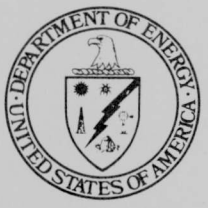
MLM-2735

Development of Ultrafiltration and Adsorbents: October 1979-March 1980

Raymond C. Roberts and C. Mark Colvin

July 2, 1980



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Foreword

Under the sponsorship of the DOE Division of Waste Management, Production and Reprocessing, and the direction of the Idaho Operations Office which is responsible for the management of Low Level Waste Programs, Mound is responsible for the development and demonstration of separation methods for removing radionuclides from intermediate-level and low-level liquid processing wastes.

This report is submitted by W. R. Cave, Director, Nuclear Operations, and B. R. Kokenge, Manager, Nuclear Technology, from contributions prepared by members of the Nuclear Waste Technology Section, K. V. Gilbert, Manager and the Liquid Volume Reduction Technology Group, W. H. Bond, Leader.

To provide an easier understanding of the relationship of the work described herein to the entire project, a work breakdown structure and a FY-1979 milestone chart are provided.

Previous reports on this project are listed below:

Development of Ultrafiltration and Inorganic Adsorbents for Reducing Volumes of Low-Level and Intermediate-Level Liquid Waste:

January-March 1978	MLM-2513
April-June 1978	MLM-2538
July-September 1978	MLM-2566
October 1978-March 1979	MLM-2611
April-September 1979	MLM-2684

Contents

Abstract

Tests on a sample of trench water from the Maxey Flats burial ground effectively demonstrated the new Reverse Osmosis Pilot Plant. The effluent from the 50% salt-rejection membrane was decontaminated well enough with the exception of tritium to be discharged to the environment. The performance of the 97% salt-rejection membrane was superior to that of the 50% membrane.

A breakthrough and capacity experiment was conducted with Durasil 10 on a simulated Three Mile Island solution. The maximum decontamination factor was extrapolated to be 10^6, which would reduce the cesium level of TMI water to below the discard limit. Capacity (1/DF = 0.5) was reached at 1260 column volumes.

Several adsorbents were tested in the engineering columns for decontamination of cesium-bearing solutions. Under the conditions of the experiment, these adsorbents were ineffective in removing cesium from the solution.

Introduction

This report is organized to conform to the Work Breakdown Structure (WBS) for the Ultrafiltration and Adsorbents program. A copy of the WBS is shown in Figure 1. Figure 2 is the FY-1980 Milestone Chart for the program.

1.2 Reverse osmosis pilot plant demonstration

R. C. Roberts

In October 1979, the new Reverse Osmosis (RO) pilot plant was fabricated by Osmonics, Inc., of Minneapolis, Minnesota. This unit consists of a transfer pump; two feed pumps connected in series and capable of a combined pressure up to 600 psi; all necessary monitoring equipment such as flow meters, pressure gauges, pH meter, and thermometer; and three types of membranes that can be used either in series or separately. Figure 3 is a flow diagram of the RO unit. The three membranes are: an Osmonics PU-192-43-SS-0(PS)-8WPT polysulfone membrane rated at 0% sodium chloride rejection, a PU-192-43-SS-50-8WPT cellulose acetate membrane rated at 50% sodium chloride rejection, and a PU-192-43-SS-97-8WPT cellulose acetate membrane rated at 97% sodium chloride rejection. Hereafter, in this report, these membranes will be referred to as 0, 50, and 97 membranes, respectively.

In addition to their different salt rejections, these membranes have other different characteristics. For example, the 0 membrane is fabricated of polysulfone and is tolerant to solutions ranging in pH from about 1 to 12. The 50 and 97 membrane material is cellulose acetate and should be used only in the pH range from 3 to 6. The maximum recommended operating pressure varies for each membrane also. This pressure is 100 psi for the 0 membrane, approximately 200 psi for the 50 membrane, and 600+ psi for the 97 membrane.

Although the unit arrived in late October and was installed by late November, a series of leaks and pumping problems necessitated some remedial action, and the system did not actually go on line until late January 1980.

