

REMOVAL OF CESIUM FROM NUCLEAR WASTE SOLUTIONS BY  
 POTASSIUM COBALT HEXACYANOFERRATE(II) COLUMNS

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ABSTRACT

Removal of  $^{137}\text{Cs}$  from nuclear power plant waste solutions by ion exchange using potassium cobalt hexacyano-ferrate(II) columns was studied. The highly alkaline (pH 14) waste solutions contained high concentrations of sodium (2.3 - 2.7 M) and potassium (0.11 - 0.24 M) ions. The cesium breakthrough capacity (at 0.01 % cumulative breakthrough) was 2400 - 4800 bed volumes, depending on the exchanger grain size and the flow rate used.

INTRODUCTION

Organic ion exchange resins are routinely used at nuclear power plants for the decontamination of radio-active waste solutions, e.g. for the purification of reactor coolants and fuel pond waters. Due to their low selectivity, organic resins are not applicable for the specific separation of  $^{137}\text{Cs}$ , which is the most harmful waste nuclide in low- and medium-level solutions. For this purpose zeolites, which exhibit higher selectivity for cesium, have been utilized (1, 2). However, high concentrations of other ions can severely interfere with the selective separation of Cs by zeolites. Therefore, even more selective ion exchangers for cesium are often required.

Mixed hexacyanoferrate(II)s of transition and alkali metals show very high selectivity for cesium (3, 4, 5). The general disadvantage of these materials is their often limited chemical and physical stability, which can make their use in fixed-bed ion exchange columns impractical. However, some of these compounds, such as potassium cobalt hexacyano-ferrate(II), can be prepared in granular form suitable for column operations. Potassium cobalt hexacyano-ferrate(II) is insoluble in most mineral acids, but peptizes to some degree in alkaline solutions with low salt content (6).

From a number of inorganic ion exchangers studied in our laboratory, potassium cobalt hexacyano-ferrate(II) was found to be the most useful for the selective separation of  $^{137}\text{Cs}$  from nuclear waste solutions with high sodium and potassium ion content (7, 8, 9). Sodium ions even at 5.0 M concentration have no effect on the uptake of  $^{137}\text{Cs}$ , potassium ions decrease the uptake at concentrations higher than 0.01 M (7). Potassium cobalt hexacyanoferrate(II) under study is a mixture of two phases,  $\text{K}_2(\text{CoFe}(\text{CN})_6)$  (85 - 88 %) and  $\text{Co}(\text{CoFe}(\text{CN})_6)$  (12 - 15 %). Absorption of cesium on this mixed compound is stoichiometric ion exchange, the exchangeable ions being  $\text{K}^+$  (88 %) and  $\text{Co}^{2+}$  (12 %). The effective capacity for cesium is 0.35 meq/g. This is 6 % of the theoretical capacity, since cesium exchange takes place only in the outermost monolayer of the crystallites (8).

At the Loviisa Nuclear Power Plant (PWR, VVER-440), Finland, radioactive waste streams are combined and evaporated, yielding waste concentrates with high salt content. After ageing, the only harmful waste nuclide in the solutions is  $^{137}\text{Cs}$ . Solidification of these waste concentrates in concrete has been

considered. This would produce large volumes of final waste. The purpose of this study is to selectively remove  $^{137}\text{Cs}$  from the concentrates and thereby obtain a substantial reduction in the final waste volume. Based on the results of the pilot plant experiments described in this paper, the design of a full-scale plant has been completed by Imatran Voima Power Company.

EXPERIMENTAL

Potassium cobalt hexacyanoferrate(II) was prepared from  $\text{Co}(\text{NO}_3)_2$  and  $\text{K}_4(\text{Fe}(\text{CN})_6)$ . The dried (110 °C) product ( $\text{K}_{1.70}\text{Co}_{0.12}\text{Fe}(\text{CN})_6 \times 1 \text{H}_2\text{O}$ ) was crushed and sieved to desired particle size fractions ( $\phi$ ). It will later be referred as  $\text{K}_2(\text{CoFe}(\text{CN})_6)$ .

Two different evaporator concentrates, designated B01 and B03, were used in the experiments. Their major chemical constituents together with radiochemical composition are given in Table I.

