UPTAKE OF RADIOSTRONTIUM FROM AQUEOUS SOLUTIONS BY BIOMASS AND NATURAL ZEOLITES: IMPLICATIONS IN THE TREATMENT OF CONTAMINATED WATERS BY AECL'S CHEMIC™ PROCESS

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ABSTRACT

AECL's CHEMIC™ process has effectively treated in excess of 4 million gallons of radiostrontium-contaminated water since 1993. One aspect of the ongoing effort to expand the application of the process involves the use of powdered sorbents such as biomass in addition to natural zeolites in conjunction with precipitation for the removal of different contaminants including radiostrontium from waste solutions. In this paper, laboratory-scale test results are presented on removal performance of radiostrontium from synthetic and actual waste solutions by different natural zeolites and biomass. The natural zeolites included calcium-chabazite, sodium-chabazite, sodium-clinoptilolite, mordenite, potassium-clinoptilolite, zeobrite and zeobrite 100. The biomass used in the tests included S. faccium, B. subtilis, L. plantarum, L. acidophillos, P. cerevisial and M. luteus. Results showed that strontium was preferentially removed by chabazite with high removal efficiencies even in the presence of the competing calcium ion. Clinoptilolite performed similar to chabazite, but only at low concentrations of the competing ion. The initial sorption rates of strontium by powdered zeolites were generally rapid at low concentrations of the competing calcium ion, and removal efficiencies in excess of 90% occurred within 30 minutes of contact between the solution and zeolite. The behaviour of different biomass sorbents for radiostrontium removal was found to be similar in many respects to that of the natural zeolites. Among the biomass tested, L. plantarum and P. cerevisial gave the highest removal efficiencies for radiostrontium when the concentration of the competing calcium ion was low. It appears that contaminant binding to specific regions on the cell surface is a key mechanism for cation removal by the biomass. The majority of the cation removal by biosorption was found to occur within a 20-minute exposure of the biomass to the contaminated solution.

INTRODUCTION

The presence of trace amounts of radionuclides and toxic metals along with alkali-earth metals and iron is common in the majority of contaminated waters around nuclear material processing and storage facilities. The concentrations of toxic metals are in the order of a few mg/L, whereas concentrations of commonly present radionuclides such as strontium-90 and cesium-137 in waste solutions are typically a few microgram/L or lower. The alkali-earth metals, calcium and magnesium, combined with iron are present in relatively higher concentrations, tens to hundreds of mg/L. Also, waters have anionic species, in particular, HCO_3/CO_3 ions, in the order of 100 mg/L. The challenge is to devise appropriate processes involving one or a combination of physico-chemical methods that remove the contaminants with high removal efficiencies. Depending on the methods, the presence of non-contaminants can aid or impede the contaminant removal efficiencies, and also can contribute to the generation of large volumes of secondary waste from the treatment. The evolving stringent environmental regulatory limits for such contaminants require that efficient and cost-effective, closed-loop treatment methods must be developed. These methods need to have high decontamination factors while generating a minimum of secondary-waste generation that requires further treatment before storage/disposal.

Under a cooperative agreement between US Department of Energy and Atomic Energy of Canada Limited (AECL) Buckley et al. (1) developed and patented (2) a generic process for the treatment of wastewaters containing mixed contaminants of radionuclides, heavy metals and organics. In their study, powdered natural zeolite and activated carbon were used to promote contaminant removal. They identified that using powdered zeolite has several advantages: (a) direct contact of contaminants with powdered ion-exchange material provides high contaminant removal efficiencies and fast kinetics; (b) powdered ion-exchange material may have lower cost because it is usually considered as waste by-product, and (c) choice of materials provides flexibility to change process conditions easily, depending on the waste being treated. This process is referred to as the AECL's CHEMIC™ technology and is offered for application in the treatment of ground waters and wastewaters. Details of the technology can be found elsewhere (3, 4).

The above studies showed that sequestering of low concentrations of cationic contaminants such as radioactive and toxic metals from aqueous waste streams can be accomplished effectively by precipitation techniques. Maximum removal of the contaminant also requires an optimum precipitation temperature. It is well known that depending on the precipitated material composition, contaminant removal also occurs through "sorption" mechanisms. For example, the presence of iron and aluminium precipitates has the ability to remove significant amounts of contaminants (20 to 30% is not uncommon) by sorption mechanism. To achieve treatment flexibility and to meet very low discharge limits (e.g., near drinking water limit in many applications), there is also a need to add either a "polishing" step after the precipitation treatment or to add small amounts of powdered sorbents to the precipitation process. Adding powdered sorbent to the contaminated solution provides process flexibility and offers the potential for the use of a wide array of natural zeolites and biomass to achieve a high quality treated water.

Depending on the nature of the chemicals added to the waste solution, the combined precipitation and sorption steps allow contaminant removal by a combination of mechanisms including: ion exchange, adsorption, precipitation and particle entrapment. The final contaminant-laden particles in the suspension can be separated from the waste stream by advanced filtration methods such as cross-flow microfiltration and dewatering.

The present version of the CHEMIC process (Fig. 1) includes caustic-sodium carbonate or CO_2 precipitation at optimum temperature, sorption by a natural zeolite using direct addition to the waste solution followed by microfiltration and gravity settling or vacuum drum filtration to remove radiostrontium from waste waters. The CHEMIC process generates a high-quality effluent by incorporating a polishing treatment in fixed-bed natural zeolite columns.

