

FLOWSHEET DEVELOPMENT STUDIES FOR THE DECONTAMINATION OF
HIGH-ACTIVITY-LEVEL WATER AT THREE MILE ISLAND UNIT 2

E. D. Collins, J. E. Bigelow, D. O. Campbell, L. J. King, and J. B. Knauer

Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37830

MASTER

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

For Presentation at the 89th National Meeting of the
American Institute of Chemical Engineers, Portland, Oregon
August 17-20, 1980

By acceptance of this article, the publisher or recipient acknowledges the U.S. Government's right to retain a non-exclusive, royalty-free license in and to any copyright covering the article.

* Operated by Union Carbide Corporation under contract W-7405-eng-26 with the U.S. Department of Energy.

FLWSHEET DEVELOPMENT STUDIES FOR THE DECONTAMINATION OF
HIGH-ACTIVITY-LEVEL WATER AT THREE MILE ISLAND UNIT 2

E. D. Collins, J. E. Bigelow, D. O. Campbell, L. J. King, and J. B. Knauer

ABSTRACT

Several chemical processing flowsheets were considered for the decontamination of high-activity-level water at the Three Mile Island (TMI) Unit 2. A zeolite ion exchange process was evaluated and recommended for absorption of the bulk of the highly radioactive cesium and strontium. Standard organic ion-exchange resins were selected to remove the remaining traces of radioactive nuclides (except tritium which cannot be removed by any practical process). Process conditions were evaluated using both synthetic, tracer-level solutions and samples of actual, high-activity level water from TMI Unit 2.

FLWSHEET DEVELOPMENT STUDIES FOR THE DECONTAMINATION OF
HIGH-ACTIVITY LEVEL WATER AT THREE MILE ISLAND UNIT 2

E. D. Collins, J. E. Bigelow, D. O. Campbell, L. J. King, and J. B. Knauer

Approximately 3000 m³ of water were contaminated with relatively large amounts of radioactive materials during the accident at the Three Mile Island (TMI) Unit 2 Nuclear Power Station in March 1979. The largest portion of this high-activity level water (HALW), about 2650 m³, spilled onto the floor of the Reactor Containment Building and collected there. However, the 340 m³ of circulating cooling water in the closed-loop Reactor Primary Coolant System (RCS) also remains highly contaminated. The first of several samples of the RCS was obtained within a few days after the accident but the larger quantity in the Containment Building floor could not be sampled until an access probe was installed about five months later. Several of the samples were sent to Oak Ridge National Laboratory (ORNL) for chemical and radiochemical analyses. A team of chemists and chemical engineers at ORNL, in conjunction with the Technical Advisory Group to the TMI-2 Recovery Staff of General Public Utilities Company (GPU), evaluated potential flowsheets for decontamination of the HALW and recommended a clarification--zeolite ion exchange process. A processing system was designed by Allied General Nuclear Services (AGNS) for Chem-Nuclear Systems, Inc. (CNSI), the prime contractor for fabrication, installation, and operation of the process equipment. The processing facility, which is called the Submerged Demineralizer System (SDS), is being installed in one of the spent-fuel handling pools at TMI.

Analyses of the Contaminated Waters

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

Both waters contain sodium borate and boric acid; the pH is 8.2 in the RCS water and 8.6 in the Containment Building water. Of the radio-nuclides now present, ^{137}Cs and ^{90}Sr will require the greatest amount of decontamination to reach limits specified by 10CFR20, Appendix B, Table II, Column 2. Although these limits do not represent specifications for discharge from TMI-2, they do indicate the relative hazards of the radio-nuclides and are useful for estimating the degree of decontamination required. (The degree of decontamination is expressed herein as the decontamination factor, or DF, which is the ratio of the concentration of a particular nuclide in the process feed solution to its concentration in the product solution.) In the case of decontaminated water from TMI, special NRC approval will be required for final disposition. Since an approved method has not been chosen, the utility is building tanks which will be used for on-site storage of the decontaminated water for an indefinite period.

In addition to cesium and strontium, one of the important radioactive contaminants present in the waters is tritium (half-life = 12.3 y). This heavy isotope of hydrogen is present as tritiated water in concentrations that are minute but are still slightly more than the 10CFR20 limits.

TABLE 1. CONTAMINATED WATER COMPOSITION

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

	Reactor Coolant System		Containment Building Water		Total Present
Volume	340 m ³		2650 m ³		3000 m ³
Sodium	1350 mg/l		1200 mg/l		3600 kg
Boron	3870 mg/l		2000 mg/l		38000 kg (as H ₃ BO ₃)
Cesium	8 mg/l		0.8 mg/l		4.8 kg
Strontium	0.5 mg/l		0.1 mg/l		0.4 kg
Nuclide	Conc., MBq L	Relative Ingestion Hazard ^a	Conc., MBq L	Relative Ingestion Hazard ^a	Total, TBq
³ H	6.3	60	37	300	100
⁸⁹ Sr	190 ^b	2,000,000	20	200,000	120
⁹⁰ Sr	930 ^b	80,000,000	85	8,000,000	540
¹⁰⁶ Ru	3.7	10,000	0.07	200	1.4
¹²⁵ Sb	0.4	100	0.74	200	2.1
¹³⁴ Cs	370	1,000,000	970	3,000,000	2,700
¹³⁷ Cs	2100	3,000,000	5800	8,000,000	15,400
¹⁴⁴ Ce	1.1	2,000	0.02	50	0.4

^a Expressed as multiples of limits of 10CFR20, Appendix B, Table II, Column 2.^b Values vary, probably because of precipitation.

The tritium cannot be removed by any current practical process but can be handled easily by dilution with uncontaminated water after the other radioactive materials have been removed.

The radiocesium isotopes in both bodies of contaminated water are by far the predominant sources of gamma activity. Until the cesium concentrations have been reduced by several orders of magnitude, the decontamination process equipment must be both shielded and operated remotely to prevent excessive exposure to operating personnel.

The concentration of ^{90}Sr in the RCS water increased from 15 to 450 MBq/L during the first month following the accident and has increased further to about 1000 MBq/L.¹ This behavior is in contrast to the concentrations of cesium and tritium which have decreased in a manner consistent with observed leakage rates of the contaminated water from the RCS (and with dilution by makeup water). The increased strontium concentration may have been due to continued leaching of exposed fuel, but, more likely, it has been caused by redissolution of a precipitated strontium form, such as strontium sulfate. Whatever the cause, the practical implication is that additional strontium may be dissolved during the decontamination process.

A significant concentration of strontium has been 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 be non-representative of the total solids within the building since the sample could be taken from only one location. The key chemical and radiochemical constituents in the solids are listed in Table 2. Also, Table 2

TABLE 2. SOLIDS IN CONTAINMENT BUILDING WATER

Chemical Element	Conc., mg/L Solids	Percent Insoluble ^a	Radioactive Nuclide	Conc., MBq/L Solids ^b	Percent Insoluble ^a
Copper	7500	99	⁹⁰ Sr	1400	8
Nickel	2500	≥98	⁸⁹ Sr	320	8
Aluminum	1450	88	¹³⁷ Cs	170	0.04
Iron	850	81	¹²⁵ Sb	54	28
Silicon	650	10	¹⁴⁴ Ce	50	93
Calcium	450	7	¹³⁴ Cs	30	0.04
Zinc	400	≥87	¹⁰⁶ Ru	28	66
Chlorine	400	10	⁹⁵ Nb	5.2	97
Magnesium	150	10	⁶⁰ Co	2.7	88
Sulfur	100	c	¹⁰³ Ru	0.37	66

^aPercentage of element or nuclide in total sample (liquid plus solid) that is insoluble. Calculation based on solids content of 0.5% (vol.) in sample, as determined by centrifugation.