TABLE I  
 Composition of Two Nuclear Waste Concentrates from Loviisa Nuclear Power Plant, Finland.

| Constituent                     | B01  | B03  |
|---------------------------------|------|------|
| $\text{Na}^+$ (mol/l)           | 2.7  | 2.3  |
| $\text{K}^+$ (mol/l)            | 0.24 | 0.11 |
| $\text{H}_3\text{BO}_3$ (mol/l) | 0.75 | 0.56 |
| pH                              | 13.7 | 13.9 |
| $^{137}\text{Cs}$ (kBq/l)       | 401  | 151  |
| $^{134}\text{Cs}$ (kBq/l)       | 157  | 57   |
| $^{60}\text{Co}$ (kBq/l)        | 6    | 3    |

Laboratory scale column experiments (bed volume 2.0 cm<sup>3</sup>) were first carried out to determine the suitable operating conditions for the pilot plant experiments and to design the apparatus.

In the pilot plant experiments, the effects of flow rate, exchanger grain size and alkali metal ion concentration on column performance were studied. The pilot plant procedure contained three major stages:

- I. Adjustment of the solution pH to 11.5-12.0
- II. Filtration of solid fines
- III. Removal of  $^{137}\text{Cs}$  by  $\text{K}_2(\text{CoFe}(\text{CN})_6)$  column

Figure 1 shows the procedure in more detail. First, solid matter was removed from the solution by filtration. The pH of the solution was then adjusted with concentrated (50 - 70 %) nitric acid, 7 - 9 l of which was consumed per 100 l of the solution. Precipitation of fine solids occurred after the pH adjustment, necessitating an additional filtration between the feed tank and the ion exchange column. Columns were packed with 90 g of  $\text{K}_2(\text{CoFe}(\text{CN})_6)$  (bed volume 150 cm<sup>3</sup>, bed height 30 cm). Samples were taken from the effluent at 1 - 3 day intervals and their  $^{137}\text{Cs}$ -activity was measured using a Ge(Li)-detector and a multichannel analyzer.

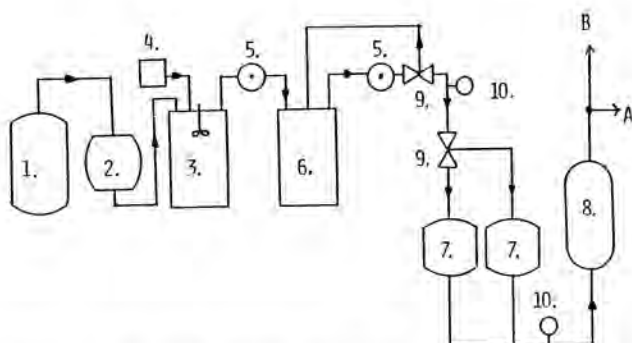


Fig. 1. The Pilot Plant Flowsheet for Cesium Removal from Nuclear Waste Concentrates. 1. Sampling Tank 2. Prefilter 3. pH Adjustment Vessel 4. Nitric Acid Tank 5. Pump 6. Feed Tank (Volume 1000 l) 7. Cartridge Filter, 0.2  $\mu\text{m}$  8.  $\text{K}_2(\text{CoFe}(\text{CN})_6)$  Column (Bed Volume 150 cm<sup>3</sup>, Bed Height 30 cm) 9. Relief Valve 10. Pressure Gauge A. Sampling B. Drain

## RESULTS AND DISCUSSION

Laboratory scale column experiments showed that cesium breakthrough capacities of several thousands of bed volumes (BV) were obtainable. However, in alkaline solutions with pH > 13 reddish-brown color was leached from the column to the solution indicating peptization of the exchanger. Moreover, a low cesium capacity was obtained at this pH. On the other hand, boric acid crystallized from the solution at pH < 11 causing blocking of the feed tubing. On this basis, the operational pH range 11.5 - 12.0 was chosen.

Precipitates formed after the pH adjustment blocked columns in some experiments. The higher cesium breakthrough capacities obtained with filtered solution indicated that the coating of the exchanger grains by the precipitate appreciably decreased the column capacity. No chemical analysis of the precipitates was made, possibly they are hydroxides of the transition metals that are present at 1 ppm level in the solutions. These hydroxides are slightly soluble at very high pH values. Radiochemical analysis showed that the precipitate had a low specific activity mainly comprised of  $^{60}\text{Co}$ .

