

DEVELOPMENT OF A SELECTIVE CESIUM AND STRONTIUM REMOVAL SYSTEM  
FOR THE JAERI TOKAI-MURA SITE - LABORATORY TESTS

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## ABSTRACT

New selective inorganic ion exchange medias, CsTreat<sup>®</sup> and SrTreat<sup>®</sup>, were tested in laboratory using minicolumns and simulated waste liquid for the treatment of medium-active reprocessing waste effluents. The test results indicated that decontamination factors (DF) in the range of 1000-10,000 could be obtained for <sup>137</sup>Cs and <sup>90</sup>Sr, which is well above the required purification efficiency, <sup>137</sup>Cs DF > 400 ( <sup>90</sup>Sr DF > 200). The results also showed that the processing capacity of CsTreat<sup>®</sup> and SrTreat<sup>®</sup> columns was larger than the required 850 bed volumes with a large safety margin. These minicolumn test results were in fair to good agreement with results obtained in the test use of the full-scale system at Japan Atomic Energy Research Institute (JAERI).

## INTRODUCTION

Due to their high radiation stability and high selectivity for specific radionuclide ions, inorganic ion exchange materials are finding increasing applications for the treatment of nuclear waste effluents. Zeolites have been commonly used in this field, but during the past decade more efficient materials, able to perform in a wider pH-range and in high-salt effluents, have entered the market<sup>1</sup>. These include highly selective CsTreat<sup>®</sup> and SrTreat<sup>®</sup> media, which have found a number of industrial applications worldwide since 1991 for the removal of <sup>137</sup>Cs and <sup>90</sup>Sr, respectively, from radioactive waste effluents<sup>2</sup>.

The Japan Atomic Energy Research Institute's (JAERI) Tokai-Mura site has produced and accumulated considerable amounts of medium-active waste effluents in its nuclear fuel

reprocessing research. . The major radioactive contaminants in the waste are  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$  and TRU-nuclides<sup>3</sup>. Laboratory tests were carried out at the University of Helsinki for the removal of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  from the effluents. Based on the results, the selective ion exchange column process was designed and integrated in the new treatment system which was constructed at JAERI during 1995-96. In this paper, laboratory test results are presented and compared with the performance of the full-scale system during test operation<sup>4</sup>.

## LABORATORY SCALE TESTS

The highly selective CsTreat<sup>®</sup> and SrTreat<sup>®</sup> ion exchange medias used in the tests are totally inorganic. CsTreat<sup>®</sup> is a hexacyanoferrate material, which is applicable over a wide pH-range (1-13)<sup>5</sup>. SrTreat<sup>®</sup> is based on titanium oxide and has a weak-acid ion exchange functionality, which means that Sr uptake is low in acidic solution and increases with increasing pH<sup>6</sup>. These materials have been developed by the Laboratory of Radiochemistry (University of Helsinki) and Fortum Engineering Oy (formerly IVO Power Engineering Oy) and are manufactured by Selion Oy.

The tests were carried out using minicolumns (bed volume 1 mL, bed height 5 cm), which were packed with 0.3 g of CsTreat<sup>®</sup> and 0.4 g SrTreat<sup>®</sup> (grain size 0.85-0.30 mm) media, the latter was at the top of the column. The bed volume of both medias was approximately 0.5 mL. Simulated reprocessing waste effluent (Table 1), traced with  $^{85}\text{Sr}$  and  $^{134}\text{Cs}$  nuclides and neutralized to pH = 8.0-11.5 with NaOH, was fed to the column from the bottom at a rate of 8-13 mL/h. Neutralization of the acidic solution was necessary to obtain a reasonable capacity for the weakly-acidic SrTreat<sup>®</sup> exchanger. After neutralization, i.e. before the column tests, the solution was filtered using a 1.6  $\mu\text{m}$  glass fiber or 0.45  $\mu\text{m}$  polymer membrane filters. Part of  $^{85}\text{Sr}$  was removed from the solution in the neutralization and filtration. At pH = 8, the removal was about 20 % and increased to 80 % when the solution was neutralized to pH = 11.5. The removal of  $^{134}\text{Cs}$  was negligible. The columns were operated either in continuous (24 h/day) or intermittent mode (3-5 h/day). Samples were taken frequently from the column effluents and analyzed for  $^{85}\text{Sr}$  and  $^{134}\text{Cs}$ . Column decontamination factors were calculated for the samples using the formula  $DF = A_0/A$ , where  $A_0$  is the activity of radionuclide in the neutralized and filtered feed solution and A that in the column effluent.

