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## DEVELOPMENT OF THE FLOWSHEET USED FOR DECONTAMINATING HIGH-ACTIVITY-LEVEL WATER AT TMI-2

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## DEVELOPMENT OF THE FLOWSHEET USED FOR DECONTAMINATING HIGH-ACTIVITY-LEVEL WATER AT TMI-2

Soon after the accident at Three Mile Island Unit 2 Nuclear Power Station (TMI-2), samples of the Reactor Coolant System (RCS) water were sent to the Oak Ridge National Laboratory (ORNL) for analysis of the chemical and radiochemical constituents. The samples were also used for evaluation of potential methods for decontaminating the highactivity-level water and concentrating the radioactive contaminants into a readily disposable form.

Based on the analyses and test results, potential decontamination processes were considered, and recommendations were made to the TMI-2 Technical Advisory Group (TAG). The TAG selected a process which was based primarily on sorption of the bulk radioactive components, cesium and strontium, onto an inorganic ion exchanger, Linde Ionsiv IE-96, the sodium form of a chabazite-type of zeolite that was commercially available and had a history of successful, large-scale usage. Standard organic ion exchange resins were to be used to sorb the remaining traces of radioactive contaminants.

The processing system was designed by Allied General Nuclear Services for the Chem Nuclear Company, the prime contractor for equipment fabrication and installation. The process was designed so that the equipment items that were to contain high levels of activity were housed in one of the spent fuel handling pools in order to use the pool water for shielding. Therefore, the process was called the "Submerged Demineralizer System," or SDS--although the process was not intended to demineralize the water during its decontamination. The original SDS flowsheet was evaluated in a series of tests made at ORNL using 3 L of TMI-2 Reactor Building sump water.<sup>1</sup> The evaluation showed that the bulk of the cesium and strontium were sorbed on the zeolite, as expected, but that the subsequent treatment with organicbased polishing resins would not provide additional decontamination from cesium and strontium or removal of the minor contaminants, <sup>125</sup>Sb and 106<sub>Ru</sub>.

Process improvement tests were then made.<sup>2,3</sup> The initial step (removal of the bulk contaminants) was improved by evaluating mixtures of zeolite ion exchangers and selecting a mixture which enabled a significantly greater volume of water to be processed through the exchanger. During this work, a mathematical model was developed to predict the performance of the SDS process. Also, a special deionization/sorption technique was developed to remove the remaining radioactive contaminants from the zeolite effluent.

## Composition of the High-Activity-Level Water

The most important chemical and radiochemical components, the total amount present, and the concentrations in each body of water which existed at the time of process development are listed in Table 1. The total amount present was about 100 times that generated annually at all nuclear power stations in the United States. However, both the total amount and the concentrations were several orders of magnitude lower than would be typical at a fuel reprocessing plant.

The high-activity-level water consisted of two bodies----340  $m^3$  that remained in the closed loop, recirculating reactor coolant system and

	Reactor coolant system	Containment building water	Total
Volume	340 m <sup>3</sup>	2440 m <sup>3</sup>	2780 m <sup>3</sup>
Sodium	1350 mg/L	1200 mg/L	3400 kg
Boron	3870 mg/L	2000 mg/L	38,000 kg <sup>a</sup>
Cesium	1.5 mg/L	0.8 mg/L	2.5 kg
Strontium	<0.05 mg/L	0.1 mg/L	0.3 kg

Table 1. Composition of high-activity-level water

(Values are corrected for radioactive decay to July 1, 1980.)

Nuclide	Conc. (µCi/mL)	Relative ingestion hazard <sup>b</sup>	Conc. (µCi/mL)	Relative ingestion hazard <sup>b</sup>	Total (Ci)
3 <sub>H</sub>	0°11	60	1.0	300	2,500
89 <sub>Sr</sub>	5 <sup>c</sup>	2,000,000	0.53	200,000	3,000
90 <sub>Sr</sub>	25 <sup>c</sup>	80,000,000	2.3	8,000,000	14,000
106 <sub>Ru</sub>	0.1	10,000	0.002	200	40
125 <sub>Sb</sub>	0.01	100	0.02	200	50
<sup>134</sup> Cs	10	1,000,000	26	3,000,000	67,000
137 <sub>Cs</sub>	57	3,000,000	160	8,000,000	410,000
144 <sub>Ce</sub>	0.03	2,000	0.0005	50	10

<sup>a</sup>As boric acid.

