

INDUSTRIAL SCALE REMOVAL OF CESIUM WITH HEXACYANOFERRATE EXCHANGER - PROCESS DEVELOPMENT

Jukka Lehto and Risto Harjula
Department of Radiochemistry
P.O.Box 5 (Unioninkatu 35)
00140 University Of Helsinki, Finland

Esko Tusa
IVO International Ltd
Vantaa, Finland

Asko Paavola
Imatran Voima Oy
Loviisa NPP
Loviisa, Finland

ABSTRACT

An industrial scale process utilizing hexacyanoferrate ion exchangers in columns was developed for the selective separation of radioactive cesium from nuclear evaporator concentrates. This process was taken into operation at the Loviisa NPP (PWR, VVER-440), Finland, at the end of 1991. This paper summarizes the work that was carried out in the development of this process. In the first stage of the work, the performance of several Cs-specific precipitants and ion exchangers (eg. zeolites and hexacyanoferrates) was tested by laboratory experiments. Based on these initial test, two precipitants, sodium hexanitrocobaltate and tungstophosphoric acid, and two hexacyanoferrate exchangers, were chosen for pilot-scale experiments. These experiments showed that the hexacyanoferrate ion exchangers were the most efficient materials for the removal of Cs-137,134, and suitable for large-scale column operation. With hexacyanoferrates, decontamination factors (DF) of several thousands, and concentration factors (CF) in the range of 2000-10 000, were obtained for Cs-137,134. By using the Cs-specific precipitants, DF's and CF's in the order of 100 were feasible in the Loviisa concentrates. After the pilot experiments, an exchanger based on hexacyanoferrate was chosen to be used in the full-scale Cs-separation plant constructed at the Loviisa NPP.

INTRODUCTION

At the Loviisa NPP various aqueous waste streams are being combined and concentrated by evaporation. The resulting evaporator concentrates are highly alkaline and contain high concentrations of sodium and potassium (Table I). After aging for a few years Cs-134,137 typically constitute more than 95 % of the radioactivity in the solutions. If the cesium activity is removed, the residual activity should be well within the legislative level for discharge into the sea.

Concentrates of higher radiocesium levels have been stored and a concept for their treatment has been that of solidification in concrete. This method would, however, produce large volumes of final waste to be disposed of in the repository. In this work an alternative method, selective separation of radiocesium from the concentrates was investigated, with an emphasis of minimizing the final waste volumes. The high salt content in the concentrates required highly Cs-selective sorbents for efficient separation.

Several hexacyanoferrates of transition metals are known to be highly selective for cesium (1-3) and some of these are being used as precipitation agents for the removal of cesium from nuclear waste solutions. Precipitation with hexacyanoferrates is rather effective compared to most other precipitation agents, but yields a colloidal sludge, which is very difficult to be removed from the solution. Some hexacyanoferrates, such as potassium cobalt hexacyanoferrate (4), can be prepared in granular form, suitable to be used as ion exchangers in packed bed columns. So far no large-scale applications utilizing hexacyanoferrates in this fashion have been reported. Using hexacyanoferrates in columns instead

TABLE I
Main Chemical and Radiochemical Constituents in a
Typical Evaporator Concentrate (Aged for Several Years)
From the Loviisa NPP

Constituent	Concentration (mol/L)	Activity (kBq/L)
Na ⁺	3.0	
K ⁺	0.2	
BO ₂ ⁻	0.7	
NO ₃ ⁻	0.7	
Cs-137		400
Cs-134		100
Co-60		6
pH > 13.5		

of batch precipitation is likely to make the separation process more efficient and more straightforward. The limiting factor in the use of hexacyanoferrates in columns has been their poor mechanical or chemical stability.

PRECIPITANTS

After an initial screening of a number of Cs-specific precipitants, tungstophosphoric acid (TPA) and sodium hexanitrocobaltate (SNC) were taken under further study (5). Laboratory experiments showed that the efficiency of SNC for removal of Cs-137 was practically insensitive to the solution

pH (range studied 2.5-13.5). TPA functioned efficiently over a very narrow pH range of 0.5-1 only. In the pilot-scale experiments (200 L batches of evaporator concentrate treated), 6 kg/m³ of TPA and 50 kg/m³ of SNC were needed to obtain decontamination factors in the order of 100 for Cs-137. The precipitate resulting from the SNC treatment could be easily removed from solution by using a continuously operating decanter centrifuge. TPA precipitate was of finer particle size and could be removed by 0.45 m filtration.

