

Pilot Plant Test of Removal of Co-60 and Cs-137 from the Evaporator Concentrates of Forsmark unit 3 – 17158

Jussi-Matti Mäki *, Leena Malinen **, Hans Daniels ***

* Fortum Power and Heat Oy

** University of Helsinki

*** Forsmark Kraftgrupp AB

ABSTRACT

A pilot plant test has been conducted to treat evaporator concentrates at Forsmark BWR NPP unit 3 in Sweden using Fortum's selective ion exchanger technology. The concentrate contains an array of radionuclides of which C-60 and Cs-137 are radiologically the most important ones. Concentrate also contained a high salt content ~ 20 g/l and high organic carbon loading ~ 1 g/l. The pilot system consisted of pre-treatment (mechanical filters, activated carbon, UV oxidation) and Cs and Co selective ion exchangers. CsTreat ion exchanger was very effective in removing Cs from the evaporator concentrate: ^{137}Cs activity was lowered from the initial value 280 MBq/m³ to below detection limit 550 Bq/m³. Removing Co was more complicated: results suggest that Co is bound to organic chelating compounds, thus fairly compete oxidation of organic carbon was required in order to achieve good ion exchange results. Finally, after total organic carbon (TOC) was treated to below 50 ppm, ^{60}Co activity was lowered from the initial value of 57 MBq/m³ to 2.7 kBq/m³.

INTRODUCTION

Minimizing waste volume is an important factor when dealing with radioactive waste. Evaporation is a typical volume minimization method. One way to further minimize the volume of an evaporator concentrate is to use ion exchangers that have high selectivity towards target nuclides and release the concentrate after the treatment. Treating concentrates is a challenging task as they can contain very high concentration of radionuclides, inactive salt ions, organic carbon, and in the case of PWR, borates. ^{60}Co and ^{137}Cs are typically two of the most problematical nuclides in nuclear power plant's waste waters. ^{60}Co is a corrosion product which contributes a major part of dose to plant's personal especially if plant's water and material chemistry is unfavorable. Co, like other transition metals, has a high affinity for organic chelating agents used in the decontamination solutions, making its removal a difficult task. ^{137}Cs on the other hand is a fission product with a high fission yield. It is volatile and is easily released from the fuel in the case of fuel leaks. It is soluble and very difficult to remove using traditional cation ion exchange resins.

In this paper we report results of a pilot plant test of removing radionuclides, especially Cesium and Cobalt, from evaporator concentrates at Forsmark NPP unit 3. The pilot treatment system consisted of pre-treatment (mechanical filters, activated carbon), a commercial UV-based oxidation reactor (Wallenius AOT 5) to destroy chelating agents that bind ^{60}Co , and Fortum's Co and Cs selective ion exchangers CoTreat® and CsTreat® in 300 ml columns. The UV oxidation reactor contained a

fixed TiO₂ catalyst on the reactor wall and a low-pressure Hg vapor lamp. A lab scale test was conducted in Finland at the University of Helsinki before the actual pilot test.

Goal of this pilot project was to test the feasibility of using selective ion exchangers in treating some of the more problematical evaporator concentrates at Forsmark. Possible options include releasing the treated concentrates to the Baltic sea if activity is below the very tight release limits. Other option is the removal of the major dose contributors (¹³⁷Cs, ⁶⁰Co) from the liquid so that after further conditioning it could be disposed of in one of the lower category storage spaces at SKB's SFR repository.

