SrTreat is an inorganic ion exchanger whose structure is based on a sodium titanate. It is available in granular form and is suitable for use in packed-bed operations. This exchanger has proved to be highly effective in the removal of radioactive strontium from alkaline nuclear waste solutions. SrTreat was used for the first time in an industrial-scale separation process in 1996 in Murmansk, Russia. During that operation 2500 bed volumes of low-active (22 kBq/L) waste solution with a moderate salt concentration was decontaminated from \(^{90}\text{Sr}\) with an average decontamination factor of 7400. The exchanger is especially suited for the decontamination of alkaline concentrated sodium nitrate solutions that are characteristic of neutralized stored wastes from some nuclear-fuel-reprocessing plants.

At the Japanese Atomic Energy Research Institute (JAERI), a new radionuclide-removal system, successfully utilizing SrTreat for the removal of \(^{90}\text{Sr}\) (7.4 GBq/L) from a neutralized alkaline reprocessing waste solution, was commissioned in the summer of 1997. In the laboratory-scale tests with a JAERI simulant, adjusted to pH 10 and having 2.4 mol/L of NaNO\(_3\), strontium could be removed from more than 1000 bed volumes with an SrTreat column, thereby obtaining a decontamination factor between 2000 and 15000. In addition to the performance of SrTreat columns in strontium removal, basic studies on the ion exchange equilibrium of strontium on SrTreat and the effects of pH and interfering cations on strontium exchange are discussed.

I. INTRODUCTION

Waste solutions produced at both civil and military nuclear-fuel-reprocessing plants contain considerable amounts of radioactive strontium, i.e., \(^{90}\text{Sr}\). In many cases strontium creates most of the radioactivity after cesium. In the fission process, cesium and strontium are produced in approximately the same yields, and in acidic reprocessing solutions, their activity concentrations are almost equal. In the neutralization of these solutions with sodium hydroxide, cesium remains almost exclusively in solution, but strontium is partially coprecipitated with hydroxides of other metals and as a carbonate. Most other radionuclides are precipitated as hydroxides, leaving only traces of these nuclides behind in the solution phase. Therefore, cesium is always the greatest contributor to the total radioactivity of neutralized alkaline waste solutions, and strontium is the second greatest.

All waste solutions must be solidified for final disposal. One way to do this is to directly calcine and vitrify the solutions. Since vitrification and final disposal of high-level waste are very expensive, it would be extremely beneficial to minimize the waste volumes. This can be achieved by the selective separation of radionuclides from solutions.\(^1\) After the removal of key radionuclides from solutions, the residuals can be solidified as medium- or low-active waste, for which the processing and final disposal regulations are much less rigorous.

An extremely selective ion exchange material, a potassium cobalt hexacyanoferrate(II) product called...
CsTreat\(^a\) has been developed\(^2\) for the removal of radioactive cesium. This material has proved to be a superior ion exchange material not only in the removal of cesium from nuclear reprocessing waste but also from many other aqueous wastes. It has been successfully used on an industrial scale in the removal of cesium from both concentrated and dilute salt solutions.\(^3\) This paper discusses the performance and properties of the strontium selective ion exchanger SrTreat,\(^b\) which is a sodium titanate. These two exchangers in combination will result in very good decontamination of reprocessing waste solutions and remarkable reductions in volume of wastes to be disposed of.

Strontium is usually removed from waste solutions by precipitation aided by calcium phosphate, calcium carbonate, or barium sulphate or by flocculation with iron(III). For example, at the La Hague reprocessing plant in France, strontium is removed from low-active waste streams by iron flocculation at pH 10.5 and from medium-active waste streams with barium sulphate at pH 8.5 (Ref. 4). Decontamination factors of 100 and above for strontium have been obtained in these processes.