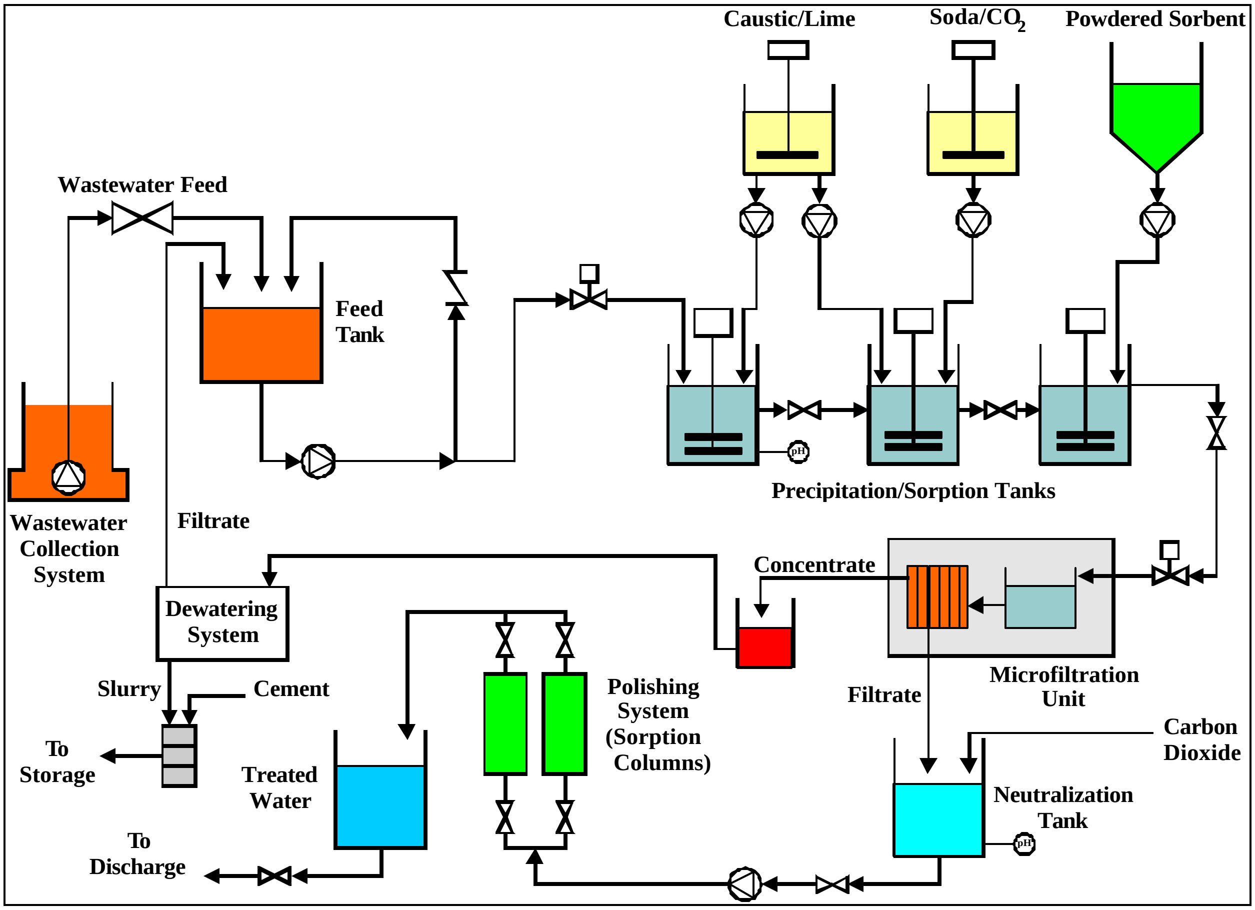

Fig. 1: AECL's CHEMIC™ Process for Removal of Radionuclides and Metals from Contaminated Water

AECL has been operating a field CHEMIC treatment facility at the Chalk River Laboratories (CRL) to decontaminate groundwater contaminated with ^{90}Sr. The treatment process, which is conducted under effective temperature control, involves precipitation of strontium as strontium carbonate followed by filtration of the dilute suspension using hollow-fibre cross-flow microfiltration and has provided a filtrate water quality as low as 27 Bq ^{90}Sr/L (Table I). Because of the similar physical and chemical characteristics of calcium and radiostrontium, the removal of calcium to below 2 mg/L has been found to produce the highest radiostrontium removal efficiency. Performance data (5) based on treating over 2.5 million gallons of radiostrontium-contaminated groundwater reveal that the CHEMIC™ plant has performed effectively to treat ground/surface waters containing approximately 3000 Bq ^{90}Sr/L to produce a discharge water that is less than 5 Bq/L (<135 µCi/L) of radiostrontium. It should be noted that the 5 Bq/L limit represents the Method Detection Limit for the quality-assured measurement established for ^{90}Sr at CRL.

Table I: Effect of Temperature on Calcium and ^{90}Sr Removal by CHEMIC™ Process from Ground/Surface Waters at Spring B Facility, Chalk River Laboratories

Temperature Range During Precipitation (^{o}C)	**Calcium Concentration in the Filtrate After Precipitation and Microfiltration (mg/L)**	**^{90}Sr Concentration in the Filtrate After Precipitation and Microfiltration (Bq/L)**
5.5 – 10.0	3.8 – 9.2	300 – 600
15.5 – 17.0	1.6 – 3.6	48 – 112
20.0 – 22.0	1.2 – 3.0	32 – 57
24.5 – 26.5	1.1 – 1.8	27 - 35

One aspect of AECL's ongoing effort to improve the chemistry and equipment performance of the CHEMIC™ process has involved testing to select low-cost, efficient sorbents that can be used in conjunction with precipitation to achieve a high removal of radiostrontium from contaminated wastewaters. This paper presents preliminary results of screening tests with different natural zeolites and biomasses to assess their relative ability for the removal of radiostrontium (^{85}Sr/^{90}Sr) from synthetic solutions and actual groundwater samples. It should be noted that the actual groundwater in this study, also contains 0.8 to 1 mg/L of stable strontium in addition to radiostrontium.

BACKGROUND

Sorption By Natural Zeolites

The removal of radionuclides from waste solutions using naturally occurring zeolites (6) has been studied since 1950s. The natural zeolites are a class of aluminosilicate minerals with favourable cation-exchange properties and resistance to radiation. 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 (7).

Zeolites are three dimensional, microporous, crystalline solids with well-defined structures that contain aluminum, silicon and oxygen in their regular framework. The silicon and aluminum atoms are tetrahedrally coordinated with each other through shared oxygen atoms. The SiO_4 is neutral, but the AlO_4 results in a net negative charge (Al^{+3} / $4O^{-}$). The net negative charge (8) is balanced by cations (e.g., alkali and alkaline-earth metals, such as sodium, potassium and calcium) that are present during the formation. These cations and water are located in the pores of the zeolite and the cations can be readily exchanged for other cationic species. In addition, the porous framework of the zeolites enables them to act as molecular sieves (i.e. they are used to separate molecular mixtures on the basis of the size and shape of molecular compounds or for the selective adsorption of gases). The zeolites have reversible hydration properties in addition to their cation-exchange properties (9). Estimates of pore volume accessible to water provide a measure of pore space. For example, the pore volume (cm^{3} as liquid water per cm^{3} of crystal) of a clinoptilolite with an idealized unit cell composition of $Na_6[Al_6Si_{30}O_{72}]24H_2O$ is 0.34 whereas a chabazite with a unit cell composition of

$Ca_2[Al_4Si_8O_{24}]13H_2O$ is 0.48; this implies that chabazite has more pore space or capacity to retain cations and certain compounds.

