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MARITIME REACTOR WASTE DISPOSAL STUDIES: SOLIDIFICATION OF ION-EXCHANGE RESIN WITH PORTLAND CEMENT FOR RADIOACTIVE WASTE DISPOSAL

R. R. Holcomb

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On page 11, the top curve Fig. 4a is labeled 10-mc block, should be changed to read 20-mc block. Lower curve Fig. 4a is labeled 20-mc block, should be changed to read 10 mc block.

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

MARITIME REACTOR WASTE DISPOSAL STUDIES: SOLIDIFICATION OF ION-EXCHANGE RESIN WITH PORTLAND CEMENT FOR RADIOACTIVE WASTE DISPOSAL

R. R. Holcomb

Date Issued

AUG 1960

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ABSTRACT

A procedure is reported for the sea disposal, by fixation in concrete with Portland cement, of ion-exchange resins containing sorbed fission products and filtered corrosion products. The results of sea disposal of both treated and untreated resins is presented.

For the fixation of nuclear-reactor-system demineralizer resin in cement, a mixture of 2 parts of cement, 1 part of resin, and 1 part of water was found to be optimum. A concrete block prepared by this receipt showed only 0.44% of the gross gamma activity leached after 2540 hr of contact with simulated sea water. The data indicate that very little or no further leaching will occur.

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1.0 INTRODUCTION

The fixation of radioactively contaminated ion-exchange resins in concrete was investigated as a means of preparing for disposal of the wastes formed in the operation of nuclear merchant ships of the N. S. Savannah type. The activity on the resin beds used to demineralize the primary loop coolant water could be immobilized in this medium prior to disposal in the sea, and the activity in the liquid wastes—the primary coolant blow-down water, laboratory waste, and shield water—could be concentrated on ion-exchange resins and handled similarly. The relatively small volumes of contaminated resin could be easily and economically contained aboard ship for dockside disposal or regeneration or they could be disposed of in the sea if dispersion of the activity could be prevented. The decontaminated effluent from the resin columns could be discharged, after monitoring, directly to the sea.[1] Radioactive off-gases, which are mostly short-lived activities, will be adsorbed on charcoal and allowed to decay before discharge to the atmosphere.[2] Laboratory-scale studies were made on methods of preparing resin-in-concrete blocks and on leaching of activity from the blocks by sea water.

Both total containment of all wastes aboard ship while at sea, with subsequent treatment and disposal on land, and total release of the active material at sea have been considered. The total containment philosophy was adopted for the N. S. Savannah. However, storage tanks for the large volumes of liquid waste are space-consuming and a possible source of contamination of the ship, and the method is relatively expensive and not always feasible. A recent National Academy of Sciences report[3] provides for total discharge of both used ion-exchange resins and liquid wastes in prescribed areas of the marine environment. Although discharge of untreated wastes directly into the ocean as prescribed is possible, it seems wiser to afford some control over the activity released. Fixation of the activity in a medium such as concrete will isolate the bulk of the radioactivity and prevent its plaguing the world in future years. Control of the activity, which is released to the sea, by treatment of waste prior to discharge will become increasingly important as the world nuclear fleet increases.

Several problems connected with this type of disposal need further study and evaluation: (1) the engineering problems involved in the operation of such a system aboard ship; (2) the effect of pressure in the depths of the ocean on the integrity of the concrete; and (3) the feasibility of concentrating the activity in liquid wastes on ion-exchange resins as proposed in this report.

Acknowledgment is made to W. J. Neill, formerly of this division, for the initial planning of the development program and the preliminary experimental work[4] and to J. T. Roberts for technical assistance. The tracers used in these studies were obtained from the Isotopes Division of Oak Ridge National Laboratory.

2.0 EXPERIMENTAL WORK

The ion-exchange resin in the primary purification loop demineralizers is the largest source of concentrated activity, as can be seen by comparing the predicted activity of the primary coolant water with the activity associated with the ion-exchange resin after 50 days' operation (Table 1). Aboard the N. S. Savannah the resin bed will be a mixture of hydrogen-form strong-acid cation-exchange resin and hydroxyl-form strong-base anion-exchange resin. All studies were made with these resins in a 1 to 1 mixture, the ratio being chosen for simplicity rather than for sorption capacity.

Table 1. Activity in Water During Operation and Total Activity on Resin[a] (N. S. Savannah)[b]

Isotope	Half-Life	Specific Activity in Water During Operation, $\mu c/ml$	Total Activity on Resin after 50 days' Operation, curies
Na^{24}	15h	1.11×10^{-2}	1.09
Co^{60}	5.3y	3.68×10^{-4}	1.98
Co^{58}	71d	1.26×10^{-3}	5.25
Fe^{55}	2.9y	1.49×10^{-2}	79
Fe^{59}	47d	3.14×10^{-4}	1.19
Cr^{51}	27d	2.16×10^{-2}	67
Ni^{65}	2.56h	1.22×10^{-4}	0.002
Mn^{56}	2.58h	1.91×10^{-2}	0.32
Mn^{54}	300d	2.25×10^{-4}	1.15
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[a] Calculations made by H. N. Culver, "Cooling Water and Demineralizer Activities in NMSR," ORNL-CF-58-5-83, May 14, 1958, p. 4.

[b] Similar calculations are presented in BAW-1109, September 1958, pp. 3A-4A.