Organic ion exchange resins have also been used for strontium separation. For example, in the aforementioned La Hague low-active waste treatment process, an end-polishing step for strontium removal after iron flocculation is carried out with a weakly acidic carboxylic acid cation exchange resin.\(^5\) Due to low selectivity, strongly acidic resins are usually used in radionuclide removal processes only for dilute solutions in conjunction with anion exchangers to completely demineralize the solution. Carboxylic acid resins, which are more selective for divalent ions than sulfonic acid resins, can be used in moderate salt concentrations as well. For example, at the Marcoule reprocessing plant, strontium could be removed with a carboxylic acid resin from 300 bed volumes of medium-active waste solution containing 0.6 mol/\(\ell\) of sodium and 0.001 mol/\(\ell\) of magnesium.\(^6\)

Zeolites, which are aluminosilicate ion exchangers, have been used for strontium removal since the beginning of the 1980s. The largest zeolite ion exchange facility, SIXEP at the Sellafield reprocessing plant in the United Kingdom, uses two 10-m\(^3\) zeolite beds in series to remove cesium and strontium from 3600 m\(^3\) of fuel storage bond water every day.\(^7\) The zeolite used is a natural mineral, clinoptilolite. Synthetic zeolites, manufactured by UOP, have been utilized for strontium and cesium removal at the Three Mile Island nuclear power plant in the United States for the decontamination of high-active waste solutions originating from the 1979 reactor accident.\(^8\) Zeolite selectivities for strontium are, however, fairly low; thus, they can be used only in dilute solutions. Another limitation is that they cannot be used in alkaline solutions with pH above 10 due to their framework instability under these conditions.

Recently, a new type of inorganic ion exchangers, called crystalline silicotitanates, has been developed at Sandia National Laboratories and Texas A&M University in the United States.\(^9\) Silicotitanates are commercially available as IONSIV IE-910/911 from UOP. These exchangers have been reported to have a high selectivity for both \(^{137}\)Cs and \(^{88}\)Sr, and they have been tested in the purification of Hanford site tank wastes.\(^10\) However, no industrial processes utilizing silicotitanates have been reported.

II. PROPERTIES OF SrTreat

SrTreat is typically used with a particle-size fraction of 0.30 to 85 mm (20 to 50 mesh); however, other grain-size fractions are also available. The specific gravity of SrTreat is 5.6 g/ml, and its bulk density is 0.8 kg/\(\ell\). The practical ion exchange capacity for strontium of SrTreat was found to be 5.0 \pm 0.3 meq/g (dry weight), as determined by batchwise equilibration of 1-g exchanger samples with 100 ml of 0.03 M \(\text{Sr(NO}_3\text{)}_2\) solution. This value is equal to the total ion exchange capacity, as will be seen later. It has been proved that the radiation resistance of SrTreat is very good: there was no degradation in the framework structure nor any decrease in strontium uptake observed even after exposing the material to an irradiation dose of 10 MGY.

III. DEFINITIONS

The distribution coefficient \(K_D\) (Figs. 1, 2, and 3) is the ratio of equilibrium concentration of the ion in the exchanger phase to that in the solution phase, i.e., \(K_D = [\text{Sr}]_r/[\text{Sr}]_s\), where [Sr], and [Sr], refer to the strontium ion concentrations in the solid and solution phases, respectively. The \(K_D\) values were calculated as follows:

\[
K_D (\text{ml/g}) = \left(\frac{A_0}{A} - 1\right) \times \frac{\text{V}}{\text{m}},
\]

where

\[
A_0 = \text{initial activity of the } ^{85}\text{Sr tracer}
\]

\[
A = \text{equilibrium activity of the } ^{85}\text{Sr tracer}
\]

\[
V = \text{solution volume (ml)}
\]

\[
m = \text{exchanger mass (g)}.
\]

The selectivity coefficient for the sodium/hydronium ion exchange was calculated as follows:

\[
k_{H/Na} = \frac{[\text{H}_3\text{O}]_r[\text{Na}]_s}{[\text{H}_3\text{O}]_s[\text{Na}]_r}.
\]

The decontamination factors (DFs) given in the breakthrough curves (Figs. 4, 5, and 6) are the ratios of the