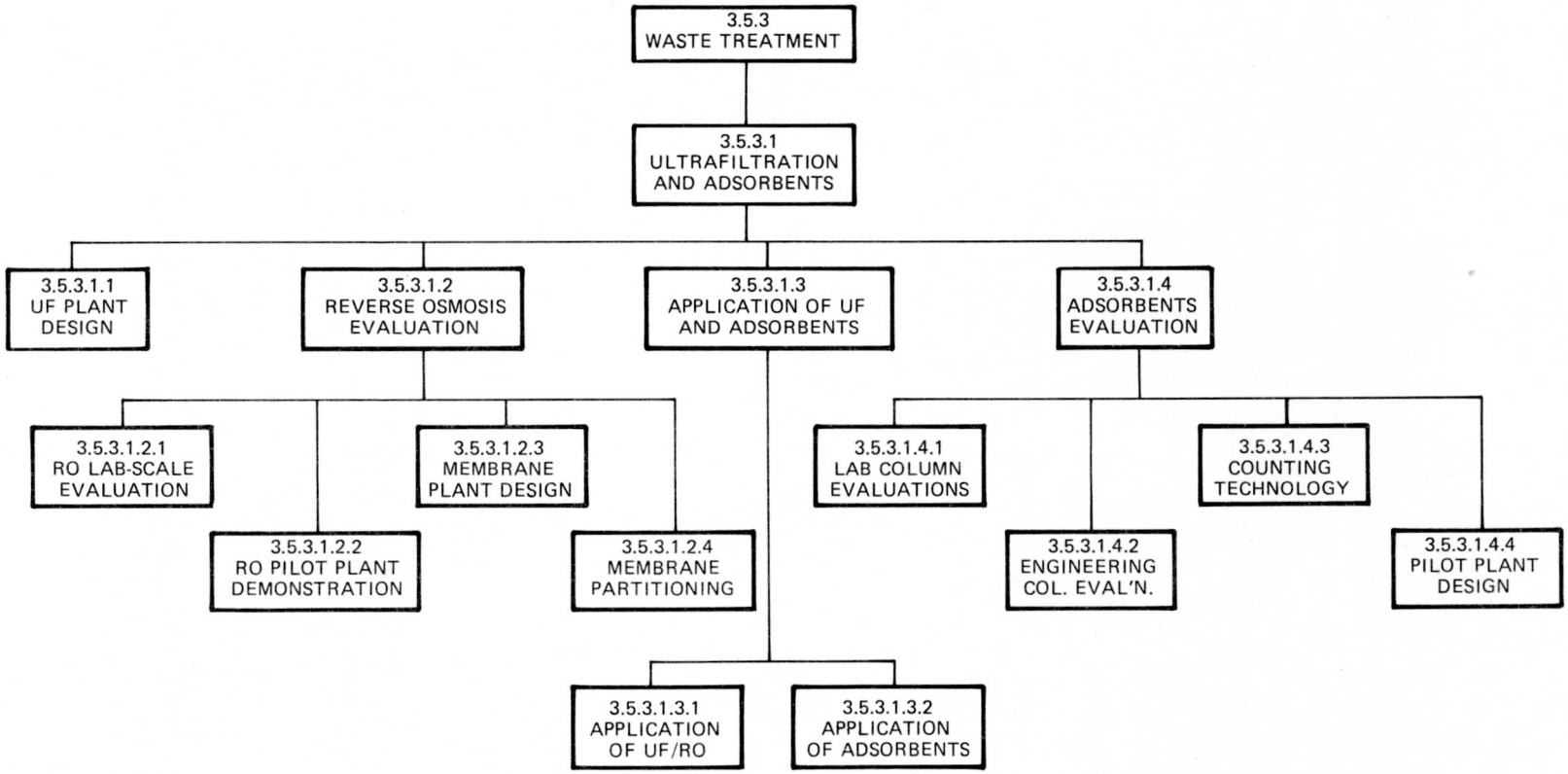

FIGURE 1 - Work breakdown structure.

Milestone No.	Milestone	Milestone Schedule															
		FY-1980												FY-1981			
		O	N	D	J	F	M	A	M	J	J	A	S	1Q	2Q	3Q	4Q
1	Complete Reverse Osmosis Pilot Plant Demonstration																
2	Complete Membrane Plant Design																
3	Complete Laboratory-Scale Partitioning Experiments																
4	Application of UF/RO																
5	Application of Adsorbents																
6	Complete Engineering Column Evaluations																
7	Complete Adsorbent Pilot Plant Design																