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<sup>b</sup>Expressed as multiples of the concentrations listed in 10 CFR 20, Appendix B, Table II, Column 2.

CValues vary, probably because of precipitation.

~2440 m<sup>3</sup> that had spilled into the reactor containment building floor. The first samples of RCS water were obtained within only a few days after the accident and subsequent samples were taken periodically. However, the larger volume in the Containment Building Floor could not be sampled until an access probe was installed about 5 months after the accident.

Both bodies of water contained primarily sodium borate and boric acid and the pH values were 8.2 and 8.6. The boron content of all of the water represented a total of 38 tons of boric acid. This was particularly significant when considering evaporation or total demineralization as a method for concentrating the radioactive contaminants and decontaminating the bulk of the water.

In relation to the sodium and boron concentration, it is also significant to note the concentrations of cesium and strontium which were the primary radioactive materials. The radiocesium isotopes in both bodies of contaminated water were by far the predominant sources of gamma activity. They required that the decontamination process equipment be both shielded and operated remotely to prevent excessive exposure to operating personnel. The strontium concentrations were somewhat lower than the cesium, in terms of radioactivity, but were equally hazardous to human ingestion.

In addition to cesium and strontium, one of the important radioactive contaminants present in the waters was tritium. This heavy isotope of hydrogen was present as tritiated water in concentrations that were minute. This was fortunate because the tritium could not be removed by any practical separations process.

In addition to the water-soluble contaminants, a significant concentration of strontium was found in an insoluble form in samples of water taken from the bottom of the Containment Building. In each sample, the concentration of solids in the slurry (liquid plus solids) was about 0.5% by volume, as determined by centrifugation; however, both the amount and nature of the solid material in the slurry sample may not have been representative of the total solids within the building since the sample was taken from only one location. The key chemical and radiochemical constituents in the solids are listed in Table 2. Also, Table 2 shows the calculated percentage of each element and nuclide in the total sample (liquid and solid) that was in the solid phase.

## Process Flowsheets Considered for Decontamination of the Water

All the processes considered for the decontamination included ion exchange or evaporation, or both, as indicated by the flowsheets shown in Fig. 1.

The process flowsheets were compared on the basis of the estimated volume of waste concentrates generated and on the potential operating and maintenance problems. In general, the flowsheets that would generate the smaller volumes of waste were those that would allow selective removal of the radioactive contaminants while leaving the boron and sodium in the water.

The first flowsheet is that of a conventional ion exchange process such as used for decontamination of low-activity-level "radwaste" water during normal operation at nuclear power stations. Processes of this type are designed to sorb both anions and cations and, depending on the

Chemical element	Conc., mg/L solids	Percent in solid phase <sup>e</sup>	Radioactive nuclide	Conc., MBq/L solids	Percent in solid phase <sup>g</sup>
Copper	7500	99	90 <sub>Sr</sub>	1400	8
Nickel	2500	>98	89 <sub>Sr</sub>	320	8
Aluminum	1450	88	137 <sub>Cs</sub>	170	0.04
Iron	850	81	125 <sub>Sb</sub>	54	28
Silicon	650	10	144Ce	50	93
Calcium	450	<b>7</b> N	134 <sub>Cs</sub>	30	0.04
Zinc	400	>87	106 <sub>Ru</sub>	28	66
Chloride	400	10	95 <sub>Nb</sub>	5.2	97
Magnesium	150	10	60 <sub>Co</sub>	2.7	88
Sulfur	100	c	103 <sub>Ru</sub>	0.37	66

Table 2. Solids in containment building water

<sup>a</sup>Percentage of element or nuclide in total sample (liquid plus solid) that is in solid phase. Calculation based on solids content of 0.5% (vol.) in samples, as determined by centrifugation. <sup>b</sup>Concentration on July 1, 1980. <sup>c</sup>Not measured in water.

