TESTING OF CoTREAT INORGANIC ION EXCHANGE MEDIA FOR THE REMOVAL OF $^{Co-60}$ 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 as a pre- coat to existing Funda filters in THORP feed pond plant (Sellafield, UK). This is a novel way of application of CoTreat, which is usually utilized in fixed-bed ion exchange columns in a granular form. The results present the effect of operating conditions (CoTreat dose, pond water chemistry) on CoTreat performance for the removal of Co-57 tracer from simulated pond water. Major findings include the strong dependence of Co-57 decontamination factor (DF) on feed activity. At the 200 Bq/L feed level, the observed DF was 10-20 but rose to 1000 and above when the feed level was increased to 20000 Bq/L. Calcium present in the feed was found to decrease the DF at concentrations higher than 1 ppm. The laboratory studies showed significantly higher DF's than what has been observed in large-scale THORP tests. This discrepancy is likely to be due to the technique used in applying the Co Treat layer to the Thorp HEFP Funda filter. Options for improving Co Treat performance (i.e. application technique) under Funda filter operating conditions are being investigated by BNFL based on this laboratory work.

INTRODUCTION

CoTreat is a novel all-inorganic ion exchange media selective for Co-60 and other activated corrosion product nuclides such as Mn-54, Fe-55,59 and Ni-63.CoTreat has exhibited efficient removal of these radionuclides from NPP Floor Drain Waters in recent tests [1,2], being able to achieve decontamination factors (DF) as high as 1000 and processing capacities in excess of 50 m^3/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, but new experience is emerging on a more efficient way of application as finely divided powders on precoated filters [3].

This paper describes laboratory tests carried out to support the application of CoTreat to existing pre-coated Funda filter operations at BNFL Sellafield (UK) Thorp Head End Feed Pond (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^2 Funda filter and to provide a framework for assessing the performance of CoTreat under HEFP operating conditions. Additionally, knowledge on the effect of varying given chemical parameters of Thorp Pond Water (e.g. concentration of Co-60, Na, Ca) on CoTreat performance was sought.

BACKGROUND

Thorp 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^3. 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 Co Treat has been investigated by loading a second ion exchange layer to an existing Pre Coated Funda filter. An example of the plant data gathered during this exercise is shown (Fig. 1).

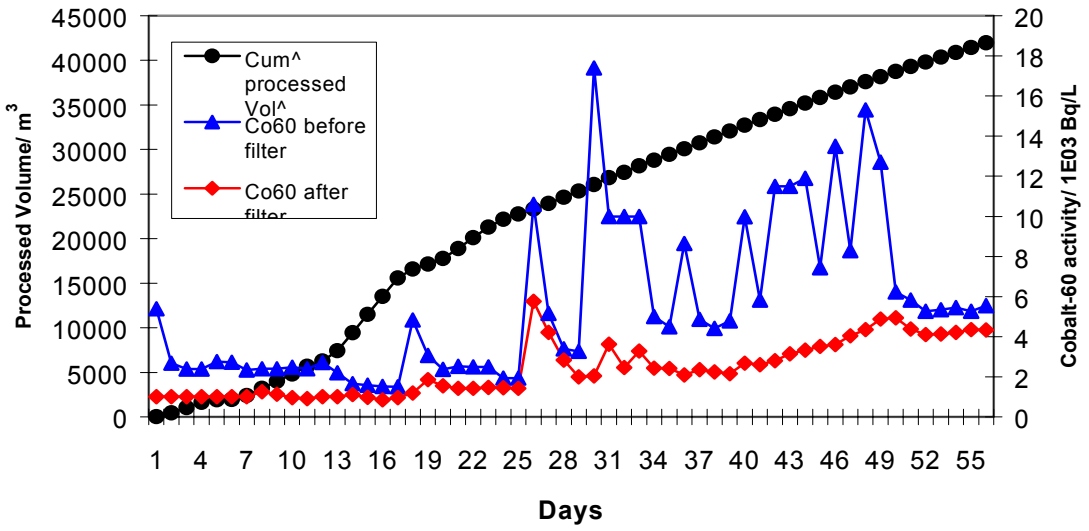

Fig. 1. Thorp Head End Feed Pond Plant data showing cobalt-60 removal performance for a Celatom coated Funda filter with a second coating of Co Treat (21 kg) against cummulative volume of water processed.

The main findings from the plant trial were CoTreat did selectively remove cobalt under HEFP plant conditions, but at much reduced DFs (1.3-8.5) compared with reported data [1-3]. The main difference between these results and those perviously reported is the volume of water being treated (average flow rate through the filter was 763 m^3/day with peak through puts of 2000 m^3/day) and the application technique; i.e. to an existing engineered Funda filter system without any modification.