FIGURE 2

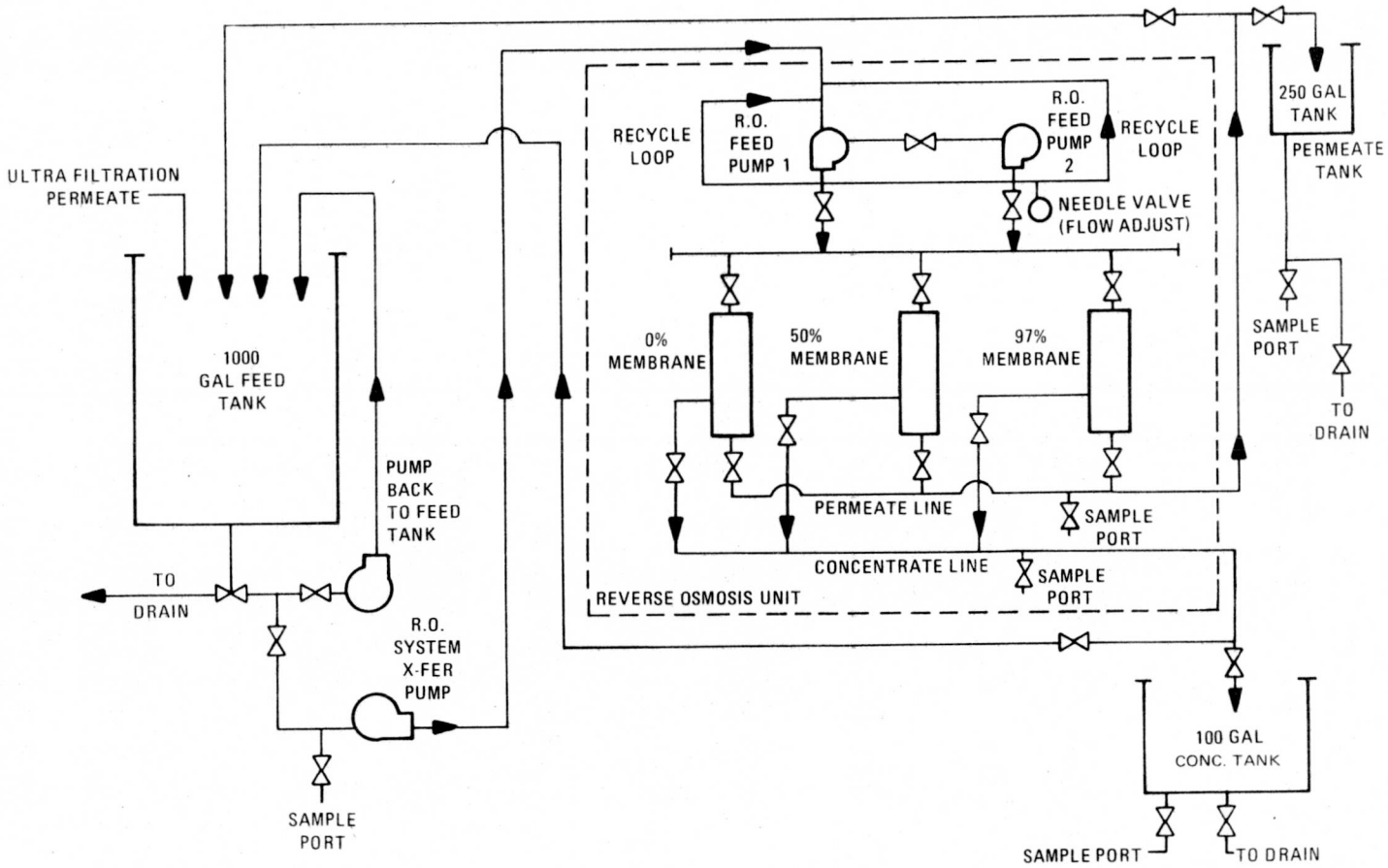

FIGURE 3 - Flow diagram - pilot plant reverse osmosis system.

The first "hot" run on the unit was made on a sample of trench water obtained from the Maxey Flats burial site in Kentucky. The experiment proceeded as described in the following section.

1.3 Application of ultrafiltration and adsorbents

About 80 gal of Maxey Flats trench water were pumped into the ultrafiltration (UF) feed tank. A sample (#1) was taken and analyzed for gross alpha, gross beta, tritium, total dissolved solids (TDS), chemical oxygen demand (COD), and chloride ion. A gamma spectrum analysis was also performed to determine what radioisotopes were present (see Table 1 for the results of these analyses). The solution was then run through the UF system, primarily to remove the suspended solids (600 mg/liter in the original feed) in preparation for RO processing. A sample (#2) of the UF processed solution was analyzed (see Table 1). The solution was then transferred to the RO feed tank and run through each membrane in the RO unit. Samples from the three membranes were submitted for gross alpha and gross beta determinations, and a sample (#3) of the solution from the 97 membrane was submitted for a complete analysis (see Table 1).

The remaining solution, by now somewhat diluted and contaminated by detergent, was returned to the RO feed tank and again sampled (#4) for a complete analysis (see Table 2). This solution was then run through the 50 membrane and again sampled (#5). Table 2 shows the results of this second run.

The results of this experiment show that the combination of UF and RO did an excellent job of decontaminating the trench water (except for tritium). Processing the water through the 97 membrane produced a gross alpha drop from 23.1 dis/min/ml to nondetectable amounts and gross beta from 781 dis/min/ml to below the lower limit of detection (<7.5 dis/min/ml). Also, the level of dissolved solids decreased by more than a factor of 10, and there was a significant decrease in levels of Cl^- and $S^=$ in solution. Any change in the tritium level was the result of dilution by water held up in the UF and RO units. (Total dilution was ~25 to 30% during the course of the run.) The only factor that appears out of line is the result obtained in the COD analysis. This analysis is being rerun, and the result is not yet known. All in all, a system utilizing a combination of UF and RO could well be used for the decontamination of the low level waste water found at Maxey Flats and other burial sites.

