrTreat is recommended for more alkaline applications, the natural neutral pH of the contaminated stream was consequently adjusted to a pH of 9.8 before performing ensuing column tests. Adjusting the pH of the feed solution had the effect of precipitating hydroxides out of solution (namely Mg(OH)₂) as well as some carbonate from absorption of atmospheric CO₂ at the higher pH. Subsequently after filtering the solid precipitate, the calcium concentration in the solution had been reduced from 25 to 11 ppm and the ⁹⁰Sr level fell from 1,700 Bq/L to 800 Bq/L. When the SrTreat column test was repeated using this pH-adjusted and filtered water, the column operated past 2,500 BV, at which point the ⁹⁰Sr level had reached 25 Bq/L. The poor ⁹⁰Sr removal efficiency of SrTreat can be attributed to its lack of selectivity over calcium [7.]. Evidently the SrTreat sorbent would not be suitable for use in simple ion-exchange processes of neutral pH waters without prior conditioning.



Figure 3: Sr-90 Breakthrough Curves Using Synthetic Selective Sorbents for SW Water

The data obtained from the column tests were used to estimate the sorbent requirements for a groundwater remediation plant. A summary of the results including feed and discharge water quality, and method performance is given in Table 4.

Option Description	Groundwater Stream Feed Concentration	⁹⁰ Sr in Treated Water (Bq/L)	Volume Reduction Factor	Annual Volume of Sorbent
Non-selective Sorption Column with Chabazite	SW 1,700 Bq/L [Ca] = 25 ppm 800 µS/cm	<50	450	42 m ³
Selective Sorption Column with CST	SW	<50	3,500	5.45 m^3
Non-selective Sorption Column with Chabazite	CP 1,500 Bq/L [Ca] = 2 ppm 60 μS/cm	<5	2,800-5,000 (4200 average)	4.52 m ³

Table 4: Summary of Sorbent Requirements for Groundwater Remediation ^a

<u>Note:</u> (a) Reference plant capacity of 38 L/m (10 US gpm); the sorbent usage and secondary wastevolume would increase proportionately with the rate at which water is treated); Total volume of contaminated water treated per annum = 19 million litres. Direct sorption tests using natural zeolites (\$5-\$10/kg) for strontium removal from SW waters with high levels of calcium and conductivity, have suggested that an inordinately high volume of spent zeolite material would be generated to attain low Sr discharge limits, rendering this option unattractive. Since the synthetic sorbent CST has exhibited a higher selectivity for strontium in the presence of these species, direct sorption of ⁹⁰Sr by CST is technically feasible to meet low ⁹⁰Sr discharge limits. Evidently, this sorbent provides for greater removal efficiency than chabazite (by a factor of 7.5), and would reduce the volume of sorbent required considerably. However, the high cost of the reagent (\$1,075/kg in June 2011) still exceeds the cost saving benefits from the disposal of lower amounts of waste.

For ground waters with low conductivities and calcium concentrations, a non-selective ion exchange technology based on natural zeolite sorbents is still the preferred option.

In the absence of a low-cost, selective inorganic sorbent for Sr removal from ground waters containing high concentrations of calcium, it appears that calcium removal as a pre-treatment step using precipitation followed by sorption using natural or commercially available sorbents such as CST or SrTreat is the most promising option. In this context, AECL's CHEMICTM technology, implemented for groundwater remediation in mid 1990s, appears to be the best process [36.]. The CHEMICTM process involves a chemical precipitation with NaOH/Na₂CO₃, followed by microfiltration and a sorption-based polishing step using a chabazite or clinoptilolite sorbent. While the initial capital costs for this option are higher, this approach is technically superior and offers the desired flexibility.

3.3 Preliminary Sr Removal Results with Selected Calixarene-Impregnated Inorganic Sorbents

3.3.1 <u>Removal Test Results Based on Simulated Water Sample with Non-Radioactive Sr</u>

Three solid substrates, a hydrogel of methyl silicic acid, a natural mordenite and a synthetic hydroxyl apatite, all with inherent sorbent properties for Sr were selected to produce modified sorbents by impregnating them with a pre-selected calixarene agent. The chosen calixarene compound, 5,11,17,23,29,35,41,47-octakis(tert-butyl)-49,50,51,52,53,54,55,56-octakis[(N,Ndiethyl-aminocarbonyl)methoxy]calix[8]arene octamide, (or calix[8]arene octamide) was systemesized and impregnated into the substrates at the Institute of Organic Chemistry, National Academy of Sciences of Ukraine in Kiev. Calix[8]arene octamide was previously determined to be a promising solvent extraction reagent for Sr and other cations.