The cation-exchange mechanism, for example, between strontium ions and zeolite may be expressed as:

$$\begin{array}{l} Sr^{+2}(H_2O) + 2\,SiAlO_7^{-1} \quad \rightarrow \quad SiAlO_7^{-1} \cdot Sr^{+2} \cdot (OH^{-1}) + SiAlO_6(OH) \\ Sr^{+2} + 2(SiAlO_7^{-1}) \cdot M^{+1} \quad \rightarrow \quad (SiAlO_7^{-1})_2 \cdot Sr^{+2} + 2M^{+1} \end{array} \qquad \text{(Eq. 1)}$$

Although ion exchange is the most predominant mechanism for cation removal by natural zeolites, physical adsorption of cations cannot be ruled out. Consequently, we will use the terminology, "sorption", to denote the combined action of ion exchange and adsorption by zeolites. Because of the favourable cation removal capacities and low costs of many natural zeolites (either in column mode or direct addition treatment), they are being used increasingly for treatment of wastewaters containing the most prevalent radiostrontium and radiocesium ions (10, 11, 12, 13).

Sorption by Biomass

Biosorption is the property of certain types of dead microbial biomass to bind and concentrate contaminant metals dissolved in solutions (14, 15). Contaminant-saturated biomass can be either burned or stabilized directly into suitable waste forms, or reused by regeneration using appropriate electrolyte solutions. Biosorption can be a viable alternative to other sorption methods for the removal of trace amounts of toxic metals and radionuclides from aqueous waste solutions. Biomass can remove specific contaminants from contaminated aqueous streams in short contact times. Several advantages have been recognized in using of dead microbes than live cells in the biosorption process. They include: a) no extra nutrients need to be added to the waste stream; b) the biomass can be concentrated to a smaller volume-requiring disposal as waste; and c) the cost of biomass is generally low. Some disadvantages associated with the dead biomass may include: a) potential solid-liquid separation issues in continuous flow processes where the biomass is dosed directly to the waste stream, as a result of small particle size and low mechanical strength of the mass; and b) potential difficulties in the preparation of the biomass for fixed-bed sorption-column applications.

Previously (14), biosorption studies have primarily focussed on cations such as uranium, thorium, radium, cadmium, gold, cobalt, copper, lead and nickel. Few investigations have been reported on strontium removal by biosorption. A preliminary study (16) showed that Citrobacter, which is known to retain in the order of 9 g uranium per gram of biomass (17), removed only limited quantities of strontium from dilute solutions. Oak Ridge Laboratories (18) screened over twenty microorganisms for their ability to remove low concentrations of strontium from solutions. The highest rates of strontium removal from a 100-mg/L strontium solution after 14 days of contact were Rhizopus (distribution coefficient: 26,240) and Micrococcus (distribution coefficient: 9,980). In comparison, Citrobacter, showed only a distribution coefficient of 1,800. [Note that distribution coefficient is defined as microgram of Sr bound per gram of biomass (on dry weight basis) divided by microgram of Sr in solution per gram of solution.].

Because of the difficulty in immobilizing Rhizopus in a support medium (inert medium or active medium such as sorptive biopolymers), Oak Ridge Laboratories only performed a detailed examination of Micrococcus luteus (19). The study with M. luteus cells immobilized in gelatin and bone gel suggested that batch equilibration tests, consisting of approximately 100 mL of 10-mg/L Sr with 16 mL of gelatine and 4 mL of M. luteus pellet, produced a residual concentration of about 0.8-mg/L Sr after 4-h contact time and 0.25 mg/L Sr after 24-h contact. The column tests with a 10-mg/L Sr solution and a 52-mL column with bone gelatin beads (4.2 mm dia.) containing 20% M. luteus cells showed breakthrough after 70 column volumes. Although the results indicated high overall strontium removals, strontium adsorption was only partially attributed to M. luteus cells; the gel retained significant amounts of strontium by adsorption. On the basis of these results, the usefulness of M. luteus was found to be only marginal for adsorption operations if the active adsorbing cells are retained within immobilizing gels.

The selectivity of the adsorbent for Sr over Ca is important for practical applications involving wastewater containing appreciably more calcium over strontium. Column experiments using biomass/gelatin beads have shown (19) a slight selectivity for Sr over Ca but the selectivity is not significant for practical purposes. Because the gelatin beads can act as a sorbent for Ca and Sr, it was not confirmed if the slight selectivity comes from the biomass or from the gelatin. A follow-up study (20) suggested loadings of 25 mg per gram of M. luteus (dry weight) when contacted with 50 mg/L Sr as $SrCl_2$ at neutral pH. It was observed that: a) Sr binding occurred in the absence of nutrients and metabolic activity; b) although initial removal of strontium within 30 min was rapid, long-term release of Sr occurred; c) Sr removal was inhibited by the presence of polyvalent cations such as calcium, magnesium and barium, and similarly chelating agents and other cations, including H^+, displaced bound-strontium; and d) indications were that Sr removal by M. luteus occurs through ion exchange-mediated, surface biomass cell components and intracellular uptake.

For other metal ions, such as thorium and iron, the uptake mechanisms by biomass such as R. arrhizus are believed to involve binding of the metal ions to the cell surface, or an ion-exchange process where the cations of the polysaccharides on the cell wall exchange with the metal cations in solution (21). The uptake of heavy metals and radionuclides by biomass has also been explained (22) by a mechanism in which the metal cations bind to specific regions on the cell surface. There is evidence of carboxyl groups on the proteins in the cell wall, which can effectively bind the metal ions. It seems that the entire biosorption process occurs within short contact times (e.g., less than 20 min) between biomass and contaminated solutions.

