

REMOVAL OF RADIOACTIVE COBALT FROM  
HIGHLY SALINE STREAMS

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ABSTRACT

The removal of radioactive cobalt by ion-exchange from saline waters such as streams which contain high levels of brackish water or seawater is complicated by the complex chemical spectrum of cobalt in such streams and by the high concentrations of other ions such as sodium. Side by side comparisons of strong acid organic ion-exchangers typically used in nuclear power plant waste water clean-up and a novel new ion-exchanger, Durasil 70 have been carried out in the laboratory using synthetic waste streams and in an operating nuclear power plant (Salen Generating Station) using actual plant waste water. The results show the Durasil 70 to have a capacity at least 15 times greater than the organic resin. Durasil 70 also gives improved decontamination factors (DF) and allows for faster process times.

INTRODUCTION

The cobalt isotopes Co-60 ( $T_{1/2} = 5.27$  yr.), Co-58 ( $T_{1/2} = 71.3$  d.) and Co-57 ( $T_{1/2} = 270$  d.) are three of the most abundant and most important radionuclides which are present in the coolant and effluent streams of nuclear power plants. Part of the cobalt is generally present in the form of dissolved ions or compounds, but a large fraction of this element may be present in the form of colloids and solid particles of various sizes. Such solids may also contain other scarcely soluble species such as oxides, hydroxides, silicates and carbonates of various metals (e.g., Fe, Al, Mn, Mg, Ca). The distribution of cobalt species is highly dependent on the pH and on the salinity of the stream. In aqueous solutions with  $pH > 7$  and low salinity, most of the cobalt is present in a solid form, and it can be removed from the stream by filtration. At pH levels below neutral and low salinities, cobalt is mostly present in a dissolved cationic form, and is efficiently removed from solution by means of conventional ion-exchange media.

However, some nuclear power plants use brackish water for cooling of components. When service water is combined with plant waste streams, high salinity levels can occur in radioactive streams. Concentrations as high as 10-20% seawater have not infrequently been recorded. The average

composition of seawater includes 19.5 g/L (0.550 M)  $Cl^-$ , 2.72 g/L (0.02 M)  $SO_4^{2-}$ , 0.067 g/L (0.001 M)  $Br^-$ , 0.144 g/L (0.002 M)  $HCO_3^-$  and 0.001 g/L (0.0001 M)  $F^-$ .<sup>1</sup> All of these anions can form soluble complexes with cobalt. When the stability constants of these various complexes<sup>2</sup> are taken into account, it can be calculated that in a solution of 20% seawater in deionized water, pH (8.1), only 41% of the cobalt will be present as free  $Co^{2+}$  (more accurately, as  $Co(H_2O)_6^{2+}$ ). The other important species (omitting the aquo groups of the following complexes) are  $CoSO_4$  (54%),  $CoCl^+$  (4%),  $CoOH^+$  (1%),  $Co(OH)_2$  (0.02%),  $CoCl_2$  (0.01%) and  $CoBr^+$  (0.01%). The concentrations of anionic species such as  $CoCl_3^-$  are below 0.1%. Accordingly, the effectiveness<sup>3</sup> of ion exchange beds in removing cobalt from solutions containing high levels of brackish or seawater is expected to be quite small. In addition, seawater contains high concentrations of cations<sup>1</sup>, 10.5 g/L (0.457 M)  $Na^+$ , 1.35 g/L (0.056 M)  $Mg^{2+}$ , 0.40 g/L (0.010 M)  $Ca^{2+}$  and 0.38 g/L (0.010 M)  $K^+$ . The presence of these competing ions, including the divalent  $Mg^{2+}$  and  $Ca^{2+}$ , is expected to result in exhaustion of the removal capacity of cation exchange beds for cobalt when a relatively small number of column volumes of the saline stream have passed through.