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Fig. 1. Process flowsheets considered for decontamination of high-activity-level water.

forms of the resins used, the process can be designed to totally demineralize the water or to sorb only the radioactive contaminants. For the special case at TMI-2, even the selective sorption of the radioactive contaminants would have generated a relatively large volume of highactivity-level solid waste because the use of large volumes of resin would have been necessary to keep the concentrations of sorbed nuclides low enough to prevent excessive radiation damage to the resin. Degradation of the resins would interfere with subsequent resin solidification, transfer, and storage operations.

In the second flowsheet, a periodic removal of cesium and strontium from the cation exchange resin by means of elution with acid would minimize the long-term radiation exposure and enable the use of a smaller volume of resin. The acid solution, containing most of the sodium originally in the water as well as the highly radioactive isotopes, would be concentrated by evaporation. The minimum volume obtained would be limited by the sodium sulfate concentration which, in typical operations, can be increased to about 22%. However, experience at nuclear power stations had indicated that evaporators required frequent maintenance, and since the maintenance of an evaporator containing highly radioactive materials would have to be done remotely, it would be significantly more difficult.

The maintenance problems would be even more severe if direct evaporation was attempted, as illustrated in the third flowsheet. In addition, a larger volume of high-level waste would be generated because the concentrate would contain the 38 tons of boric acid and typically the

concentration of such solutions is limited to about 6% boric acid to prevent plugging problems.

The fourth flowsheet would utilize an inorganic ion exchanger for sorption of most of the highly radioactive cesium and strontium, followed by evaporation for removal of all remaining radionuclides, except tritium. Inorganic ion exchangers, such as zeolites, were known to have a much greater degree of radiation stability than organic-based resins and a very high selectivity for cesium. Large-scale, successful operations using zeolites were a matter of record at several installations. In this flowsheet, the evaporator used would not contain the highly radioactive material; therefore, its operation and maintenance would not be as difficult. Another advantage of this flowsheet was that the use of evaporation as a polishing step would provide a dependable decontamination of the water in comparison to ion exchange processes which could be ineffective if non-ionic species and colloids were present. The only disadvantage to this flowsheet was that the evaporation would produce a large volume of boric acid concentrate; even though, in this case, the concentrate would be low-level wastes.

The fifth flowsheet also would use an inorganic ion exchanger for removal of most of the cesium and strontium but would use organic-based resins for polishing. The latter step would be effective for decontaminating the water if non-ionic species and colloids were not present in significant concentrations. Overall, this process would generate the lowest volume of waste concentrates. It is this flowsheet that, eventually, was selected for use at TMI-2.

## Evaluation of Potential Sorbents

Because of the desire to expedite the process design and equipment fabrication, an early process selection was made on the basis of the flowsheet considerations described above and the results of a few tests that could be made with the small samples of RCS water that was available.

Distribution coefficients between the RCS water and selected sorbents were measured and small scale ion exchange column tests were made using synthetic solutions traced with radioactive cesium or strontium. These tests were made to compare the loading performance of the various sorbents of interest and to indicate the effect of some of the process variables.

The breakthrough curves shown in Fig. 2 indicate the superiority of the zeolites for cesium sorption. IE-95 is a chabazite type of zeolite in the calcium form. It was selected for use at TMI-2, but in the sodium form, which is called IE-96.

Sodium titanate was not a good sorbent for cesium, but it was the best found for strontium. However, the titanate had only been produced in experimental amounts, and it had a soft, powdery texture which made it undesirable for use in large scale columns. It was tested as a mixture with IE-95, as shown in Fig. 3, but was not considered further.

The kinetics of strontium sorption were found to be generally slower than for cesium. IE-96 zeolite was found to be an acceptable sorbent for strontium if the column residence time was at least 10 minutes. Thus, IE-96 zeolite was selected by the TAG as the best sorbent for both cesium and strontium.



Fig. 2. Effectiveness of several inorganic sorbents for cesium loading.



Fig. 3. The effect of residence time on strontium loadings for a variety of sorbents.

