

## **ADDITIONAL TESTING OF CoTREAT INORGANIC ION EXCHANGE MEDIA FOR THE REMOVAL OF <sup>60</sup>Co FROM THORP POND WATER**

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### **ABSTRACT**

CoTreat, a new inorganic ion exchange media, has been studied in the laboratory to support its application trials as a pre-coat to existing Funda filters in THORP feed pond plant (Sellafield, UK).

The performance of separate CoTreat and Celatom layers at different configurations (Celatom on bottom/CoTreat on top, CoTreat on bottom/Celatom on top) as well as that of intimately mixed layer of the two materials was evaluated. Results indicated that an intimately mixed layer of Celatom and CoTreat performed better than separate layers with corresponding CoTreat dose, increasing the decontamination factor (DF) for Co-57 by 50-100 %. This can be rationalized by assuming that Celatom acts as a filler that helps to distribute CoTreat more evenly on the filter and decreases the pressure drop and compaction of the CoTreat precoat. Additional tests were carried out to study of the effect of mixing ratios of CoTreat and Celatom on performance with a view to optimise the ratio. Finally, long-term experiments were carried out observe the exhaustion capacity of CoTreat media. This was found to be 513,300 L/kg when the feed level of Co-57 was 200 Bq/L. However, when the feed level increased after first exhaustion to 600 Bq/L, CoTreat material resumed Co-57 uptake and was exhausted finally at this feed level when the throughput reached 1,200,000 L/kg.

### **INTRODUCTION**

CoTreat is a novel all-inorganic ion exchange media selective for <sup>60</sup>Co and other activated corrosion product nuclides such as <sup>54</sup>Mn, <sup>55,59</sup>Fe and <sup>63</sup>Ni. Granular CoTreat material has exhibited efficient removal of these radionuclides from NPP Floor Drain Waters in recent column tests [1,2], being able to achieve decontamination factors (DF) as high as 1000 and processing capacities in excess of 50 m<sup>3</sup>/kg even in high-conductivity waters. Application of CoTreat, and of it's sister medias CsTreat and SrTreat, is usually carried out using granular formulation in a fixed-bed ion exchange column. The problem in the column operation of these medias is that for efficient performance, relatively low flow rates (10-50 bed volumes per hour)

must be used due to the slow kinetics of the crystalline inorganic materials. However, new experience is emerging on a more efficient way of application of these materials as finely divided powders on precoated filters, enabling a 100-fold increase of the flow rates [3,4].

THORP (BNFL, Sellafield) Head End Feed Pond (HEFP) is where spent fuel destined for reprocessing is removed from its storage containers and is fed to the reprocessing plant. A water channel connects the facility to the much larger Thorp Receipt & Storage facility (TR&S) resulting in a common water volume of around 30,000 m<sup>3</sup>. TR&S primarily stores light water reactor fuel (LWR), the basis of design for the facility is on fuel containerisation; i.e. fuel stored in gas sealed containers. This storage technique results in main pond water activity levels being very low (~2-3 Bq/ml) which facilitates direct discharge of the pond water to sea after filtration and sentencing; as a means of maintaining pond water chemistry. Prior to fuel discharge in the HEFP the containers are flushed and the resultant relatively small amount of medium active effluent is treated in the enhanced actinide removal plant (EARP). Any particulates displaced during fuel removal operations are filtered at source by the HEFP Pre Coated Funda Filters or will be removed by the pond floor cleaner.

During the processing of heavily cruded LWR fuel HEFP pond purge discharges have been noted to be subject to considerable fluctuation in cobalt-60 content. A reappraisal of the system has concluded that the soluble cobalt has arisen from leaching of crud deposited on the Funda filter and settled solids within the HEFP by the high quality deionised water used in the storage ponds. As a means of capturing any dissolved cobalt prior to pond water discharge the cobalt selective ion exchanger CoTreat has been investigated at the plant by loading a second ion exchange layer to an existing PreCoated Funda filter [5].

## **SCOPE OF WORK**

Laboratory test program has been conducted to support the application trials of CoTreat at the THORP HEFP plant. The aim of the tests was to optimise the operating conditions (e.g. quantity applied and formulation) of CoTreat for application to a pre-coated 30m<sup>2</sup> Funda filter and to provide a framework for assessing the performance of CoTreat under HEFP operating conditions. The first part of the program was mainly concerned to study various CoTreat formulations and the effect of pond water chemistry on CoTreat performance [5]. As there was some indications that Celatom material used as filtration aid in the Funda filters might have some effect on CoTreat performance, e.g. causing channelling in the CoTreat layer. Further tests, described in this report, have been carried out to assess the combined performance of CoTreat and Celatom and their possible interactions.

