

Removal of Trace Amounts of Co-60 from NPP Waste Water Using UV-C Irradiation, TiO₂ and CoTreat Inorganic Ion Exchange Media - 16025

Leena Malinen*, Jussi-Matti Mäki**

*University of Helsinki, Finland, leena.k.malinen@helsinki.fi

**Fortum Power and Heat Oy, jussi-matti.maki@fortum.com

ABSTRACT

The removal of Co-60 from an aqueous nuclear liquid waste obtained from a BWR NPP was tested using a two-step process. In the first phase the liquid waste was oxidized with ultraviolet irradiation at 254 nm (UV-C irradiation) together with a photocatalyst, TiO₂ P25 AEROXIDE, to degrade the organic complexing agents present in the solution. During some of the experiments it was noticed that TiO₂ P25 AEROXIDE also removed Co-60 from the solution. In the second phase the UV-C irradiated solution was mixed with inorganic ion exchange media, CoTreat, to remove the rest of Co-60 from the solution. The effect of pH and contact time with UV-C irradiation were evaluated and both had a noticeable effect on the results. Best results were attained when pH of the initial test solution was lowered to 3.5 ± 0.2 before the UV-C irradiation. From the initial Co-60 activity, 2.2 Bq/ml, the activity decreased to 0.03 ± 0.01 Bq/ml after 24 hours of UV-C irradiation together with the photocatalyst and mixing with CoTreat.

INTRODUCTION

Co-60 is one of the most problematic waste nuclides in NPP waste streams due to its relatively long half-life (5.2 a) and high gamma decay energy (1.3 and 1.2 MeV). Many of these waste streams contain complexing agents, such as EDTA and oxalate, originating from cleaning solutions used to remove the radioactive metals, such as Co-60, from contaminated structures and equipment of NPPs. In addition, the liquid waste often contains high amount of inactive metal ions and only low chemical concentration of Co-60. Therefore, the method for its removal has to be highly selective.

Cation exchange resins have normally been used for the removal of Co-60 but as soon as cobalt is complexed, for example with EDTA, the resins turn out to be quite inefficient. An additional step in the purification process is required to degrade the organic complexing agents and to liberate radioactive metal ions in the solution. In this study, UV-C irradiation together with a photocatalyst, TiO₂ P25 AEROXIDE (Evonik Industries), was used for the degradation. The treated solution was then mixed with a highly selective inorganic ion exchange media, CoTreat (Fortum), to remove Co-60 from the solution.

TiO₂ P25 AEROXIDE was selected as the photocatalyst in this study since it is a widely used photocatalyst which is easily commercially available. CoTreat is an all-inorganic, titanium-based ion exchange media which has a significant sorption capacity towards cobalt. CoTreat has been tested for radiocobalt removal from THORP pond water [1, 2] and extensive laboratory scale studies have been made about its capacity to remove radiocobalt from real floor drain effluents [3, 4]. *Harjula et al.* [5] have

indicated in their studies that the prevailing mechanism for trace transition metal uptake on CoTreat is surface complexation.

In this study, the effect of pH and contact time with UV-C irradiation with TiO₂ P25 AEROXIDE was clear. After 24 hours of UV-C irradiation with the photocatalyst and mixing with CoTreat, the Co-60 activity decreased to 0.6 Bq/l from the initial Co-60 activity 2.2 Bq/l. When the pH of the waste solution was adjusted to 3.5 prior to UV-C irradiation, the corresponding result for Co-60 activity was 0.03 Bq/ml.

DESCRIPTION

Methods

Co-60 activity before and after the experiments was counted with a Genie 2000 Ge-detector (Canberra Industries) from 5, 10 or 15 ml samples depending on the experiment. The pH adjustments of the liquid waste were done with varying amounts of HNO₃ or NaOH as necessary. The solutions were allowed to stand in the dark for at least 24 hours with occasional mixing after adjusting the test solution pH.

Ultrafiltration experiments were made to clarify whether the radioactive cobalt ions were in the solution or in possible particles present in the solution. 100 kDa and 5 kDa ultrafiltration membranes (Biomax High-flux polyethersulfone membranes) were used in a Sartorius Ultrasart Ultrafiltration System (Cell 10 SM 16666) using 1.5 bar pressure during the filtration. Aliquots (15 ml) before and after the experiments were counted for Co-60 activity.