^bConcentration on July 1, 1980.

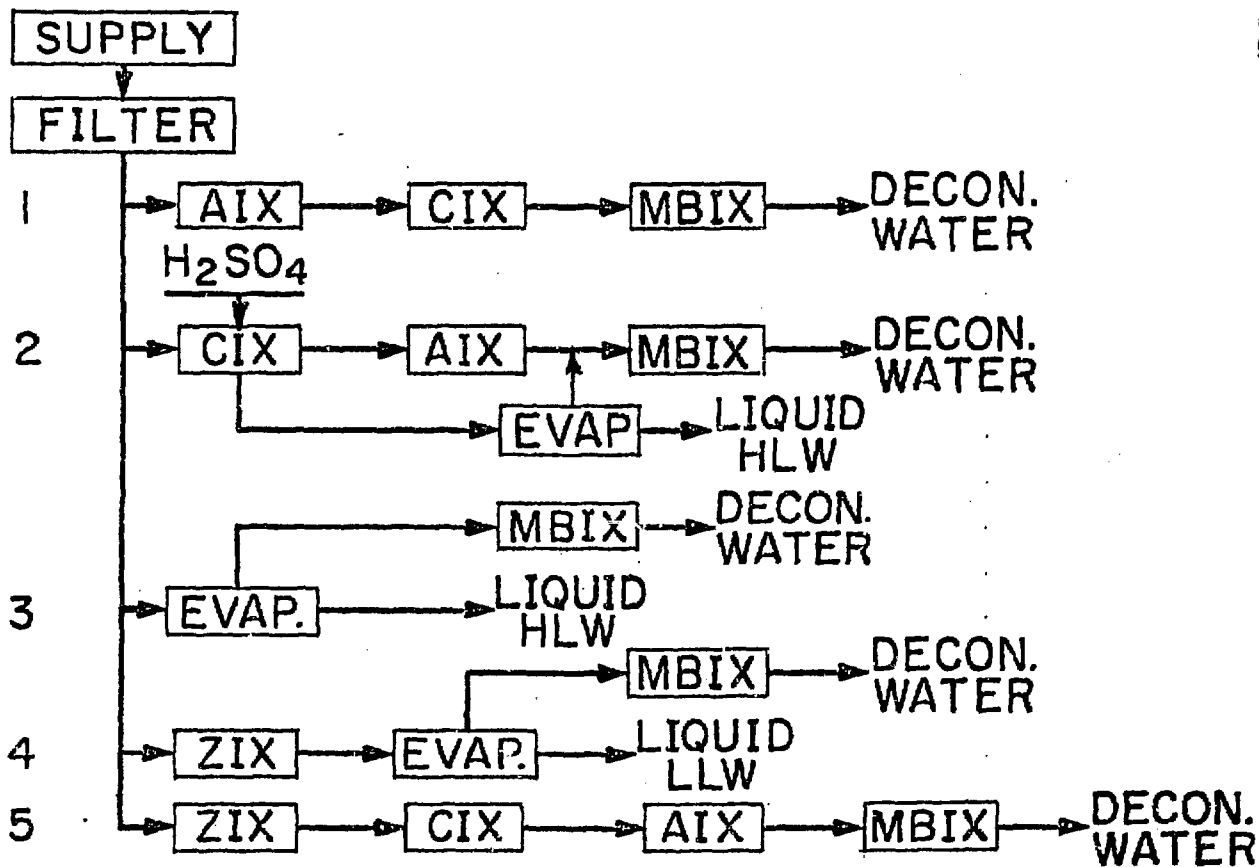
^cNot measured in water.

shows the calculated percentage of each element and nuclide in the total sample (liquid and solid) that was insoluble. Although the strontium was the predominant radionuclide in the solids, 92% of the total strontium in the sample was in the liquid phase. Essentially all of the cesium was in the liquid phase. Thus, even if these solids are dissolved during the decontamination process, the total amount of radioactive materials in the water should not be increased significantly.

Process Flowsheet Considerations

All processes considered for concentration of the radioactive nuclides and decontamination of the excess water have included ion exchange or evaporation or combinations of both. Clarification of the contaminated water by means of filtration has been considered in all cases. Several of the process flowsheets initially considered are illustrated in Fig. 1 and are compared on the basis of the estimated volume of waste concentrates that would be generated. In general, the flowsheets that would generate the smaller volumes of waste are those that would allow selective removal of the radioactive contaminants while leaving the predominant solutes, boron and sodium, in the decontaminated water. In addition to the volumes of waste, potential operating and maintenance problems were considered in the selection of an appropriate process.

The first flowsheet illustrated in Fig. 1 is that of a conventional ion exchange process such as that used for decontamination of low activity level water during normal operation at nuclear power stations. Processes of this type are designed to sorb both anionic and cationic contaminants; depending on the forms of the resins used, the process can be designed to totally demineralize the water or to sorb only the radioactive contaminants.



EST. WASTE VOL., m ³	
HIGH LEVEL	LOW LEVEL

1600	20
80	40
400	20
15	400
15	15

LEGEND

AIX = ANION EXCHANGE
 CIX = CATION EXCHANGE
 MBIX = MIXED RESIN ION EXCHANGE
 DECON. WATER = DECONTAMINATED WATER

ZIX = ZEOLITE ION EXCHANGE
 EVAP. = EVAPORATION
 HLW = HIGH LEVEL WASTE (Cs + Sr)
 LLW = LOW LEVEL WASTE

FIG. 1. PROCESS FLOWSHEETS CONSIDERED FOR DECONTAMINATION OF HIGH ACTIVITY LEVEL WATER.

For the special case of decontaminating the HALW at TMI, even the selective sorption of only the radioactive contaminants would generate the relatively large volume of high-activity-level waste shown if organic-based resins are used. The use of large volumes of resin would be necessary to keep the concentrations of sorbed, radiation-emitting nuclides sufficiently low to prevent excessive radiation damage to the resin. Degradation of the resins could interfere with subsequent resin transfer, solidification, and storage operations. In radiochemical processing, resin damage has been observed at integrated doses above 0.1 MGy (10^7 rads) for anionic resins and 1 MGy (10^8 rads) for cationic resins.² For a maximum dose of 1 MGy (10^8 rads), integrated over a 10-year period, the allowable loadings of ^{137}Cs and ^{90}Sr are 1 and 13 TBq/m³. The average loading of resins in columns must be even lower if localized loading occurs as it usually does.

In the second flowsheet shown in Fig. 1, periodic removal of cesium and strontium from the cation exchange resin (by means of elution with sulfuric acid) would minimize the long-term radiation exposure and enable the use of a smaller volume of resin. The acid eluate solution, containing most of the sodium originally in the water as well as the highly radioactive cesium and strontium isotopes, would be concentrated by evaporation. The minimum volume obtainable would be limited by the sodium sulfate concentration which, in typical operations, can be increased to a maximum of about 22% (wt.). Experience at nuclear power stations has indicated that, in comparison to the operation of ion exchange columns, evaporators require more frequent maintenance. Since the maintenance of an evaporator containing highly radioactive materials probably would have to be done remotely, it would be significantly more difficult.

The operating and maintenance problems would be even more severe if direct evaporation of the HALW were attempted, as illustrated in the third flowsheet shown in Fig. 1. In addition, a larger volume of high level waste would be generated because of the large amount (38,000 kg) of boric acid contained in the HALW and because the concentration of boric acid solutions is typically limited to about 6% to prevent plugging problems.