In the first phase, the performance of separate CoTreat and Celatom layers at different configurations (Celatom on bottom/CoTreat on top, CoTreat on bottom/Celatom on top) as well as that of intimately mixed layer of the two materials was evaluated. In addition, the uptake characteristics of Celatom alone for <sup>57</sup>Co was measured to estimate the possible bleeding of the radionuclide from the material. As the first phase results indicated that an intimately mixed layer of Celatom and CoTreat performed better than separate layers with corresponding CoTreat dose, second phase of tests comprised a study of the effect of mixing ratios on performance with a view to optimise the ratio. Due to high capacity of CoTreat, it was not possible to measure the

exhaustion capacity of the material for Co-57 routinely. Therefore, at the end of the tests series a long-term “exhaustion” test was carried out with the optimised mixing ratio.

## EXPERIMENTAL

All tests were carried out using a planar Millipore filter unit (Fig. 1) comprising a planar housing for a 142 mm disc filter (filter surface area 120 cm<sup>2</sup>). CoTreat and Celatom powders (dose 20-50 mg/cm<sup>2</sup>) were packed on a filter by using a packing cylinder filled with water. The powder was slurred in the packing cylinder and allowed to settle on top of the filter (Whatman SMWP with 5.0 µm pore size). Water was removed by suction from below after which the packing cylinder was replaced by the upper lid of the filter housing (Fig. 1). Feed liquid was simulated THORP pond water (Na 0.1 ppm, Ca 0.1 ppm, pH = 6.5) recirculated to the filter unit via a 50-L feed vessel (flow rate 18 L/h). Fresh Co-57 was added continuously to the feed vessel with a small peristaltic pump to replenish the Co-57 taken up in the filter and to keep the Co-57 activity level on constant level (200-300 Bq/L). Filter effluent was sampled regularly and analysed for Co-57. The decontamination factor DF for Co-57 was calculated as  $DF = A_0/A$ , where  $A_0$  and  $A$  are the activity concentrations of Co-57 (Bq/L) in the filter influent and effluent, respectively.



Fig. 1 Millipore filter unit that was used in the tests.

In the first phase, tests were conducted using different ordering in the Celatom and CoTreat layers. (Table I). Also a layer of intimately mixed materials and single Celatom layer were tested.

Table I Conditions for Phase 1 Tests. CoTreat Dose 5.85 g (50 mg/cm<sup>2</sup>) Celatom Dose 2.51 g (21 mg/cm<sup>2</sup>) Except in Run 4.

RUN No.	Material on bottom	Material on top
1	Celatom	CoTreat
2	CoTreat	Celatom
3	mixture	mixture
4	Celatom 5.02 g (43 mg/cm <sup>2</sup> )	none

It was found that the intimately mixed layer of CoTreat and Celatom performed significantly better than separate layers. Therefore, in the second phase, the proportions of Celatom and

CoTreat in the mixture were varied (Table 2) in with a view to confirm the improved performance and optimise the mixture formulation. Also a long-term test was carried out to measure the exhaustion capacity of the optimized formulation. The feed solution in the long-term test was traced with Cs-134 in addition to Co-57 in order to check possible concurrent uptake of radiocesium.

Table II Conditions for the Phase 2 Tests

RUN No.	CoTreat dose (g/%)	Celatom dose (g/%)
5	5.85/70	2.51/30
6	4.18/50	4.18/50
7	2.09/25	6.27/75
8	5.85/100	0
9	5.85/70	2.51/30

## RESULTS

### Phase 1- Separate Layers

The order of Celatom/CoTreat layers, i.e. whether one of the materials was on top or on bottom, had no practical effect on DF of  $^{57}\text{Co}$  (Fig. 2) except at very low throughputs (Fig. 2). The DF's were about 35-45 initially and decreased to about 10 when 900 L of solution had been processed. Coupled with the finding that the performance of the double-layers is very similar to that of the single CoTreat layer (Fig. 2) it is possible to conclude that the presence of Celatom layer does not have any detrimental effect on the performance of the CoTreat layer. Thus, the assumption that mixing of Celatom with the CoTreat layer might cause channeling proved invalid. In fact, intentional mixing of the two materials was found to improve the performance significantly (DF = 90 initially, DF = 20 at 900 L, Fig. 2). This can be rationalised by assuming that Celatom acts as a filler that helps to distribute CoTreat more evenly on the filter. Celatom itself had practically zero uptake for Co-57.