EXPERIMENTAL

Materials

Seven natural zeolites from different suppliers were employed in the tests. ZS500H (Ca-chabazite) was purchased from GSA Resources, Inc., Cortaro, Arizona through Fisher Technical Development Inc. TSM-140 (Na-clinoptilolite) and TSM-310 (Na-chabazite) were obtained from Steelhead Specialty Minerals, Spokane, Washington. Mordenite (Ca-mordenite), K-clinoptilolite, Zeobrite 100 (Ca-clinoptilolite) and Zeobrite (Ca/K-clinoptilolite) were obtained from Zeotech Corporation, Albuquerque, New Mexico. The zeolites were used as received, except some zeolites were ground and sieved to the proper size for the tests. The particle size (average particle diameter) of all zeolites tested was less than 44 µm (-325 mesh).

Physical properties and composition of the zeolites employed in the present study are summarized in Table II.

Table II: Composition and Properties of Zeolites Used in Our Study

	TSM-310 (Na-chabazite)	**ZS500H** (Ca-chabazite)	**TSM-140** (Na-clinoptilolite)	**K-clinoptilolite**	**Zeobrite** (Ca-clinoptilolite)	**Zeobrite 100** (Ca/K-clinoptilolite)	**Mordenite** (Ca-mordenite)
	Weight %						
SiO_2	54.60	55.30	66.03	69.54	62.80	68.40	79.60
Al_2O_3	14.90	13.20	10.47	9.86	11.60	12.10	14.30
CaO	0.22	3.25	1.55	0.88	4.10	2.40	3.31
MgO	0.60	0.98	0.58	0.17	0.94	0.70	0.31
TiO_2	-	-	0.13	0.32	0.18	-	-
Na_2O	6.67	2.85	3.25	1.16	0.85	0.60	0.21
K_2O	0.90	1.15	1.81	4.65	1.54	1.70	0.31
Fe_2O_3	2.28	3.40	1.12	1.92	0.77	0.80	0.19
MnO	-	-	0.027	0.03	0.013	0.70	-
Density (kg/L)	-	1.73	1.60	1.60	-	-	-
Bulk Density (kg/L)	0.79-0.72	-	0.72-1.28	0.72-1.28	0.64-0.93	0.78	0.46-0.64
Pore Size (A)	4-12	3.7-4.1	4.0	-	3-6	3-6	-
Stability pH	4-12	3-12	3-10	3-10	3-10	3-10	-
Cation Exchange Capacity (meq/g)	2.37	2.50	1.65-1.80	1.55	1.50	1.50	1.33

The industrial biomass samples, B. subtilis, S. faccium, L. plantarum, L. acidophillos and P. cerevisial were obtained as steam-sterilized, dried powders from Environmental Microbial Services Inc., Calgary, Alberta (23). Micrococcus luteus was obtained from Laurentian University, Sudbury, Ontario (24) as a steam-sterilized suspension.

The strontium-85 (^{85}Sr) source was obtained from Dupont Canada Inc., Mississauga, Ontario. The source was diluted to the designed concentrations as standard solutions for the preparation of feed samples. Strontium-85 feed solutions were prepared by adding pre-determined amounts of ^{85}Sr with or without calcium chloride in distilled water. The pH of the feed solutions was adjusted to the desired value with $NaOH/H_2SO_4$ prior to the addition of biomass. For ^{90}Sr removal tests, actual contaminated ground/surface water samples from Chalk River Laboratories, Ontario (13) were used. Typical assay (13) of the contaminated water was: [^{90}Sr] = 2,500 Bq/L; other cations (mg/L): [Ca] = 45; [Mn] = 3;

[Mg] = 7; [Na] = 30; [Fe] = 5-30; and [HCO_3] ~100 mg/L. All chemical reagents employed in the experimental study were of analytical grade.

Determination of Radiostrontium Removal Performance

Tests involving direct addition of sorbents (powdered zeolite or biomass) in simulated or actual waste solutions were conducted with varying sorbent concentrations (typically 500 and 1000 mg sorbent per litre of solution). For tests with natural zeolites, fifty millilitres of the feed solution, which contained ^{85}Sr and calcium was shaken with 0.05 g of zeolite at room temperature (~23°C) for a pre-determined 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 analysed for contaminants.

The selected biomass of was added to 400 mL of waste solution (synthetic or actual) solution and mixed for a conditioning time (e.g., 20 min) at a solution pH of 4 or 7. The suspension was filtered in a filtration cell purchased from Amicon Corporation, USA. The cell consisted of a special membrane holder to allow for easy insertion or removal of the filter membrane sheet without damage. The cell design facilitated the suspension to be poured in and out easily, and to provide maximum recovery of the separated liquid (filtrate) with virtually no fluid loss. The stirring bar allowed efficient mixing of the suspension during filtration. A flat-sheet polypropylene microfilter with a 0.2-µm pore-diameter was used. The cell pressure was maintained at about 68 kPag (~10 psig) by a nitrogen gas cylinder. The temperature of the operation was kept at room temperature (~25°C). Samples of the starting feed solution and the fully mixed filtrate after the solution was filtered were analyzed for contaminants.

It should be noted that because the sizes of the zeolite particles (less than 44-µm diameter) were significantly larger than the biomass particles, a coarser filtration, 6-µm pore diameter Whatman filter was determined to be adequate (through separate tests, not reported in this paper). However, for the lower particle-size biomass filtration, a tighter 0.2-µm pore-diameter microfilter was required to obtain reliable results. The use of a microfilter or an ultrafilter for zeolite suspension filtration, or an ultrafilter (~0.01-µm pore-diameter) for biomass suspension filtration (except for a few tests with M. luteus), showed no significant advantage for improving radiostrontium removal.

The percent contaminant removal efficiency, PCRE (%), for a given conditioning time was calculated by:

$$PCRE = \frac{C_i - C_f}{C_i} x100 \qquad \text{(Eq. 2)}$$

Where, C_f represents concentration of the contaminant in the treated water (after sorption by zeolite or biomass and filtration) and C_i is the initial concentration of the contaminant in the untreated (feed) water.

Water samples were preserved at 4°C in polyethylene bottles at a pH <2 with nitric acid. All analyses were completed within 15 days of sampling. The concentration of ^{85}Sr in water samples was determined by gamma spectrometry, and ^{90}Sr was determined using liquid scintillation. Calcium was analysed using Inductively Coupled Plasma and colorimetric methods.