Before impregnating the solid substrates with the selected calixarene, the substrates were prepared as follows: 1) the hydrogel of methyl silicic acid was was heated at 120 - 140°C for 8 hours; 2) the mordenite was converted into its sodium form by saturation with 1 M NaCl solution for 24 hours at room temperature; and 3) the hydroxyl apatite was synthesized by mixing 10 wt.% aqueous solutions according to the following reaction:

$10Ca(NO_3)_2 + 6KH_2PO_4 + 14NaOH = Ca_{10}(PO_4)_6(OH)_2 + 6KNO_3 + 14NaNO_3 + 12H_2O$

The three solid substrates were modified by impregnating them with the calixarene compound at room temperature. The substrate matrix impregnation was carried out by soaking the prepared solid substrates (~10 g each) in a 50 mL solution containing $9 \cdot 10^{-3}$ M of calix[8]arene octamide and the chosen volatile organic solvent. The volatile organics used were 1) dichloromethane and 2) a mixture of dichloromethane and 3-nitrobenzotrifluoride. After impregnation of the solvent mixture, the volatile organic solvent was removed at an elevated temperature (50°C).

Batch sorption tests were carried out by by contacting the impregnated sorbent with the Sr containing solution at different pH values (1 to 9.5), and mixing at a slow rate at room temperature (~20°C) for approximately 30 min. Samples of the initial and final solution, after separating the sorbent, were analyzed by ICP-AES for Sr. The cumulative maxium errors (analysis and, experimental) in the Sr removal efficient data reported in Table 5 were within 5%. For the simulated Sr test solutions, the strontium removal results (columns 2, 3 and 4 in Table 5), with one exception, did not show any favourable Sr removal efficiency as a result of incorporating the chosen calixarene into the sorbent substrate matrix. In fact, the addition of the calixarene agent to the substrate appeared to reduce the Sr removal efficiency. For the acidic solutions (pH 1- and 2.5), no Sr was removed by modified or non-modified sorbents. These observations were very surprising, considering the favourable performance of calyx[8]arene octamide in solvent extraction processes. A simple reason for the observed reductions in Sr removal efficiencies could not be afforded. One possible reason could be conformational changes resuting from the introduction of the calyx[8]arene octamide agent into the substrate. One result with the hydroxylapatite substrate modified with calyx[8]arene octamide in dichloromethane and 3-nitrobenzotrifluoride appears to suggest a slightly increased removal efficiency for Sr under alkaline pH conditions.

3.3.2 <u>Removal Results for ⁹⁰Sr wtih Actual CP Groundwater Sample</u>

Batch sorption tests were carried out in glass vessels with mixing stirrers to ensure good contact between the sorbent and solution. The mixing time was limited to 2 h at room temperature $(25\pm2^{\circ}C)$. All tests were done with 1 g of sorbent (Table 5) in 100 mL of water sample. The natural calcium concentration in the CP ground water was 3.5 mg/L. To understand the effect of calcium on ⁹⁰Sr removal, selected sorption tests were conducted by spiking the water samples with additional calcium (as CaCl₂) to to provide a calcium concentration of ~13.5 mg/L. The ⁹⁰Sr removal results are summarized in Table 5 (columns 5 and 6). Again, similar to the results with simulated solutions, for the groundwater samples with low Ca/Mg concentrations, the introduction of calyx[8]arene octamide did not produce any improvement in Sr removal. Increasing the calcium from 3.5 mg/L to 13.5 mg/L further reduced the ⁹⁰Sr removal efficiencies by approximately a factor of 2, thus showing low selectivity for Sr over Ca.

The overall poor Sr removal results, using the calyx[8]arene octamide impregnated sorbents, have suggested a need for more detailed investigation of the complexation and conformational aspects of this reagent in the solid substrates in the presence of interfering cations.

