PILOT SCALE TESTING OF INORGANIC ION EXCHANGERS FOR PRECOAT APPLICATIONS

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ABSTRACT

New selective inorganic ion exchange medias were tested for precoat application, in which the exchangers were layered as fine powders on a filter element. The scope of the treatment was the removal of $^{137}$Cs and $^{60}$Co from simulated NPP Floor Drain waters. Preliminary results indicate that very high processing capacities are obtained with the novel precoat materials, e.g. CoFloc material (Graver Technologies Inc.) showed no sign of exhaustion after 40,000 L of simulated floor drain water had been purified using a 80-g precoat dose. This corresponds to a minimum processing capacity of 500,000 L/kg (60,000 gal/lbs.). The decontamination factors (DF) depended on the radioactivity level in the feed. When $^{57}$Co tracer activity concentration was 50-70 Bq/L, the DF’s were modest (between 3 and 4) but increased to 40-70 when the feed activity was increased to 1000-1600 Bq/L. CsTreat® powder (Selion Oy) and CsFloc (Graver Technologies Inc.) gave mostly DF’s larger than 100 for $^{134}$Cs tracer even when the feed activity concentration was 50-70 Bq/L. At 4200 Bq/L activity level the DF was 1400 for CsFloc.

INTRODUCTION

Inorganic ion exchange materials are increasingly applied for the treatment of radioactive waste effluents as they often show superior performance compared to the conventional organic resins. A large majority of applications involve granular ion exchange materials and column operation. This is often not the optimal way of using the new highly selective materials. Especially when a high throughput rate is required, the slow kinetics in the granular material may detract from the advantage of high-selectivity. One way to improve the kinetics is to decrease the ion exchanger particle size.

In the treatment of nuclear waste effluents, inorganic ion exchange materials have several advantages, e.g. higher radiation stability and higher selectivity, which make them superior to organic ion exchange resins in certain situations. Zeolites have been commonly used in the removal of $^{137}$Cs and $^{90}$Sr from low-salt liquids, but they are generally inefficient for the treatment of higher salt effluents such as US DOE tanks wastes or NPP evaporator concentrates. Several new efficient inorganic exchangers, e.g. titanates, silicotitanates and hexacyanoferrate compounds have been developed and brought to market recently. These include CsTreat®, SrTreat® and CoTreat, which are manufactured by Selion Oy, Finland and which have found applications all over the world in recent years. CsTreat® was first taken into use at Loviisa
NPP (Finland) in 1991 for the purification of high salt (240 g/L NaNO₃) evaporator concentrates and has been used since at several other NPP's and nuclear sites to process both high-salt and low-salt cesium-bearing waste waters. A recent application of CsTreat® and SrTreat® involves purification of medium-active waste streams from ¹³⁷Cs and ⁹⁰Sr, respectively, at the JAERI Tokai-Mura site in Japan. CoTreat is a new selective inorganic exchanger for the removal of radiocobalt and other activated corrosion product nuclides, and it is in test use in several nuclear sites.

The application of inorganic materials almost always involves column operation utilizing granular ion exchange materials. The rate of ion diffusion in the crystalline inorganic materials is relatively low – hence the ion exchange rate is low and the flow rates in columns packed with granular material (particle size typically 0.25-0.85 mm) need to be low, typically 10-50 BV/h, to obtain a good decontamination factor for the radionuclide ions. This means that large beds, containing a very high excess of ion exchange capacity, need to be used when large throughputs are required. Most of this excess capacity often remains unused. Because the cost of efficient selective inorganic materials is relatively high, the unused capacity presents an extra cost, which may reduce the economical gains resulting from the high selectivity and processing capacity.

The ion exchange rate can be increased by decreasing the exchanger particle size. Precocat applications utilizing ground organic resins of very small particle size are common in nuclear power plants. However, inorganic materials other than zeolites have not been used in this fashion to date. CsFloc and CoFloc are new precocat materials that are manufactured by Graver Technologies Inc. These materials have been formulated using finely divided CsTreat® and CoTreat exchangers and additives.

Pilot scale tests have just been started at the University of Helsinki in mid-1999 to assess the efficiency of CsFloc and CoFloc, as well as that of CsTreat® and CoTreat precursors for the removal of ¹³⁷Cs and ⁶⁰Co from simulated NPP wastewaters.