RESULTS AND DISCUSSION

Radiostrontium Removal Performance by Selected Natural Zeolites

In general as shown in Table III, 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 calcium). It should be noted that with one exception, TSM-140, all zeolites screened in our study showed approximately 90% removal efficiency for strontium at a conditioning time of 30 min. As expected, the similarity in physical-chemical properties of strontium and calcium resulted in significant reduction of strontium removal efficiency when calcium concentration was increased, for example, to 100 mg/L. It should be noted that the strontium concentrations used in the tests were several orders of magnitude lower than calcium concentrations in the solution.

Table III: Effect of Conditioning Time on Radiostrontium Removal Efficiency at Low and High Concentrations of Calcium

Zeolite	**Calcium Concentration**	**10 mg/L**		**100 mg/L**	
	Conditioning Time (min)	**30 min**	**60 min**	**30 min**	**60 min**
	^{85}Sr conc. In Feed (Bq/L)	**569.9**	**633.4**	**484.2**	**484.2**
TSM -310 (Na-chabazite)	^{85}Sr conc. in Filtrate (Bq/L)	24.6	<10	20.3	<10
	Percent Removal Efficiency	93.7	>97.4	95.8	>97.9
ZS500H (Ca-chabazite)	^{85}Sr conc. in Filtrate (Bq/L)	59.5	59.2	28.4	25.3
	Percent Removal Efficiency	84.6	90.7	94.1	94.8
TSM -140 (Na-clinoptilolite)	^{85}Sr conc. in Filtrate (Bq/L)	125.4	<10	290.6	294.6
	Percent Removal Efficiency	67.6	>97.4	40.0	39.2
Clinoptilolite (K-clinoptilolite)	^{85}Sr conc. in Filtrate (Bq/L)	49.5	79.6	356.5	404.5
	Percent Removal Efficiency	91.3	87.4	26.4	16.5
Zeobrite (Ca-clinoptilolite)	^{85}Sr conc. in Filtrate (Bq/L)	51.6	82.9	255.8	389.3
	Percent Removal Efficiency	91.0	86.9	47.2	19.6
Zeobrite 100 (Ca/K-clinoptilolite)	^{85}Sr conc. in Filtrate (Bq/L)	45.8	59.2	294.7	260.0
	Percent Removal Efficiency	92.0	90.8	39.1	46.2
Mordenite (Ca-mordenite)	^{85}Sr conc. in Filtrate (Bq/L)	70.4	23.8	37.2	192.0
	Percent Removal Efficiency	87.7	96.2	92.3	60.4

The relative performance of the zeolites for radiostrontium removal from feed water containing approximately 5,000 Bq ^{85}Sr/L for different concentrations of the competing calcium ion is shown in Fig. 2.

At low concentrations of competing calcium ions (e.g., 10 mg Ca/L), with the exception 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 100, a Ca/K-clinoptilolite, produced the lowest strontium removals. Zeobrite (Ca-clinoptilolite) had a lower strontium removal performance (~75%). 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. The cations are situated along with water molecules in most cases in these interconnected channels, which provide paths for the cations to diffuse freely throughout the structure. Studies (e.g., 26) have shown that diffusion of cation is dependent on the size of the cation relative to the smallest free diameter of the channel and on the charge on the cation. This latter coulombic interaction arises because the channel walls are lined with oxygen atoms that are negatively charged.

It appears that strontium removal behaviour of the zeolites may be related to certain key elemental composition of the zeolites, although elemental compositions alone may not be the only mechanism for the observed performance. For a zeolite with a relatively high Si/Al ratio, the negative charge on the framework would be reduced and also the coulombic interaction energy. 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 less favourable environment for the cation-ion exchange (e.g., low cation exchange capacity). As expected, based on the lowest Si/Al ratio values among the zeolites tested (Table II), 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 easily displaced than calcium ions in the zeolite by strontium ions. Although the diameters of Na^+ (1.90 Å) and of Ca^{2+} (1.98 Å) are similar, the self-diffusion coefficient of Ca^{2+} was found to be lower (26). These Ca^{2+} 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 the experimental errors, approximately 93% of 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 calcium ion is 1.98 Å and the diameter of strontium ion is 2.26 Å) and the coulombic interaction is the main control mechanism. For mordenite, because of 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 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 (Table II) expressed as ratios of dominant species (Table IV) 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.

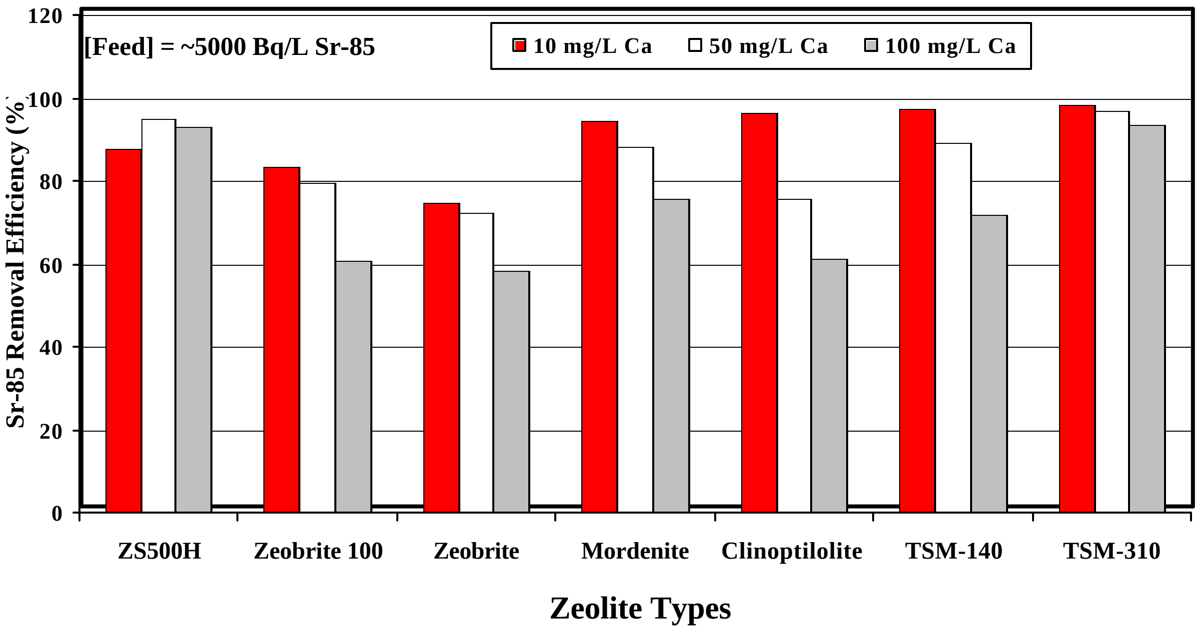

Fig. 2: Sr-85 Removal Efficiencies for Different Zeolites

The clinoptilolites performed similar to Chabazite for strontium removal, but only at low concentrations of the competing calcium ion. 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 reasoned 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 IV).