UV-C irradiation experiments were carried out in a 100-ml immersion well reactor (Photochemical Reactors Ltd., Model 3312) equipped with a 6 W low-pressure mercury lamp with major emission wavelength of 254 nm (Fig. 1). A quartz tube separated the lamp from the reaction mixture (80 ml of test solution and 160 mg of TiO₂ P25 AEROXIDE). Stirring was provided by a bubbling system delivering compressed air through sintered glass with a constant flow rate of 0.15 – 0.2 l/min. The reaction mixture was allowed to balance in the dark for one hour before the UV-C irradiation, which was continued for 4, 6 or 24 hours. A thermostat TTM-000 Series (TOHO Electronics Inc., Japan) was used to control the temperature (22-24 °C) during UV-C irradiation. Solid material was removed from the solution by centrifugation (Sepatech Megafuge 1.0, Heraeus) for 10 minutes at 4,000 rpm (3000 G). The solution was filtered with a 0.2 µm Acrodisc filter (PALL Life Sciences) and its pH was measured. Aliquots (5-15 ml) of solution before and after the experiments were counted for Co-60 activity.



Fig. 1. UV reactor used in the UV-C irradiation experiments.

After removing TiO_2 P25 AEROXIDE, the UV-C irradiated solution was mixed with CoTreat. These batch experiments were carried out at room temperature. Constant rotary mixing (50 rpm) was used to equilibrate 20 mg of CoTreat with 10 ml of the test solution for 24 hours in the dark. Solid material was removed by centrifugation and filtration before the activity measurement.

Results

The BWR NPP waste water used in this study contained approximately 14 g/l Na, 1 g/l K, 61 mg/l Mg and 16 mg/l Ca. The amount of TOC was approximately 119 mg/l, chemical concentration of Co-60 was $9\text{E-}13$ M ($5\text{E-}11$ g/l) and pH was 8.4. The initial activity of Co-60 was 2.2 Bq/ml. After the ultrafiltration experiments with 100 kDa and 5 kDa ultrafiltration membranes, the activity of Co-60 and the solution pH were the same as for the initial solution, indicating that the radioactive cobalt ions were in a soluble form.

When the liquid waste was oxidized by UV-C irradiation together with TiO_2 P25 AEROXIDE for 4, 6 or 24 hours, the cobalt activity decreased to 1.3, 1.0 and 0.9 Bq/ml, respectively (Fig. 2, blue symbols). Solution pH rose to 9.3 in every

experiment. After centrifugation and filtration, batch experiments were carried out for the UV-C irradiated solutions with CoTreat. Co-60 activity further decreased to 1.2, 0.8 and 0.6 Bq/ml, respectively (Fig. 2, orange symbols) and pH stayed at the same level as before the experiment. Operating pH area of CoTreat is at pH 4-8. Therefore, the batch experiments were repeated after decreasing the test solution pH to 7.0-7.5 (Fig. 2, grey symbols). Co-60 activity decreased to some extent as is seen in Fig. 2.