\(^a\)Manufactured by Selion Oy, Vantaa, Finland.
\(^b\)Manufactured by Selion Oy, Vantaa, Finland.
distribution coefficient of strontium was determined as a function of pH in 2 M NaNO₃ solution (Fig. 1). Second, the column breakthrough of strontium in 2 M NaNO₃ solution was determined at three solution pH values: 9.0, 10.0, and 11.5 (Fig. 4). As can be seen from these graphs, the pH of solution has a tremendous effect. At pH 7, strontium uptake by SrTreat is rather low, but in alkaline solutions, \( K_D \) increases more or less linearly with pH and has high values at pH 10 and above. Column tests gave the same picture: At pH 9 the column performance is rather poor (DF < 100), but at pH values 10 and above, SrTreat works much more efficiently (DF 100 to 10000). The effect of pH indicates that the exchanger is weakly acidic and prefers hydronium ions. Thus when strontium in trace concentrations is equilibrated with SrTreat in sodium form, the ion exchange system always has three components: trace strontium, sodium, and hydronium ions. The equilibrium of this system is discussed in more detail in Sec. V.

IV. EFFECT OF pH ON STRONTIUM REMOVAL WITH SrTreat

The effect of pH on the performance of SrTreat in strontium removal was studied in two ways. First, the

V. SELECTIVITY OF SrTreat FOR STRONTIUM AND COMPETING IONS

V.A. Effect of Hydronium Ions

Studies on the pH dependence of strontium uptake indicated that SrTreat does not dissociate appreciably at neutral pH, which means that the exchanger is weakly acidic in nature. To obtain a more detailed view of the acidity of the material, the sodium form of SrTreat was titrated with 1 M HNO₃ to convert it into hydrogen form (Fig. 2). The titration was carried out batchwise in a 3 M

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Fig. 1. Distribution coefficient \( K_D \) of strontium on SrTreat as a function of pH in 2 M NaNO₃ solution.

Fig. 2. Titration curve of SrTreat in 3 M NaNO₃ traced with \(^{85}\)Sr Batch titration with 1.0 M HNO₃. Distribution coefficient \( K_D \) determined simultaneously with the titration.
NaNO₃ solution containing a ⁸⁵Sr tracer. The pH and ⁸⁵Sr activity were measured in the solution at equilibrium. Since the initial sodium concentration in solution was high and the sodium-hydrogen exchange did not affect the total sodium content of the solution markedly, it was assumed constant at 3.0 M. Sodium concentration in the exchanger at equilibrium was measured after treatment with concentrated acid. The hydrogen ion concentration in the exchanger was then calculated from the difference between sodium concentration and ion exchange capacity, 5.0 meq/g, which was derived from the inflection point in the titration curve. From these equilibrium measurements, the distribution coefficient $K_D$ of ⁸⁵Sr and the selectivity coefficient $k_{H/Na}$ were determined.

The titration curve for SrTreat was very sharp, and only one inflection point was observed (Fig. 2). This indicates that the exchanger is monofunctional in character. In the initial stages of titration, when the exchanger is mostly in the sodium form, the $K_D$ values for ⁸⁵Sr were very high—close to 1000 000 ml/g in 3 M sodium ion concentration. However, with increasing conversion into hydrogen form, the $K_D$ decreased and dropped sharply with pH as the point of equivalence was approached. In

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**Fig. 3.** Distribution coefficient of ⁸⁵Sr for SrTreat in different salt solutions as a function of solution concentration. SrTreat was in the same ionic form as the solution cation.

**Fig. 4.** Breakthrough of strontium in 2 M NaNO₃ solution from SrTreat columns using solutions adjusted to three different pH values.

**Fig. 5.** Breakthrough of strontium from a 0.5-ml SrTreat column using continuous and intermittent pumping (5 h of pumping and 19 h of inactivity). Solution: 2.4 mol/l of sodium and pH of 10.0. Grain size of SrTreat, 0.30 to 0.85 mm. Flow rate of 25 bed volumes (BV)/h.