DESCRIPTION

Methods

Pilot plant treatment system consisting of pre-treatment, UV oxidation and ion exchange was built in-house by Fortum. A 500-liter stainless steel vessel was used as a feed tank. The feed tank contained a mixer, pH measurement and a chemical dosing system. Peristaltic pumps were used for transferring the liquid from the feed tank for the treatment process. The pre-treatment consisted of a 10 and 1 µm cartridge filters (by Pall Corporation), and 2 liter activated carbon column (Sigma Aldrich). An commercial 42 W UV oxidation reactor (Wallenius AOT 5) was added to the system after initial tests resulted in poor Co abatement. Other components of the UV oxidation system included two 70-liter treatment vessel, and a circulating pump. Wallenius AOT 5 contains a low-pressure Hg vapor lamp with total power of 42 W. The reactor walls contained a fixed TiO₂ catalyst. As the distance between the UV lamp quartz sleeve and the catalyst on the reactor wall was some millimeters, good UV transparency is necessary for efficient oxidation. AOT 5 contains a built-in UV flux measurement that indicates a too low a photon flux. Reason for a too low a flux can be, e.g., aging of the UV lamp, turbidity of the liquid, or stained UV lamp quartz sleeve. UV system was built to be able to run autonomously without operator interruption for several days. UV oxidation was conducted in 60 l batches.

Ion exchanger system included two 300 ml CoTreat® columns (granular material, 0.3-0.85 mm) in series followed by two CsTreat® columns (granular material, 0.25-0.85 m). The system contained sample points after each filter or treatment step. Gamma activity was measured using HPGe-detector and Apex-Gamma software (Canberra Industries). TOC was measured using TOC-analyzer (Shimadzu TOC-VWP) and metal cations were measured using ICP-OES (Thermo iCAP 6500Duo).

The evaporator concentrate used in the pilot plant test at Forsmark contained 15 g/l Na, 2.3g/l K, 5.0 ppm Mg, 16 ppm Ca, and 4.0 ppm Fe. TOC was 1300 ppm before the treatment. ⁶⁰Co, ¹³⁴Cs, ¹³⁷Cs, and ¹²⁵Sb were the detected radionuclides. Activity of other radionuclides were below the detection limit (in the kBq/m³ range). The liquid was dark brown due to strong absorption in the blue end of the visible spectrum caused by the high organic carbon load (1300 ppm). Exact origin of the organic carbon load is not known; however, it can be assumed that it includes at least greases and oxalic acid.

Roughly 100 liters of evaporator concentrate was taken to the feed tank for the treatment. Initial pH of the evaporator concentrate was 9.2 and TOC content 1300 ppm. The liquid was dark brown and very turbid, an indication of a high organic content. pH was lowered to 3.5 with nitric acid in order to achieve best possible TOC reduction in UV oxidation. In neutral and alkaline conditions sorption of Co^{2+} ions on the catalyst surface is possible, lowering the efficiency of the treatment [2]. Lowering of pH resulted in precipitation of mainly organic origin. The precipitate was filtered out using the 10 μm and 1 μm cartridge filters. The liquid was considerably less turbid after the filtration. After this the concentrate was filtered with an activated carbon to further improve the UV transparency. Flow rate of the circulating pump was high in order to achieve oxygen saturation of the liquid which is beneficial for the treatment. TOC was measured during the oxidation. After sufficiently low TOC value was achieved, ion exchange treatment was started. Modes flow rate of 1.5 l/h, corresponding to 5 bed volumes/h, was used in the ion exchange treatment. Radiochemical samples were taken after each of the four ion exchange columns.

The lab tests conducted at University of Helsinki before the pilot plant tests included oxidation conducted using a 100 ml immersion-well deep UV reactor and TiO_2 based Degussa P25 catalyst and subsequent batch ion exchange tests. Additionally 100 kDa and 5 kDa ultrafiltration was tested. Ultrafiltration did not remove any activity, thus most of ^{60}Co was in soluble form. Oxidation and subsequent ion exchange were effective in removing ^{60}Co when treatment pH was low. The results and methods of the lab tests have been reported earlier[1].

Results

Initial pilot plant test were conducted without UV oxidation. The test resulted in good Cs abatement efficiency but only very minor Co abatement. As ^{60}Co activity correlated strongly with TOC, it was decided to conduct lab oxidation tests and to add pilot scale UV reactor to the system. All the results reported in this paper are for the later tests which utilized the UV reactor.

