

Separation of Radiocobalt and Radionickel from NPP Evaporation Concentrates – 14395

Risto Koivula *, Risto Harjula *, Maria Kaipainen *

*Laboratory of radiochemistry, Department of chemistry, University of Helsinki

A.I.Virtasen aukio 1, PO Box 55,, P.O.Box 55, FI-00014 Helsinki, Finland

ABSTRACT

Selective removal of radiocobalt and radionickel from nuclear power plants (NPP) high salt evaporation concentrate is a challenge for every separation technique. This study demonstrates that ion exchange process, applying selective materials, can be used to separate cobalt and nickel from this difficult solution. Typical organic ion exchange resins and inorganic metal oxides, mainly four valent oxides were tested. The ion exchange experiments were done in high concentrated salt solution (2.75 M Na, 2M NO₃, 0.2M K, 1M B) representing evaporator concentrate. Based on the speciation data of nickel and cobalt and batch experiments it was concluded that practically all anionic species are taken up by the inorganic materials, representing about 90% and 15% of Ni and Co, respectively, at pH 11.7. From organic materials, the chelating materials reached the same uptake level but more typical strong/weak anion/cation exchange resins showed clearly lower uptake level with one exception. In dynamic column experiment at pH 11.5 sodium titanate showed promising uptake curve with approx. 5% break through level for over 2 500 bed volumes at feed rate of 20 bed volumes per hour.

INTRODUCTION

Nuclear power plants (NPP) produce large volumes of liquid radioactive waste and typically the volume of these waste solutions is decreased by evaporation. This evaporation concentrate contains high amounts of inactive metal ions such as K⁺, Na⁺ and Ca²⁺ and quite often only trace concentrations of radionuclides. Since further volume reduction of these liquids is favored highly selective separation techniques are required. For this selective ion exchange materials such as zeolites, titanosilicates, sodium-titanates and hexacyanoferrates have been used and large volume reductions have been achieved [1,2]. The advantage of inorganic ion exchangers over organic resins is their ability to resist decomposition at elevated temperatures and in ionizing radiation. Also the possibilities of safe storage and final disposal of the used materials have made these materials very interesting in nuclear waste management. Nevertheless inorganic ion exchangers have some serious disadvantages. The operating pH-range is usually rather narrow due to the low acidic nature of the exchange material (typical pK_a ~4), thereby limiting ion exchange use. Furthermore, the chemical stability of inorganic materials can be problematic, for example, the dissolution of aluminium from zeolites at pH extremes.

Selective removal of radiocobalt and radionickel from nuclear power plants (NPP) high salt evaporation concentrate is a challenge for every separation technique. This study demonstrates that ion exchange process, applying selective materials, can be used to separate cobalt and nickel from this difficult solution.

MATERIALS AND METHODS

Several different ion exchange materials were chosen ~~to~~ for this study. Typical strong and weak, cation/anion (Purolite C145/A500 and C106/A105) ion exchange resin were tested but also two chelating, iminodiacetate and aminophosphonate (Purolite S930 and S950), exchangers were chosen from organic materials. From inorganic materials, the main focus was on four valent metal oxides and their metal doped counterparts. Six different tin dioxides, two zirconium dioxides, alumina and sodium titanate (CoTreat®) were selected for the ~~to~~ test program. The ion exchange experiments were done in high concentrated salt solution (2.75 M Na, 2M NO₃, 0.2M K, 1M B) representing the evaporator concentrate of pressure water reactor and the pH of that solution was varied using concentrated nitric acid or NaOH solutions. The majority of the ion exchange experiments were static batch experiments at pH 7 or 11.7 but also a few dynamic minicolumn experiments were done to better verify the materials ion exchange properties in real application.

Static batch experiments were used to evaluate the metal uptake properties of the material. In batch experiments 20 mg of solid ion exchange material was equilibrated in 10 ml of test solution in a constant rotary mixer (50 rpm) for 24 hours during which time the solid/solution system reached equilibrium. The solid phase was then separated by centrifuging the vials for 10 minutes at 3000 G, and 5 ml aliquots of the supernatant were pipetted and filtered through a 0.2 µm filter (I.C. Arcodisc, Gellman Sciences) for the measurements of cobalt concentration by gamma spectrometric counting (Wallac 3" Wizard) and beta counting for nickel concentration measurements (Perking Elmer TriCarb). The equilibrium pH was measured from the remaining solution. The results from batch experiments are presented as distribution coefficients (K_d , ml/g) that reveal how the element of interest is distributed between the initial sample solution and the solid material after 1 day equilibration time. It was calculated as follows:

$$K_d = \frac{(A_i - A_{eq}) * V}{(A_{eq}) * m} \quad (1)$$

, where A_i = initial metal concentration (tracer activity) of the solution, A_{eq} = metal concentration of the solution at equilibrium, V = volume of the solution, m = mass of the solid material.