		Percent Sr/ ⁹⁰ Sr Removal Efficiency (%R)				
Sorbent (Solid sorbent substrates modified by impregnation with calyx[8]areneamide in organic	Simulated Water (Note 1) [Sr] = 1 mg/L			Actual Ground Water (CP) (Note 2) [Sr] = $0.03 \text{ mg/L}; [^{90}\text{Sr}] = 1,800 \text{ Bq/L}$		
unuents)	[Ca] = [Mg] = 1 mg/L			[Ca] = 3.5 and [Mg] = 1.06 mg/L	[Ca]~13.5 and [Mg] = 1.06 mg/L	
		$T = 20 \pm 5^{\circ}C$		T = 25	5±2°C	
	pH = 4.6	pH = 7.3	pH = 9.5	pH = 6.5	pH~6.5	
Hydroxylapatite	91	48	35	99	55	
Hydroxylapatite modified with calyx[8]arene octamide in dichloromethane	81	40	56	39	15	
Hydroxylapatite modified with calyx[8]arene octamide in dichloromethane and 3- nitrobenzotrifluoride	81	71	66	99	40	
Na-mordenite	85	67	78	94		
Na-mordenite modified with calyx[8]arene octamide in dichloromethane, or in nitrobenzotrifluoride	80	56	70	95 or 92		
Hydrogel of methyl silica acid	40	75	95	24		
Hydrogel of methyl silica acid modified with calyx[8]arene octamide in dichloromethane, or in nitrobenzotrifluoride	36	72	90	5 or 22		

Table 5: Strontium Removal Performance of Sorbent Substrates with and without Impregnation Using Calix[8]arene Octamide

Note:

(1) Simulated Water samples: [Sr] = 1 mg/L; [Ca] = [Mg] = [A1] = [Mn] = [Ba] = [Fe] = 1 mg/L; Na] = n/a; [K] = n/a

(2) CP Ground Water: $[^{90}Sr] = 1,800 \text{ Bq/L}$; [Sr] = 0.03 mg/L; [Ca] = 3.5 mg/L; [K] = 1.5 mg/L; [Mg] = 1.06 mg/L

4. CONCLUSIONS AND RECOMMENDATIONS

- Most natural zeolites are attractive media for strontium removal for a relatively wide range of pH values (e.g., 4 to 12) from dilute aqueous solutions such as ground waters, provided that the total dissolved solids concentration is low (e.g., 500 mg/L) and the Ca and Mg concentrations are similarly low (e.g., 1-5 mg/L). For waste solutions containing high concentrations of salt with Ca and Mg (e.g., tens and hundreds of mg/L), natural zeolites are not suitable, and synthetic sorbents are required.
- Most synthetic inorganic sorbents give good Sr removal performance (e.g., K_d values in the order of 10^4 - 10^5 mg/L) in alkaline solutions when the interfering ions are low or absent. The K_d value decreases (on the order of 10^2 - 10^3 in the presence of interfering ions including Na, Ca and Mg).
- The commercially available sorbents, CST and SrTreat, show favourable removal performance in slightly to highly alkaline solutions. These sorbents exhibit high selectivity for Sr over Na, but their selectivity is affected as the concentration of other cations (e.g., Ca) increases. Only a few synthetic sorbents such as tin antimonates and potassium metal sulphides work favourably in acidic solutions.
- The cost of the synthetic sorbents is high compared to that of natural zeolites, because most of the materials are still in the R&D and laboratory-scale stage of their commercial development. The industrial-scale availability of sorbents such as CST and SrTreat is attractive, although diminished by the relatively long delivery times and high costs. Increased use of the existing sorbents, such as CST and SrTreat, combined with the development of newer, low-cost synthetic inorganic materials is expected to increase the demand of these compounds.
- An industry involving the mass production of sorbents for strontium removal is still in the early stage of development. A need for development efforts towards the synthesis and fabrication of solid sorbent beads suitable for packing in column configurations, significant laboratory testing of the sorbents under various aqueous effluent conditions, and separation process flowsheet development must be considered before the implementation of a selective strontium removal process can be accomplished.
- Advancement of low-cost sorbents based on zeolite materials modified with selective organic complexing reagents can be a promising approach for selective removal of strontium from solutions with a wide pH range. However, further research and development efforts are needed in the selection, synthesis and testing of appropriate complexing agents with suitable conformational and sorption characteristics when introduced to the substrate inorganic materials.