In addition to the results published earlier, TOC measurement was conducted at Forsmark for the concentrate samples treated with UV oxidation in Helsinki. There was strong correlation between TOC and ^{60}Co activity after ion exchange as can be seen in Figure 1.

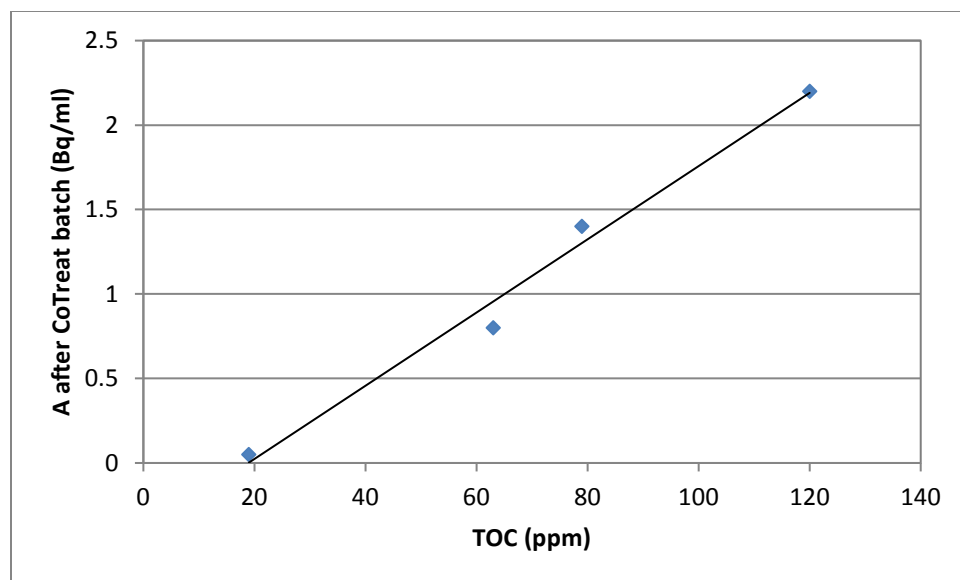


Figure 1. TOC vs. Co-60 activity after a lab batch ion exchanger treatment.

Correlation between TOC and ^{60}Co activity was also evident in the pre-treatment as can be seen in Table 1. When the precipitate originating from pH adjustment was filtered out with the cartridge filter, TOC was lowered from 1300 ppm to 900 ppm and further to 500 ppm after activated carbon filtration. Correspondingly ^{60}Co activity was lowered from 70 MBq/m³ to 50 MBq/m³ and finally to 30 MBq/m³ after the activated carbon filtration.

Table 1. Activity and TOC values of the evaporator concentrate during the different pre-treatment stages.

	^{60}Co (Bq/m ³)	^{134}Cs (Bq/m ³)	^{137}Cs (Bq/m ³)	^{125}Sb (Bq/m ³)	TOC (ppm)
Before treatment	6.8E+07	1.5E+07	3.0E+08		1300
Activity after mechanical filtration	5.0E+07	1.2E+07	2.6E+08	2.6E+06	970
After activated carbon filtration	2.9E+07	8.1E+06	1.8E+08	1.0E+06	520
After UV oxidation					50

Untreated concentrate had very little transmittance in the UV wavelengths. The concentrate was considerably less turbid once activated carbon filtration was conducted. Even then the UV flux measurement indicated that the flux was too low, i.e. the liquid absorbed UV photons before they reached the TiO₂ catalyst on the reactor wall. Oxidation rate, as indicated by TOC, was slow at first due to aforementioned absorption of UV photons. Thus, it was decided to add hydrogen peroxide (H₂O₂) to speed up the process. H₂O₂ is distributed homogeneously in the liquid and thus oxidation is less influenced by the UV transmittance. Hydrogen peroxide and TiO₂ both produce hydroxyl radicals, •OH, when illuminated with deep

UV light (UV/catalyst systems form hydroxyl radicals via the optical excitation of electron/hole pairs). •OH production by UV light is especially effective at low pH.