Durasil - Three Mile Island water experiment

Although the work described below was performed in April and, therefore, is chronologically out of place in this report, it is considered to be of too much immediate interest to delay publication for the proper report.

Much of the credit for the success of this experiment must go to representatives of the Vitreous State Laboratory of Catholic University of America for their recommendations and assistance during the experiment.

Table 1 - RADIOISOTOPES PRESENT IN MAXEY FLATS WATER BEFORE AND AFTER TREATMENT

	Gross α (dis/min/ml)	Gross β (dis/min/ml)	H^3 (μCi/liter)	T.D.S. (mg/liter)	C.O.D. (mg/liter)	Cl^- (moles/liter)	$S^=$ (moles/liter)
Raw Maxey Flats Water (#1)	23.1[b]	781[b]	82.1	1570/1690 (SS=772/468)	434.5 96.6	10^{-2}	
After UF Before RO (#2)	19.3	318	58.0	700	310	5.9×10^{-3} 6.2×10^{-3}	2.0×10^{-6}
After RO 97[a] (#3)	N.D.	< 7.5	53	60	342.7	6.4×10^{-4} 7.6×10^{-4}	1.0×10^{-6}

[a] A sample after the 0% membrane showed 13.9α, 310β while an after 50% membrane sample showed 0.4α, 14.5β.

[b] A gamma spectrum showed only ∿1.2 pCi/ml cesium and less than 1 pCi/ml of anything else; therefore, nearly all the beta had to come from strontium which emits no gamma. Nearly all the alpha came from plutonium-238 and plutonium-239.

Table 2 - MAXEY FLATS WATER AFTER FURTHER TREATMENT

	Gross α (dis/min/ml)	Gross β (dis/min/ml)	H^3 (μCi/liter	T.D.S. (mg/liter)	C.O.D. (mg/liter)	Cl^- (moles/liter)	$S^=$ (moles/liter
Before RO 50 (Sample #4)	6	160	28	810	16.3	7.2×10^{-3} 7.8×10^{-3}	1.8×10^{-6}
After RO 50 (Sample #5)	N.D.	∿7	28	155	16.3	3.9×10^{-4} 4×10^{-4}	1.2×10^{-6}

Test results for Durasil-10

INTRODUCTION

The approximately 700,000 gal of water at Three Mile Island (TMI) which are to be processed for radionuclide removal contain ∿130 mCi/liter of radioactive cesium in a solution that is ∿1000 ppm sodium and ∿2000 ppm boron. Decontamination of this water by ion exchange requires an exchange medium that has a high decontamination factor (the maximum permissible concentration for cesium release is 2×10^{-5} mCi/liter and a large capacity and selectivity for cesium in the presence of high concentrations of sodium and boron. In addition, the final form of the exhausted medium should be such that shipment to a waste repository is both safe and convenient.

Durasil 10 is an ion exchange medium with a high-silica glass base developed at the Catholic University of America (CUA) under the sponsorship of the National Patent Development Corporation (NPDC). Tests conducted at CUA on cold, simulated, TMI water showed that Durasil 10 has a high decontamination factor (DF), capacity, and selectivity for cesium, strontium, and cobalt. Once exhausted, Durasil 10 can be collapsed into a monolithic structure suitable for safe disposal. The test described below was made at Mound as an independent evaluation of the performance of Durasil 10 on radioactive, simulated TMI water.

TEST DESIGN

A schematic of the test system is shown in Figure 4. The column consisted of a filter tube having an inner diameter of 19 mm and a sintered glass plate of coarse porosity. The backwashed and forward flow

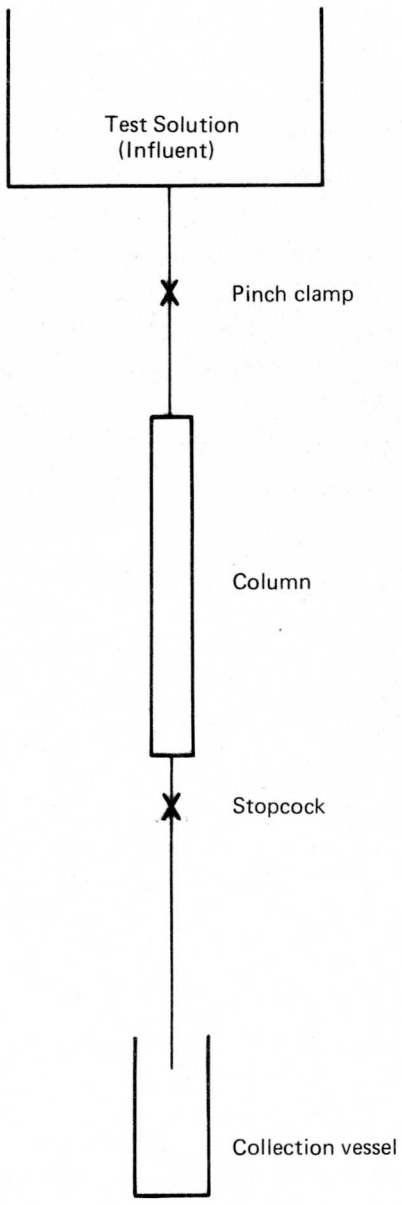

FIGURE 4 - Test system schematic.