The fourth flowsheet illustrated in Fig. 1 would utilize zeolite ion exchange (ZIX) for sorption of the bulk of the highly radioactive cesium and strontium and evaporation for removal of all remaining radionuclides except tritium. Zeolite ion exchangers are known to have a much greater degree of stability than organic-based resins when exposed to radiation and have a high selectivity for cesium. Also, successful operations using ZIX are a matter of record; ZIX has been used on a large scale for removal of cesium from irradiated fuel storage pool water^{3,4} and for recovery of high concentrations of cesium from fuel reprocessing wastes.⁵ The evaporator that would be used in the fourth flowsheet would not contain the highly radioactive material; thus, its operation and maintenance should not be as difficult. The use of evaporation as a polishing step would provide effective decontamination of the water whereas the use of ion exchange processes for polishing could be ineffective if non-ionic species and colloids are present. A negative effect of the evaporation would be the production of the large volume of boric acid concentrate; however, in this case, the waste concentrate would contain only a small amount of radioactive material (less than 3 TBq).

The last flowsheet shown in Fig. 1 also would use zeolite ion exchange for removal of the bulk of the cesium and strontium but would use conventional

organic-based resins for polishing. The latter step would be effective for decontaminating the water if non-ionic species and colloids are not present in significant concentrations. Overall, this process would generate the lowest volume of waste concentrates. It is this flowsheet that, subsequently, was selected for use at TMI.

Process Development, Selection, and Evaluation

Because of the desire to expedite the process design and equipment fabrication, an early process selection was made on the basis of the considerations described and the results of a few tests that could be made with the small volume of RCS water that was available. Distribution coefficients (K_d) between RCS water and selected absorbents were measured and small-scale column tests (2-mL volume of sorbent) were made, using synthetic solutions traced with either ^{89}Sr or ^{137}Cs , to compare the loading performance of the various sorbents of interest and to indicate the effects of some of the process variables. Many of the column tests were made with a synthetic solution that contained 4000 mg/L of sodium because this was the calculated composition for the Containment Building Water (CBW); later, when the CBW was sampled, the sodium concentration was found to be only 1200 mg/L. Nevertheless, the column test results were useful for comparative purposes.

The results of the distribution measurements for the RCS water are shown in Table 3 and the results of the small column loading tests are shown in Figs. 2-4. The K_d measurements listed in Table 3 and the breakthrough curves shown in Fig 2 indicate the superiority of the zeolites, especially Ionsiv IE-95 (manufactured by Union Carbide Corp., Linde Division, and formerly called AW-500) and Zeolon-900 (manufactured by Norton Company,

TABLE 3. DISTRIBUTION COEFFICIENTS (K_d) FOR REACTOR COOLANT
WATER USING VARIOUS ABSORBENTS

(Reactor coolant water contained 960 mg/L sodium)

Exchanger	Sr K_d			Cs K_d			Final pH	Phase Ratio, (mL/g)
	5 min	2 h	Second Stage	5 min	2 h	Second Stage		
Nalco HCR-S	50	230	20	3700	8700	>330	3.6	27
Amberlite IR-200	120	290	28	85	200	250	8.3	71
Zeolon-900	~0	50	39	280	1800	1400	-	144
Ionsiv IE-95	~2	100	-	180	1300	-	-	136
Clinoptilolite	22	96	130	135	990	3000	8.6	67
Durasil Glass	96	250	54	160	440	400	8.6	68
Activated Charcoal	20	50	60	0	0.7	2	8.7	42

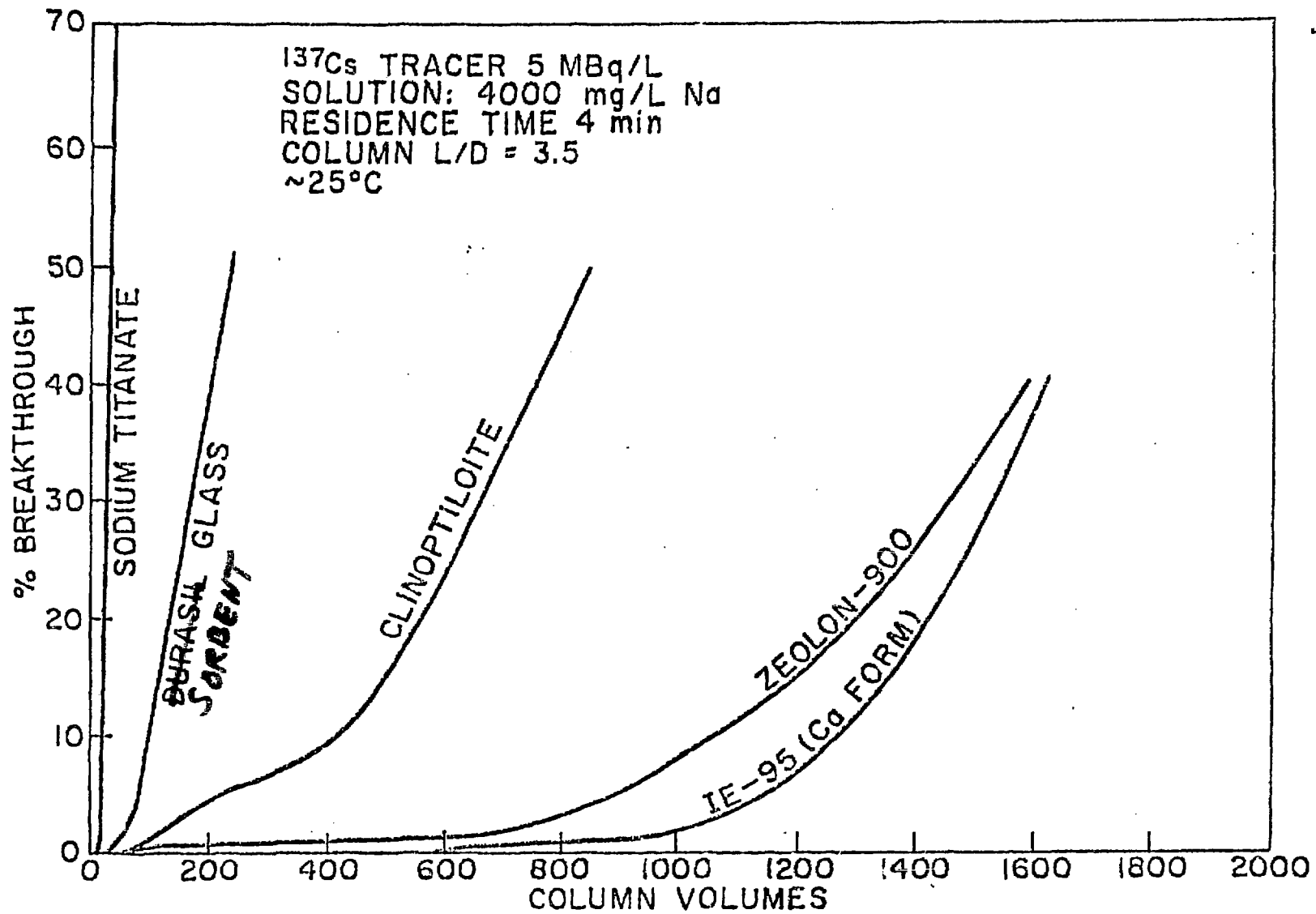


Fig. 2. Effectiveness of several Inorganic sorbents for cesium loading.