 $^{89}$ Sr tracer (150 µC1/L - 4000 mg/L Na - 25°C)

#### Evaluation of the Original Flowsheet

The original SDS flowsheet, shown in Fig. 4, called for the contaminated water to be clarified and then passed through a series of ion exchange columns. Four small columns, each containing about 225 L of sorbent, were to be located within the spent fuel pool. The first three were to contain IE-96 zeolite and the fourth was to contain a strongacid type cation exchange resin. The manner of operation was designed to accommodate the needed contact time (>10 minutes) for strontium sorption.

The columns were modular and were intended to be used as the radioactive waste containers after being loaded. The flowsheet called for the columns to be moved after processing each  $50 \text{ m}^3$  of water. This was equivalent to about 200 bed volumes, based on each column. At that point, the column in the first position was to be discharged, the other two moved forward one position, countercurrent to the flow of water, and a new column installed in the third position. In this manner, the cesium would be loaded in the column in the first position and all three columns would provide a sufficient contact time for strontium sorption.

The original flowsheet was conservatively designed and would have required at least 60 columns to process all of the high-activity-level water.

The SDS process was evaluated in a series of small-scale tests using 3 L of TMI-2 Containment Building water. These tests showed that the bulk of the cesium and strontium were effectively adsorbed on the zeolite, but that the subsequent treatment with organic-based cation and polishing resins would not provide additional decontamination.

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#### Process Flowsheet Improvements

Process improvement tests were then begun. The objectives were (1) to obtain increased loadings of cesium and strontium in the zeolite columns and (2) to develop an effective method for the polishing decontamination of the effluent water from the zeolite columns.

Improved Loading of Zeolite Columns. During evaluation of the SDS flowsheet, a 1000 bed volume test had been made. The results had indicated that as much as about 600 bed volumes could be processed before strontium breakthrough from the third column would occur. Since the organic cation resin, which originally was to be used in the fourth column, was found to be ineffective for providing additional decontamination, consideration was given to using zeolite in the fourth column in order to provide backup capability. Then, the throughput could be increased to 600 bed volumes while maintaining a sufficient safety margin.

A further increase in loading was envisioned after a more "strontium specific" zeolite, Linde A-51, was identified. The use of both IE-96 zeolite for cesium sorption and A-51 zeolite for strontium sorption in either mixed beds, layered beds, or in alternate columns was considered. The use of alternate columns would mean that two types of columns would have to be kept up with and perhaps treated differently during subsequent waste solidification operations. The use of layered columns could mean that the bottom layer could be adversely affected if flow distribution at the bottom of the column was not efficient. Therefore, the use of mixed columns appeared to be most appropriate.

A 1500-bed volume test was then made with TMI-2 Containment Building water and a mixed zeolite containing equal parts of IE-96 and A-51. The breakthrough curves obtained in that test for cesium and strontium are compared in Fig. 5 with those obtained while using only IE-96.

The cesium breakthrough when using only IE-96 was less than 0.01% during the entire test, but the strontium broke through early. When using the mixed zeolite, the capacity for strontium sorption was increased by a factor of about 10, even though the kinetics of the strontium sorption, as indicated by the lesser slope of the breakthrough curve, were somewhat slower. The capacity for cesium was adequate for a throughput of about 200-bed volumes. That loading would still allow a ten-fold increase in column throughput.

A series of tracer-level tests was made to determine the effect of the mixed zeolite ratio on cesium and strontium breakthrough. A sufficient volume of TMI-2 water was not available for these tests, so a synthetic solution was formulated to a chemical composition similar to the TMI-2 Containment Building water and was traced with radioactive cesium and strontium.

Ratios of IE-96 to A-51 of 3/1, 2/1, and 1/1 were tested. A balanced loading of cesium and strontium was the goal but, if any uncertainty existed, the choice was to obtain better cesium loading because breakthrough of the gamma emitters (radiocesium isotopes) would not be satisfactory. The results of the single column tests, shown in Fig. 6, indicated that the proper ratio for balanced loading of cesium and strontium was between 2/1 and 1/1.



Fig. 5. Comparison of performance of single zeolite and mixed zeolite.



Fig. 6. Results of tracer-level column tests.

<u>Modeling of Zeolite Column Performance</u>. The tests provided breakthrough data for only one column. Therefore, the data were fitted by means of the mathematical "J-function", using the constant separation factor model developed by Thomas,<sup>4</sup> to enable calculation of the mass transfer coefficients and extrapolation of the data to obtain the estimated performance of a second, third, and fourth column in series.