5. **REFERENCES**

- [1.] Human Health Fact Sheet, Argonne National Laboratory, EVS, November 2006; www.evs.anl.gov/pub/doc/Strontium.pdf
- [2.] Amphlett, C.B., Inorganic Ion Exchangers, Elsevier Publishing Company, Amsterdam, 1964.
- [3.] Clearfield, A. (Edr.), Inorganic Ion Exchange Materials, CRC Press, Boca, Raton, FL, USA (1982).

- [4.] Abe, A., "Ion-exchange selectivities of inorganic exchangers", in Inorganic Ion Exchange Materials, ch. 9, A. Clearfield (Edr.), CRC Press, Boca, Raton, FL, USA (1982).
- [5.] Barrer, R.M., Hydrothermal Chemistry of Zeolites, Academic Press (1982).
- [6.] Vaughan, D.E.W., "Properties of natural zeolites" in Natural Zeolites: Occurrence, Properties, Use, L.B. Sand and F.A. Mumpton (Edrs.), Pergmon Press, New York, 353 (1978).
- [7.] Sheppard, R.A., Zeolites in Sedimentary Deposits of the Northwestern United States -Potential Industrial Minerals, Montana Bureau of Mines and Geology, Special Publication, 74, 69 (1976).
- [8.] Munson, R.A. "Properties of Natural Zeolites", U.S. Bureau of Mines, Report of Investigation, 7744 (1973).
- [9.] Mimura, H., and Kanno, T., "Distribution and fixation of cesium and strontium in zeolite A and chabazite", *J. Nucl. Sci. & Tech.*, Vol.22, Iss.4, p.284 (1985).
- [10.] Semmens, M.J., and Martin, W.P., "The Influence of pretreatment on the capacity and selectivity of clinoptilolite for metal ions", *J. Water Res.*, Vol.22, Iss.5, p.537 (1988).
- [11.] Robinson, M., Begovich, J.M., and Scott, C.B., "Low-activity-level process wastewaters:treatment by chemical precipitation and ion exchange", *J. Water Pollut. Control Fed.*, Vol.60, pp.2120-2127 (1988).
- [12.] Vesely, V., and Pekarek, V., "Synthetic inorganic ion-exchangers-I hydrous oxides and acidic salts of multivalent metals", *J. Talanta*, Vol.19, Iss.3, pp.219-262 (1972).
- [13.] Clearfield, A., "Inorganic Ion Exchangers: A technology ripe for development", J. *Industrial & Engineering Chemistry Research*, Vol.34, Iss.8, pp.2865-2872 (1995).
- [14.] Clearfield, A., "Inorganic ion exchangers, past, present and future", J. Solvent Extraction and Ion Exchange, Vol.18, Iss.4, pp.655-678 (2000).
- [15.] Bray, L., High Capacity, Selective Solid Sequestrants for innovative chemical separation: inorganic ion exchange approach", Presentation at the <u>ESPIP Technical Exchange Meeting</u>, Gaithersburg, Maryland, Pacific Northwest Laboratory, PNL-SA-25549/CONF-950171-1, Richland, Washington, USA, 1995.
- [16.] Behrens, E.A., Sylvester, P., and Clearfield, A., "Assessment of a sodium nonatitanate and pharmacosiderite.-type ion exchangers for strontium and cesium removal from DOE waste simulants", *J. Environ. Sci. Technol.*, Vol.32, pp.101-107 (1998).
- [17.] Park, Y., Shin, W.S., Reddy, S., Shin, S.-J., and Choi, S.-J., "Use of nano crystalline silicotitanate for the removal of Cs, Co, Sr from low-level liquid radioactive waste", *J. Microelectronics and Optoelectronics*, Vol.5, pp.238-242 (2010).
- [18.] Bostick, D.A., and Guo, B.B., "Evaluation of improved technique for the removal of fission products from process water and groundwater: FY 1996 status", Oak Ridge National Laboratory Report ORNL-/TM-13306, TN, USA, July (1997).
- [19.] Lehto, J., and Clearfield, A. "The Ion exchange of strontium on sodium titanate", J. *Radioanalytical and Nuclear Chemistry*, Vol.118, Iss. 1, pp.1-13 (1987).