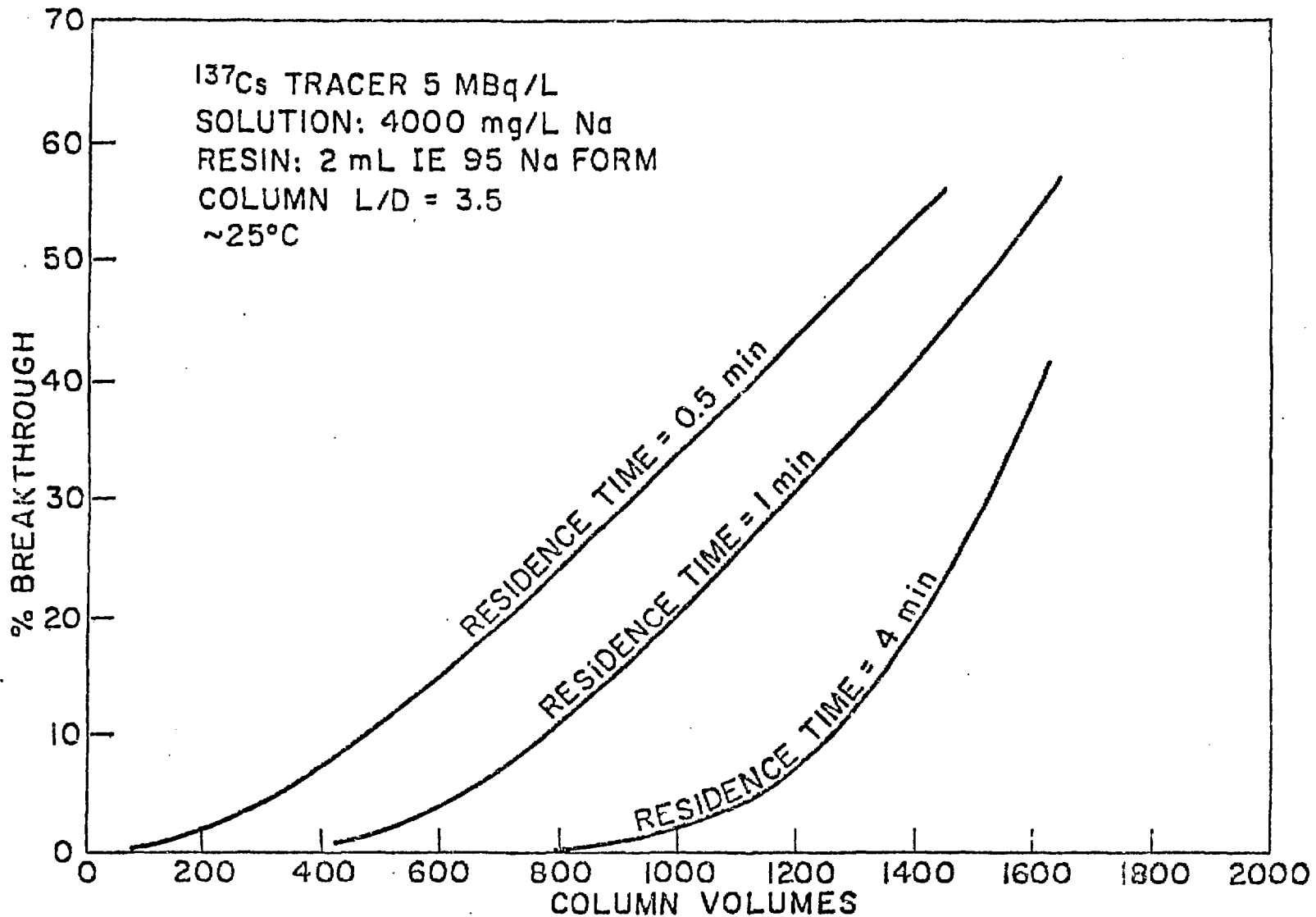


Fig. 3. Effect of residence time on cesium loading of IE-95 zeolite.

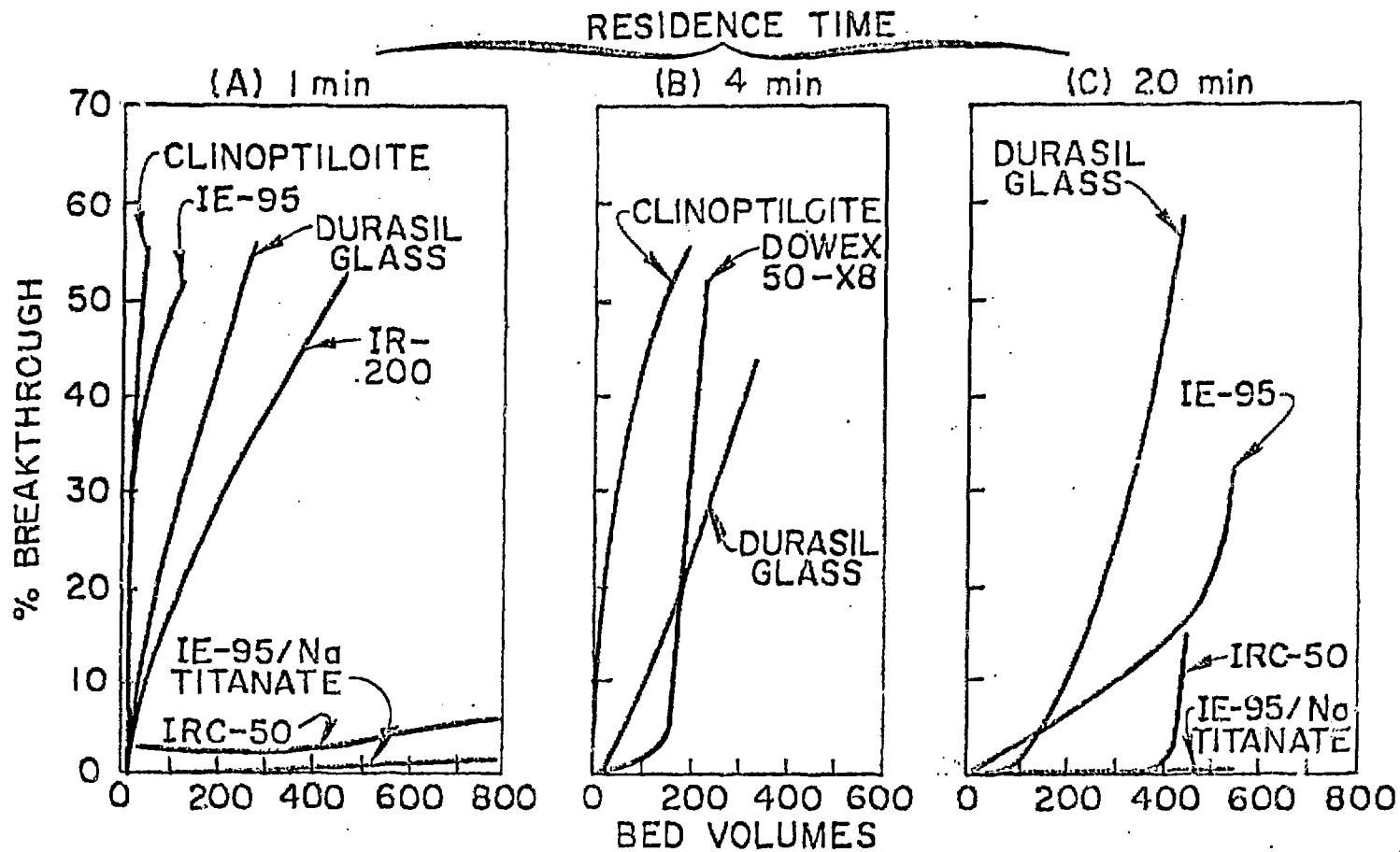


Fig. 4. The effect of residence time on strontium loading for a variety of sorbents

^{89}Sr tracer (5 MBq/L - 4000 mg/L Na - 25°C)

Chemical Process Products Division), for sorption of cesium. Comparison of the K_d 's after a short contact time (5 min) with those after a longer period (2 h) shows that the kinetics of the sorption of cesium on the zeolites is slow and that of strontium is even slower. These effects also can be seen in Fig. 3 for cesium, and in Fig. 4, for strontium. The data of Fig. 4 also show that sodium titanate is the best sorbent for strontium. However, this material has been produced only in experimental amounts and it has a soft, powdery texture which could cause plugging difficulties in large-scale columns. Figure 4 shows that a significant amount of strontium can be sorbed on the IE-95 zeolite if a sufficiently long residence time is allowed (about 15 min).