H₂O₂ addition speeded up the oxidation process considerably. Progress of the TOC reduction as a function of UV time is shown in Figure 2. Three large H₂O₂ doses were added to the reactor and this speeded up the process considerably. Continuous dosing would have been even more effective as excess H₂O₂ react with hydroxyl radicals to form water and oxygen [3]. After TOC reached 100 ppm, the liquid was much more clear, showing only a slight brown color. Photon flux at the catalyst had improved at that point so that no more H₂O₂ was required.

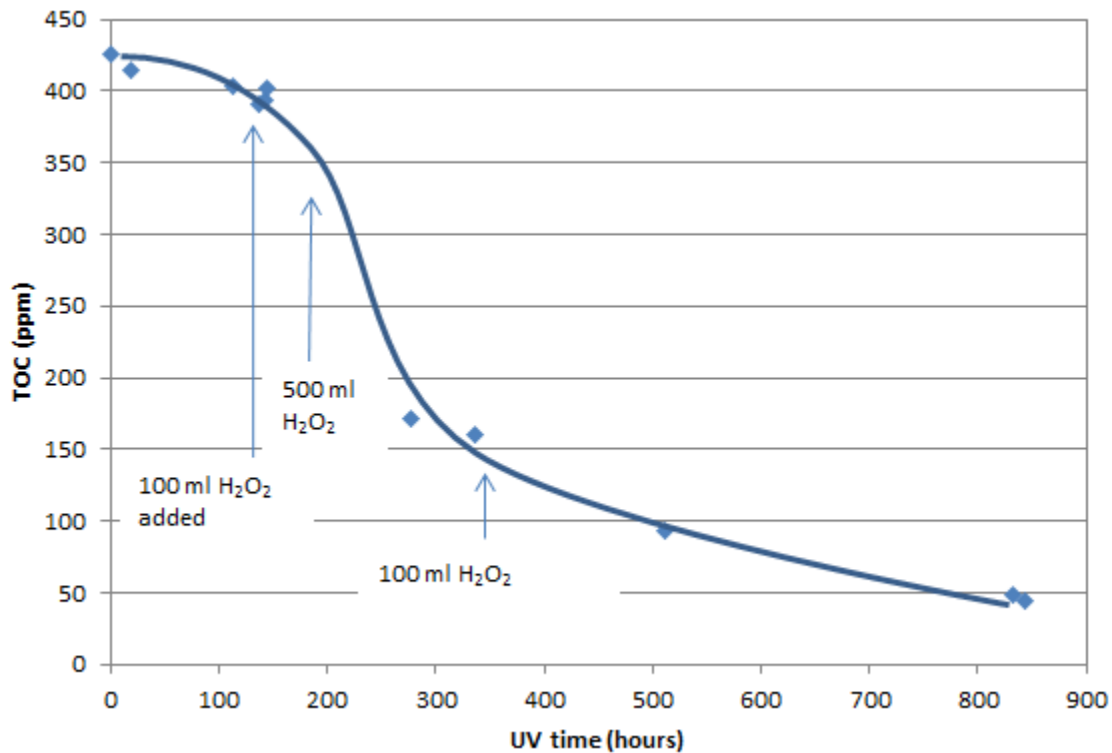


Figure 2. TOC reduction as a function of UV time. Solid line is to guide the eye. TOC reduction was very slow before hydrogen peroxide dosing.

Ion exchange treatment was started once 50 ppm TOC was reached after 800 hours of UV operation. Very good results were achieved: ¹³⁷Cs activity was below the detection limit of 5E+02 Bq/m³ (decontamination factor DF more than 3.0E+05) and ⁶⁰Co activity was 2.7 E+03 Bq/m³ (DF 1.0E+04). Ion exchanger was running during dayshift only, thus roughly 10 litres of liquid was treated per day. Complete daily results after treating roughly 20 liters of liquid (corresponding 70 ion exchange column volumes) are shown in Table 2. The ion exchangers did not show signs of exhaustion during the treatment and there was activity only in the lead IX columns. The used Cs and Co selective ion exchangers were not effective in removing ¹²⁵Sb.