## TEST RESULTS

### Laboratory

The above conclusions were confirmed in the following experiment: A solution of 600 nCi./L Co-60 (obtained from New England Nuclear Co. in the chloride form) was prepared in a medium which contained 80% of boric acid solution (500 mg/L boron) and 20% of simulated seawater<sup>1</sup> (27.2 g/L NaCl, 8.13 g/L MgCl<sub>2</sub>·6H<sub>2</sub>O, 1.59 g/L CaSO<sub>4</sub>·2H<sub>2</sub>O, 0.86 g/L K<sub>2</sub>SO<sub>4</sub>, 0.12 g/L CaCO<sub>3</sub>, 0.12 g/L MgBr<sub>2</sub>·6H<sub>2</sub>O, adjusted to pH 8.1 with 0.008 g/L NaOH). The pH of the mixed solution was 6.4-7.0. This solution was passed through a glass column containing a volume of 1 mL of Dowex HCR-S Nuclear Grade hydrogen form strongly acidic cation exchange resin, which is 8% cross-linked with a dry mesh size of 20-50 (0.30 - 0.85 mm). As shown in Fig. 1, extremely low decontamination factors for Co (below 2) were obtained even at the beginning of the experiment (100 column volumes). Similar experiments showed that plain silica powder is also ineffective. On the other hand, the specialized ion-exchange medium DURASIL 70, developed at The Catholic University of America, proved quite effective in removing Co-60 from the solution described above. When 10,500 column volumes of this solution were passed through the column the decontamination factor remained at a level of 120-300 throughout the run without showing significant decrease (see Fig. 1). When the number of column volumes exceeded 10,500 the decontamination factor started to decrease gradually, but it remained above 17 even at 13,000 column volumes. The residence time used in the column experiment was 4.6 minutes.

### Plant

Reactor waste streams are much more complex than the synthetic waste stream used above. Trace components such as oils and complexing species are often unique to a given plant and virtually impossible to analyze for. Subtle variations in pH and the oxidative or reductive nature of the stream can also affect stream chemistry and exchanger performance. Thus, the only meaningful test of an exchanger is its performance in the actual waste stream.

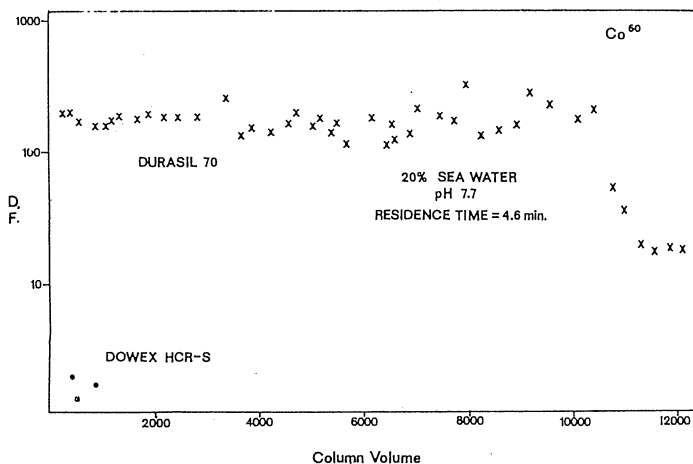


Fig. 1. Laboratory comparison of Dowex HCR-S and Durasil 70.

An on-site test of the Durasil 70 ion-exchanger media was conducted at the Public Service Electric & Gas Company's Salem Nuclear Generating Station between August 15 and 19, 1983. The purpose of this demonstration was to establish the relative performance of Durasil 70 and the organic resins similar to those currently in use at Salem under actual plant conditions and using plant waste water.

The Salem Nuclear Generating Station is a twin unit, 1100 MWe (each) PWR located on the tidal reaches of the Delaware River in southern New Jersey. Salem currently collects all waste streams including floor drains, equipment drains, laundry drains, laboratory drains, and other waste streams in a single tank and processes this waste through organic mixed-bed ion-exchange resin. The effluent from the demineralizers is sampled and discharged to the Delaware River. The expended resins are dewatered and disposed of at a nuclear land burial facility.