Table 1. Chemical composition of the simulated reprocessing waste solution

Constituent	Concentration (mol/L)
HNO <sub>3</sub>	1.75
Na <sup>+</sup>	0.036
Fe <sup>2+</sup>	0.0035
Cr <sup>3+</sup>	0.00055
Zr <sup>4+</sup>	0.00020
Al <sup>3+</sup>	0.0015
Ca <sup>2+</sup>	0.00004
Mg <sup>2+</sup>	0.00015
Ni <sup>2+</sup>	0.00030
Sr <sup>2+</sup>	0.000015 <sup>a</sup>
Cs <sup>+</sup>	0.000015 <sup>a</sup>

<sup>a</sup>concentration corresponds about 7.4 GBq/L (0.2  $\mu\text{Ci/L}$ ) of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$

## RESULTS OF LAB SCALE TESTS

The weak-acid nature of SrTreat<sup>®</sup> exchanger was reflected in the column tests carried out at different pH-values (Fig. 1). The column decontamination factors (DF) for Sr-85 increased with pH. When the influent pH was 8, the column DF's were initially above 5000 but dropped to about 100 when 400 bed volumes (BV) had been processed. When pH was increased to 10.0 or 11.5, the DF-level increased and remained high (DF > 1,000-10,000) until the termination of the tests at about 1,000 BV. The activity of <sup>134</sup>Cs in treated solution was below the detection limit at all pH-values. Calculated from the detection limit, the column DF's for <sup>134</sup>Cs were greater than 6,500 in these cases.

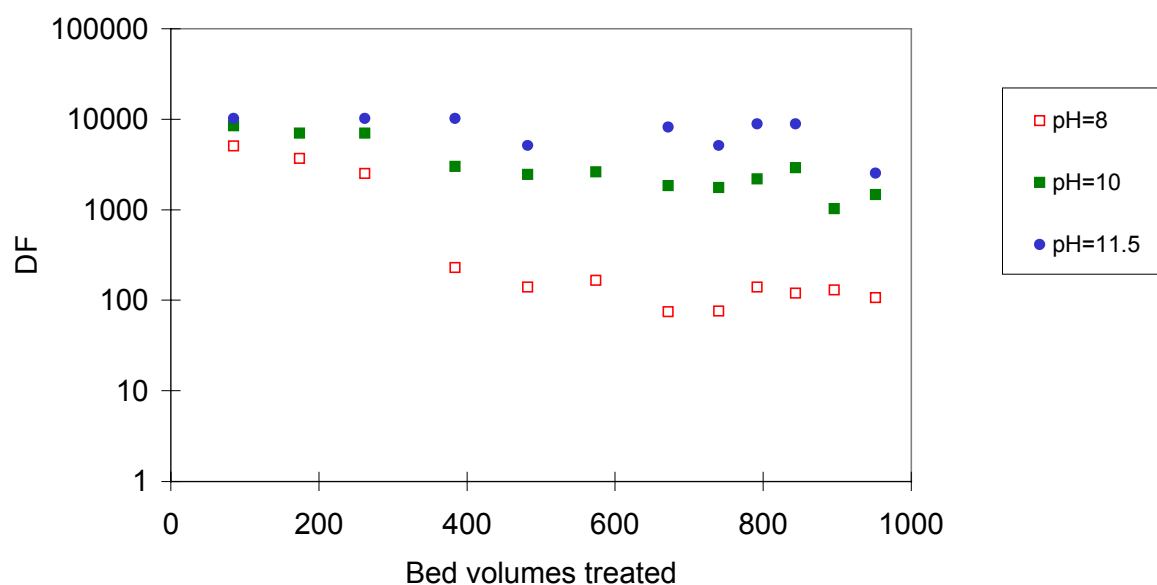


Figure 1. Effect of solution pH on the <sup>85</sup>Sr column decontamination factor (DF)  
Bed volume 0.5 mL.

For further tests, the feed solution pH was adjusted to 10, which value was a compromise in an attempt to minimize the co-precipitation of <sup>85</sup>Sr and to maximize the DF. In addition, the activity concentration of <sup>134</sup>Cs tracer in the solution was increased so that the true column DF's for <sup>134</sup>Cs could be measured. The DF's for both radionuclides were slightly better in intermittent mode than in continuous mode (Figs. 2-3). In intermittent operation, the DF-level for <sup>85</sup>Sr remained high (DF ≈ 10,000) until 1500 BV had been treated (Fig. 2). In continuous operation, the <sup>85</sup>Sr DF had dropped to about 1,000 at 1500 BV. The DF's obtained for <sup>134</sup>Cs were somewhat higher than for <sup>85</sup>Sr and no sign of column exhaustion was observed at the termination of the tests at 1500-1800 bed volumes (Fig. 3).