ION EXCHANGERS

The most abundant ions to compete with trace Cs exchange in the evaporator concentrates were Na⁺ and K⁺. Therefore, in the initial laboratory experiments, the effects of these ions, as well as that of solution pH, on the static performance of several Cs-selective ion exchangers was studied. These were zeolites Zeolon-900 (synthetic mordenite), AW-500 (synthetic chabazite), ammonium phosphomolybdate (AMP) and potassium cobalt hexacyanoferrate (KCoCF). KCoCF was prepared as described by Prout et al. (4), the rest of exchangers studied were commercial products.

Compared to the zeolites, or conventional organic resins, KCoCF and AMP were found to have superior efficiency in the removal of Cs-137 (Table II). Uptake of Cs-137 by KCoCF was practically unaffected by the concentration of Na⁺ in the solution (6). K⁺ ions decreased Cs-137 uptake at concentrations higher than 0.1 M, but the uptake was still very high in 1.0 M K⁺ concentrations (Table II). In evaporator concentrates, the performance of KCoCF was found to be practically independent on the solution pH, too, over the range of 2-12. At pH > 12, the exchanger started to dissolve with a concurrent decrease in the uptake of Cs-137. The performance AMP was slightly poorer than that of KCoCF. In addition, AMP was not available as granules suitable for column operation. Based on these facts, KCoCF was chosen for further study.

TABLE II

Absorption-% of Trace Cesium from 1 M NaCl and KCl Solutions on Different Exchangers

Exchanger	Absorption-% 1M NaCl	1M KCl
Hexacyanoferrate	99.95 %	99.8 %
Ammonium phosphomolybdate	99.90	96
Zeolite (mordenite)	85	36
Organic resin	13	4

Small-scale column experiments (bed volume BV = 2 cm³) were conducted with granular KCoCF using an evaporator concentrate from Loviisa NPP. These experiments showed that column breakthrough capacities as high as about 3000 BV for Cs-137 (1% breakthrough) were feasible with this material.

PREPARATION OF HEXACYANOFERRATE RATE EXCHANGERS

During the time this work was carried out, large quantities of granular KCoCF were available from one commercial supplier only. However, this product was found unsuitable for

column operation due to the poor stability of the exchanger grains. Therefore, study was directed into the preparation of this material. Two options were considered: a) preparation of pure granular KCoCF, b) preparation of a composite exchanger by attaching KCoCF, or some other metal hexacyanoferrate, into a suitable support matrix. The work on the preparation and properties of different granular KCoCF-products has been summarized elsewhere (7,8). Here, some results on the composite exchangers are reported.

Several support matrices for metal hexacyanoferrates were taken under study: silica gel, granular activated carbon, zeolite Zeolon 900, porous glass, adsorption resins, an anion exchange resin (IRA-400, IRA 904) and a chelating resin (Chelex-100). Metal hexacyanoferrates were attached into these materials by treating them with alkali metal hexacyanoferrate and transition metal salt solutions. The static uptake of Cs-137 by different products was measured in the Loviisa concentrates. Hexacyanoferrate products based on Chelex-100 and IRA-904 had static uptakes comparable to those of pure KCoCF grains. Products based on activated carbon and silica gel took up Cs-137 rather strongly, but their performance was markedly poorer than that of pure KCoCF. No usable products could be obtained by using the rest of the matrices.

Small-scale column experiments with the Loviisa concentrate showed that the breakthrough (1%) capacities of the silica and carbon based materials for Cs-137 were about 500 BV. The product based on IRA-904 appeared to be unusable, as the hexacyanoferrate bound to the resins was eluted from the column by the concentrate solution. The products prepared into Chelex 100 appeared most promising with breakthrough capacities of several thousands of bed volumes.