The test used a special system (shown schematically in Fig. 2) which allows simulation of various waste water treatment techniques using actual waste streams. In order to simplify waste feed to the system and to establish the relative performance of both methods under Salem's worse case conditions, a 200 gallon polyethylene tank was used to prepare and store the test water. This tank was filled with a mixture of Salem waste water (60%) and high salt service water (40%) to achieve a waste solution of approximately 10% seawater which is the worse case condition at Salem. Under these conditions, organic ion-exchangers have two major drawbacks: (1) they are exhausted relatively rapidly, after approximately 30 column volumes; and (2) they elute radioactive species previously loaded into the column.

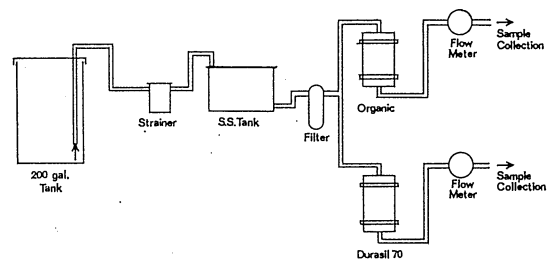


Fig. 2. Ion exchange test system.

The prepared waste water solution in the 200 gallon tank was analyzed at Salem and at the Vitreous State Laboratory at The Catholic University of America. The analyses correlate well and are presented below.

TABLE II

Sample Results  
Relative Performance of Durasil 70  
and Organic Ion-Exchangers

Sample No.	Column Volumes		Decontamination Factors				
	Organic	Durasil	Organic	Co-58	Durasil	Organic	Co-60
1	1.5	5.3	1.2	2.7	5.6	7.7	
2	5.6	26.0	14.1	9.7	50	9.8	
3	10.9	50.1	36	28	50	17.2	
4	16.8	75.4	6.8	102	5.3	50	
5	21.7	96.3	0.2*	0.6*	0.1*	0.3*	
6	27.1	119.4	2.2	100	2.1	50	
7	32.5	146.4	1.5	100	1.3	50	
8	38.4	174.9	1.3	84	1.3	50	
9		237.5		110		50	
10		297.0		0.07*		0.03*	
11		322.4		19*		9.4*	
12		384.1		32*		0.06*	
13		390.0		456		150	
14		443.3		122		50	
15		528.2		2.4*		4.4*	

\*Denotes probable sample bottle contamination

TABLE I

## Waste Water Composition

Species	VSL Analysis	Salem Analysis
Sodium	1240 ppm	1200 ppm
Chlorides	2560 ppm	2770 ppm
Boron	408 ppm	314 ppm
pH	7.7	7.9
Specific Conductivity		6830 umho
Co-58		1.34 E-4 uCi/ml
Co-60		4.00 E-5 uCi/ml

This solution corresponds to approximately 11.5% seawater.

Water from the 200 gallon tank was pumped through a coarse strainer and into the stainless steel holding tank (Fig. 2). Water from the holding tank was passed through a 5 micron filter and then split into two streams, one for each test column. The first stream was passed through a 1.2 liter column of organic mixed-bed resins, and the second through a 1.2 liter column of Durasil 70. The organic resin mix was approximately 1.05 liters of mixed-bed resins topped with approximately 0.15 liter of cation resin. This configuration corresponds to the system then in use at Salem. Residence time in the organic exchanger was 45 minutes, also corresponding to Salem's system. The Durasil 70 column contained 1.2 liters of Durasil 70. Residence time for this column was 10 minutes. The effluent from each stream was collected in a graduated plastic collection bottle for sampling and flow monitoring.

Throughout the test pump pressures ranged between 10 and 13 psi. Most of this pressure drop was across the 5 micron filter. Pressure drops across both columns were uniformly less than 1 psi throughout the test.