The general Thomas equation for the reaction kinetics of ion exchange in a fixed bed is as follows:

$$- \frac{\partial X}{\partial N} = \frac{\partial Y}{\partial NT} = X(1 - Y) - RY(1 - X), \qquad (1)$$

where X and Y are the dimensionless concentrations of the solute ion in the fluid and solid phases, respectively, and R is the separation factor. The variable X is defined as  $C/C_0$ , where C and  $C_0$  are the concentrations of the solute ion of interest in the effluent and feed solutions, respectively. The variable Y is defined as  $q/q^*$ , where q is the actual concentration in the solid phase, and  $q^*$  is the concentration in the solid phase when it is in equilibrium with fluid at the inlet concentration,  $C_0$ . When the concentration of the solute ion is small relative to the concentration of the replaceable ion in the feed (as it is in this case), R approaches unity, and the isotherm is linear.

The variable N represents the length of the exchange column in transfer units and is defined by the expression

$$N = K_d \rho_B K_a / (f/v) , \qquad (2)$$

in which  $K'_d$  is the distribution coefficient when X = 1,  $\rho_B$  is the bulk density of the ion-exchanger,  $K_a$  is the mass-transfer coefficient characteristic of the system, f is the rate of flow of solution through the column, and v denotes the overall volume of the sorbent bed, including the void spaces. The throughput parameter, T, is defined approximately by:

$$T = (V/v)/K_{A}\rho_{B}, \qquad (3)$$

where  $\nabla$  is the volume of solution processed through the column. Note that  $\nabla/v$  is the number of "bed volumes" of solution.

Since  $\rho_B$  is essentially constant, it is convenient to define a volume-basis distribution coefficient,  $K_d = q_v/C_0$ , where  $q_v$  is the concentration of the solute ion per unit volume of the sorbent bed (sorbent plus void space) and  $C_0$  is the concentration in the feed solution. Equations (2) and (3) can then be expressed as

$$N = K_{d}K_{a}/(f/v) , \qquad (2a)$$

and

$$T = (V/v)/K_d$$
 (3a)

Equation (1) has been integrated [Eq.(16-128a) in ref. 5] for the special case of reversible second-order reaction kinetics (appropriate to ion exchange) with the solution being

$$X = C/C_0 = \frac{J(RN, NT)}{J(RN, NT) + [1 - J(N, RNT)] \exp[(R - 1)N(T - 1)]}, \quad (4)$$

where J is a mathematical function<sup>5</sup> related to the Bessel function,  $L_0$ .

For large values of RN (a condition approached in SDS operation and in the small-scale tests),  $C/C_0 = \sim 0.5$  when T = 1, independent of the values of RN. This characteristic can be employed in the data analysis. Experimental data can be used to construct logarithmic-probability plots of  $C/C_0$  vs V/v. These plots are nearly linear and can be used to estimate K<sub>d</sub>, which is approximately equal to V/v at the point where  $C/C_0 =$ 0.5. Values of R and N can then be obtained from the experimental data through the iterative use of Eqs. (3a) and (4).

A numerical solution model of the Thomas equation was developed to accept input data in a form that simulates the cyclical mode of operation proposed for the SDS. A numerical solution was required to analyze the multibed system in which the partially loaded columns are ved forward (countercurrent to the water flow) periodically, because an analytic solution is not practical unless the initial loading on each bed is zero.

The four columns of the SDS were represented in the model by two 4000-point arrays (one each for X and for Y), using 1000 points for each column. Calculations were carried out to simulate the passage of the desired volume of feed through the four columns in series, with initial values of zero for X(n) and Y(n) for all points.

At the end of the first feed cycle, the values of X(n) and Y(n)were replaced by the previously calculated values of X(n + 1000) and Y(n + 1000) for values of n between 1 and 3000 and were set equal to zero for values of n between 3001 and 4000. This procedure simulated removing the first column, moving the last three columns forward one

position, and putting a new column in the fourth position. The calculations were then repeated for another cycle, using this configuration as the initial condition. This modeled rotation procedure was repeated for the number of cycles necessary to process the total volume of HALW.