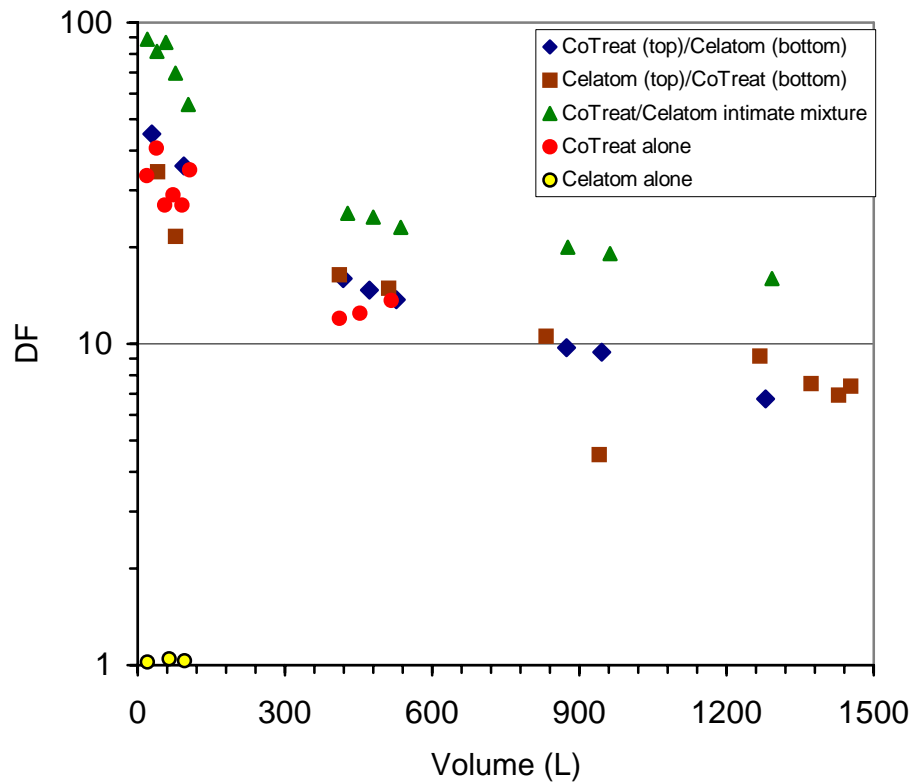


Fig. 2. Decontamination factor of Co-57 versus processed Volume (L) in Phase 1 Tests.

### Phase 2 - Mixed Layers

When the proportion of CoTreat in the mixture was decreased, DF's for Co-57 decreased as expected (Fig. 3). 50/50 mixture (containing 4.18 g CoTreat) performed better than CoTreat alone (5.81 g) initially and until about 800 L of solution was treated. Decreasing the proportion of CoTreat to 25 % caused a large drop in DF. Based on these tests, the 70/30 ratio (5.85 g CoTreat) in the mixture gives the optimal performance that is clearly better than that of corresponding amount of CoTreat alone.

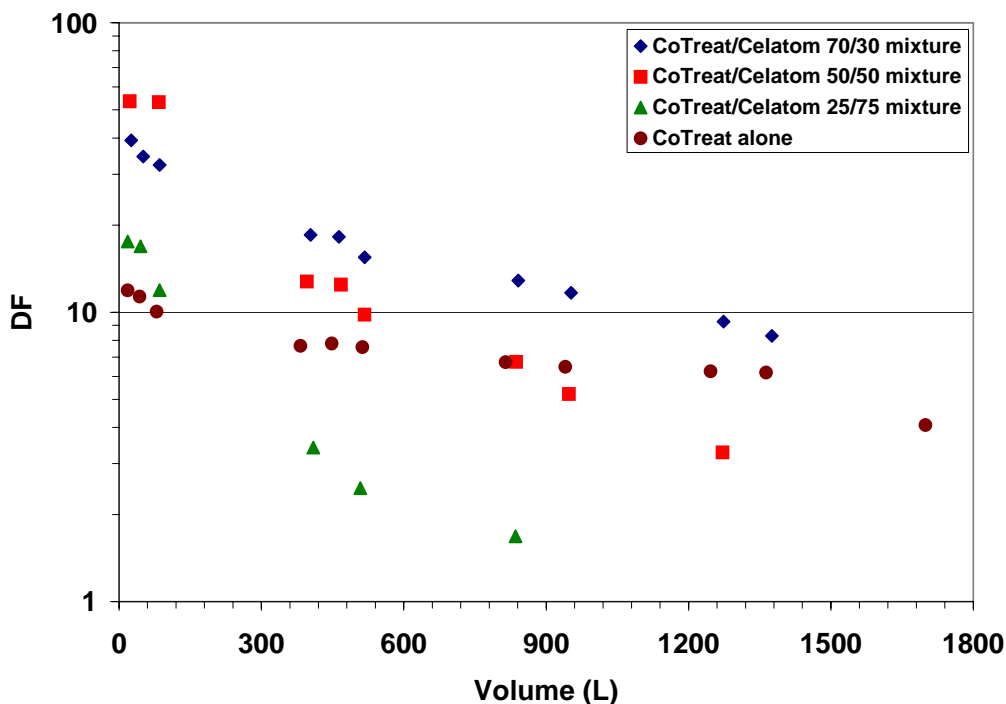


Fig. 3 Decontamination Factor of Co-57 Versus Processed Volume (L) in Phase 2 tests.

