

SEPARATION OF ^{60}Co FROM A LOW-ACTIVE EVAPORATOR CONCENTRATE USING ULTRAFILTRATION, PRECIPITATION, POLYELECTROLYTES, ION EXCHANGE AND ACTIVATED CARBON

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ABSTRACT

Removal of ^{60}Co from a highly alkaline low-active evaporator concentrate solution was studied. Ultrafiltration with a 2-3 nm membrane showed a cobalt removal of about 14%. Precipitation with Co^{2+} , CO_3^{2-} , Fe^{3+} , $\text{Fe}(\text{CN})_6^{4-}$ and S^{2-} removed 4-89% of ^{60}Co at pH 11.5; the highest removal was obtained with sulphide. Of the polyelectrolytes tested only cationic species showed slight removal with flocculation, varying in the range of 10-13.5%. Several chelating organic ion exchange resins, inorganic ion exchangers and activated carbons were also tested. Most of these did not remove any cobalt. The most effective chelating resin was Imac GT 73 which removed 17% of cobalt. The highest uptake obtained with inorganic exchangers (modified phlogopite mineral and manganese sulphide) was 11-13%. The cobalt adsorptions on activated carbons varied in the very wide range of 7-77%.

INTRODUCTION

A highly effective method was previously developed for the separation of ^{137}Cs from nuclear waste solutions with hexacyanoferrate exchangers. A full-scale process utilizing hexacyanoferrates in columns for the separation of cesium from low-active evaporator concentrates was taken into operation in 1991 at the Loviisa NPP, Finland (1). After separation of cesium the main radiochemical component is usually ^{60}Co . This study was performed to assess the feasibility of cobalt removal from alkaline waste solutions, in which ^{60}Co is not primarily present as divalent cation, but also, or entirely, as small particles and complexes. Ordinary precipitation and ion exchange separation methods have often been unable to remove cobalt from these alkaline solutions.

EXPERIMENTAL

The waste solution used in the experiments was a low-active and highly alkaline (pH about 14) evaporator concentrate, which contains high concentrations of alkali metals and borate. Because of the high pH of solution the transition metals (Co, Fe, Mn, Ni) in the waste are present mostly as hydroxide precipitates on the bottom of the waste tanks. Approximately 90% of ^{60}Co is in the precipitate and the rest in the solution in ionic and/or colloidal form. The activity of ^{60}Co in the solution phase is 6 kBq/L. Prior to the experiments, the pH of the solution was adjusted with nitric acid to a desired value and the solution was filtered through a 0.22 μm membrane filter, except in the filtration test described below.

^{60}Co -activity of the samples was determined with a Ge(Li) crystal and a multichannel analyzer.

Filtration test was carried out by using an evaporator concentrate sample containing solid precipitate from the bottom of the waste tank. After adjusting the pH to 11.5 the solid matter was separated by centrifugation. Particulate fractions containing ^{60}Co were determined by successive filtrations of the residual solution through filters with pore sizes of 1.6, 0.45, 0.22, 0.05 μm and 5,000 NMWC (Daltons). 5,000 Daltons correspond approximately to 2-3 nm.

Flocculation of cobalt was tested by using cationic, anionic and non-ionic Fennopol polyelectrolyte products and a cationic Fennofix polyelectrolyte (Kemira Co., Finland). Polyelectrolytes were added as 0.1-0.5% solutions into the waste solution of pH 11.5 and mixed with a magnetic stirrer for 0.5-1 hours. The dosages of the polyelectrolytes were 1, 10 and 100

mg/L. The Fennopol solutions were first filtered through a 0.22 μm and then through a 0.1 μm membrane filter. The Fennofix solution was filtered through a 10,000 NMWC membrane filter.