**Fig. 6.** Breakthrough of strontium from Hanford DSSF and NCAW simulants from SrTreat columns. DSSF composition: 5 M Na, 0.64 M Al, 0.95 M K, 2 mM Ca, 0.6 μM Sr, 1.8 M NO₃, 0.43 M NO₂, 0.15 M SO₄, 0.09 M F⁻, 0.025 M PO₄³⁻. NCAW composition: 5 M Na, 0.4 M Al, 0.1 M K, 0.2 mM Ca, 0.6 μM Sr, 3.5 M NO₃, 1.5 M NO₂, 0.008 M SO₄, 0.12 M Cl⁻, 0.014 M PO₄³⁻; pH = 13, temperature = 42 to 47°C, BV = 2 ml, flow rate = 5 BV/h.
the hydrogen form, the $K_D$'s were very low. The selectivity coefficient for sodium-hydrogen exchange, $k_{H/Na^+}$, was $10^{76}$ when the exchanger was mostly in the sodium form. This result reflects the high preference of the material for hydrogen ions. As a result, the uptake of strontium from solution is low when the material is in the hydrogen form, which dominates in neutral and acidic solution media.

Even though strontium could possibly be efficiently removed from strontium-loaded SrTreat, regeneration and reuse of the exchanger has not been studied. This may not be practically viable anyway because all inorganic ion exchangers, unlike organic resins, are slightly soluble, especially in acids and alkalis; this alone would restrict their cyclic use.

V.B. Effect of Common Cations

The selectivity of SrTreat for common cations ($H^+$, $K^+$, $Li^+$, $Ca^{2+}$, $Mg^{2+}$, and $NH_4^+$) and their effect on $^{85}Sr$ uptake was determined. This was done by equilibrating samples of SrTreat, converted into the respective ionic forms, in corresponding salt solutions of varying concentrations. Cations $K^+$ and $Li^+$ appeared to have practically no effect on strontium uptake (Fig. 3). The $Mg^{2+}$ and $NH_4^+$ cations decreased strontium uptake, but strontium removal was still high at concentrations that are typically present in waste solutions. Even when present at relatively low concentrations, $Ca^{2+}$ decreases strontium uptake strongly. It can be calculated from Fig. 3 that the selectivity coefficient $k_{Sr/Ca} \approx 1$; i.e., SrTreat has no selectivity difference between strontium and calcium. Note, however, that calcium is not usually soluble in the pH range (>9) in which SrTreat works in an optimal way. The reason is that alkaline waste solutions that have been in contact with the atmosphere take up carbon dioxide, which eventually results in the precipitation of calcium as the carbonate. For example, at pH 9 the concentration of the carbonate in a solution that has been in contact with the atmosphere can be as high as 0.0001 mol/L. As the solubility product of calcium carbonate is $5 \times 10^{-9}$, the maximum solution concentration of the calcium ion will be as low as $5 \times 10^{-3}$ mol/L. At a pH value of 10, the calcium concentration in solution will be two orders of magnitude lower than for solution at pH 9. Such low concentrations of calcium in solution will have a negligible effect on the strontium ion exchange by SrTreat.

By comparing the various data sets in Fig. 3, we can conclude that the selectivity of SrTreat for the ions studied decreases in the following order: $H^+ > Sr^{2+} > Ca^{2+} > Mg^{2+} > NH_4^+ > K^+ > Li^+$. Considering removal of $^{90}Sr$ removal from waste solutions, critical factors in the capacity of SrTreat are solely the solution pH and the concentration of calcium ions (in circumstances where calcium is soluble).

VI. LARGE-SCALE UTILIZATION OF SrTreat—EXPERIENCES AND POTENTIAL

VI.A. Purification of Low-Active Waste Effluents in Murmansk, Russia

In Murmansk, Russia, there is a naval base that has a nuclear-operated fleet composed mainly of icebreakers that work on the Arctic Sea. In refueling these ships, large volumes of low- and medium-active-waste solutions are generated. IVO Power Engineering, Finland, started a demonstration project in 1996 to purify these waste solutions from radioactive elements. A total of 300 m$^3$ of waste liquid was treated with a compact transportable purification system, NURES, which was constructed in a container. The composition of NURES is as follows: 0.1-$\mu$m prefiler, activated carbon bed, and two parallel lines that each have 12-ℓ CsTreat and SrTreat beds in series. In the treatment of the first 60-ℓ batch (2500 bed volumes), an average DF of 7400 was obtained. This batch of solution contained 0.4 g/ℓ of mixed salts (sodium, calcium, magnesium, and iron; the exact composition and concentrations of anions unknown), its initial pH was 9.8, and the $^{90}Sr$ activity was 22 kBq/ℓ (5 × 10$^{-7}$ µCi/ml). After treatment the $^{90}Sr$ activity level was very low (3 Bq/ℓ, 8 × 10$^{-8}$ µCi/ml), and the purified solution could be released into the sea because the whole NURES system also removed other nuclides efficiently, the DFs for $^{137}Cs$, $^{60}Co$, and $^{125}Sb$ being 360, 120, and 8, respectively. The average DF for the total activity was 430.