TEST METHODS AND MATERIALS

In the tests, CsFloc (GL 750) and CoFloc (GL 792) precocat exchangers, as well as CsTreat® and CoTreat powders, were tested on a pilot plant scale. CsTreat® is an all-inorganic, hexacyanoferrate ion exchanger that is highly selective for cesium ions. CoTreat is a titanium oxide material which is selective for cobalt (e.g. ⁶⁰Co), manganese (e.g. ⁵⁹Mn), iron (e.g. ⁵⁹Fe), zinc (e.g. ⁶⁵Zn) and plutonium (e.g. ²⁴⁰Pu). CsTreat® and CoTreat materials are normally supplied for column operation in granular form, but they are also available in powder forms. CsFloc and CoFloc, manufactured by Graver Technologies Inc, are made from finely divided inorganic compounds and organic polyomers. CsFloc utilizes hexacyanoferrate chemistry for selective removal of cesium and in a corresponding manner, CoFloc uses titanium oxide chemistry for the selective removal of cobalt. In addition, finely divided organic resins were tested for reference. The organic exchangers used were Powdex® GX089 (weak-acid cation resin) for cobalt removal and Powdex® PCH (strong-acid cation resin) for cesium removal. Both resins were supplied by Graver technologies and used in the supplied hydronium forms.
The precoat pilot-plant unit, supplied by Graver Technologies Inc., comprised a housing for a 10-inch precoat element, a slurry tank, a precoat pump and auxiliary piping, meters and valves (Fig. 1). 80-100 g (0.18-0.22 lbs.) of ion exchange material (particle size < 0.15 mm) was coated on the filter element. Coating was carried out by recirculating (valves Y and A-2, Fig. 1) 10-g subdoses of material from the slurry tank (valve Z, Fig. 1). The ion exchange materials were soaked overnight in the non-radioactive test solutions prior to use.

**Figure 1.** Schematic presentation of the pilot plant test equipment

Two types of simulated floor drain (FD) waters (for compositions, see Table 1) were used in the tests. First type (FDA) represented a medium-salt floor drain water contaminated with radiocesium, while the second (FDB) was a simulant of low-salt water contaminated with radiocobalt. In the test, the simulated wastewaters were circulated by a second pump through the precoated filter element (valves A-1, A-2 and U, Fig. 1) via a stirred 60 L (16 gal) feed tank. Concentrated solutions of radioactive tracer ions (\(^{134}\)Cs or \(^{57}\)Co) were fed continuously into the feed tank to replenish the radioactivity taken up by the precoat filter and to keep the radioactive feed level approximately constant at 70-50 Bq/L. In the testing of CoFloc, also higher levels of \(^{57}\)Co, between 1000-1600 Bq/L were used for short periods of time. A prolonged feed at this activity level was not possible due to the build-up of radioactivity in the precoat filter. The flow rate through the element was 3.5-4 L/min (0.9 – 1.0 gpm).
Table 1. Chemical composition of simulated floor drain waters

<table>
<thead>
<tr>
<th>Constituent</th>
<th>FDA</th>
<th>FDB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na (ppm)</td>
<td>204</td>
<td>43</td>
</tr>
<tr>
<td>K (ppm)</td>
<td>19</td>
<td>17</td>
</tr>
<tr>
<td>Mg (ppm)</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>Ca (ppm)</td>
<td>40</td>
<td>0.5</td>
</tr>
<tr>
<td>Nitrate (ppm)</td>
<td>560</td>
<td>106</td>
</tr>
<tr>
<td>PH</td>
<td>6.9</td>
<td>6.8</td>
</tr>
<tr>
<td>Cs-134 (Bq/L)</td>
<td>50-70 (4200 short-term)</td>
<td>0</td>
</tr>
<tr>
<td>Co-57 (Bq/L)</td>
<td>50-70 (1000-1600 short-term)</td>
<td>0</td>
</tr>
</tbody>
</table>

One-liter samples were taken periodically from the feed tank and precoat filter outlet (valve U, Fig. 1) to determine the activity concentration of $^{134}\text{Cs}$ or $^{57}\text{Co}$. The decontamination factor for the radionuclides was calculated from the formula $DF = A_0/A$, where $A_0$ is the activity concentration in the feed tank and $A$ that in the precoat outlet.