Dynamic column experiments were done in mini-columns (BioRad, Bio-Scale MT2 with the radius of 3.5 mm and 28-µm support). In the column experiments app. 1 g of dry material, corresponding to 1 ml as bed volume, was placed in the minicolumn and solutions were pumped through the column using ~20 bed volumes per hour flow rate. The effluent was collected by the fraction collector using 30 min collection time. From the effluent fractions the amount of nickel was measured using beta counting. The results from column experiments are presented as separation percentages.

WM2014 Conference, March 2 – 6, 2014, Phoenix, Arizona, USA

All reagents were of analytical grade. Radioactive tracers Co-57 (γ , 121 keV) and Ni-63 (β , 63 keV) were added to the test solutions at trace concentrations.

Metal speciation of the solutions was calculated using Visual Minteq program (table 1) [3].

Table 1. Nickel and cobalt speciation of the simulated evaporation concentrate solution at pH 7 and pH 11.7.

pH 7		pH 11.7	
Ni(2+)	21.864	NiOH(+)	0.044
NiOH(+)	0.028	Ni(OH)2 aq	11.198
NiNO3(+)	78.108	Ni(OH)3(-)	88.754
Cationic 100%		Anionic 88.8%, Neutral 11.2%	

pH 7		pH 11.7	
Co(2+)	13.605	CoOH(+)	0.337
CoOH(+)	0.028	Co(OH)2 aq	86.032
CoNO3(+)	30.668	Co(OH)3(-)	13.605
Co(NO3)2 aq	55.699	Co(NO3)2 aq	0.014
Cationic 44.3% Neutral 55.7%		Anionic 13.6% Neutral 86%	

RESULTS AND DISCUSSIONS

Comparing the speciation data of nickel and cobalt and the uptake percentages from batch experiments (table 2) it was concluded that practically all anionic species are taken up by the inorganic materials, representing about 90% and 15% of Ni and Co, respectively, at pH 11.7. This was a little bit surprising finding since some of the materials were considered purely as cation exchangers. The different sorption properties of different metals can be explained by the amount of neutral metal species in the solution. At lower pH, the cobalt uptake was clearly higher in comparison to its ionic speciation but here the most plausible explanation would be the drive to speciation equilibrium after the uptake of cationic species (24 h mixing time).

From organic materials, the chelating materials reached the same uptake level as the inorganic materials but the more typical strong/weak anion/cation exchange resins showed clearly lower uptake level with one exception. Weak cation exchanger showed almost 80% nickel uptake from pH11.7 solution.

WM2014 Conference, March 2 – 6, 2014, Phoenix, Arizona, USA

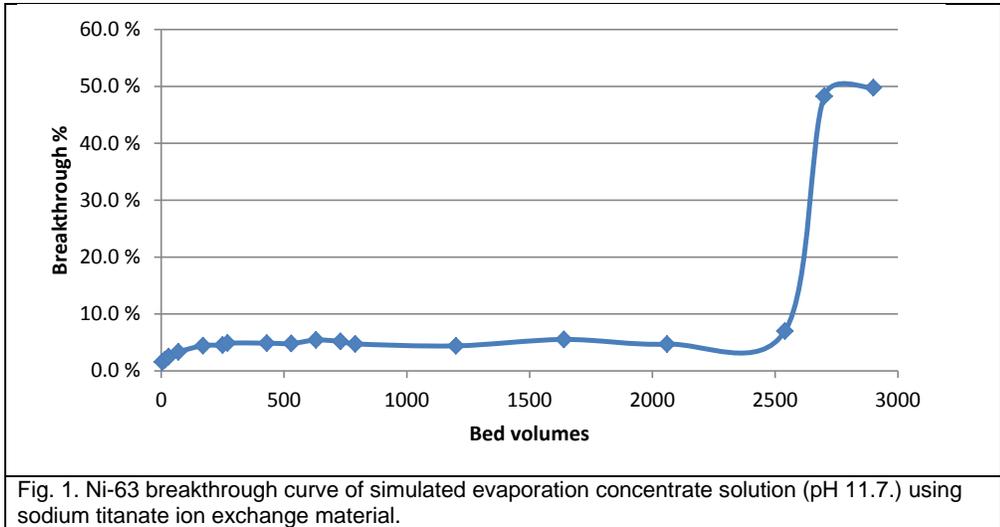
Table 2. Metal uptake percentage and distributions coefficients (Kd, ml/g) for Co-57 and Ni-63 from simulated evaporation concentrate solution using inorganic ion exchange materials.