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

	Si/Al (mole ratio)	**Ca/Mg (mole ratio)**	**Na/K (mole ratio)**	**Fe + Na (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

Radiostrontium Removal Performance by Selected Biomass

(a) Radiostrontium uptake by M. luteus and TSM-140 (Na-Clinoptilolite)

Strontium removal results with M. luteus in combination with TSM-140 zeolite are presented in Table V. The results show that as the concentration of M. luteus increases, the uptake of ^{85}Sr (last column in Table V), expressed as Bq/mg of the biomass, begins high and then decreases when the total concentration of strontium in solution is low (in the range of 4,000 to 6,000 Bq/L). A similar trend has been observed with biosorption of copper and uranium by yeast and fungi (25). One reason for this observation has been attributed to adverse electrostatic interactions between binding sites at high biomass concentrations, although a complete understanding of this behaviour is not available presently. However, the removal efficiency increases continuously and reaches a plateau as the concentration of the biomass in the solution increases. For example, strontium removal efficiency in the order of 70 to 80% can be obtained with a biomass concentration in the range of 500 to 1000 mg/L when the total strontium concentration is low (4 to 7 µg/L ^{85}Sr in the present study). As illustrated in Table V, the addition of stable strontium at a level of 40 mg/L resulted in a significant reduction of Sr removal efficiency to 20-30%. This corresponds to the calculated strontium uptake value of 18.4 and 13.2 mg/g of biomass when the solution was contacted with an arbitrary biomass concentration of 500 mg/L (dry wt.) and 1000 mg/L, respectively. The lower strontium uptake observed in our study compared with the value of 25 mg/g of biomass found in previous column tests (19, 20), involving M. luteus immobilized in gelatin over glass beads in contact with a 50 mg/L-Sr solution, may be because of additional contributions from the sorbent action of the gelatin support medium for M. luteus and the higher initial concentration of 50 mg/L Sr in the waste solution we employed in our study.

By comparison, zeolite addition at 400 mg/L to the solution resulted in 96% removal efficiency for ^{85}Sr (Table V). However, the efficiency was reduced to about 25% when the solution contained 40 mg Sr/L. The Sr uptake of 25 mg/g by zeolite is comparable to 18.4 mg Sr/g biomass uptake. This compounded effect of the addition of zeolite and biomass (refer to Table V) may be summarized as follows:

- At low concentrations of ^{85}Sr (4,142 Bq/L), the addition of 900 mg/L sorbent (400 mg/L zeolite and 500 mg/L M. luteus) gave 77% ^{85}Sr removal efficiency; this value is comparable to 79% removal efficiency for strontium obtained with 1,000 mg/L biomass;

Table V: Strontium-85 Removal Performance from Synthetic Solutions by M. luteus and TSM-140 Zeolite (pH = 7; Temperature = 25°C; Contact Time = 20 min)

[^{85}Sr] (Bq/L)	**[SrCl$_2$] (mg/L)**	**[TSM-140] Zeolite (mg/L)**	**[M. Luteus] Biomass (mg/L)**	**^{85}Sr in Filtrate (after sorbent addition) (Bq/L)**	**^{85}Sr Removal Efficiency (%)**	**^{85}Sr Uptake** (Bq/mg Sorbent)**	**Total Sr [^{85}Sr + Sr] Uptake (microgram per gram of Sorbent)**
4142	-	-	500	1283	69	5.7	6.5
4142	-	-	1000	851	79	3.3	3.4
4142	-	400	-	135	96	9.9	11.2
4142	-	400	500	939	77	3.6*	41.0
4142	-	400	1000	933	77	2.3*	32.0
4956	-	-	100	2216	55	27.4	31.2
4956	-	-	500	1402	72	7.1	8.1
5457	40	-	500	4208	23	2.5	***18.4 mg/g sorbent
5457	40	-	1000	3680	33	1.8	***13.2 mg/g sorbent
5457	40	400	500	3950	27	1.7*	***12.0 mg/g sorbent
5457	40	400	1000	3517	35	1.4*	***10.0 mg/g sorbent
5457	40	400	-	4071	25	3.4	***25.0 mg/g sorbent
6233	-	-	750	1757	72	6.0	6.8
6233	-	-	200	3159	49	15.4	17.6
6233	-	-	100	3617	42	26.2	29.9
6233	-	-	75	4913	21	17.6	20.1
6233	-	-	50	5117	18	22.3	25.4
6233	-	-	25	5535	11	27.9	31.8
6233	-	-	10	5259	15	97.4	111.0

Note: * Combined zeolite and biomass effect on the basis that the effect of sorbents is identical.
** Specific activity of ^{85}Sr is 8.77×10^{14} Bq/g; 1 Bq = 1.14×10^{-9} g ^{85}Sr, or 1.14 nanogram.
*** Stable Sr (from added SrCl$_2$) removal efficiency is the same as ^{85}Sr removal efficiency.

- At high concentrations of Sr (40 mg/L), 900 mg/L of combined sorbents resulted in 27% strontium removal efficiency, which is comparable to Sr removal efficiency of 33% by 1,000 mg/L M. luteus; and

- Increasing the concentration of the sorbents (single or combined) above 1,000 mg/L had only marginal increase in the strontium removal efficiency (increased from 27% to 35%) at 40 mg/L Sr solution and no improvement in Sr removal performance was observed at low concentrations of Sr (4,142 Bq/L).

A similar pattern of removal performance may be anticipated when the competing ion, Ca, instead of stable Sr is present in the solution being treated. The results in Table V suggest that the strontium removal performance by Na-clinoptilolite (TSM-140) and M. luteus is very similar.