**RESULTS AND DISCUSSION**

CsTreat® and CsFloc materials were precoated on the filter element using the standard procedure which involves recirculation of the ion exchange material via the openings at the bottom of the filter housing (valves A-2 and Y, Fig. 1). In this procedure, the inorganic materials, that are heavier than ordinary organic precoat formulations, tended to accumulate largely on the bottom area of the element surface while the layer of precoat on top was very thin. Nevertheless, the first tests carried out in these non-optimal conditions for FDA gave highly encouraging results (Figure 2). Initially, the decontamination factors (DF) obtained with CsTreat® and CsFloc for $^{134}\text{Cs}$ were 300-400. CsTreat powder performed well (DF>10) until about 13,000 liters of solution had been processed. After about 12,000 L had been processed, the pressure drop across the element started to increase with a concurrent decrease in DF. CsFloc still performed well (DF = 60) at about 7,000 L when the test was terminated due to time constraints. No increase of dP was observed in the CsFloc run. The performance of Powdex® PCH precoat was modest compared to that of CsTreat® or CsFloc, the DF was less than 2 throughout the resin test (Fig. 2).
Figure 2. Decontamination factor (DF) obtained for CsFloc, CsTreat and Powdex PCH as a function of solution FDA volume (L) processed through the precoat element. Flow rate 4 L/min, CsTreat dose 100 g, CsFloc and Powdex doses 80 g.

Figure 3. Decontamination factor (DF) obtained for CoFloc and CoTreat powder as a function of solution FDB volume (L) processed through the precoat element. Flow rate 4 L/min, CoTreat and CoFloc dose 80 g. Activity of $^{57}$Co in feed 50-70 Bq/L (1000 Bq/L and 1600 Bq/L short term as indicated).
For the tests of CoTreat powder and CoFloc various procedural modifications were used to improve the homogeneity of the precoat layer. It was found that by circulating the suspended ion exchange material out of the filter housing from the top of the vessel (valve V), instead of the bottom, and through the slurry tank facilitated the upward flow of the precoat suspension. This resulted in a homogenous precoat layer on the filter element. The first tests were carried out using FDB simulant. For the CoTreat powder the DF’s for $^{57}$Co were about 10 initially and fell below 3 when 20,000 L of solution had been processed (Figure 3). A similar increase of pressure drop across the filter element was observed as for CoTreat powder. For CoFloc, the DF’s were somewhat lower initially, but were still around 3 when 40,000 L had been processed. These rather modest values were obtained when the feed activity level of $^{57}$Co was low, i.e. 50-70 Bq/L. However, when the feed activity concentration of $^{57}$Co was increased there was a considerable increase in the DF, at 1000 Bq/L feed level the average DF increased to 42 and at 1600 Bq/L feed level the DF was about 70 (Fig. 3). Closer inspection of the data indicated that the DF was a linear function of the $^{57}$Co activity in the feed (Fig. 4). It is worth noting that even when 40,000 L of solution had been processed, CoFloc was still able to yield a high DF at elevated feed activity. Only 80 g of CoFloc was dosed. The minimum processing capacity is thus 40,000 L/0.080 kg = 500,000 L/kg, which corresponds to about 60,000 gallons per pound of CoFloc. The organic precoat GX089 was far less efficient than CoTreat or CoFloc (Fig. 3). The DF was only about 2 and did not increase with increasing $^{57}$Co activity level in the feed (Fig. 4).

In the first CsTreat and CsFloc tests the effect of elevated $^{134}$Cs activity concentration was not investigated. New tests that have just been initiated for CsFloc indicate that there is a similar
increase of DF with activity concentration as what was observed for CoFloc. At 4200 Bq/L activity level the DF of 1400 for $^{134}\text{Cs}$ and CsFloc has been measured.

**SUMMARY AND CONCLUSIONS**

The preliminary test results indicated that high processing capacities on the order of 150,000 L/kg (18,000 gal/lbs.) are obtainable with CsTreat® and CsFloc precoat materials. The DF’s for $^{134}\text{Cs}$ were close to 100 or more prior to media exhaustion. These estimates are probably conservative since in these preliminary tests there were problems in packing the precoat uniformly onto the filter element.

The precoat packing problems were solved for the CoFloc and CoTreat tests. The results indicate that the processing capacities for CoFloc are very high exceeding 500,000 L/kg (60,000 gal/lbs.). For CoTreat powder the processing capacity appeared to be lower, which may be due to the compacting of the material under pressure and the resulting channeling. At 50-70 Bq/L feed levels the $^{57}\text{Co}$ DF’s were considerably lower (DF = 3-10) for CoTreat and CoFloc than for the Cs-selective medias. However, at the elevated feed levels (1000-1600 Bq/L) the CoFloc yielded DF’s that were close to 100.

The performance of organic resin precoats was rather modest compared to the inorganic medias. The DF obtained by the organic materials was about 2 (50% removal) at best. The organic resins were used in their H⁺-forms, which may have not been the optimum ionic form for efficient operation.

The test results show that a considerable advantage of precoat application compared to column operation is that much higher flow rates can be applied for a given amount of exchange material.

**REFERENCES**