Exchanger	Simulant at pH 7				Simulant at pH 11.7			
	Cobalt uptake (% / Kd)		Nickel uptake (% / Kd)		Cobalt uptake (% / Kd)		Nickel uptake (% / Kd)	
SnO2 A	88.8	3920	96	11980	14.5	80	90.2	4250
SnO2 B	90	4480	90.3	4650	19.6	120	90.2	4770
SnO2 C	87.3	3370	98	24020	17.9	100	91.7	5560
SnO2 D	92.4	5970	99.4	76280	29.1	190	91.2	4930
SnO2 E	90.3	4640	95.1	7960	15.4	90	87.4	3330
SnO2 F	94.2	8040	96.6	11910	39.8	340	92.7	6050
Al2O3	60.2	730	43.2	370	27.6	180	92.4	5760
ZrO2 A	68.8	1080	41.9	350	25.9	170	92	5740
ZrO2 B	54.7	610	77.1	1670	19	120	92.2	5930
Titanate	90.1	4600	37.7	300	26.9	180	92.2	5500

Table 3. Metal uptake percentage and distributions coefficients (Kd, ml/g) for Co-57 and Ni-63 from simulated evaporation concentrate solution using organic ion exchange resins.

Exchanger	Simulant at pH 7				Simulant at pH 11.7			
	Cobalt uptake (% / Kd)		Nickel uptake (% / Kd)		Cobalt uptake (% / Kd)		Nickel uptake (% / Kd)	
Strong cation	1.8	4	82.2	920	10	20	31.8	90
Weak cation	70.1	470	0	0	15.6	35	79.8	760
Strong anion	0	1	38.8	125	8.8	18	25.8	70
Weak anion	6.5	15	96	4730	9.9	20	25.7	65
Iminodiacetate	71.6	505	97.2	7090	18.1	45	89.9	1768
Aminophosphonate	90.5	1910	97.6	8195	16.6	38	85.5	1170

Dynamic minicolumn experiments were done for three best performing materials from which the sodium titanate showed the best results. The sodium titanate column showed promising uptake curve (Fig 1.) with approx. 5% break through level for over 2 500 bed volumes of simulated evaporation concentrate at pH 11.7 with a feed rate of 20 bed volumes per hour. This result correlates very well with the batch results suggesting that this material can be used for selective ion exchange of nickel.



The batch and minicolumn experiments demonstrated that the selectivity of inorganic materials is high enough for successful cobalt and nickel separations from the evaporation concentrate if only ion exchange process is considered. However, evaporation concentrates can have other components that seriously affect the ion exchange process, complexing agents for example. The effect of 4g/L of oxalate in the evaporation simulant at pH 11.5 decreased the metal uptake percentage only about 5 to 10% is consistent with the speciation data and metal oxalate species content. We did only a few batch tests with real evaporation concentrate from Loviisa NPP (PWR). In these tests, the sodium titanate again showed the best results but now reaching only 25% nickel uptake indicating that something is preventing the ion exchange process. Whether this is due to complexing agents or **something else what** is under further study at the moment.

CONCLUSIONS

From the batch and minicolumn tests done with several inorganic and organic ion exchangers in simulated evaporation concentrate it was concluded that in ion exchange perspective, selective ion exchange can be used to separate radio nickel and cobalt from highly concentrated waste solutions typical for pressure water nuclear power plant. From the tested materials the CoTreat®, sodium titanate showed overall best performance with high distribution coefficients and good column performance. However, in real applications other issues hindering ion exchange process has to be considered before the separation process. Particularly complexing agents and colloidal particles are seen as potential problems for the technique.

WM2014 Conference, March 2 – 6, 2014, Phoenix, Arizona, USA

REFERENCES

[1] J. Lehto, L. Brodtkin and R. Harjula, E. Tusa. Separation of radioactive strontium from alkaline nuclear waste solutions with the highly effective ion exchanger SrTreat. Nucl. Technol.. 127 (1999). 81.

[2] J. Lehto and R. Harjula. Selective separation of radionuclides from nuclear waste solutions with inorganic ion exchangers. Radiochim. Acta. 86 (1999). 65.

[3] J. P. Gustafsson. Visual Minteq. <http://www.lwr.kth.se/English/OurSoftware/vminteq/> (verified 10.01.2010). 51. 2 (2006).

Formatted: English (U.S.)