(b) Radiostrontium uptake by Different Industrial Biomass

Strontium removal results obtained from industrial biomass (S. faccium, B. subtilis, L. plantarum, L. acidophillos, P. cerevisial) at 1,000 mg/L with different concentrations of the competing calcium ion (0, 10 mg/L and 100 mg/L) are presented in TableVI.

Table VI: ^{85}Sr Removal Performance from Simulated Wastewater by Selected Biomass (Solution pH = 7; Temperature = 25^{o}C; Conditioning Time = 20 min)

Biomass	**Biomass Conc. (mg/L)**	**Ca (mg/L)**	**^{85}Sr Remaining in Filtrate (Bq/L)**	**Removal (%)**
Feed	**-**	**-**	**5043**	-
S. faccium	1000	-	850	83
B. subtilis	1000	-	3878	23
L. acidophillos	1000	-	189	96
P. cerevisial	1000	-	ND <48	>99
L. plantarum	1000	-	ND <50	>99
Feed	**-**	**-**	**4030**	-
P. cerevisial	1000	100	971	76
P. cerevisial	500	100	2270	44
P. cerevisial	100	100	3730	7
P. cerevisial	1000	10	ND <20	>99
L. plantarum	1000	100	981	76
L. plantarum	500	100	2420	40
L. plantarum	100	100	3710	8
L. plantarum	1000	10	ND <20	>99

The results in Table VI show that:

- When test solution contained no calcium or low concentrations of calcium (10 mg/L), L. plantarum and P. cerevisial gave greater than 99% ^{85}Sr removal efficiency;
- Biosorption of ^{85}Sr by L. plantarum and P. cerevisial for 100 mg/L of calcium was reduced significantly (from 99% to 76%). This behaviour is similar to zeolite sorption performance in the presence of the competing calcium ion; and reducing the concentration of the biomass produced almost a proportional decrease in the strontium removal efficiency.

As shown in Fig. 3, L. plantarum and P. cerevisial also had the highest removal for ^{90}Sr from actual groundwater containing about 45 mg/L Ca (and also [Sr] ~1 mg/L; [Mn] = 3 mg/L; [Mg] = 7 mg/L; [Na] = 30 mg/L; [Fe] = 5-30 mg/L) as compared with other biomass. It should be noted that the test condition was: pH = 4, conditioning time = 20 min, and the biomass concentration = 1,000 mg/L. The slightly lower ^{90}Sr removal efficiency can be attributed to higher concentration of calcium present in the actual groundwater. This trend is in conformance with the strontium removal performance of natural zeolites such as clinoptilolite and Chabazite.

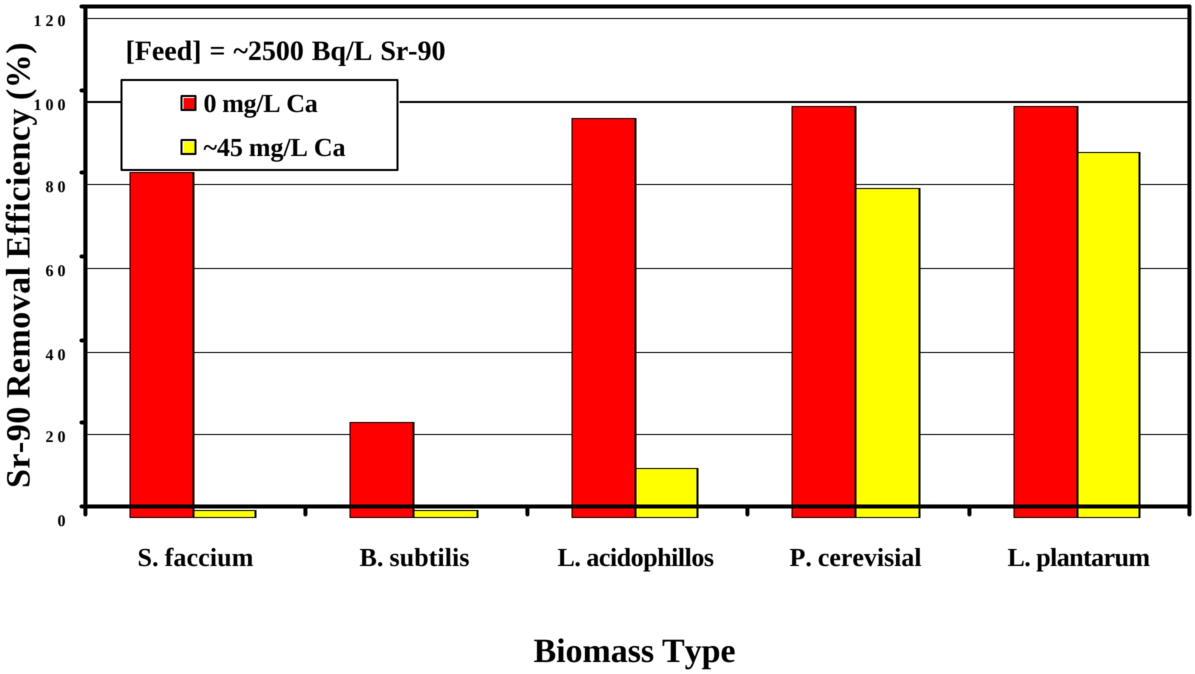

Fig. 3: Strontium-90 Removal Efficiencies for Selected Biomass from Groundwater (Solution pH = 4; Conditioning Time = 20 min; Biomass Conc. = 1,000 mg/L)

IMPLICATIONS FOR CHEMIC^{TM} PROCESS

The ability of sorbents such as natural zeolites and biomass to remove cations from waste solutions suggest that direct addition of powdered natural materials can be a viable option for removing metal contaminants in the CHEMIC^{TM} process. The high radiostrontium removal performance of some zeolites and biomass even in the presence of relatively high concentrations of the competing calcium ions suggest that these materials can be used favourably to improve the efficiency of radiostrontium removal. The resulting combined actions of precipitation and sorption processes provide flexibility to treatment facilities and can improve the cost effectiveness of producing discharge waters with extremely low concentrations of radiostrontium to meet existing and evolving stringent discharge limits.

At AECL's Chalk River Laboratories, in excess of 4 million gallons of surface and ground waters contaminated with low concentrations of radiostrontium has been treated using a combined precipitation-zeolite sorption process in the CHEMIC treatment facility with a continuous 2-gpm throughput capacity. The relative ability of using different process schemes in this treatment facility for radiostrontium removal is summarized in Fig. 4.