volumes of the Durasil 10 were 45 cm^3 and 38.5 cm^3, respectively. Column dimensions were thus close to the ASTM recommended dimensions of 20-mm diameter and 30-ml capacity [1]. Since the Durasil 10 provided by CUA was 355-710 m in diameter, the ratio of column diameter to resin particle size was well above the minimum 10 necessary to avoid major wall effects [2].

The composition of the simulated TMI influent solution is given in Table 3. The boron, sodium, lithium, cesium, and zinc analyses were obtained at Mound and confirmed at CUA using atomic absorption spectroscopy. Sulfur and chlorine concentrations were computed from the weights of reagents added to solution. The cesium-137 concentrations of the influent and of all effluent samples were obtained using a Packard Tri-carb 460-CD Liquid Scintillation System. Residence time of the solution on the column was ~4 min.

Table 3 - SIMULATED TMI INFLUENT SOLUTION

Element	Concentration
B	1900 ppm
Na	966 ppm
Li	1.53 ppm
Cs	1.72 ppm
Zn	0.564 ppm
^{137}Cs	0.1 mCi/liter
S (as $SO_4^{=}$)	8 ppm
Cl (as Cl^-)	11 ppm

RESULTS

Figures 5 and 6 are plots of DF and 1/DF as functions of the volume of effluent measured in column volumes. (The backwashed column volume of 45 cm^3 was used in these computations.) The data obtained in this test are plotted along with results obtained [3] in cold tests at CUA. The CUA test column was 10% longer than the one used at Mound, and the cesium concentration of the influent was 25% lower.

Decontamination factors obtained at Mound remain in excess of 10^5 for the first 250 column volumes, falling to 10 at ~900 column volumes. The CUA results show a DF of 10 at 1075 column volumes. (Because of limitations of analytical procedures, CUA could not determine DF values in excess of 100.) The 20% disagreement is not unexpected since tests at CUA show that both longer column length and lower cesium concentration lead to a higher DF [3].

The capacity of the Durasil 10 can be reliably estimated by noting the point where 1/DF = 0.5. The result obtained in this test (from Figure 6) is 1260 column volumes, in substantial agreement with the CUA result of 1460 column volumes. The 15% difference is to be expected on the basis of the dependence of capacity on cesium concentrations [3].

IMPLICATIONS FOR TMI

The DF values obtained in this test indicate that a column configuration having a total length greater than 1 ft and a residence time greater than 8 min would suffice to give a total DF value well in excess of that needed at TMI. The capacity figure obtained means that the cleanup of 700,000 gal of TMI water would lead to an amount of spent Durasil 10 that would fill approximately 10 55-gal drums and weigh approximately 5000 lb. Onsite processing of the spent Durasil 10 would result in a collapsed monolithic structure, simplifying safe transportation to a suitable repository.

1.4 Adsorbents evaluation

C. M. Colvin

The expected result of the adsorbent project is to have one, or more, adsorbent systems in operation decontaminating actual waste streams. The engineering-scale column experiments are an intermediate step