Separation of ^{60}Co by precipitation at varying pH values was studied using the following precipitating reagents: Co^{2+} , CO_3^{2-} , Fe^{3+} , $\text{Fe}(\text{CN})_6^{4-}$ and S^{2-} solutions. After addition of the reagents into the waste solution the mixtures were shaken overnight, whereafter the precipitates were separated by centrifugation. Precipitations with CO_3^{2-} , $\text{Fe}(\text{CN})_6^{4-}$ and S^{2-} were also performed with cobalt carrier using $\text{Co}(\text{NO}_3)_2$ solution.

Uptake of cobalt on ion exchangers and adsorbents were tested by shaking 0.08 g samples of the sorbents with 8 ml of waste solution. After 20 hours' shaking the solid was separated by centrifugation or filtration with a 0.22 μm filter. Chelating ion exchangers tested in the experiments are listed in Table I and activated carbons in Table II. Prior to the tests the activated carbons were crushed and sieved for 0.14-0.30 mm particle size fraction. Synthetic organic adsorbents, XAD-2, XAD-7 and Bio-Beads SM-4, were also tested, as were the following inorganic ion exchangers: phlogopite mineral, modified phlogopite mineral, zeolite 13X-Na, serpentine mineral and manganese sulphide.

RESULTS

Filtration

The solid matter in the evaporator concentrate at pH 11.5 separated by centrifugation (G value 10,000) contained 92% of ^{60}Co . Filtration of the supernatant through the 1.6 μm glassfibre filter removed 15% of the residual ^{60}Co . The fractions of cobalt filtered out by the membrane filtration were: 0.45 μm no removal, 0.22 μm about 6% and 0.05 μm no removal. Ultrafiltration with the 5,000 NMWC (2-3 nm) membrane yielded 14% removal of cobalt. The filtration tests indicate that ^{60}Co is mainly present in the waste solution either as very small particles (diameter smaller than 2 nm) or as soluble ions and/or complexes. The inability of cation exchangers to remove cobalt from the solution, described below, suggests that most probably ^{60}Co is present as very small colloids or complexes.

Flocculation with Polyelectrolytes

Due to the high salt concentration and high pH, 11.5, no or very low flocculation of cobalt with polyelectrolytes were observed. Anionic and non-ionic polyelectrolytes Fennopol A392 and N200 (MW about 10^5) yielded no removal and cationic

Fennopol K1912 only about 10% removal. Use of these high molecular weight polyelectrolytes resulted in very viscous solutions, filtration of which was very time consuming. The highest removal, 13.5%, was obtained with a cationic polyelectrolyte Fennofix (MW ~ 50,000).

Precipitation

The efficiencies of common precipitation agents for the removal of cobalt from the evaporator concentrate at pH 7.0, 11.5 and ~13.6 are presented in Fig. 1. Coprecipitation with $\text{Co}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$, formed by addition of cobalt and iron(III) salt solutions, respectively, resulted in about 10% removal of ^{60}Co . Addition of $\text{Fe}(\text{CN})_6^{4-}$ together with cobalt carrier results in the formation of insoluble cobalt hexacyanoferrates, which coprecipitated 30% of ^{60}Co at pH 7. This was essentially higher than at higher pH values, probably due to higher proportion of ionic cobalt in the solution. These lower pH values are, however, not applicable in this case because of precipitation of borates is to be avoided. The highest removal with precipitation agents was obtained with sulphide (Fig. 1). It is understandable that sulphide performed best, since the solubility of CoS is much lower than those of $\text{Co}(\text{OH})_2$ and CoCO_3 (solubility products are $2 \cdot 10^{-25}$, $2 \cdot 10^{-16}$ and $1.4 \cdot 10^{-13}$, respectively). Optimization of pH, sulphide and cobalt carrier dosages yielded in 89% removal of ^{60}Co .

Ion Exchange

The uptakes of cobalt by chelating ion exchangers were very low or there was no uptake at all in many cases (Table I). The most effective resin was Imac GT 73 (Room & Haas) which removed 17% of cobalt. Chelating resins were ineffective under these severe conditions of high pH, high salt and interfering ion concentrations. Most probably only a small fraction of ^{60}Co was present in ionic form, capable for ion exchange reaction.