In addition to the above findings it was also observed during the trial that Co Treat's capacity for caesium ions became exhausted which raised an issue of whether radionuclides could be leached from the material either on filter or during filter slurry transfer operations on plant.

To rationalise the plant findings and to investigate alternative formats of Co Treat for Funda filter application under Thorp HEFP operating conditions a development programme was placed through Fortum Engineering with Helsinki University.

EXPERIMENTAL

In the first stage of the tests, alternative CoTreat formulations to the standard powder (10-150 μm) were tested to find an optimal formulation for minimising differential pressure (DP) build-up across the Thorp Funda filter when applying the additional CoTreat coating. Alternative formulations under study included CoTreat powder that has been depleted of finer (10 - 50 μm range) particles ("coarse CoTreat") and regular powder that has been treated with milled glass microfibres ("MGM CoTreat"). In the first stage, these new formulations were tested for improved filterability (pressure drop dP) and Co-60 uptake (decontamination factor DF). The tests were carried out using a planar Millipore filter unit comprising a cylindrical housing (h= 140 mm) for a 142 mm disc filter (filter surface area 120 cm^2). Feed liquid was simulated pond water recirculated to the filter unit via a 50-L feed vessel (flow rate 6-66 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 (200-400 Bq/L).

In the second stage, "Coarse CoTreat", which was found to have the best overall performance of the different formulations, was used as the basis for further investigations. These investigations evaluated the response of "Coarse CoTreat" to changes in operating conditions; i.e. adsorbent dose, and concentrations of Ca, Na and Co in the feed (as given in Table 1). The experimental procedure used was the same as in the first stage, except the level of Co-57 tracer in the feed liquor was elevated for short periods of time. In addition, leaching tests for radiocobalt and radiocaesium were carried-out (Table 1, Test No 2) by adding Cs-134 at the same levels as Co-57.

After the CoTreat on the Millipore filter had been loaded with the double-traced simulant and the uptake data had been recorded, the filter was leached with deionised water at 18 L/h for 44 h to demonstrate a "worst case" scenario. The leaching was carried-out by circulating the water via the 50-L feed vessel and samples were taken from the feed vessel for the analysis of Co-57 and Cs-134.

Table 1. Operating conditions for hot tests of coarse CoTreat

TEST No.	Dose (mg/cm^2)	Ca (ppm)	Na (ppm)	Co-57 feed level (Bq/L)
1	25	0.1	0.1	200, increased to 2000 and 20000 periodically
2*	50	0.1	0.1	
3	75	0.1	0.1	
4	50	0.1	1	
5	50	0.1	10	
6	50	0	0.1	
7	50	1	0.1	

*feed liquid traced with $^{Cs-134}$ in addition to $^{Co-57}$

RESULTS AND DISCUSSION

Tests of different CoTreat formulations

CoTreat powder produced the lowest DF-values (24-10), which was rather unexpected considering that the smallest grain fractions have the highest uptake rate for Co-57. The MGM material produced DF's that were similar to those obtained with coarse CoTreat, except at the end of the test when it showed clearly lower performance (DF= 11-13) than coarse CoTreat (DF = 22-25). The relationship between DF and dP was investigated in more detail by plotting the DF's as a function of dP corresponding to the $^{Co-57}$ sampling times (Fig. 2). Plotting reveals an inverse linear correlation of DF with dP. This suggests that increasing dP causes compression of the CoTreat layer on the filter, which may result in channelling of flow through the material. This is obviously the explanation for the better performance of coarse CoTreat in comparison with the finely powdered formulation.