Predicted and Actual Zeolite Column Performance. By interpolating between the experimentally derived distribution coefficients and the calculated mass transfer coefficients and separation factors for 1:1 and 2:1 zeolite mixtures, values were derived for the 3:2 mixture. These values are shown in Table 3, along with corrected values obtained from early SDS operations. The observed differences were not greatly significant, even though the scaleup factor from the test column size to the SDS column size was  $\sim 10^5$ . Whereas the test column data indicated nearly balanced loading of cesium and strontium, the actual data showed similar performance for strontium but better performance for cesium. As shown in Table 4, using the early SDS data, cesium and strontium breakthroughs were calculated for six loading cycles in which 2760 m<sup>3</sup> of HALW are processed (460  $m^3$  in each cycle). Although the strontium breakthrough continued to increase throughout the six cycles, the breakthrough from the fourth column did not exceed the concentration (0.1%) of the nonexchangeable species of strontium which had been experimentally observed in the HALW. The number of zeolite columns used to process the bulk of the HALW at TMI-2 was reduced to ~10.

Improvement of Polishing Decontamination Method. Results from the evaluation tests on the original SDS flowsheet showed that the effluent water from the zeolite columns contained residual radiocesium and

	Test col	umn data	SDS column data	
Parameter	Cesium	Strontium	Cesium	Strontium
Distribution coefficient $(K_d)$	2805	3760	3800	3000
Mass transfer coefficient (K <sub>a</sub> )	$8.0 \times 10^{-4}$	2.9 x $10^{-4}$	$2.2 \times 10^{-3}$	5.6 x 10 <sup>-3</sup>
Separation factor (R)	1.15	1.65	1.0	1.0

Table 3. Comparison of predicted and actual performance parameters for cesium and strontium

		Cu	mulative	breakthro	ugh (% of	feed)			
		Cesium				Strontium			
Cycle	Column	Column	Column	Column	Column	Column	Column	Column	
number	1	2	3	4	1	2	3	4	
1	0.62	a	а	a	13.8	0.18	a	a	
2	0.71	a	a	а	22.9	0.92	a	а	
3	0.73	а	а	а	29.5	2.14	а	а	
4	0.73	а	а	a	34.5	3.62	0.17	а	
5	0.73	a	а	a	38.3	5.21	0.35	а	
6	0.73	а	а	a	41.4	6.81	0.60	8	

## Table 4. Calculated cumulative breakthrough of cesium and strontium for six cycles of column replacement

<sup>a</sup>Calculated breakthrough less than observed concentrations (0.003% of cesium and 0.1% of strontium) of nonexchangeable species.

radiostrontium with concentrations of about  $10^{-3} \mu \text{Ci/mL}$ . Also, the effluent water contained anionic radionuclides, <sup>125</sup>Sb and <sup>106</sup>Ru, with concentrations of  $10^{-2} \mu \text{Ci/ML}$  and  $10^{-3} \mu \text{Ci/mL}$ , respectively.

Filtration tests were made and indicated that the residual cesium and strontium were in the form of either non-ionic colloids or absorbed on colloids of other materials. Thus, these contaminants could not be removed by ion exchange methods unless the water was treated to change the chemical nature of the residual cesium and strontium.

During the flowsheet evaluation tests, indications were that, if the zeolite effluent water could be allowed to age for at least several hours before contact with the polishing sorbents, further decontamination could be obtained. The theory was that the residual species were ionic but were sorbed on colloids of other materials in the water and that, if the exchangeable species were first removed from the water, the material sorbed on the colloids would reequilibrate with the water during the aging period and become susceptible to removal by subsequent ion exchange treatment.

A series of tests was designed to investigate the effects of aging times from 3.6 to 605 ks (2 h to 7 d) at ambient conditions, at an elevated temperature (75°C), at a reduced pH level (pH = 6), and at combinations of these conditions. Further, a comparison was made of the use of either IE-96 zeolite or a cation exchange resin (Nalcite HCRS, in the sodium form) for the polishing treatment after the aging period. The results of these tests showed that significant reductions of the cesium and strontium concentrations could be obtained by aging for at least 2 h at 75°C.