Thus, IE-95 zeolite was selected as the sorbent to be used for cesium and strontium. Conventional organic-based ion exchange resins were selected for the polishing decontamination by the Technical Advisory Group and AGNS/CNSI because of previous experience. (At the time of the initial tests, the existence of non-ionic species had not yet been proven.)

The flowsheet designed by AGNS for the Submerged Demineralizer System (SDS) is shown in Fig. 5. The contaminated water will be clarified by filtration during transfer into the ion-exchange feed tank. The clarified water will be pumped through either or both of two trains of ion exchange columns. Each train consists of a series of three columns containing zeolite and a column containing an organic cation exchange resin. Finally, the effluent water from each train is combined and passed through a large polishing column containing layers of cation resin, anion resin, and mixed resins. The operating procedure provides that 200 bed volumes of water will be passed through each zeolite column while it is in the first position.

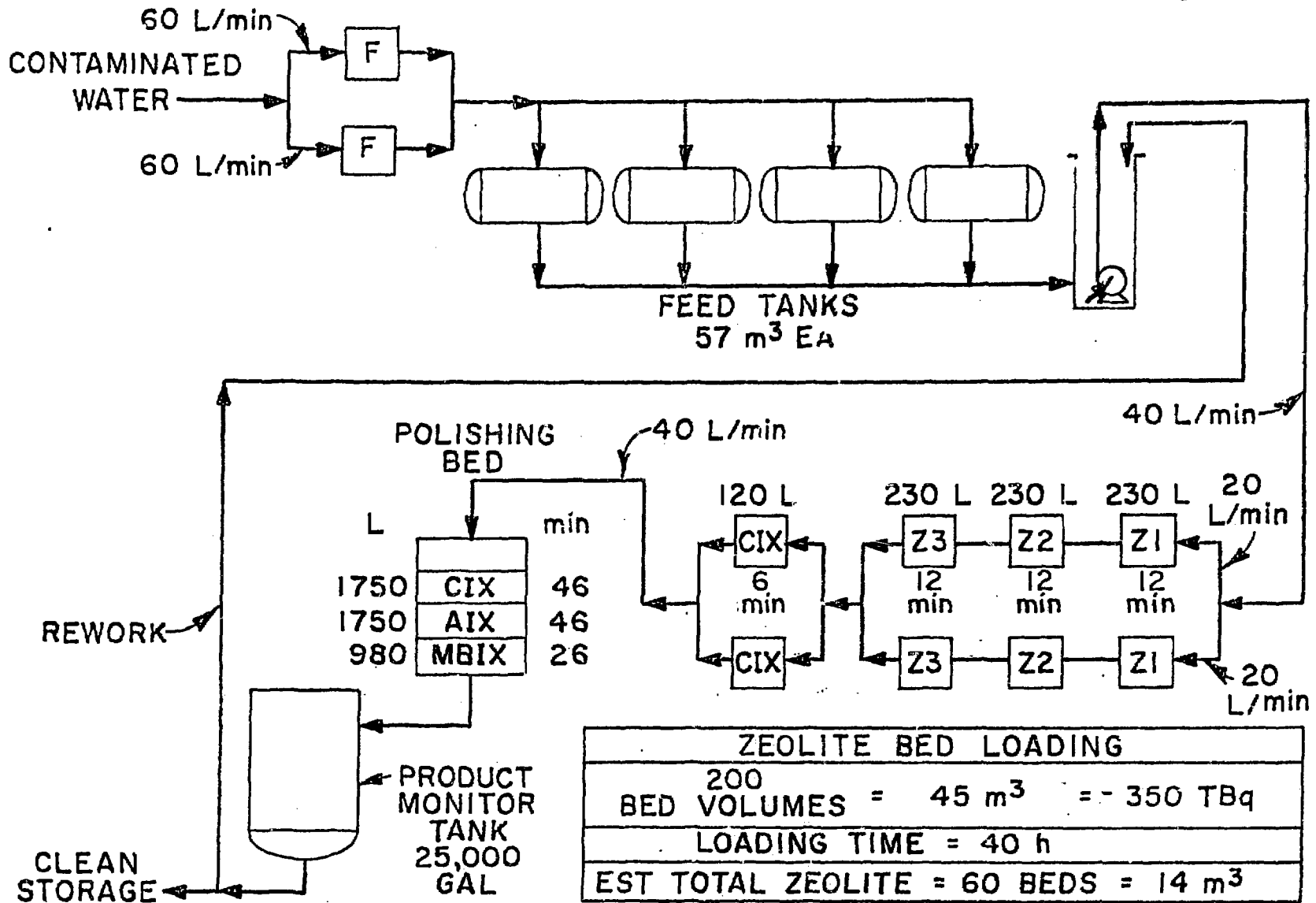


FIG. 5. SDS FLOWSHEET.

At that time, the column containing the loaded zeolite will be removed from the system, the other zeolite columns moved forward one position (counter-current to the water flow), and a new zeolite column will be installed in the third position. In this manner, the zeolite columns in the first position will sorb most of the cesium and those in the second and third positions will provide the necessary residence time to allow the strontium to be sorbed. The cation resin columns will be changed if in-line monitors or periodic sample results indicate that a bed has become loaded.

Access to the Containment Building Water was achieved after the SDS had been designed. When samples of the CBW were obtained and distribution measurements were made (results are shown in Table 4), the presence of non-ionic species of both strontium and cesium was indicated; estimated concentrations were 0.08% and 0.04%, respectively. Also, the sample taken from the bottom of the building contained a significant volume of flocculent solids that appeared to require a more efficient filtration system than that provided in the SDS design.

Because of these potential difficulties, flowsheet evaluation tests were initiated. Three one-liter samples were obtained from the bottom of the Containment Building and were used for the tests. The evaluation consisted of filtration tests, small-column ion exchange tests, and a few, selected distribution measurements that were made to interpret some of the column test results and to indicate appropriate process modifications.

Concentrations of the key constituents of the solids were determined and are listed in Table 2. The copper and iron were observed (by the color of the solid material) to be in their chemically reduced states. Since the total volume of solids in the available sample was not large enough for extensive filtration tests, a synthetic slurry was formulated to the same

TABLE 4. DISTRIBUTION COEFFICIENTS (K_d) FOR THE CONTAINMENT
BUILDING WATER USING TWO ABSORBENTS

Stage	Sorbent	K_d (Sr)	K_d (Cs)	pH	mL/g
1	IE-95	480	890	8	10
2	IE-95	280	380	8	10
3	IE-95	30	40	8	10
4	HCR-S	40	16	6	8

chemical composition as the actual slurry and was used in the tests to evaluate a variety of filter media and filtration methods. Care was taken to ensure that the chemically reduced states were maintained and that the synthetic slurry was formulated in such a way that the settling characteristics were similar to those observed for the actual slurry. Sintered metal filters having porosity ratings of 5, 10, 20, and 40 μm were used, with and without precoats of a diatomaceous earth (Johns-Manville Celite 535 was found to be the best filter aid). The mixed slurry was pumped either upflow through the filter housing, with the filter located in the top of the housing, or downflow with the filter at the bottom of the housing. The tests were terminated when the pressure drop reached 240 kPa; the turbidity of the filtrate solution was compared to the turbidity of the feed slurry to provide a measure of the filtration efficiency. At the flow rates used (270-880 $\mu\text{m/s}$), the holdup time in the test filter housing was similar to that of the SDS filter housing.