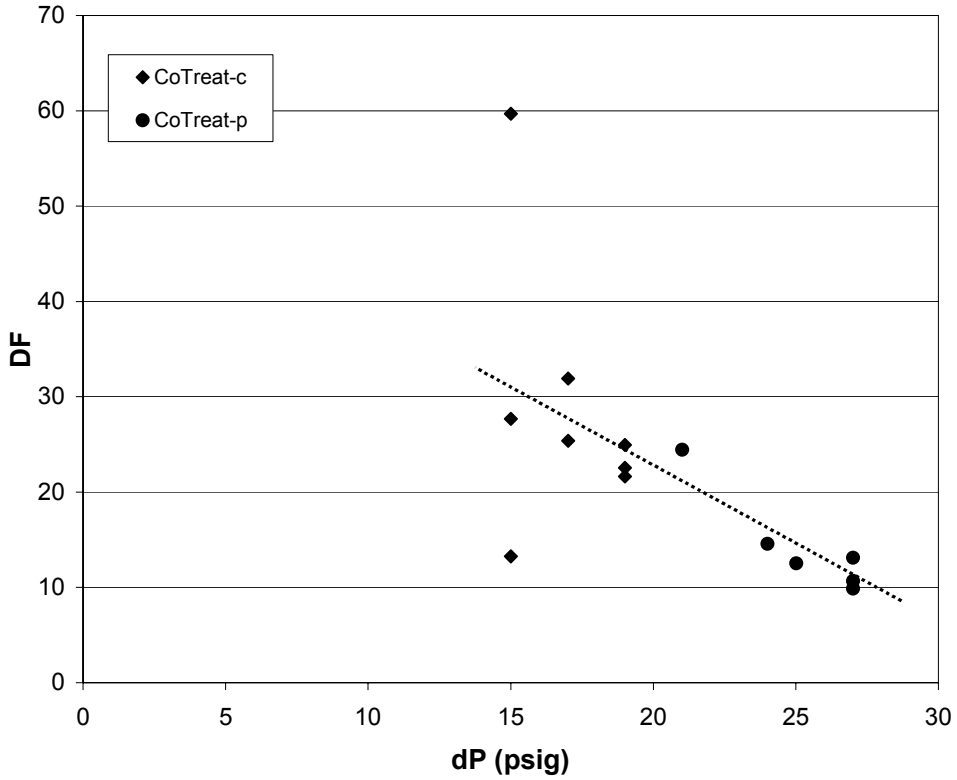

Fig. 2. Decontamination factor (DF) as a function of pressure drop (dP) across the pure CoTreat formulations in the hot tests (CoTreat-MGM omitted).

Tests with Different Operating Conditions

Effect of CoTreat dose: When Co-57 in the feed was at the 200 Bq/ level, the DF's obtained with the two lowest doses (25 and 50 mg/cm^2) were similar, between 30-50 initially and decreasing to about 10 at high feed volumes (Fig. 3). The highest dose of 75 mg/cm^2 produced clearly higher DF's (100 initially and about 20 at higher volumes). When the feed activity was increased to 2000

Bq/L and 20000 Bq/L, DF's increased to 7000 at maximum. Thus when the efficiency is considered in absolute terms, i.e. DF for a given volume of liquid, increasing the dose above the 50 mg/cm^2 level increases the efficiency.

Effect of Ca concentration: The concentration of Ca in the feed had a decreasing effect to Co-57 DF (Fig. 4). The effect was not very strong initially but was rather significant at higher throughputs (> 70000 L/kg) at 1 ppm Ca level as the DF for Co-57 fell to about 2. The decreasing effect of Ca on Co uptake could be expected, as Ca competes strongly with Co exchange due to their similar hydrated ionic radii (2.95 Å for Co^{2+} and 2.71 Å for Ca^{2+}).

Effect of Na: There appeared to be no clear trends between the Na concentration in the feed and Co-57 DF that would support the hypothesis that low background salt content might be a reason for the low Co-57 DF's