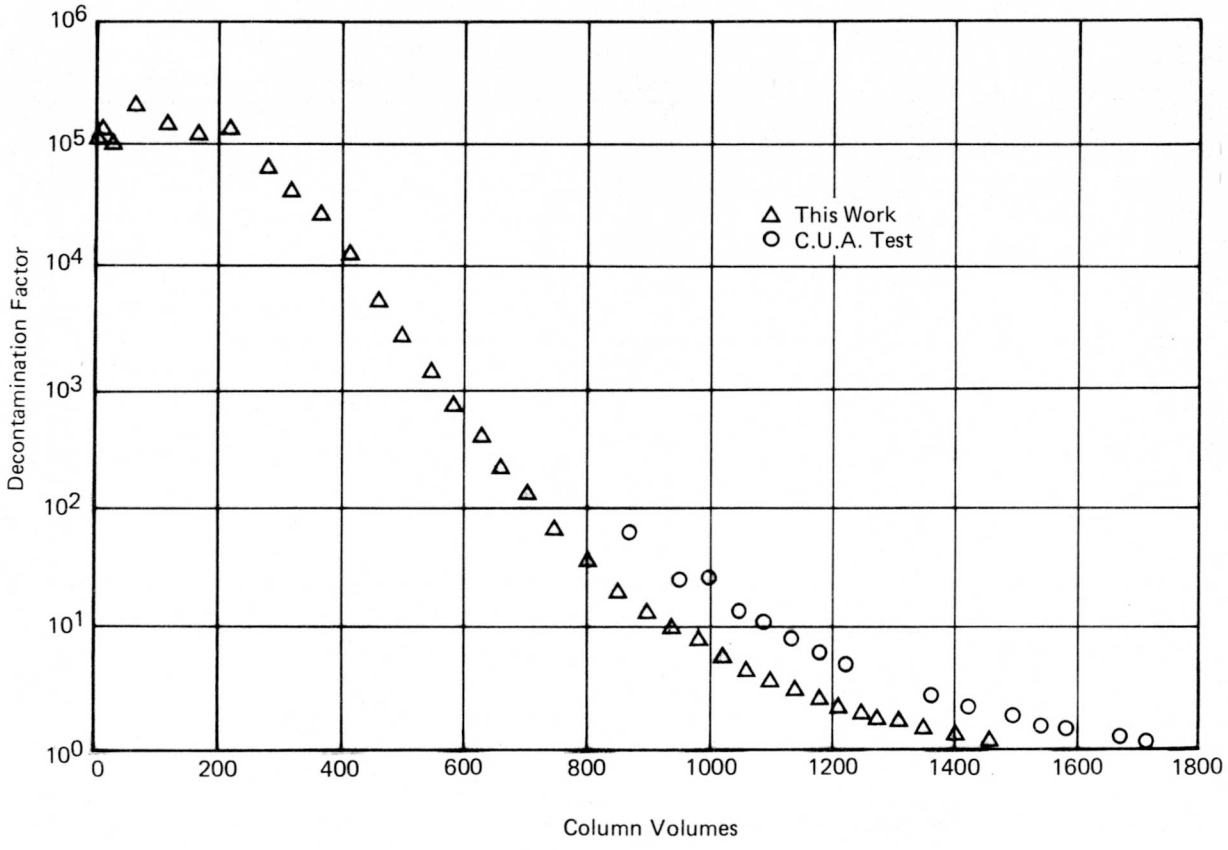

FIGURE 5 - Decontamination of Three Mile Island simulant as a function of effluent volume using Durasil.

between the laboratory-scale column experiments and actual use in an industrial-scale column. The purpose of the engineering column experiment is to determine the effects of scaling up from the laboratory column experiments. The effects of variables such as flow rate, pH, and radioisotope concentration on the decontamination ability of a particular resin for each isotope are measured and expressed by decontamination factors. The decontamination factor (DF) is the ratio of the concentration of the radionuclide in the feed divided by the concentration of the radionuclide in the raffinate.

The raw data for the individual isotopes and adsorbents are listed in Tables 4-9. The tables are displayed for easy evaluation of the effects of pH and flow rate on each adsorbent and the resultant DF.