Figure 2 shows the cumulative breakthrough curves for  $^{137}\text{Cs}$  from the pilot plant experiments. The cesium breakthrough capacity (at 0.01 % cumulative breakthrough) dropped from 4800 BV to 2400 BV as the flow rate was increased from 11 BV/h to 22 BV/h (Fig. 2a). The capacity shows direct proportionality to contact time. With smaller grains (0.20 - 0.30 mm) a higher capacity of 8500 BV was obtained compared to the capacity of 4800 BV obtained with bigger grains (0.30-0.85 mm) (Fig. 2b). This was due to the faster cesium exchange rate on the smaller grains. The only major component in the solutions that was expected to suppress cesium exchange on  $\text{K}_2(\text{CoFe}(\text{CN})_6)$  was the potassium ion (7). Potassium ion concentrations in B01 and B03 were 0.24 and 0.11 M, respectively. The obtained capacities, 2400 BV for B01 and 3800 BV for B03, correlate with potassium ion concentration in the solutions (Fig. 2c). The data collected is insufficient to establish the precise relation of the breakthrough capacity to the parameters studied, and thus gives an approximation of the column performance.

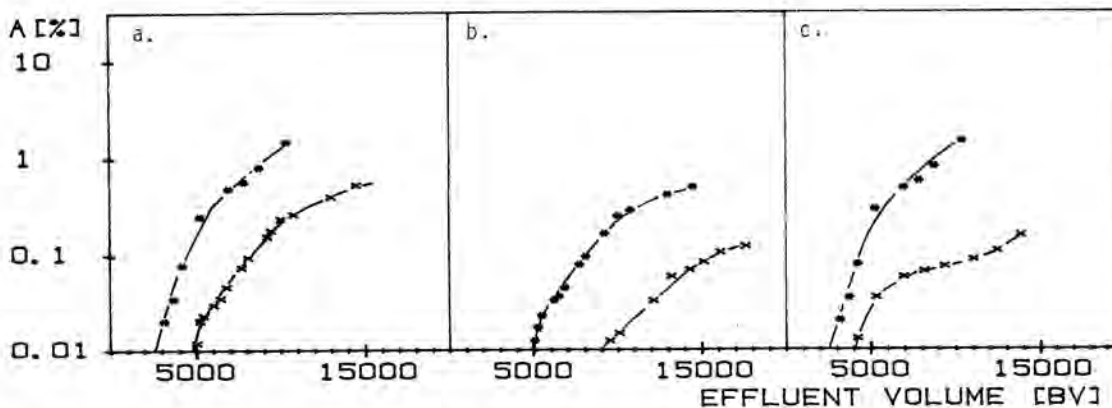


Fig. 2. The Cumulative Breakthrough of  $^{137}\text{Cs}$  from  $\text{K}_2(\text{CoFe}(\text{CN})_6)$  columns. A (%) Indicates The Ratio of The Specific Activity of  $^{137}\text{Cs}$  in The Total Volume of Effluent to That in The Feed. The Effect of a) Flow Rate (\* = 22 BV/h, x = 11 BV/h), b) Exchanger Grain Size (\* = 0.30 - 0.85 mm, x = 0.20 - 0.30 mm), c) Solution Composition (\* = B01, x = B03, for Compositions, See Table I.). Bed Volume (BV) 150 cm<sup>3</sup>, Bed Height 30 cm, Column Diameter 2.54 cm.

Prout reported much higher breakthrough capacities (40000 BV) in 4.25 M NaCl solution, which contained no potassium. On the other hand, the capacity was only 250 - 500 BV in a high-level waste concentrate containing 0.03 M potassium and 0.0003 M cesium ions (6).

Compared to synthetic zeolites mordenite and chabazite,  $K_2(\text{CoFe}(\text{CN})_6)$  has a far superior selectivity for  $^{137}\text{Cs}$ . In the zeolite columns, an instant cesium breakthrough occurred with BO1 (9).

The results presented above show that  $K_2(\text{CoFe}(\text{CN})_6)$  is an extremely selective ion exchanger for cesium even in the presence of large excess of other alkali metal ions. In the solutions studied the molar ratio of Cs to Na and K was of the order  $10^9$  -  $10^{10}$ . According to the pilot plant experiments, a decontamination factor of 10000 with a volume reduction factor as high as 8500 can be achieved for the waste concentrates. Thus, each 100 m<sup>3</sup> of concentrate can be reduced to 12 l (7 kg) of solid material.

#### CONCLUSIONS

$^{137}\text{Cs}$  can be efficiently removed from nuclear waste solutions containing high concentrations of salts by ion exchange using potassium cobalt hexacyanoferrate(II) columns. In contrast to solidification in concrete, this method provides a high volume reduction factor for the final waste.

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