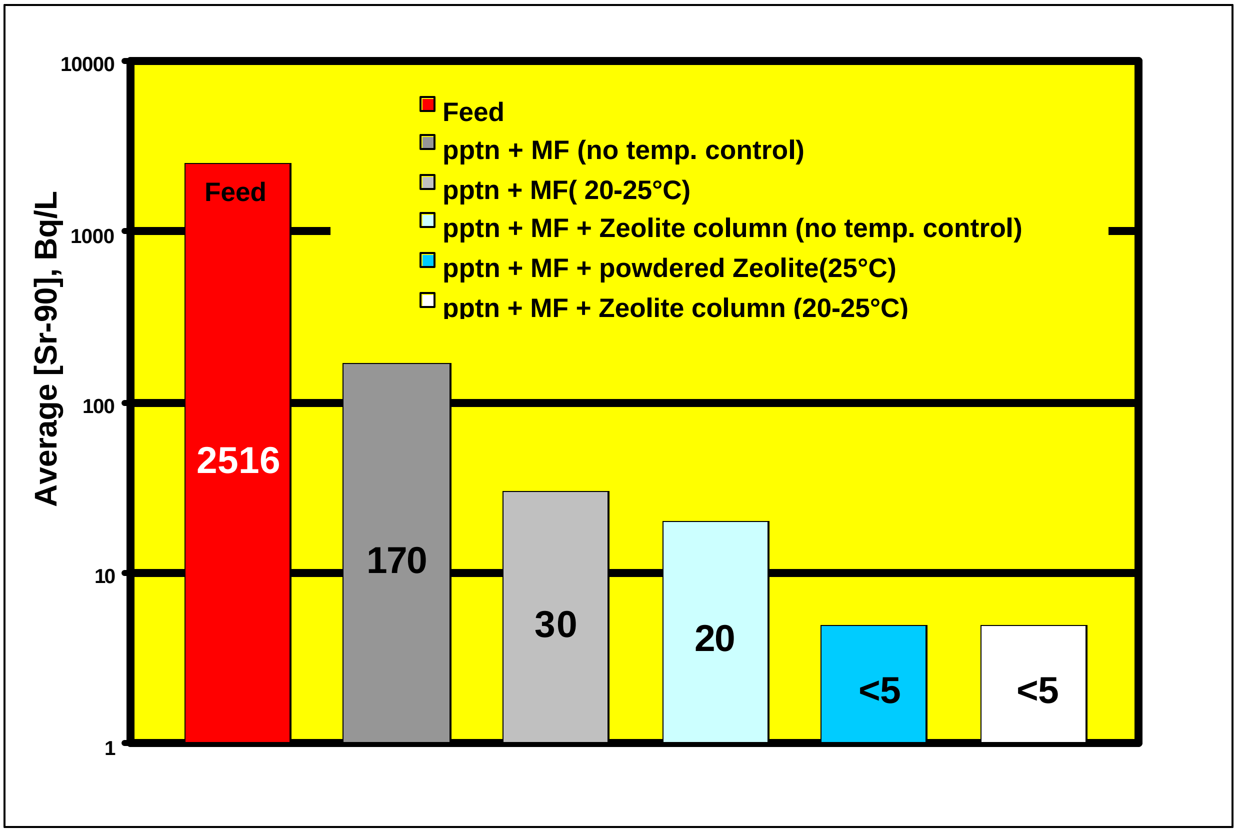

Fig. 4: Strontium-90 Removal Performance by AECL's CHEMIC^{TM} Process for Different Processing Schemes Involving Precipitation and Sorption

The different process schemes are:

- Precipitation of wastewater with NaOH-Na_2CO_3 without temperature control, followed by cross-flow microfiltration.
- Precipitation of wastewater with NaOH-Na_2CO_3 with temperature control, followed by cross-flow microfiltration.
- Precipitation of wastewater with NaOH-Na_2CO_3 without temperature control, followed by cross-flow microfiltration, and a polishing step with natural zeolite (clinoptilolite or chabazite) sorption columns.
- Precipitation of wastewater with NaOH-Na_2CO_3 with temperature control, followed by powdered zeolite (clinoptilolite or chabazite) addition and cross-flow microfiltration.
- Precipitation of wastewater with NaOH-Na_2CO_3 with temperature control, followed by cross-flow microfiltration, and a polishing step with natural zeolite (clinoptilolite or Chabazite) sorption columns.

On the basis of our screening results of the strontium removal efficiency of biomass, it is feasible to replace the zeolite powder-addition step with biomass (L. plantarum or P. cerevisial) addition to the wastewater either as powder or as a suspension. It may be also possible to replace using a zeolite sorption column for the polishing step with a biomass column, when stable, inexpensive methods for supporting the biomass in a fixed-bed column configuration becomes available. Presently, such methods are not available, although improvements to supporting the biomass over glass or silica particles (20) in gelatin or similar medium could prove to be attractive. Our results for strontium removal suggest that when the competing calcium is present in low concentrations (e.g., less than 10 mg/L) in the wastewater, Na-clinoptilolite, Na-chabazite, L. plantarum or P. cerevisial are the most promising sorbents. However, at relatively high concentrations (e.g., 20 to 50 mg/L) of the competing calcium, the superior performance of chabazite or L. plantarum is the preferred choice.

CONCLUSIONS

The major conclusions from our preliminary evaluations of selected natural zeolites and biomass in the context of AECL's CHEMIC^{TM} process are as follows:

- The radiostrontium removal performance of different biomass was similar to that of the natural zeolites, and thus provides choices in the use of natural sorbent materials for contaminant removal from wastewaters.
- Depending on the characteristics of the wastewater, natural zeolites or biomass can be used for direct sorbent-addition treatment in the CHEMIC process.

- Chabazite and L. plantarum are the preferred sorbents for strontium removal from wastewaters containing relatively high concentrations of the competing calcium ion.

- When the concentration of competing calcium is low, the use of lower-cost clinoptilolite would be the preferred choice for treatment of radiostrontium-contaminated waters.

- Controlling the precipitation temperature and optimising the sorbent concentration in the CHEMIC process provides the basis for efficient removal of radiostrontium from contaminated waters to meet different discharge water quality targets.

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