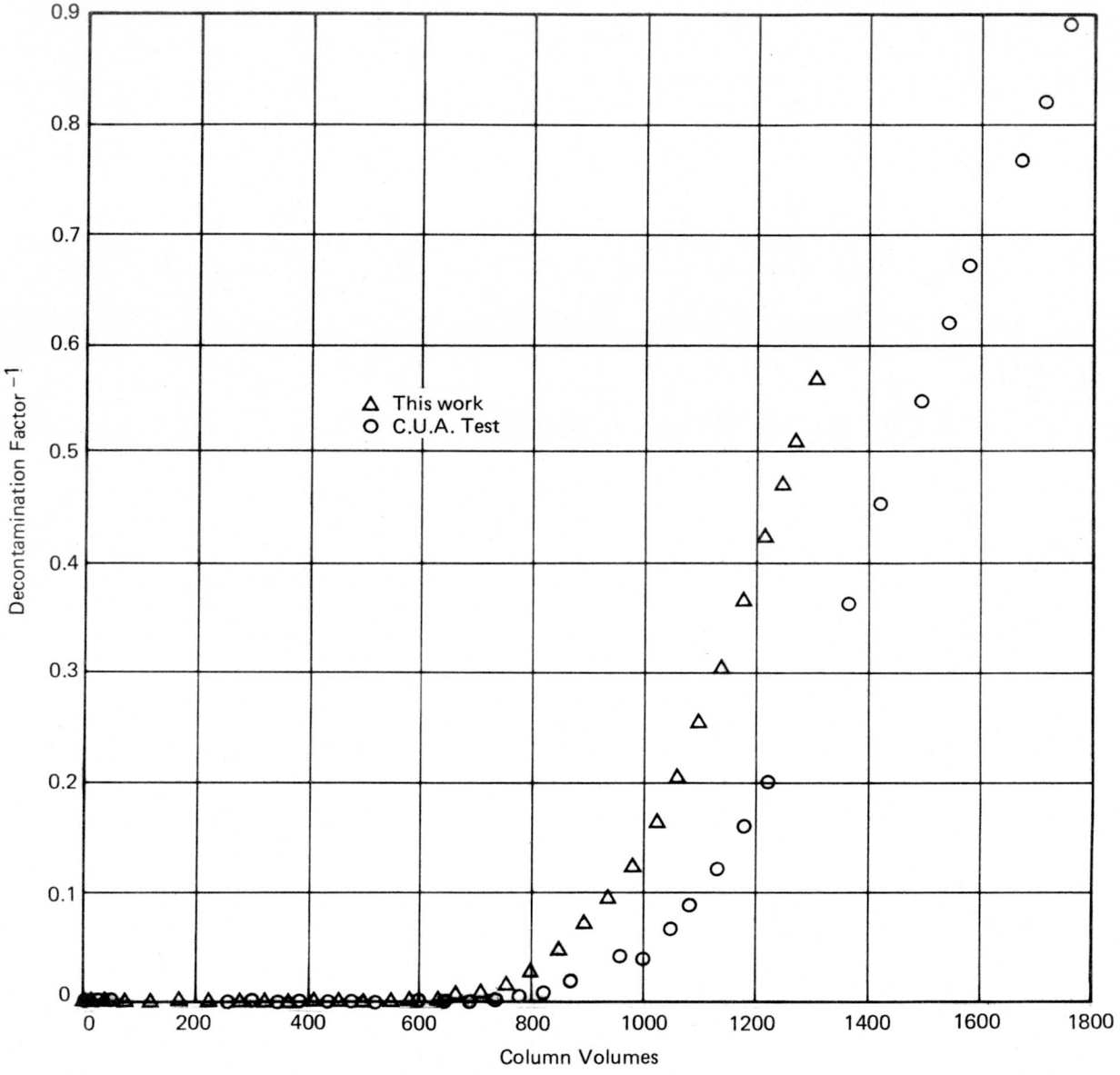

FIGURE 6 - Capacity (1/DF = 0.5) of Durasil in Mound and CUA tests.

The following is a description of the procedure used in preparing the ion exchange columns for the tests on iodine-131. Three engineering columns, 50-mm i.d., were prepared with a different resin in each. The resins used were MSA-1, IRA-938, and bone char. The resin bed volumes were approximately one liter. The quantity of the resins was more accurately determined by weight. The resins were weighed in 1500-ml beakers, and then were poured into the columns until they reached a 50-cm mark, which indicated a volume of approximately one liter. After the columns were filled to the bed volume level, the beakers and the remaining resins were again weighed and the bed volume weights were obtained by difference.

The feed solution for the iodine experiments was prepared by filling the feed tank with approximately 1000 liters of

Table 4 - DATA SUMMARY OF ENGINEERING COLUMN TESTS WITH IODINE-131 AND MSA-1

One Bed Volume Weight (g)	Flow Rate (ml/min)	Initial Feed pH	Initial Feed Beta (count/min/ml)	Product Beta (count/min/ml)	Temp (°F)	DF
535	100	3	968	813	71	1.2
	100	3	912	755	71	1.2
	100	7	1066	659	71	1.6
	100	7	1300	709	71	1.8
	100	10	1559	1391	71	1.1
	100	10	1657	1271	71	1.3
	150	3	1196	736	71	1.6
	150	3	1058	896	71	1.2
	150	7	873	656	71	1.3
	150	7	899	613	71	1.5
	150	10	1626	1004	71	1.7
	150	10	1318	1253	71	1.1

Table 5 - DATA SUMMARY OF ENGINEERING COLUMN TESTS WITH IODINE-131 AND IRA-938

One Bed Volume Weight (g)	Flow Rate (ml/min)	Initial Feed pH	Initial Feed Beta (count/min/ml)	Product Beta (count/min/ml)	Temp (°F)	DF
648	100	3	968	597	71	1.6
	100	3	912	985	71	<1
	100	7	1066	642	71	1.7
	100	7	1300	666	71	1.9
	100	10	1559	160	71	9.7
	100	10	1657	152	71	10.9
	150	3	1196	672	71	1.8
	150	3	1058	754	71	1.4
	150	7	873	631	71	1.4
	150	7	899	654	71	1.4
	150	10	1626	304	71	5.3
	150	10	1318	186	71	7.1

Table 6 - DATA SUMMARY OF ENGINEERING COLUMN TESTS WITH IODINE-131 AND BONE CHAR

One Bed Volume Weight (g)	Flow Rate (ml/min)	Initial Feed pH	Initial Feed Beta (count/min/ml)	Product Beta (count/min/ml)	Temp (°F)	DF
720	100	3	968	103	71	9.4
	100	3	912	91	71	10.0
	100	7	1066	110	71	9.7
	100	7	1300	98	71	13.3
	100	10	1559	155	71	10.1
	100	10	1657	77	71	21.5
	150	3	1196	81	71	14.8
	150	3	1058	79	71	13.4
	150	7	873	90	71	9.7
	150	7	899	92	71	9.8
	150	10	1626	165	71	9.9
	150	10	1318	147	71	9.0