PILOT

SCALE EXPERIMENTS Based on the results of the laboratory-scale experiments, granular KCoCF (KCoCF-P) and a hexacyanoferrate product based on Chelex-100 (CF-CX) were chosen to be tested on a pilot plant. In these experiments, 30 cm high columns were used (BV = 0.15 L) and an evaporator concentrate from the Loviisa NPP (for composition, see Table I).

By using KCoCF-P in the pilot-scale columns, breakthrough capacities (0.1%) higher than 10 000 BV were obtained for Cs-137. For KCoCF-P it was found that the breakthrough capacity was directly proportional to the mean radius of the KCoCF grains, to the flow rate and to the concentration of K⁺ in the solution. An example of the effect of the flow rate is shown in Fig. 1. The results obtained showed that the rate of trace Cs exchange in KCoCF was very slow. Because of this, most of the capacity available in the columns remained unused. More efficient operation could be achieved by reducing the flow rate from the values of 10-20 BV/h used. For treating large volumes of solution, much lower flow rates might, however, be unfeasible due to long processing times. An alternative means to increase column utilization would be connecting several columns in series.

Also CF-CX demonstrated a high breakthrough capacity for Cs-137, although its efficiency was somewhat lower than that of pure KCoCF (Fig. 1). It should be noted, however, that the fraction of active hexacyanoferrate in the total mass of CF-CX was very low (< 10 %). Fig. 1. a) Examples of Cs-137 breakthrough curves from pilot-scale columns. Curves 1&2: KCoCF-P, grain size 0.85-0.30 mm, flow rate 20 BV/h (1) and

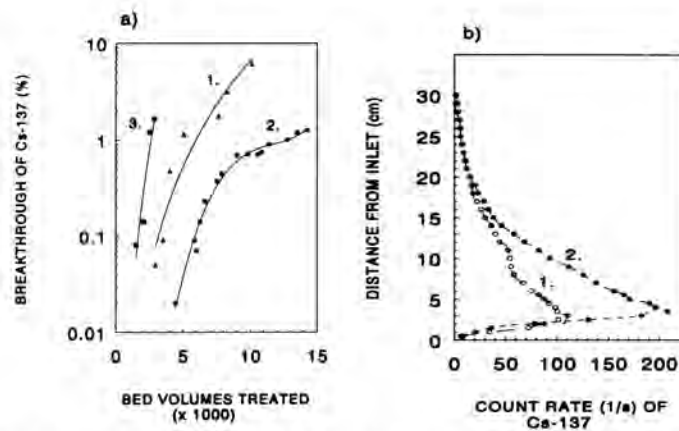


Fig. 1. a) Examples of Cs-137 breakthrough curves from pilot-scale columns. Curves 1&2: KCOCF-P, grain size 0.85-0.30 mm, flow rate 20 BV/h (1) and 10 BV/h. Curve 3: CF-CX, grain size 0.08-0.04 mm, flow rate 5 BV/h. b) distribution of Cs-137 inside the columns corresponding to the breakthrough curves 1 and 2 in a).

10 BV/h (2). Curve 3:CF-CX, grain size 0.08-0.04 mm, flow rate 5 BV/h. b) Distribution of Cs-137 inside the columns corresponding to the breakthrough curves 1 and 2 in a).

FULL-SCALE OPERATION

Based on the experience gained in the preparation studies, a full-scale industrial plant was designed and constructed for the production of hexacyanoferrate exchangers at larger scales. The full-scale Cs-separation plant for the evaporator concentrates, called IVO-CsTreatSystem, has been constructed in the Waste Storage Building at the Loviisa NPP. Also the storage tanks (volume 300 m³) of the evaporator concentrates are located in the same building. The actual Cs-separation unit, consisting of prefilters and heavily shielded ion exchange columns (BV = 8 L), is very compact, taking up only about 8 m³ of floor space. The design and operation of the IVO-CsTreatSystem has been described in more detail in another paper of this session (9).