In contrast to the nature of the residual cesium and strontium, none of the antimony and only about one-third of the ruthenium were indicated by ultra-high-speed centrifuging tests to be in a colloid form. The antimony and ruthenium were initially sorbed in anion exchange column tests; however, breakthrough occurred early at a point which coincided with breakthrough of sodium from the preceding cation exchange beds. Subsequently, distribution measurement tests were made to obtain an understanding of this effect. First, the sodium was removed from the water by cation exchange with an acid-form resin. This lowered the pH of the water, as shown in Table 4, and enabled an exponential increase in the distribution coefficients of ruthenium and antimony in the subsequent distribution tests with a strong-base anion exchange resin (Nalcite SBR, in the borate form). These results can be explained by the hypothesis that the contaminants were not sorbed effectively by the anion exchange resin because of competition from the large concentration of borate ions in the water. Further, by removing the sodium, the borate ions were converted to weakly-ionized boric acid, thereby removing the competitive effect. Thus, removal of the sodium was, in effect, a deionization of the water.

The results also indicated that a smaller, but still significant, reduction of the residual cesium and strontium concentrations could be obtained at the lower pH levels.

The penalty for using this method would be the generation of a relatively large volume of low-activity-level waste ion exchange resin, which would be necessary to sorb the sodium. In comparison to the highactivity-level zeolite wastes that would be generated during removal of

Distribution coefficient with SBR (H <sub>2</sub> BO <sub>3</sub> -)						
106 <sub>Ru</sub>	125 <sub>Sb</sub>	90 <sub>Sr</sub>	137 <sub>Cs</sub>			
16	29	1	1			
54	210	1	5			
2200	1500	21	23			
	106 <sub>Ru</sub> 16 54 2200	106 <sub>Ru</sub> 125 <sub>Sb</sub> 16 29   54 210   2200 1500	IO6Ru I25Sb 90Sr   16 29 1   54 210 1   2200 1500 21			

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# Table 4. Sorption of residual radioactive components by strong-base anion exchange resin

<sup>a</sup>pH adjustment by means of cation exchange.

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the cesium and strontium, a 20-fold greater volume of cation and anion exchange resin would be required for removal of the sodium and the anionic contaminants.

Other methods were tested. These included neutralization of the sodium by addition of various acids, evaluation of other anion exchange resins, use of a boron-complexing agent, and use of a variety of other sorbents, such as high-surface-area glass, titanates, zeolites, and molecular sieves. However, none of the methods appeared to be usable except that in which the pH is reduced by means of sodium removal on a cation exchange resin followed by sorption of the contaminants on anion resin.

#### Summary

Using a few small samples of high-activity-level water from TMI-2, a chemical processing flowsheet was developed for decontamination of the water and concentration of the radioactive contaminants in a form suitable for disposal. The initially selected process was evaluated and significantly improved. The improved process included (1) sorption of the bulk radioactive materials, cesium and strontium, onto a mixture of inorganic zeolites and (2) sorption of the anionic contaminants, antimony and ruthenium, plus the remaining traces of cesium and strontium onto standard organic ion exchange resins. The latter step was accomplished by means of a special deionization/sorption technique.

## References

- Campbell, D. O., et al., "Evaluation of the Submerged Demineralizer System (SDS) Flowsheet for Decontamination of High-Activity-Level Water at Three Mile Island Unit 2 Nuclear Power Station," ORNL/TM-7448 (1980).
- Campbell, D. O., et al., "Process Improvement Studies for the Submerged Demineralizer System (SDS) at the Three Mile Island Nuclear Power Station, Unit 2," ORNL/TM-7756 (1982).
- Collins, E. D., et al., "Water Decontamination Process Improvement Tests and Considerations," AIChE Symposium Series 213, <u>78</u> (1982) 9.
- Hiester, N. K., Vermeulen, T., Klein, G., Chemical Engineers' Handbook, Fourth ed. (Perry, J. H., et al., Eds) McGraw-Hill, New York (1963) 16-2.
- 5. Hiester, N. K., Vermeulen, T., Chem. Eng. Prog., <u>48</u> (1952) 505.

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