Table 2. Activity values of the evaporator concentrate during the treatment.

	⁶⁰ Co (Bq/m ³)	¹³⁴ Cs (Bq/m ³)	¹³⁷ Cs (Bq/m ³)	¹²⁵ Sb (Bq/m ³)
Before IX treatment (after oxidation)	2.9E+07	8.1E+06	1.8E+08	1.0E+06
Day 1	3.6E+03	MDA 6.0E+02	MDA 5.4E+02	5.0E+05
Day 2	3.1E+03	MDA 5.0E+02	MDA 4.5E+02	5.1E+05
Day 3	2.7E+03	MDA 5.5E+02	MDA 6.0E+02	5.6E+05

DISCUSSION

Treatment of evaporator concentrates is a difficult task due to the high salt concentration and also due to presence of organic compounds. High salt content means that the ion exchangers have to be selective towards the target nuclides, otherwise the capacity would be consumed very quickly. Presence of chelating agents means that transition metals, such as Co, are not in ionic form and that pre-treatment is required. If only moderate Co abatement is required, activated carbon filtration for example could be sufficient. If good Co abatement is the goal, oxidation by UV or by some other means is necessary.

In this pilot Cs was always in soluble form and removing it with CsTreat® ion exchanger was a simple task. Fairly straightforward full-scale treatment setup would be sufficient to remove Cs from aqueous evaporator concentrates. Removing Co requires a setup where oxidation of chelating agents is possible. UV oxidation was effective, albeit slow, after H₂O₂ was added. Higher power UV source is necessary for practical applications. The oxidation process would have been more effective if oxidation conditions would have been optimized. Continuous H₂O₂ dosing would have been more effective instead of three larger doses, as too high H₂O₂ can lead to a self-recombination of •OH radicals. pH has also a major influence on the oxidation efficiency, as pH has influence on the free radical stability and also affects the concentration of free radical scavengers. Fixed TiO₂ catalyst like the one used in the pilot's reactor is problematical because typical evaporator concentrates will absorb photon in the UV wavelength. Plain UV without catalyst does not seem to be effective enough based on this pilot. There are also other options for the oxidation, such as, ozonation, Fenton's reagent, or photo-Fenton.

CONCLUSIONS

Pilot plant evaporator system was constructed and tested with the aim of treating Forsmark NPP unit 3's evaporator concentrate. Removing major dose contributors (^{60}Co , ^{137}Cs) would simplify the further conditioning of the concentrate or possibly enable the release of the effluent to the sea.

Cs removal was very effective using CsTreat® ion exchanger with only minor pre-treatment. ^{137}Cs activity was lowered from the initial value 280 MBq/m³ to below detection limit of 550 Bq/m³. ^{60}Co was bound to organic chelating compounds and its removal was more complicated. ^{60}Co activity was lowered from the initial value of 57 MBq/m³ to 2.7 kBq/m³ using CoTreat® ion exchanger after nearly complete oxidation of organic carbon.

REFERENCES

1. L. MALINEN, J.-M. MÄKI, "Removal of trace amounts of Co-60 from NPP waste water using UV-C irradiation, TiO₂ and CoTreat inorganic ion exchange media", *Proc. of the WM'16 Conference*, Phoenix, AZ, March 6-10, 2016.
2. L. MALINEN, J.-M. MÄKI, "Removal of trace amounts of Co-60 from nuclear power plant liquid waste", poster presentation, Ninth International Conference on Nuclear and Radiochemistry, Helsinki, Finland, August 29-September 2, 2016.
3. R. VENKATADRI, R. PETERS, "Chemical Oxidation Technologies: Ultraviolet Light/Hydrogen Peroxide, Fenton's Reagent, and Titanium Dioxide-Assisted Photocatalysis", *Haz. Waste & Haz. Mat.*, 10, 107 (1993).