The test run of the Cs- separation plant was carried out during October 1991 - June 1992. One single column was connected into the system when the test run was initiated. The performance of this column is shown in Fig. 2., together with those of laboratory and pilot- scale columns obtained under comparable conditions. As it can be seen, the separation efficiency of the system increased considerably, as the scale of operation was increased from the laboratory and pilot levels: the Cs-137 capacity obtained at 0.1 % breakthrough exceeded 20 000 BV (167 m³). Altogether 257 m³ of evaporator concentrate was purified in the test run, which took three columns. The capacities of the second and third columns were markedly lower than that of the first column. This was caused by the sudden increase of solution pH above the maximum design limit of 12 soon after the second column was taken into use. No remedial action regarding the solution pH was taken, however, as the column capacities remained at acceptable levels.

SUMMARY

This work demonstrated that hexacyanoferrates ion exchangers can be used in columns for large scale separation of radioactive cesium from highly concentrated salt solutions, such as NPP evaporator concentrates. The efficiency of hexacyanoferrate exchangers is superior compared to any

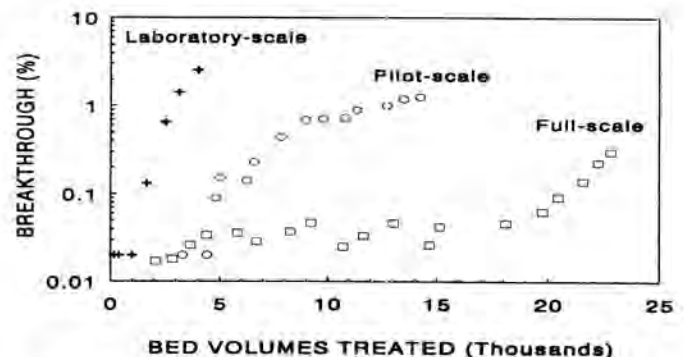


Fig. 2. Column breakthrough of Cs-137 from laboratory (BV = 2 cm³), pilot (BV = 0.15L) and full-scale columns (8L) at constant relative throughputs of 10 BV/h.

other Cs-specific ion exchanger or precipitant known at present.

REFERENCES

1. H. LOEWENSCHUSS, "Metal-Ferrocyanide Complexes for the Decontamination of Cesium from Aqueous Radioactive Waste", *Radioact. Waste Manag.* 2(1982)327.
2. V. PEKAREK, and V. VESELY, "Synthetic Inorganic Ion Exchangers II", *Talanta* 19(1972)1245.
3. W.F. HENDRICKSON, and G.K. KIEL, "Comparison of Ferrocyanides for Cesium Extraction", *Health Phys.* 28(1975)17.
4. W.E. PROUT, E.R. RUSSELL, and H.J. GROH, "Ion Exchange Absorption of Cesium by Potassium Hexacyanocobalt(II) Ferrate(II)", *J. Inorg. Nucl. Chem.* 27(1965)473.
5. J. LEHTO, E. PUUKKO and T. JAAKKOLA, "Separation of Cesium from a Nuclear Waste Solution by Precipitation with Sodium Hexanitrocobaltate and Tungstophosphoric Acid", *Radiochim. Acta*, 38(1985)53.
6. J. LEHTO and R. HARJULA, "Separation of Cesium from Nuclear Waste Solutions with Hexacyanoferrate(II)s and Ammonium Phosphomolybdate", *Solvent Extraction and Ion Exchange* 5(1987)343.

7. J. LEHTO and R. HARJULA, "Separation and Solidification of Radioactive Cesium from Nuclear Waste Solutions with Potassium Cobalt Hexacyanoferrate(II) Ion Exchangers", IAEA-TECDOC-675, International Atomic Energy Agency, Vienna, 1992, p. 131.
8. J. LEHTO, S. HAUKKA, R. HARJULA, and M. BLOMBERG, Mechanism of Caesium Ion exchange on Potassium Cobalt Hexacyanoferrate(II), J. Chem. Soc. Dalton Trans. 3(1990)1007.
9. E. TUSA, A. PAAVOLA, J. LEHTO and R. HARJULA, "Industrial Scale Removal of Cesium with Hexacyanoferrate Exchanger - Process Realization", Proceedings of WM'93, submitted.