Table 7 - DATA SUMMARY OF ENGINEERING COLUMN TESTS WITH CESIUM-137 AND MSC-1

One Bed Volume Weight (g)	Flow Rate (ml/min)	Initial Feed pH	Initial Feed Beta (count/min/ml)	Product Beta (count/min/ml)	Temp (°F)	DF
732	50	3	3757	363	81	10.3
	50	3	4386	57	81	76.9
	50	3	4439	60	81	74.0
	50	7	4560	68	81	67.1
	50	7	3962	74	81	53.5
	50	7	3969	68	81	58.4
	50	10	3806	789	81	4.8
	50	10	3722	895	81	4.2
	50	10	3836	701	81	5.5
	150	3	4378	37	81	118.3
	150	3	4505	50	81	90.1
	150	3	4445	37	81	120.1
	150	7	4395	102	81	43.1
	150	7	4119	44	81	93.6
	150	7	4173	63	81	66.2
	150	10	3986	331	81	12.0
	150	10	3692	292	81	12.6
	150	10	3823	326	81	11.7

Table 8 - DATA SUMMARY OF ENGINEERING COLUMN TESTS WITH CESIUM-137 AND IR-200

One Bed Volume Weight (g)	Flow Rate (ml/min)	Initial Feed pH	Initial Feed Beta (count/min/ml)	Product Beta (count/min/ml)	Temp (°F)	DF
751	50	3	3757	14	81	268
	50	3	4386	61	81	72
	50	3	4439	51	81	87
	50	7	4560	77	81	59
	50	7	3962	83	81	48
	50	7	3969	55	81	72
	50	10	3806	1174	81	3.2
	50	10	3722	988	81	3.8
	50	10	3836	1035	81	3.7
	150	3	4378	68	81	65
	150	3	4505	62	81	73
	150	3	4445	28	81	159
	150	7	4395	12	81	366
	150	7	4119	1	81	4119
	150	7	4173	9	81	463
	150	10	3986	707	81	6
	150	10	3692	614	81	6
	150	10	3823	666	81	6

Table 9 - DATA SUMMARY OF ENGINEERING COLUMN TESTS WITH CESIUM-137 AND XN1010

One Bed Volume Weight (g)	Flow Rate (ml/min)	Initial Feed pH	Initial Feed Beta (count/min/ml)	Product Beta (count/min/ml)	Temp (°F)	DF
442	50	3	3757	210	81	18
	50	3	4386	125	81	35
	50	3	4439	167	81	27
	50	7	4560	75	81	61
	50	7	3962	-	81	-
	50	7	3969	71	81	56
	50	10	3806	4277	81	<1
	50	10	3722	4561	81	<1
	50	10	3836	4670	81	<1
	150	3	4378	62	81	71
	150	3	4505	84	81	54
	150	3	4445	20	81	222
	150	7	4395	144	81	30
	150	7	4119	744	81	5
	150	7	4173	941	81	4
	150	10	3986	3843	81	1
	150	10	3692	4329	81	<1
	150	10	3823	4670	81	<1

simulated product from the ultrafiltration membrane process, which is a probable pretreatment to absorbent processing, and then spiking with iodine-131 until a concentration of approximately 1500 counts/min/ml was achieved. The adsorbents were tested at flow rates of 100 and 150 ml/min and pHs of 3, 7, and 10.

In order to stabilize the resin bed, the feed solution was pumped through the columns for approximately 3 hr at constant pH and flow rate before samples were taken. The feed solution was pumped by tubing pumps with variable speed drive, and the flow rate was measured with calibrated flow meters. The feed samples were taken after the solution was passed through a 10-μm filter. The filter was used to remove particles from the feed stream to maintain solution homogeneity and to reduce the filtering effect of the adsorbents. The raffinate samples were taken after the columns. Both the feed and raffinate samples were counted on a Hewlett-Packard Tri-Carb liquid scintillation spectrometer calibrated for iodine-131. The resulting counts were used to calculate the DFs.

The data gathered from the tests indicate that MSA-1, IRA-938, and bone char are inadequate for decontaminating a waste stream of this composition containing iodine-131 at pHs of 3, 7, and 10.

The procedure used for cesium-137 was similar to that used for iodine-131 except that the initial feed concentration was approximately 4500 counts/min/ml; the flow rate was only 50 ml/min; and the resins used were MSC-1, IR-200, and XN1010. The raw data from the cesium-137 experiments are displayed in Tables 4 to 9. The DFs that are less than unity are probably the result of counting error. The resin with the best performance was IR-200 at pH 7 and a flow rate of 150 ml/min.

The procedure used for the engineering columns was discussed more thoroughly in the previous report [4].

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