VI.B. Purification of Reprocessing Waste Effluents at JAERI

For the removal of cesium and strontium from reprocessing waste effluents, a new radionuclide removal system was commissioned at the Japanese Atomic Energy Research Institute (JAERI) in 1997 (Ref. 11). This process utilizes ion exchange columns containing CsTreat and SrTreat, ~1 ℓ of each. The waste solutions contain metals such as iron, chromium, zirconium, aluminum, calcium, magnesium, and nickel, the concentrations of which are in the millimolar range. Prior to cesium-strontium removal, some other nuclides, such as plutonium, are removed by other systems. The $^{90}Sr$ activity concentration in the effluent is ~7.4 GBq/ℓ (0.2 Ci/ℓ), which corresponds to a strontium concentration of 0.015 mmol/ℓ. The solution is initially acidic, ~2 M nitric acid, but to achieve the optimum efficiency of the ion exchange materials, the pH is increased to the alkaline region. Due to neutralization and previous nuclide-removal steps, cesium and strontium form most of the solution activity. It was found, however, that a large fraction of strontium, ~50%, was removed in the neutralization-filtration step. From the resulting neutralized solution, which now contains ~2 mol/ℓ of sodium due to the addition of NaOH,
CsTreat and SrTreat columns remove cesium and strontium very efficiently.

Figure 5 shows the breakthrough curves of the laboratory-scale tests done with a simulant having a pH of 10.0 and a sodium concentration of 2.4 mol/l. The tests were done in two ways: first, by continuous pumping and then by periodic pumping, i.e., 5 h of pumping following 19 h of standing stationary. Both methods gave good results regarding radionuclide removal, but when operated by periodic pumping, efficiency was considerably improved. This behavior indicates that the ion exchange rate under these conditions is controlled by particle diffusion; i.e., the break in the pumping allows the strontium to diffuse into the sodium titanate crystals and granules and enhances the strontium uptake rate. The average DF at 1500 bed volumes, when using continuous pumping, was 4400, and when using periodic pumping, this value increased to 8400. The grain size of SrTreat in these tests was 0.30 to 0.85 mm (20 to 50 mesh). In another experiment conducted with a smaller grain size of 0.14 to 0.30 mm (50 to 100 mesh), the performance was even better, and DFs as high as 15000 were obtained. As already noted (Figs. 1, 2, and 4), the pH used in these tests, 10.0, is not the optimum; at higher pHs even better strontium separation can be achieved. Moreover, these laboratory-scale tests were done with very small columns containing only 0.5 ml of SrTreat and CsTreat in each, and it is probable that on a larger scale, performances will be better.

Using three columns in series yielded DFs as high as one million.

VII. CONCLUSIONS

SrTreat, a sodium titanate, has been proved to be a highly selective inorganic ion exchanger for strontium. It removes strontium very efficiently from both concentrated and dilute waste solutions. The optimum pH range for its use is 10 and above, and it works effectively even in the highest pH values found in the waste solutions. High sodium, potassium, lithium, magnesium, and ammonium concentrations practically do not interfere with the strontium exchange; however, calcium ions have a detrimental effect on the removal of strontium. The interference by calcium is not regarded as a major problem because in the pH range where SrTreat works optimally (pH > 9), the calcium precipitates as the carbonate if the solutions are in contact with the atmosphere, which is usually the case. SrTreat has been used successfully on an industrial scale in Murmansk, Russia, and at JAERI in Japan. Preliminary experiments have shown that SrTreat has a great potential in the treatment of high-active waste solutions from the Hanford site and for other neutralized alkaline reprocessing waste solutions.

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