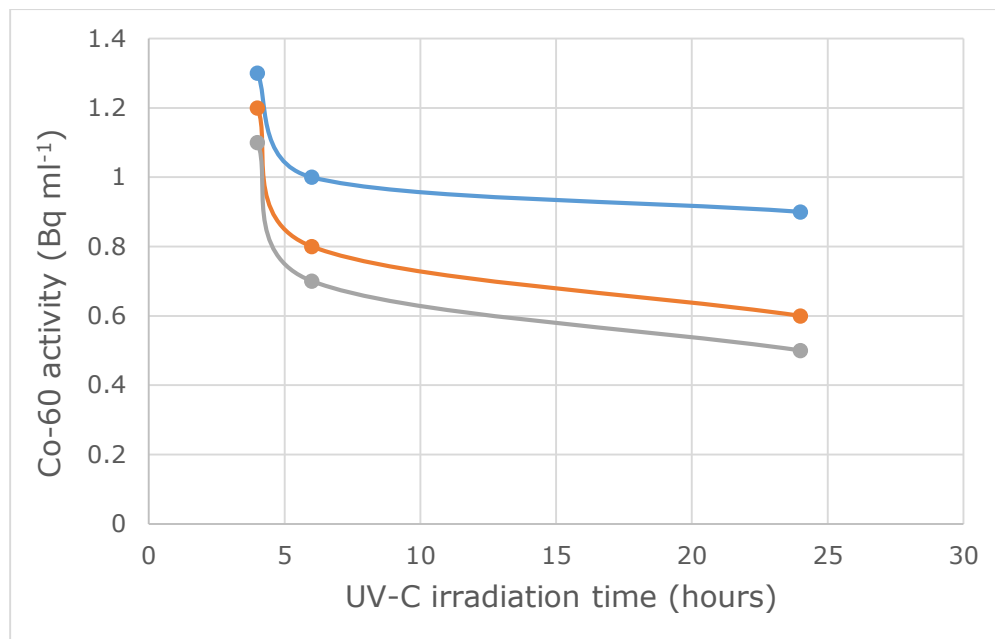


Fig. 2. Co-60 activity after UV-C irradiation with TiO₂ P25 AEROXIDE (blue) and after batch experiment with CoTreat without (orange) and with (grey) pH adjustment.

According to the safety data sheet of TiO₂ P25 AEROXIDE its pH is 3.5-4.5 (40 g/l at 20 °C). Therefore, it was tested how much the adjustment of the initial waste solution pH to approximately 3.5 would affect the results. First, the pH adjusted solution was oxidized 4 hours under UV-C light with the photocatalyst. Then the batch experiment with CoTreat was done and the Co-60 activity decreased to 1.4 Bq/ml or 0.2 Bq/ml depending on the solution pH before the batch experiment (TABLE I). When the pH adjusted solution was oxidized for 24 hours with the photocatalyst, Co-60 activity decreased to 0.5 Bq/l. The Co-60 activity was further decreased to 0.03 ± 0.01 Bq/ml after the batch experiment with CoTreat which indicates the effectiveness of the method.

TABLE I. Co-60 activity (Bq/ml) and solution pH after 4 or 24 hours of UV-C irradiation with TiO₂ P25 AEROXIDE and CoTreat batch experiments for the pH adjusted NPP liquid waste.

Test	Co-60 activity (Bq/ml)	pH
4 hours of UV-C irradiation	2.0	3.7
- for which CoTreat batch experiment	1.4	4.3
- for which pH adjustment to 6.8 prior to CoTreat batch experiment	0.2	5.9
24 hours of UV-C irradiation	0.5	7.2
- for which CoTreat batch experiment	0.03	6.2

DISCUSSION

In this study the removal of Co-60 from a BWR NPP liquid waste containing organic complexing agents was tested. In order to achieve good removal efficiency, UV-C irradiation together with a photocatalyst was used to degrade the organic complexing agents and to liberate radiocobalt ions in the solution. The suitability of CoTreat as a photocatalyst has been tested earlier [6] and the results showed that additional oxidation was needed in order to obtain efficient removal of radiocobalt. Therefore, a widely used and commercially available photocatalyst, TiO₂ P25 AEROXIDE, was selected for the experiments with UV-C irradiation.

TiO₂ P25 AEROXIDE removed Co-60 from the waste solution to some extent. The effect of waste solution pH and contact time with UV-C irradiation were emphasized. One of the most recent studies about cobalt removal from liquid nuclear waste using TiO₂ has been done by *Rekab et al.* [7] and the effect of the test solution pH was clear also in their study. The solution pH affects also the sorption capacity of CoTreat. Without pH adjustments the Co-60 activity decreased to 0.9 Bq/ml after 24 hours of UV-C irradiation with the photocatalyst and further to 0.6 Bq/ml after the CoTreat batch experiment. When the liquid waste pH was adjusted to 3.5 prior to UV-C irradiation, TiO₂ P25 AEROXIDE didn't remove Co-60 from the solution after 4 hours of UV-C irradiation and 1.4 Bq/ml of Co-60 remained in the solution after CoTreat batch experiment. The relatively low pH of the 4 hours UV-C treated solution (pH 3.7) affected the Co-60 sorption capacity of CoTreat. When the pH of the 4 hours UV-C treated solution was adjusted to 6.8, Co-60 activity in the solution was decreased to 0.2 Bq/ml after CoTreat batch experiment which is noticeably lower than the Co-60 activity after the experiments with no pH adjustments. The result indicates that the degradation of organic complexing agents was much more efficient when the liquid waste pH was adjusted prior to the experiments.