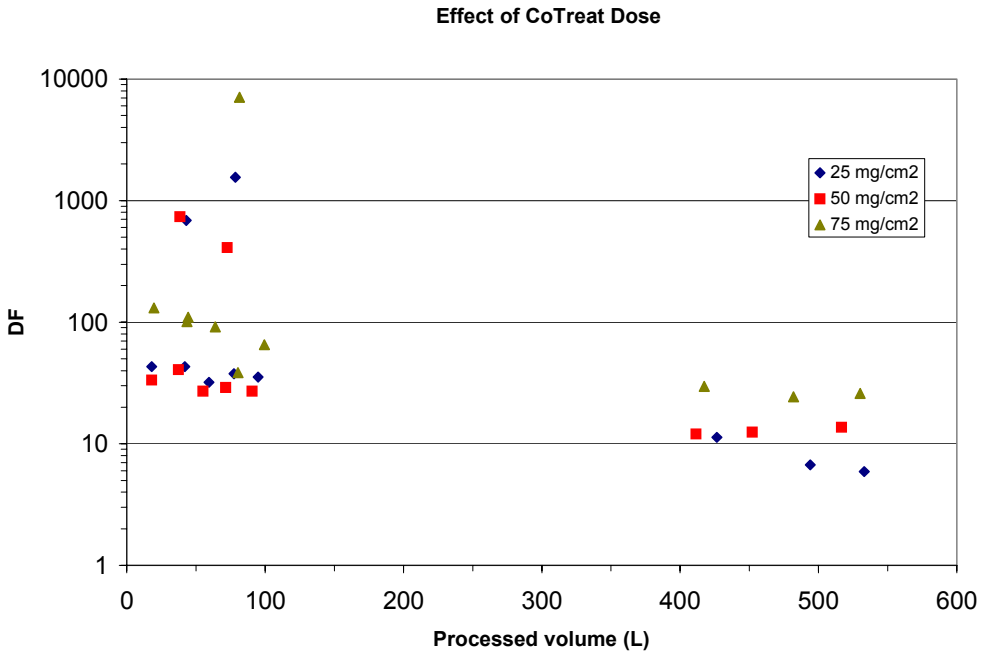

Fig. 3. Effect of CoTreat dose on Co-57 DF (plotted versus water volume processed) in simulated THORP Pond Feed (Ca=0.1 ppm, Na = 0.1 ppm). Baseline Co-57 activity in feed about 200 Bq/L. Feed activity increased to 2000 Bq/L and 20000 Bq/L for 1 hour at about 50 L and 100 L feed volumes, respectively.

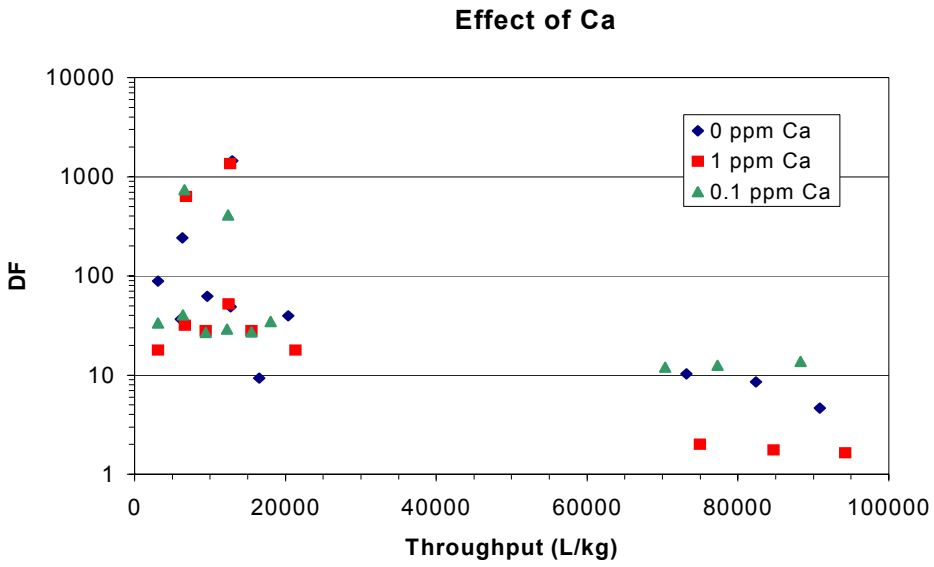

Figure 4. Effect of Ca concentration on Co-57 DF (plotted versus water volume processed) in simulated THORP Pond Feed (Na = 0.1 ppm, CoTreat dose 50 mg/cm^2). Baseline Co-57 activity in feed about 200 Bq/L. Feed activity increased to 2000 Bq/L and 20000 Bq/L for 1 hour at hour at various throughputs below 15,000 L/kg resulting increase in DF.

Effect of Co-57 feed activity: As it has been observed in earlier lab tests, Co-57 DF's increase with increasing feed activity. Obviously, other factors such as CoTreat dose and Ca level has effect on the DF-level, too. When the feed activity was in the 200 Bq/L level, the DF's were in the range of 20-100 depending on the Ca concentration (Fig. 5). When Co-57 in the feed was increased to 10-fold to 2000 Bq/L, there was almost a 10-fold increase in DF's (300-800). At 20,000 Bq/L feed level the DF's increased well above 1000. However, the DF's are considerably lower than what has been observed in large-scale tests in THORP, where DF's in the order of 10 have been measured at 10,000 Bq/L feed levels.