Results of the filtration tests, summarized in Table 5, indicate that the use of a filter aid will be necessary to achieve a satisfactory filtration efficiency and that the use of a downward direction of flow, with the filter located at the bottom of the housing will be necessary to maintain an adequate covering of the filter surface with filter aid, especially during operations in which it is necessary to stop and start the flow periodically.

The initial test of the SDS ion exchange flowsheet was divided into five parts (IX1 through IX5) in order to measure the concentrations of the various radionuclides in several of the column effluent streams. Conditions used in each part of the test are listed in Table 6. The effluent solution from each part was collected in 50-mL fractions and, except for

Table 5. Filter Loading Tests Using Synthetic Slurry^a

Filter Rating, μm	Flow Rate, $\mu\text{m/s}$	Filter Loading, mm^{b}	Filtrate Turbidity ^c	
			Avg.	EOT ^d
No Filter Aid -- Upward Flow				
5	270	27	20.5	93.5
20	270	51	49.8	73.9
40	270	57 ^e	37.5	84.1
20	270	51	49.8	73.9
20	530	27	63.8	82.1
20	880	14	69.1	86.1
3 mm Filter Aid -- Upward Flow				
5	270	25	0.3	0.2
20	270	28	0.5	1.0
40	270	45	1.5	2.4
10	880	7	9.3	17.0
20	880	13	4.1	5.5
40	880	13	22.6	28.3
38 mm Filter Aid -- Downward Flow				
20	270	78	0.4	0.2
40	270	70 ^e	0.7	0.2
40	880	143	0.4	0.3

^aSynthetic slurry contained 1.0% (volume) solids.

^bCalculated average depth.

^cFiltrate turbidity in % of feed slurry turbidity.

^dEnd of Test.

^eTest terminated before ΔP reached 240 kPa.

TABLE 6. CONDITIONS USED FOR ION EXCHANGE COLUMN TESTS
ON CONTAINMENT BUILDING WATER

Test	Number of IX Beds	Sorbent (Form)	Volume (each bed), mL	Flowrate $\mu\text{L/s}$	Residence Time (each bed), min	Total Throughput, mL
IX1	1	IE-95 (Na)	2.0	2.2	15	2000
IX2	2	IE-95 (Na)	2.0	2.8	12	1230
IX3	1	HCRS (H)	1.0	2.8	6	1140
IX4	2	HCRS (H)/SBR(OH)	7.7	2.8	46/46	1025
IX5	1	MR-3	4.4	2.8	26	950
IX6	3	IE-95 (Na)	2.0	0.72	12	400

sample aliquots, the fractions were fed sequentially to the next test column. Decontamination factors for the major contaminants, cesium and strontium, are shown in Fig. 6 and those for two of the minor contaminants, antimony and ruthenium, are shown in Fig. 7.

The presence of a non-ionic species of cesium in the effluent from the first zeolite column was suspected because the DF was essentially constant at 10^4 throughout the test (a total of 1000 bed volumes had been passed through the first column) and because a gamma profile of the column, shown in Fig. 8, indicated that the column was less than half-loaded. Thus, the relatively large DF (about 400) obtained in the second and third zeolite columns was not expected.

In the sequence of tests, the contaminated water had been passed through the first zeolite column (Test No. IX1) in a hot cell operation and, after a 4-week period in which the effluent water fractions had been transferred to a laboratory hood and additional equipment set up in the hood, the water had been passed through the second and third zeolite columns (Test No. IX2). During the time period between tests IX1 and IX2, non-ionic species present in the first column effluent could have reformed into an exchangeable species; therefore, the DF measured for the three columns could have been higher than if the water had been passed through the three columns without a time delay. This possibility was investigated by making a sixth test (IX6) in which the contaminated water was passed continuously through a series of three zeolite columns. The results of this test (shown as dotted lines on the DF curves of Fig. 6) confirmed that the time delay (aging) period between tests IX1 and IX2 had enabled higher DF's for both cesium and strontium and that the effect was more pronounced for cesium than for strontium.

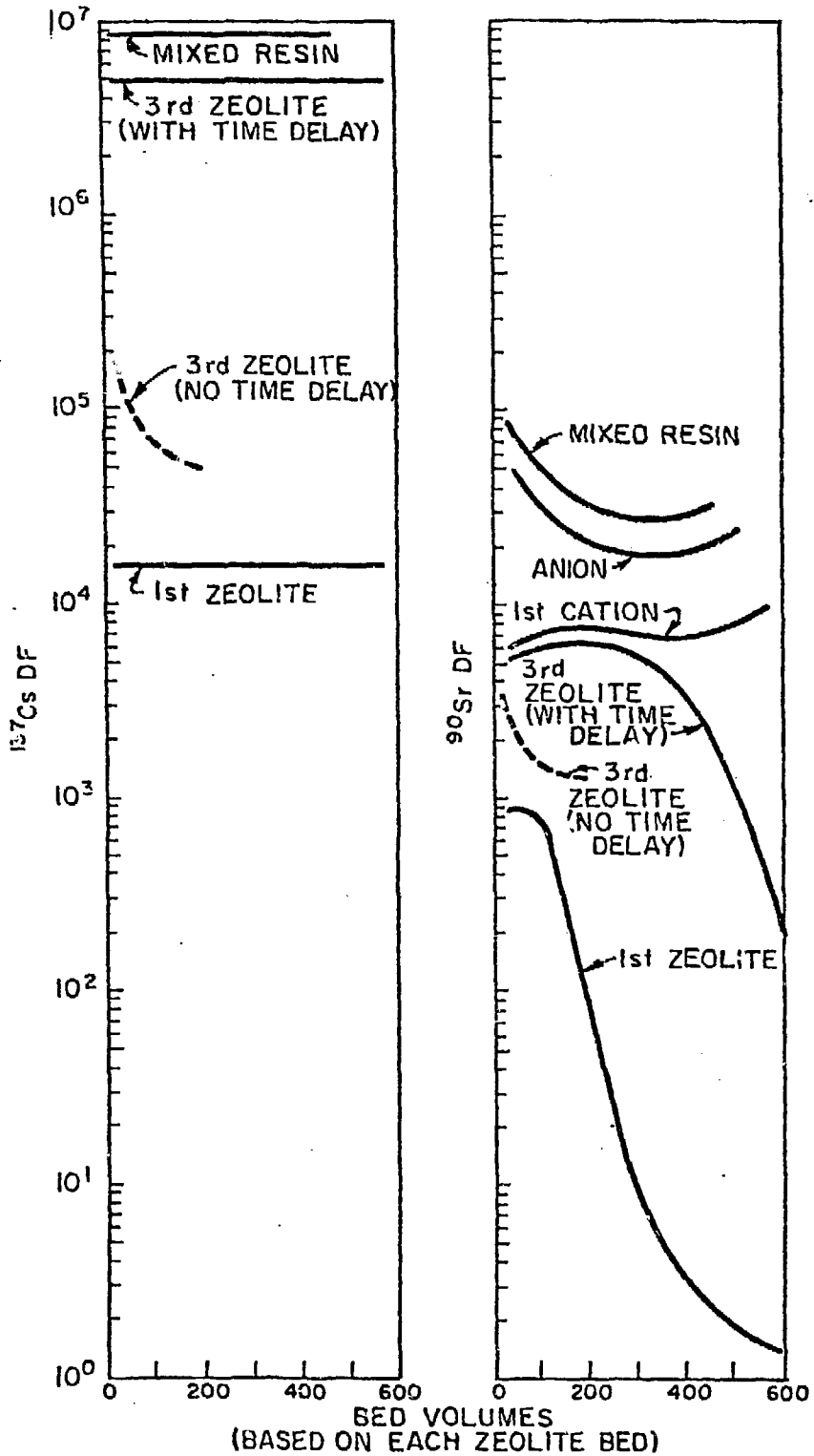


Fig. 6. Cesium and strontium decontamination factors for SDS column effluent streams.