Initially, samples were taken from each stream every four hours. These samples were taken from the collection bottles at the end of each stream. These bottles were calibrated for volume

to allow total flows to be measured. At the end of each sample period, samples were withdrawn from each bottle, the bottles emptied and the volumes recorded. After the organic resins were expended and the organic stream shut down, effluent from the Durasil column was routed directly through the accumulating flow meter on the system and then directly to a floor drain. During this period, samples were taken every twelve hours from a sample port located on the outlet side of the Durasil column.

Samples were collected in polyethylene bottles and analyzed by Salem personnel for specific activity. The results of these samples are reported in Table II and shown on Fig. 3. As noted in the following section, the bottles used in the first twelve samples were previously used for routine sampling at Salem. Some of these bottles gave evidence of contamination. The last three samples were taken in new bottles.

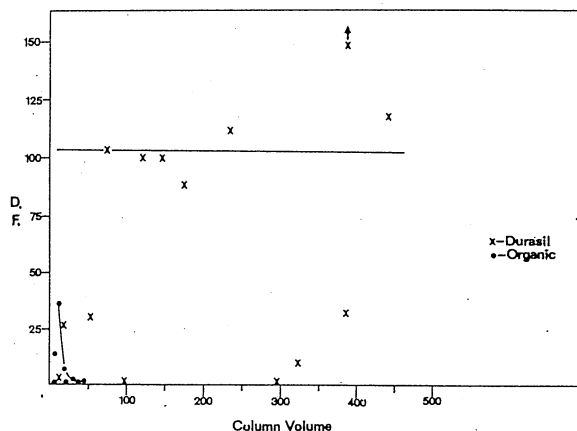


Fig. 3. Plant comparison of Dowex HCR-S and Durasil 70.

## PLANT RESULT

The results of the test are given in Fig. 3 and Table II. The organic resin was exhausted after 30 column volumes of waste were processed. The Durasil 70 column was still performing very well at the point at which the 200 gallon waste holding tank ran dry (approximately 525 column volumes). The maximum decontamination factor (DF) of the organic column was 36. For Durasil 70 the maximum DF was greater than 456 and the DF exceeded 100 for nearly the entire test.

Table III summarized the performance in the three important areas for both columns.

Table III

### Test Results

	<u>Durasil 70</u>	<u>Organic Resin</u>
Capacity (CV)	>528	30
DF (maximum)	456	36
(average)	100	10
Flow rate (CV/hr)	6	1.33

In operating terms, Durasil 70 will provide volume reduction factors of 15, reduce the amount of radioactive cobalt released to the environment by a factor of 10, while at the same time processing waste water at a rate 4.5 times faster than the organic system.

In reviewing and interpreting the specific sample data, the following points should be noted:

1. The increasing DF exhibited in samples 1 through 3 for both columns probably results from the progressive cleaning out of the system which may have contained some contamination from previous use. The increase in DF is found in both streams and is nearly identical with time.
2. The seemingly low DFs from samples 5, 10, 12 and probably 11 are most likely the result of contaminated samples. The bottles of samples 1 through 12 were obtained from the Salem count room and had been previously used. Samples 13 through 15 were taken using new bottles. Note that samples 12 and 13 were only six column volumes apart yet the DF for Co-60 for sample 12 (a used count room bottle) is 0.06 while that for sample 13 (new bottle) is greater than 150.
3. The final sample (15) was obtained from a filter housing after flow has been stopped and the liquid has sat in the housing for five to six hours. It is probably contaminated.

## CONCLUSION

The new ion-exchange media, Durasil 70, developed at the Vitreous State Laboratory of The Catholic University of America, has been shown to be significantly more effective for the removal of cobalt from highly saline waters than the strong acid ion-exchangers typically used for nuclear power plant waste stream clean-up. Side by side tests carried out in the laboratory and at the

Salem Generating Station shown the new media to have a significantly higher capacity, better DFs and a faster process rate.

## REFERENCES

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2. L. G. Sillen and A. E. Martell, Stability Constants of Metal-Ion Complexes, Special Publication No. 17, The Chemical Society, London, 1964; Supplement No. 1, Special Publication No. 25, The Chemical Society, London, 1971.