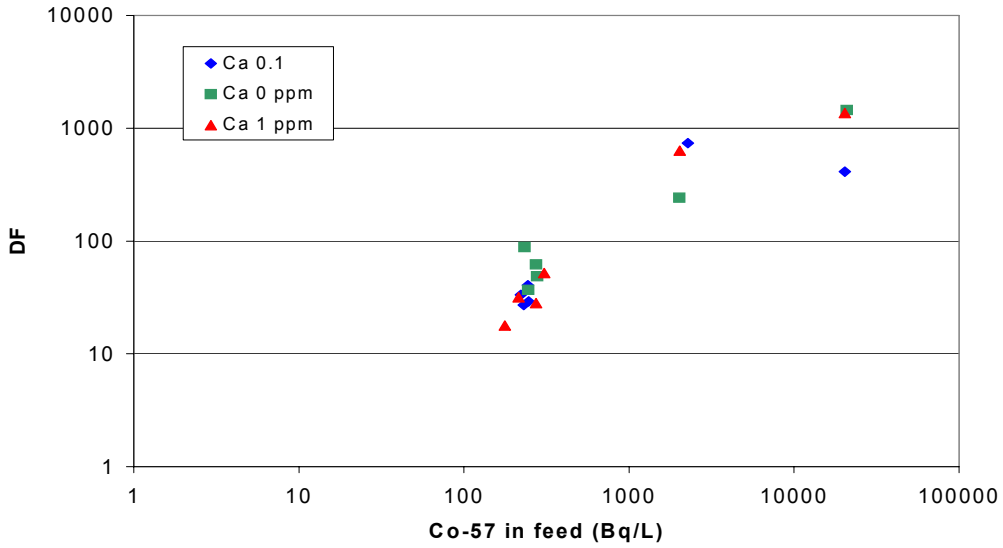

Fig. 5. Effect of Co-57 feed activity on DF in simulated THORP Pond Feed (Na = 0.1 ppm, CoTreat dose 50 mg/cm^2) at different Ca feed levels.

Leaching tests

Approximately 150 kBq of Co-57 and 108 kBq of Cs-134 were loaded on CoTreat during Run 2. After loading, CoTreat on the Millipore filter was leached by circulating deionised water (40 L) and taking samples from filter effluent. The leached activity of Co-57 in the effluent was low (1.2-2.5 Bq/L) and increased slightly towards the end of the test, when a total volume of about 800 L of water had been used. Leached Cs-134 activities were considerably higher, rising from the level of 10 Bq/L to about 50 Bq/L during the test. The total activity of C0-57 leached was only 94 Bq and that of Cs-134 1722 Bq, corresponding about 0.06 % of Co-57 and 1.6 % of Cs-134 loaded initially.

CONCLUSIONS

Test data showed that the decontamination factor of CoTreat powder could be increased using new formulations that produce a lower pressure drop across the coated filter. These new formulations can be prepared by removing the finer dust fractions from the standard CoTreat powder (coarse CoTreat) or by adding milled glass microfibre to the standard powder as a filtration aid (CoTreat-MGM).

Further tests carried out for coarse CoTreat showed that:

- DF can be increased when CoTreat dose is increased above a threshold of 50 mg/cm^2
- Ca has clear decreasing effect on Co-57 DF, but the effect comes significant at levels (1 ppm) that are higher than presently encountered in Thorp Ponds
- Na in the feed is insignificant regarding the Co-57 DF
- Leaching of Co-57 from CoTreat in filter is insignificant, but up to 1.6 % of Cs-134 is leached with extensive use of deionised water

The DF's obtained in the laboratory tests were found to be considerably higher than those measured in Thorp HEFP tests. Data gathered through the laboratory trials indicate that this discrepancy is likely to be due to the technique used in applying the CoTreat layer to the Thorp HEFP Funda filter. Options for improving Co Treat performance (i.e. application technique) under Funda filter operating conditions are being investigated by BNFL. In addition a second phase of work has been placed with the university to evaluate the impact of mixing between the filter coatings.

REFERENCES

1. R. HARJULA, J. LEHTO, L. BRODKIN, E. TUSA, J. RAUTAKALLIO AND P. AUGUSTYN, CoTreat – A New Selective Ion Exchange Media For Radioactive Cobalt And Other Corrosion Product Nuclides, Proceedings of EPRI International Low Level Waste Conference, Orlando, FL, July 15-17, 1998.
2. R. HARJULA, J. LEHTO, A. PAAJANEN AND L. BRODKIN AND E. TUSA, Testing of highly selective CoTreat ion exchange media for the removal of radiocobalt and other activated corrosion product nuclides from NPP waste waters, Proceedings of Waste Management '99, Tucson, AZ, February 28-March 4, 1999.
3. R. HARJULA, A.PAAJANEN, J. LEHTO, P. YARNELL AND E. TUSA, Pilot scale testing of inorganic ion exchangers for precoat applications, Proceedings of Waste Management 2000, Tucson, AZ, February 27-March 2, 2000.