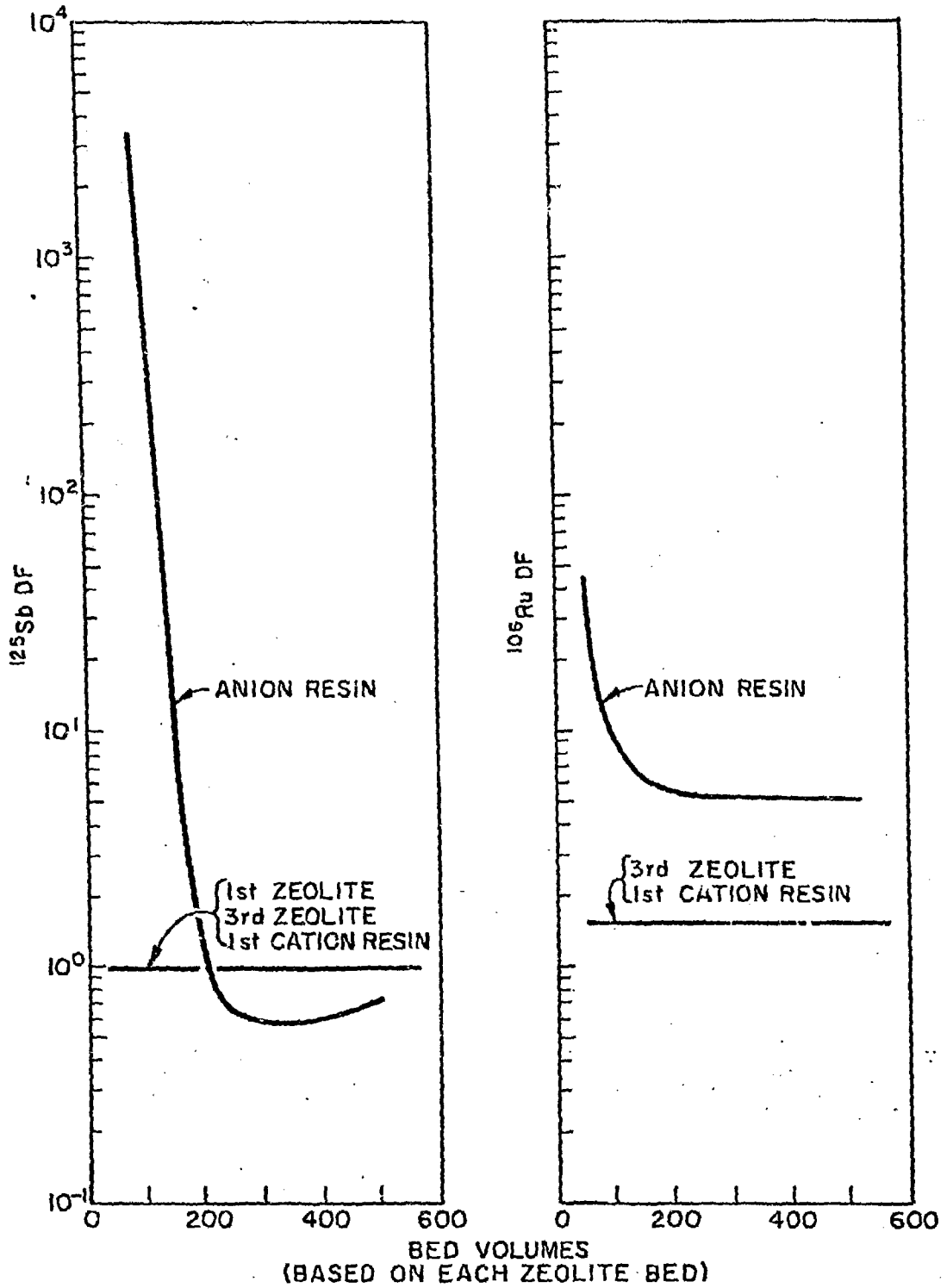


Fig. 7. Antimony and ruthenium decontamination factors for SDS column effluent stream.

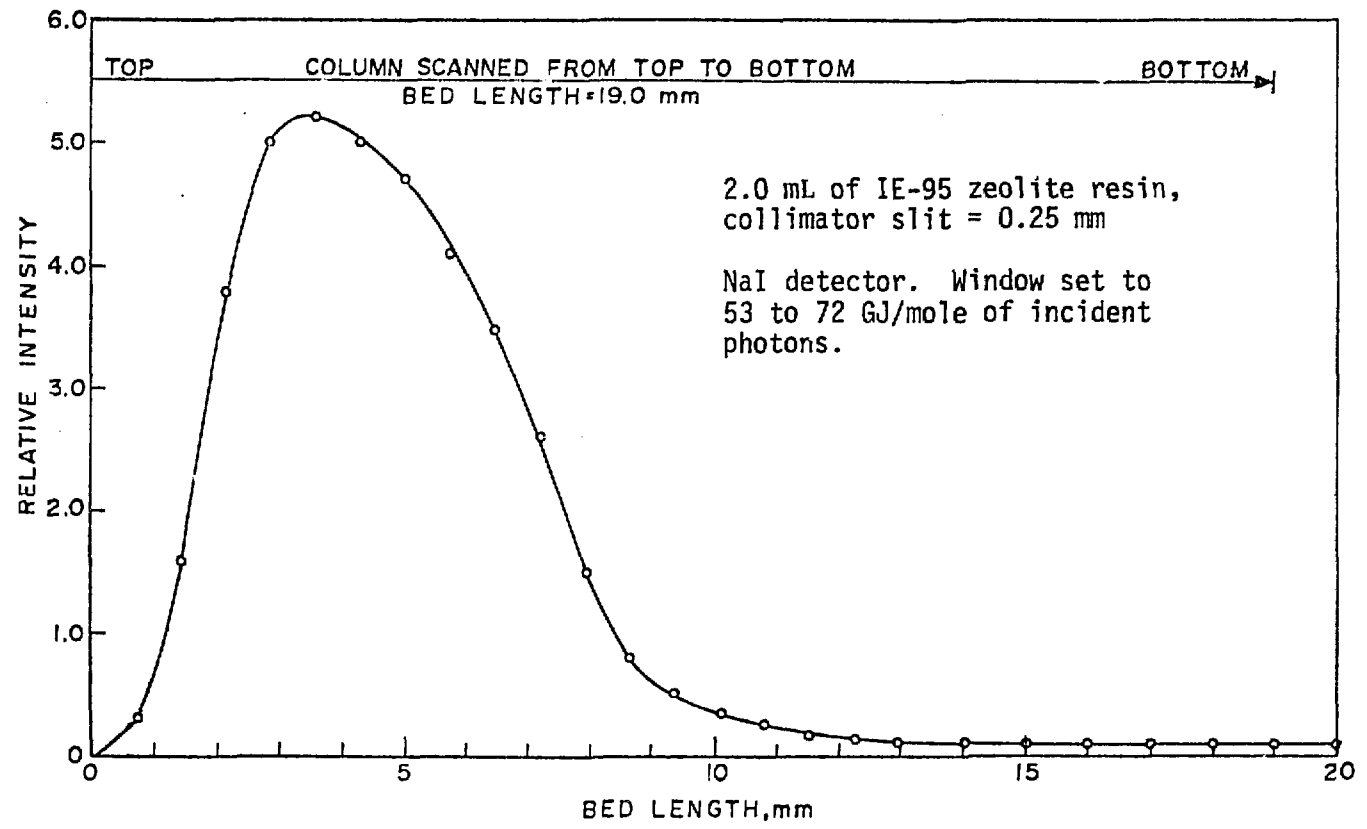


Fig. 8. Cesium activity profile of the 2 mL column after treating 1000 volumes of Containment Building water.