### Phase 2 – Long-term Tests

A total of 6880 L of feed solution, corresponding a throughput of about 1,200,000 L/kg, was treated in the long-term test. Full exhaustion for Co-57 was first measured (DF = 1) at 513,300 L/kg (Fig. 4). At this point, however, the level of Co-57 in the feed vessel started to increase due to the addition of Co-57 tracer, and CoTreat began to take up Co-57 again. The tracer feed was then decreased and the feed activity stabilised to a 600 Bq/L level, and at this level, the CoTreat material was very close to exhaustion (DF = 1.09) at 1,117,000 L/kg when the test was interrupted. The initial DF's for Cs-134 were somewhat higher than for Co-57, but the Cs-134 DF decreased with increasing throughput more strongly than for Co-57. Exhaustion for Cs-134 took first place at the same point as for Co-57 (513,300 L/kg). Increase of feed activity of Cs-134 after this point resulted in slight increase of DF, but the phenomenon was less strong than for Co-57.

It should be noted that the measured DF's for Co-57 were clearly lower in Phase 2 tests compared to Phase 1. This is due to different CoTreat batches.

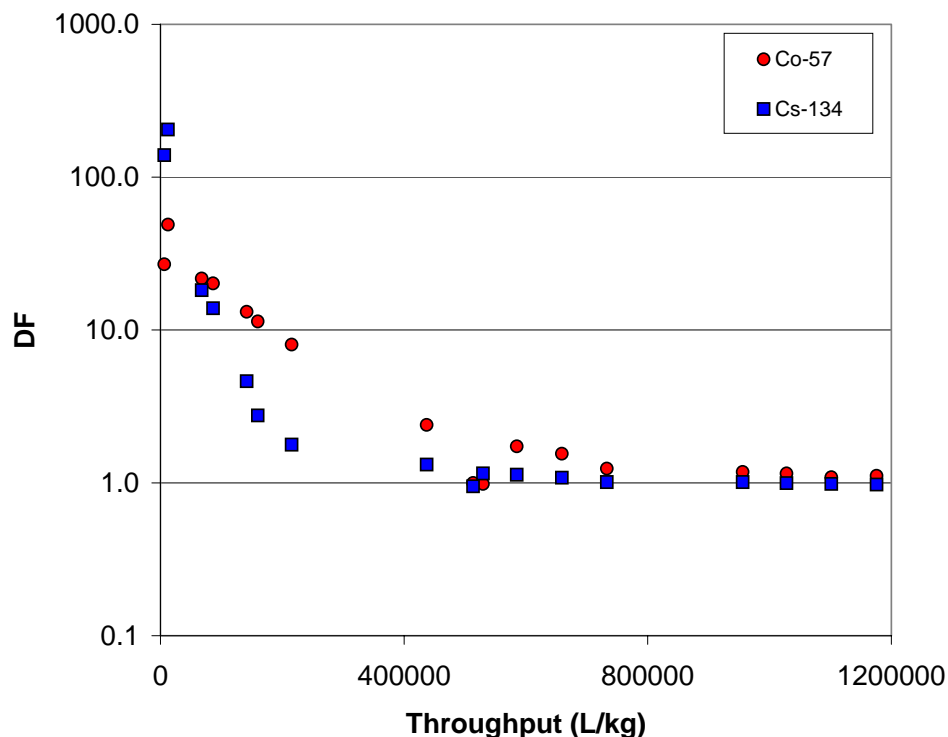


Fig. 4 Results of the Long Term Test.

## CONCLUSIONS

Use of CoTreat as a finely divided precoat instead of granular form in columns appears a new promising technique that overcomes the problem of slow kinetics associated with inorganic ion exchange and makes it possible to use high flow rates similar to organic precoat resin materials.

The major result obtained in this test series is that an intimate mixture of CoTreat and Celatom performs considerably better than CoTreat alone or as a separate layer with Celatom. The optimum mixing ratio (CoTreat/Celatom) is about 70/30 on mass basis. The long-term test indicated that the exhaustion capacity of the mixture is at least 500,000 L/kg, which is the close to what has been observed in the plant trials in Sellafield. However, the DF's measured in the plant trials have been lower than what has been observed in the laboratory tests. Even packing of the CoTreat layer is likely to highly critical for large-scale performance. Using mixtures of CoTreat and Celatom materials, instead of separate layers, may help to facilitate even packing and improve the large-scale performance.

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