- [20.] Miller, J.E., Brown, N.E., Krumkans, J.L., Trudell, D.E., Anthony, R.G., and Philip, C.V., in Science and Technology for Disposal of Radioactive Wastes, W.W. Schultz and N.J. Lombardo, Eds., Plenum, New York (1998).
- [21.] Lehto, J., Leena, B., and Harjula, R., "SrTreat- a highly effective ion exchange for the removal of radioactive strontium from nuclear waste solutions", Radioactive Waste Management and Environmental Remediation- ASME (1997).
- [22.] Koivula, R., Pajaanen, A., Harjula, R., and Lehto, R., "Decontamination of radioactive cobalt, nickel, strontium, and cesium from simulate solutions using tin antimonate columns" *J. Solvent Extraction and Ion Exchange*, Vol.21, Iss.6, pp.915-928 (2003).
- [23.] Manos, M.J., Ding, N., and Kanatzidis, M.G. "Layered metal sulfides: exceptionally selective agents for radioactive strontium removal", Argonne National Laboratory Report, (2008).
- [24.] DePaoli, S.M., and Bostick, D.T. "Process wastewater treatment with hydrogen-form CST and chabazite zeolites", Spectrum'98 Conference, Colorado (1998).
- [25.] Möller, T., Harjula, R., Pillinger, M. Dyer, A., Newton, J., Tusa, E., Amin, S., Webb, M., and Araya, A., "Uptake of ⁸⁵Sr, ¹³⁴Cs and ⁵⁷Co by antimony silicates doped with Ti⁴⁺, Nb⁵⁺, Mo⁶⁺ and W⁶⁺", J. Materials Chemistry (2001).
- [26.] Dyer, A., Pillinger, M., Newton, J., Harjula, R., Moller, T. and Amin, S., "Sorption behaviour of radionuclides on crystalline synthetic tunnel manganese oxides", *J. Chemistry* of Materials, Vol.12, Iss.12, pp.3798-3804 (2000).
- [27.] Marinin, D.V., and Brown, S.N., "Studies of sorbent/ion-exchange materials for the removal of strontium from liquid radioactive waste and high hardness ground water", *J. Waste Management*, Vol.20, pp.545- 553, (2000).
- [28.] Arafat, H.A., Aase, S.B., Bakel, A.J., Bowers, D.L., Gelis, A.V., Regalbuto, M.C., and Vandegrift, G.F., "The Application of in-situ formed mixed iron oxides in the removal of strontium and actinides from nuclear tank waste", Argonne National Laboratory Report, (2010).
- [29.] Venkatesan, K.A., Panner Selvan, G., and Vasudeva Rao, P.R., "Sorption of strontium on hydrous zirconium oxide", J. Separation Science and Technology, Vol.35, Iss.14, pp.2343-2357 (2000).
- [30.] Inan, S., Tel, H., and Altas, Y., "Sorption studies of strontium on hydrous zirconium dioxide" *J. Radioanalytical and Nuclear Chemistry*, Vol.267, Iss.3 (2005).
- [31.] Zhang, A., Xiao, C., and Chai, Z., "Spec Process II. Adsorption of strontium and some typical co-existent elements contained in high-level liquid waste on to a macroporous silicabased crownether impregnated functional composite", *J. Radioanalytical and Nuclear Chemistry*, Vol.280, Iss.1, pp.181-191 (2009).
- [32.] Mokhtari, B., and Pourabdollah, K., "A review of calixarene application in nuclear industries", *J. Radioanal. Nucl. Chem.*, Vol.287, Iss.3, pp.921-934 (2010).
- [33.] Vijayan, S., and Wong, C.F., "Uptake of radiostrontium from aqueous solutions by biomass and natural zeolites: Implications in the treatment of contaminated waters by

AECL's CHIMICTM Process", Proc. <u>Waste Management WM'01 Conf.</u>, Feb 25-Mar 01, Tucson, Arizona (2001).

- [34.] Rees, L.V.C., and Rao, A., "Self-diffusion of various cations in natural mordenite", *J. Trans Faraday Soc.*, Vol.62, pp.2103-2110 (1966).
- [35.] Rousseau, S., and Vijayan, S., Technology perspectives on the removal of radiostrontium from large volumes of groundwater", Paper #4955, Proc. <u>Waste Management WM'04 Conf.</u>, 2004 February 29-March 4, Tucson, AZ.
- [36.] S. Vijayan, S., "Experience with the application of CHEMICTM technology for treatment of ground /surface waters containing radiostrontium", <u>Waste Management '99, Proc. of the</u> <u>Symposium on Waste Management</u>, Tucson, Arizona. (1999).