When the UV-C irradiation time was increased for the pH adjusted liquid waste, Co-60 activity was decreased as low as 0.5 Bq/ml after the UV-C irradiation with the photocatalyst. Since only 0.03 ± 0.01 Bq/ml Co-60 was left in this solution after CoTreat batch experiment, it can be concluded that the two-step process for Co-60 removal presented in this study is very efficient.

Because of the uncertainty about the chemical form of Co-60 in the liquid waste, it is not possible to conclude e.g. whether the change in the surface charge of the

WM2016 Conference, March 6-10, 2016, Phoenix, Arizona, USA.

photocatalyst or the possible change in the chemical form of Co-60 due to pH adjustments of the liquid waste affected the results more. Despite of this the results provide important information for pilot scale test planning of liquid nuclear waste.

CONCLUSIONS

The removal of trace amounts of Co-60 from aqueous nuclear liquid waste containing organic complexing agents presents a difficult task. The method described in this study offers an efficient way to decrease the amount of Co-60 in NPP liquid waste. From the initial Co-60 activity 2.2 Bq/ml it was possible to decrease the Co-60 activity to 0.03 ± 0.01 Bq/ml. Commercial UV-C irradiation systems can be easily purchased. Also TiO₂ P25 AEROXIDE photocatalyst and inorganic ion exchange material CoTreat are commercial products making this method easily available.

REFERENCES

1. R. Harjula, A. Paajanen, J. Lehto, E. Tusa and P. Standring, "Testing of CoTreat Inorganic Ion Exchange Media for the Removal of Co-60 From Thorp Pond Water", *Proc. of the WM'03 Conference*, Tucson, AZ, February 23-27, 2003.
2. R. Harjula, A. Paajanen, J. Lehto, E. Tusa, R. Smith and P. Standring, "Additional Testing of CoTreat Inorganic Ion Exchange Media for the Removal of Co-60 From Thorp Pond Water", *Proc. of the WM'04 Conference*, Tucson, AZ, February 29-March 4, 2004.
3. R. Harjula, J. Lehto, A. Paajanen, L. Brodtkin and E. Tusa "Removal of Radiocobalt and Other Activated Corrosion Product Nuclides From NPP Waste Waters by Highly Selective CoTreat Ion Exchange Media", *Proc. of the 7th International Conference on Radioactive Waste Management and Environmental Remediation*, Nagoya, Japan, September 26-30, 1999.
4. R. Harjula, J. Lehto, L. Brodtkin, E. Tusa and J. Rautakallio, "Treatment of Nuclear Waste Effluents by Highly Selective Inorganic Ion Exchange Media – Experience Gained and New Developments", *Proc. of the WM'98 Conference*, Tucson, AZ, March 1-3, 1998
5. R. Harjula, M. Kelokaski and H. Leinonen, "Sorption of Radiocobalt and Other Activation Product Radionuclides on Titanium Oxide Material CoTreat", *Radiochim. Acta*, 98, 341 (2010).
6. L. K. Malinen, R. Koivula and R. Harjula, "Removal of Radiocobalt From EDTA-Complexes Using Oxidation and Selective Ion Exchange", *Water Science & Technology*, 60.4, 1097 (2009).
7. K. Rekar, C. Lepeytre, F. Goettmann, M. Dunand, C. Guillard and J-M. Herrmann, "Degradation of a Cobalt(II)-EDTA Complex by Photocatalysis and H₂O₂/UV-C. Application to Nuclear Wastes Containing Co-60", *J. Radioanal. Nucl. Chem.*, 303, 131 (2015).

ACKNOWLEDGEMENTS

Jenny and Antti Wihuri Foundation is highly appreciated for the financial support.