The higher DF's obtained in intermittent operation indicates that the rate of ion exchange was controlled by diffusion in the particle. When the flow is stopped, the concentration gradients within the particle level off, which facilitates further radionuclide uptake when the flow is

restarted. The column DF= 1000 means that 99.9 % of the radioactivity was taken up while DF = 10,000 means 99.99 % uptake. Considering the radionuclide uptake the effect of operation mode was thus not very significant.

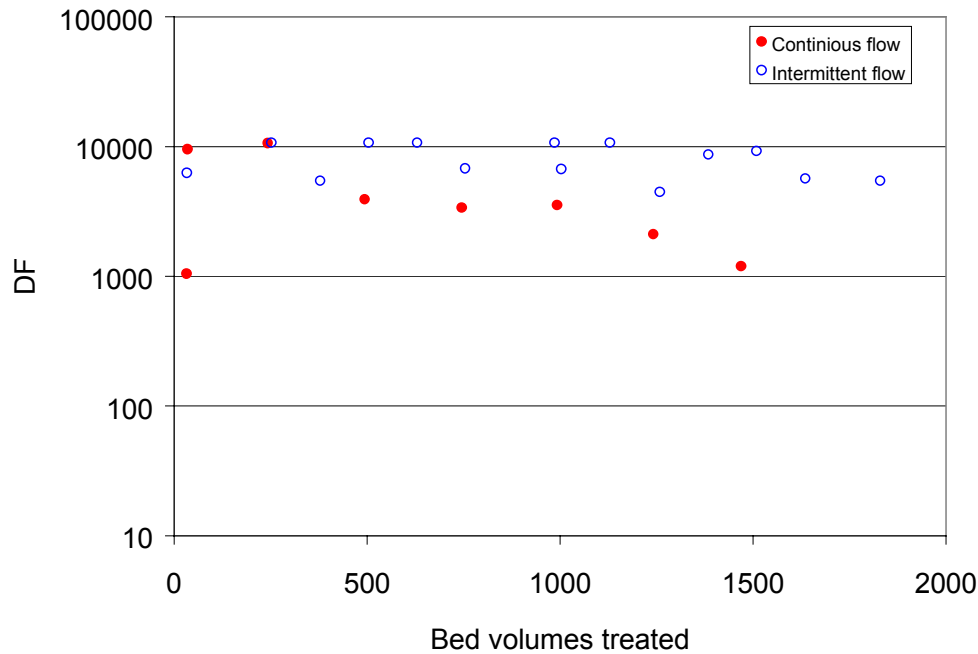


Figure 2. Column decontamination factors for  $^{85}\text{Sr}$  in continuous and intermittent operation. Feed solution pH = 10.0. Bed volume 0.5 mL.