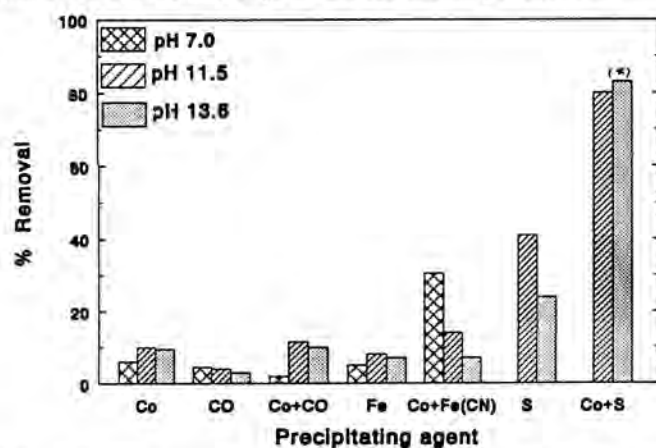


Fig. 1. Percentage removal of ^{60}Co with various precipitation agents from an evaporator concentrate at pH 7.0, 11.5 and ~13.6. Dosage of the agents 0.01 mol/L, in (*) 0.03 mol/L.

Most inorganic exchangers tested did not remove cobalt at all. Modified phlogopite mineral and manganese sulfide, however, took up 10.5% and 12.5% of cobalt, respectively, at pH 11.5.

Adsorbents

Because of the ineffective cobalt removal by ion exchangers some adsorbent resins and several commercial activated car-

bons were tested. The uptakes of cobalt by adsorbent resins were rather low: XAD-7, XAD-2 and Bio Beads SM-4 removed 11%, 21% and 27% of cobalt, respectively, at pH 11.5. More promising results were achieved by activated carbons (Table II) even though the cobalt adsorptions varied in a very wide range of 7 - 77%. Five products out of the fifteen carbons tested removed 50% or more at pH 11.5.

The number of products, fifteen, does not allow precise comparison of the products according to their raw material. However, the coconut shell based product showed somewhat poorer performance, $23 \pm 8\%$ removal, than those made of coal ($44 \pm 12\%$) and especially those made of peat ($53 \pm 19\%$).

CONCLUSIONS

None of the method tested alone yielded a satisfactory purification of the evaporator concentrate from cobalt under these conditions. However, the combination of some of the methods described has so far resulted in the removal of higher than 98%.

REFERENCES

1. J. LEHTO, R. HARJULA, E. TUSA and A. PAAVOLA, "Industrial Scale Removal of Cesium with Hexacyanoferrate Exchanger - Process Development", Proc. Waste Management '93 Symposium, Tucson, USA, February 28 - March 2, 1993, Vol. 2, p. 1693.

TABLE I
Uptake of Cobalt by Chelating Ion Exchangers
Solution pH 11.5

Exchanger	Functional Group	% Uptake
Amberlite IRC 718	iminodiacetic acid	11
Chelex 100	iminodiacetic acid	0
Chelite C	iminodiacetic acid	2
Diaion CR 20	polyamine	10
Diphonix	diphosphonic acid	0
Duolite ES 467	aminophosphonate	0
Imac GT 73	unknown	17
Lewatit TP 214	including S and N	13
Spheron Oxin	8-hydroxyquinoline	10
Spheron Salicyl	salicylic acid	0
Spheron Thiol	3-mercapto-2-hydroxypropyl	10
Varion BSM	mercaptile	11
Varion BTAM	including S and N	3
Varion BTKM	thiocarbamate	0

TABLE II
Adsorption of Cobalt from the Evaporator Concentrate on
Activated Carbons. The Particle Size 0.14-0.30 mm.
Solution pH 11.5.

Activated Carbon	Raw Material	% Adsorption
Chemviron carbons	coal	23-57
Diahope carbons	coal	46-50
Eurocarb carbons	coconut shell	7-31
Hydriffin carbons	coal	34-57
Hydriffin carbon	coconut shell	27
Norit carbons	peat	30-77