During the first part of text IX4, both ^{125}Sb and ^{106}Ru were removed from the water by the anion resin bed as illustrated in Fig. 7. During this period of operation, the replacement of Na^+ ions with H^+ ions in the preceding cation resin bed had lowered the pH of the water entering the anion resin bed and apparently made it effective for sorption of the antimony and ruthenium. Subsequent K_d tests also have shown this effect. That is, as the pH was lowered from 8.6 to 7.3 to 6.4 by means of a pretreatment with a cation exchange resin, the K_d for ^{125}Sb on the anion resin (borate form) was increased from 40 to 200 to 1500. This effect is apparently due to a reduction of the borate ion content by conversion of the sodium borate to weakly ionized boric acid and is, in effect, a deionization of the water (the boric acid is not removed).

Attempts to obtain a higher K_d by addition of acids, such as aminoacetic, acetic, formic, and oxalic, were unsuccessful.

In order to maintain the deionization of the water and the subsequent removal of antimony and ruthenium on the downstream anion bed, the amount of acid-form cation resin used must be sufficient to remove all of the sodium from the water. Removal of sodium from the Containment Building water would require the use of about 75 m^3 of a sulfonic acid-type cation resin or about 37 m^3 of a carboxylic acid-type. Even the latter choice would represent a four-fold increase of low level waste concentrate.

Samples of the effluent water from the mixed resin bed were subjected to ultracentrifugation tests to determine if any of the residual radio-nuclides were associated with particulates. From the results of these tests, estimates were made that the particulates contained about 30% of the strontium and ruthenium, 10-20% of the cesium, and less than 1% of the

antimony in the effluent water. Distribution measurements also had indicated that the antimony was mostly anionic in the TMI water.

Expected Performance of the SDS

The expected concentrations of radionuclides in the decontaminated effluent from treatment of the Containment Building water are shown in Table 7. These projections are based on the most pessimistic test results -- the zeolite effluent concentration of Text IX6 after 200 bed volumes and an additional DF of 2 for all nuclides, except ^{125}Sb , in the cation, anion, and mixed resin beds downstream of the third zeolite bed. Table 7 also lists the estimated effluent concentrations from the SDS if it is modified to enable effective removal of antimony and ruthenium and if appropriate storage tanks are provided to allow the water to be aged before its final treatment with zeolite or cation resin. The aging period would allow improvements in the removal of cesium and strontium.

Special Considerations for Processing RCS Water

The RCS is a recirculating loop which cannot be drained because it must always contain a substantial volume of water in order to cover the core. Thus, the RCS water must be decontaminated in a recirculation, or by-pass mode, as opposed to once-through operation. Also, the boric acid and sodium borate concentrations must be maintained to prevent criticality and to maintain the pH at a sufficiently high level to prevent corrosion. Thus, removal of the minor contaminants, ^{125}Sb and ^{106}Ru , will not be practical by means of the SDS. The objective will be to reduce the concentrations of cesium and strontium to levels that will permit fuel removal operations without excessive exposure to personnel. Only the zeolite columns in the SDS will need to be used for this purpose because zeolite is the best sorbent for the

TABLE 7. EXPECTED PERFORMANCE OF SDS FOR
DECONTAMINATION OF CONTAINMENT BUILDING WATER

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

Nuclide	Concentration in Effluent			
	SDS		Modified SDS ^a	
	kBq/L	Rel Hazard ^b	kBq/L	Rel Hazard ^b
³ H	37,000	300	37,000	300
⁸⁹ Sr	11	100	3.7	30
⁹⁰ Sr	52	4700	19	1700
¹⁰⁶ Ru	52	140	7.4	20
¹²⁵ Sb	740	200	7.4	2
¹³⁴ Cs	9.3	30	0.4	1
¹³⁷ Cs	59	80	1.9	3
¹⁴⁴ Ce	9.3	25	3.7	10

^aWith larger cation exchange bed, sized to remove Na⁺.

^bExpressed in multiples of limits of 10CFR20, Appendix B, Table II, Column 2.

bulk of the cesium and strontium and does not effect the boric acid and sodium borate concentrations. The time required to process the RCS water can be reduced by increasing the amount of zeolite in the SDS; this can be done by replacing the cation column with a fourth zeolite column.

In the recirculating mode, only one theoretical stage of separation is possible for each batch of zeolite used and this can be obtained only if the throughput volume is large enough to bring the batch of zeolite into equilibrium with the water in the entire RCS. In order to minimize the volume of zeolite used (and thus, the volume of radioactive waste generated), the throughput of each column in each position should be at least 1000 bed volumes; after being moved through each of the four positions, each column will have accumulated a total throughput of 4000 bed volumes, which is equivalent to 2.7 volumes of the RCS.

Summary

Of the several chemical processing flowsheets that were considered for concentration of the radioactive contaminants in the HALW and decontamination of the excess water, the SDS flowsheet should generate the smallest amount of radioactive waste concentrates. Sorption of the bulk of the highly radioactive contaminants, cesium and strontium, on an inorganic zeolite ion exchanger will minimize potential problems in the subsequent solidification and/or storage operations. If a significant volume of insoluble materials such as those found in samples taken from the bottom of the Containment Building are encountered and if efficient clarification is necessary, the SDS filtration system should be modified to enable downflow filtration through a bed of Celite 535 filter aid.

Except for tritium, the predominant radioactive contaminant remaining in the effluent water from the SDS, unless it is modified, will be ^{125}Sb ; however even if modified, the most hazardous contaminant, relative to the limits of 10CFR20, will be ^{90}Sr . The RCS water must be processed in a recirculating mode, using only the zeolite ion exchange columns of the SDS, in order to remove the highly radioactive cesium and strontium while leaving the boric acid and sodium borate concentrations unchanged. This will require circulation of relatively large volumes of the RCS water through the zeolite columns if the volume of zeolite is to be minimized.

REFERENCES

1. W. N. Bishop, D. A. Nitti, N. P. Jacob, and J. A. Daniel, "Fission Product Release from the Fuel Following the TMI-2 Accident," Proceedings of the 1980 ANS/ENS Topical Meeting, Thermal Reactor Safety, American Nuclear Society, Knoxville, Tennessee (April 1980).
2. T. E. Gangwer, M. Goldstein, and K. K. S. Pillay, "Radiation Effects on Ion Exchange Materials," Brookhaven National Laboratory, BNL 50781 (November 1977).
3. L. L. Denio, D. E. Knowlton, and E. E. Voiland, "Control of Nuclear Fuel Storage Basin Water Quality by Use of Powdered Ion Exchange Resins and Zeolites," American Society of Mechanical Engineers, 77-JPGC-NE-15 (June 1977).
4. M. W. Wilding and D. W. Rhodes, "Removal of Cesium and Strontium from Fuel Storage Basin Water," Idaho Chemical Plant, ICP-1048 (August 1974).
5. H. L. Brandt, "B Plant Recovery of Cesium from Purex Supernatant," Atlantic-Richfield Hanford Company, ARH-1639 (March 1970).