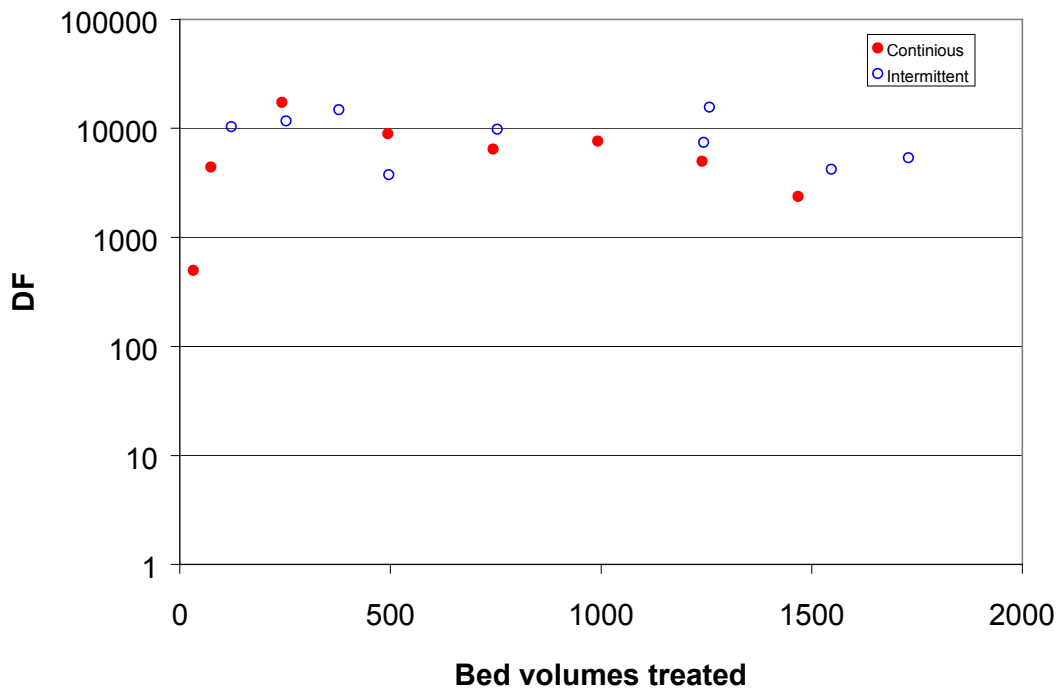


Figure 3. Column decontamination factors for  $^{134}\text{Cs}$  in continuous and intermittent operation. Feed solution pH = 10.0. Bed volume 0.5 mL.

The minimum target DF's set by JAERI were 200 for  $^{90}\text{Sr}$  and 400 for  $^{137}\text{Cs}$ . The design value for the processing capacity was 850 BV, which was mainly determined by radiological shielding constraints. Laboratory scale column tests indicated that the required DF's and processing capacity could be well obtained with CsTreat<sup>®</sup> and SrTreat<sup>®</sup> ion exchange medias.

## **COMPARISON WITH FULL SCALE PERFORMANCE**

In the test operation at JAERI Tokai-Mura site (intermittent operation), the decontamination factors obtained with the full-scale columns (bed size 0.82 L + 0.82 L) have been in general in the same range (DF = 1,000-10,000) as what was observed in lab scale tests<sup>4</sup>. These values were clearly above the minimum design values. However, certain differences could be seen in the lab-scale and full-scale performance data. These include.

- Regarding Cs-removal, the full-scale operation at pH = 9-10 gave clearly higher DF's than at pH = 8-9 or pH = 11-12. This was unexpected from earlier experience and lab-scale results. DF's for  $^{137}\text{Cs}$  in the full-scale operation were similar (DF = 2,000 – 7,000) to the  $^{134}\text{Cs}$  DF's obtained in the lab scale (DF = 3,000 – 20,000).
- Regarding Sr-removal, the effect of pH on column DF was weaker in full-scale operation and was clear only when more than 700 BV were processed. In addition, full-scale operation at pH = 9-10 gave higher DF's than at pH = 11-12, which is in contradiction with the lab-scale results (Fig. 1). DF's for  $^{90}\text{Sr}$  in the full-scale operation at pH= 9-10 were somewhat lower (DF = 200-3,000) than what was obtained in lab-scale operation (DF = 1,000 – 10,000). The corresponding uptakes were 99.97-99.50 % for full-scale operation and 99.99 – 99.9 % for lab scale operation. Considering percent uptake, the results were practically identical.

In the neutralization process, several metal hydroxides (e.g.  $\text{Fe}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ ) were precipitated. The precipitates are likely to adsorb  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  to some degree. If left in solution as suspension, the hydroxide precipitates may carry some  $^{90}\text{Sr}$  and  $^{134}\text{Cs}$  through the ion exchange columns. The full scale system utilized a ceramic 1- $\mu\text{m}$  filter while membrane filters (1.6  $\mu\text{m}$  or a 0.45  $\mu\text{m}$ ) were used in the lab-scale tests. The slightly lower DF-values obtained in the full scale operation may be partly due to the different filtration efficiencies.

## **CONCLUSIONS**

It can be concluded that the performance of the full-scale CsTreat<sup>®</sup> and SrTreat<sup>®</sup> columns for the treatment of the reprocessing waste effluent at JAERI was surprisingly close to that predicted from the lab-scale tests conducted with simulated waste solution. The lab-scale results correctly demonstrated that the design values ( $^{90}\text{Sr}$  DF > 200,  $^{134}\text{Cs}$  DF > 400, processing capacity > 850 bed volumes) could be easily obtained by the using CsTreat<sup>®</sup> and SrTreat<sup>®</sup> columns. The used minicolumn technique thus appears to be an economic and valuable aid in the process design of systems that utilize the new highly selective ion exchange medias.

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