2.1 Leaching of Activity from Contaminated Resins

The simplest method of disposing of resin contaminated aboard ship would be direct discharge to the ocean, without treatment. Consequently, the elution effect of sea water on various activities sorbed on mixed ion-exchange resin is of interest. Radioactive contaminants were rapidly eluted

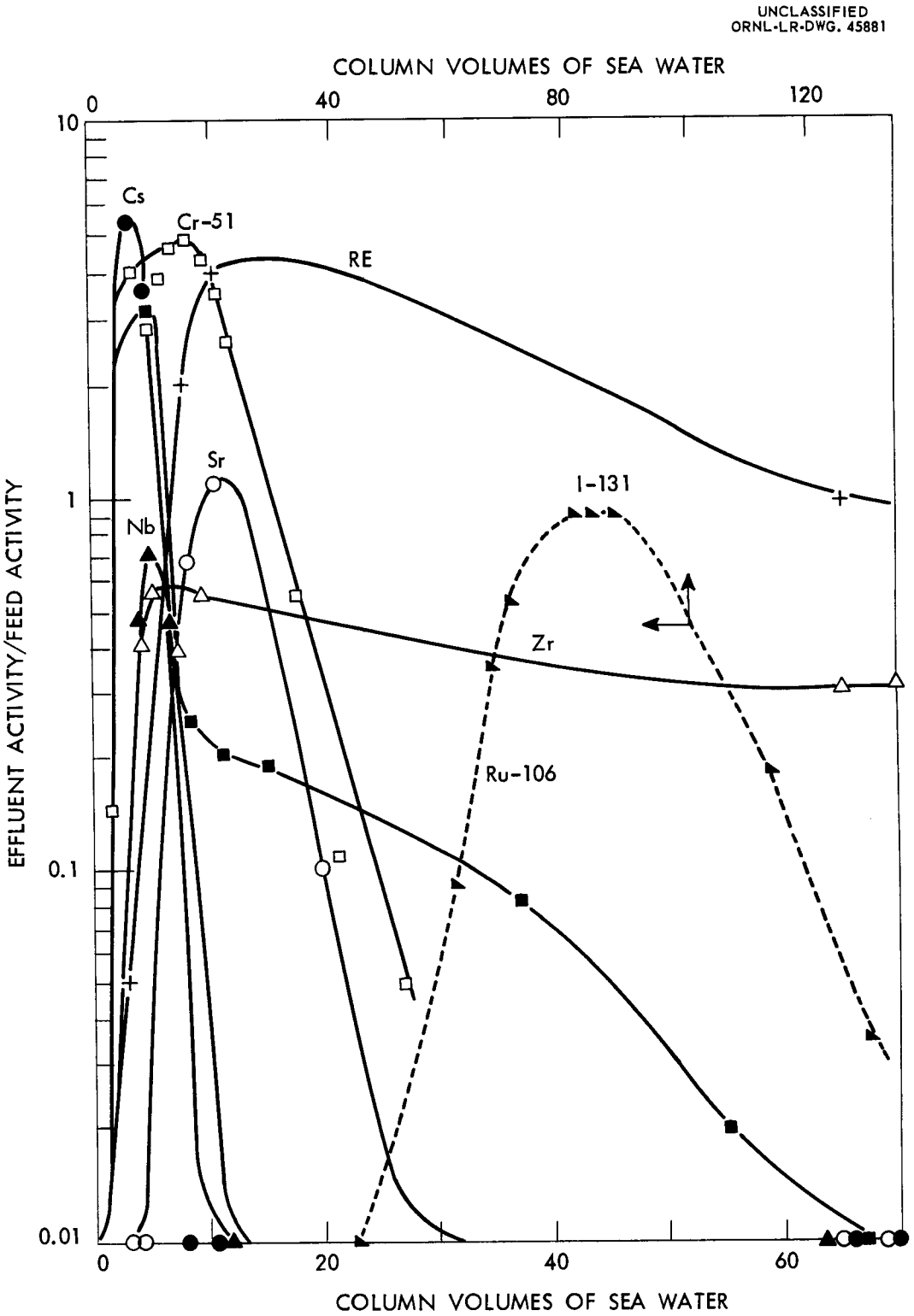

Fig. 1. Elution of fission products from a mixed resin bed with simulated sea water.

from resin by simulated sea water (Fig. 1) in the laboratory. This indicates that direct discharge of contaminated resin to the ocean without fixation or containment of some type would quickly contaminate the ocean at the site of discharge. This would create a hazard for other ships passing the site of discharge and possibly even for the ship completing the discharge.

For the experiments, one resin column was contacted with a sample of mixed fission products, a second with I-131, a third with Cr-51, and a fourth with Ru-106. The bulks of the various activities were eluted from the resins in the following column volumes of sea water (0.52 M NaCl, 0.03 M $MgCl_2$, 0.03 M $MgSO_4$): Cs, 7; Nb, 17; Sr, 21; Zr, 62; total rare earths, 62; and I, 120 (Fig. 1). Chromium-51 was 80% eluted by sea water in 15 column volumes and Ru-106 was 30% eluted in 16 column volumes. The remaining Cr-51 and Ru-106 were eluted very slowly, and it appears that these elements hydrolyzed during the elution. Sea water elution of a sample of actual demineralizer ion-exchange resin from the APPR system gave similar results (Fig. 2).

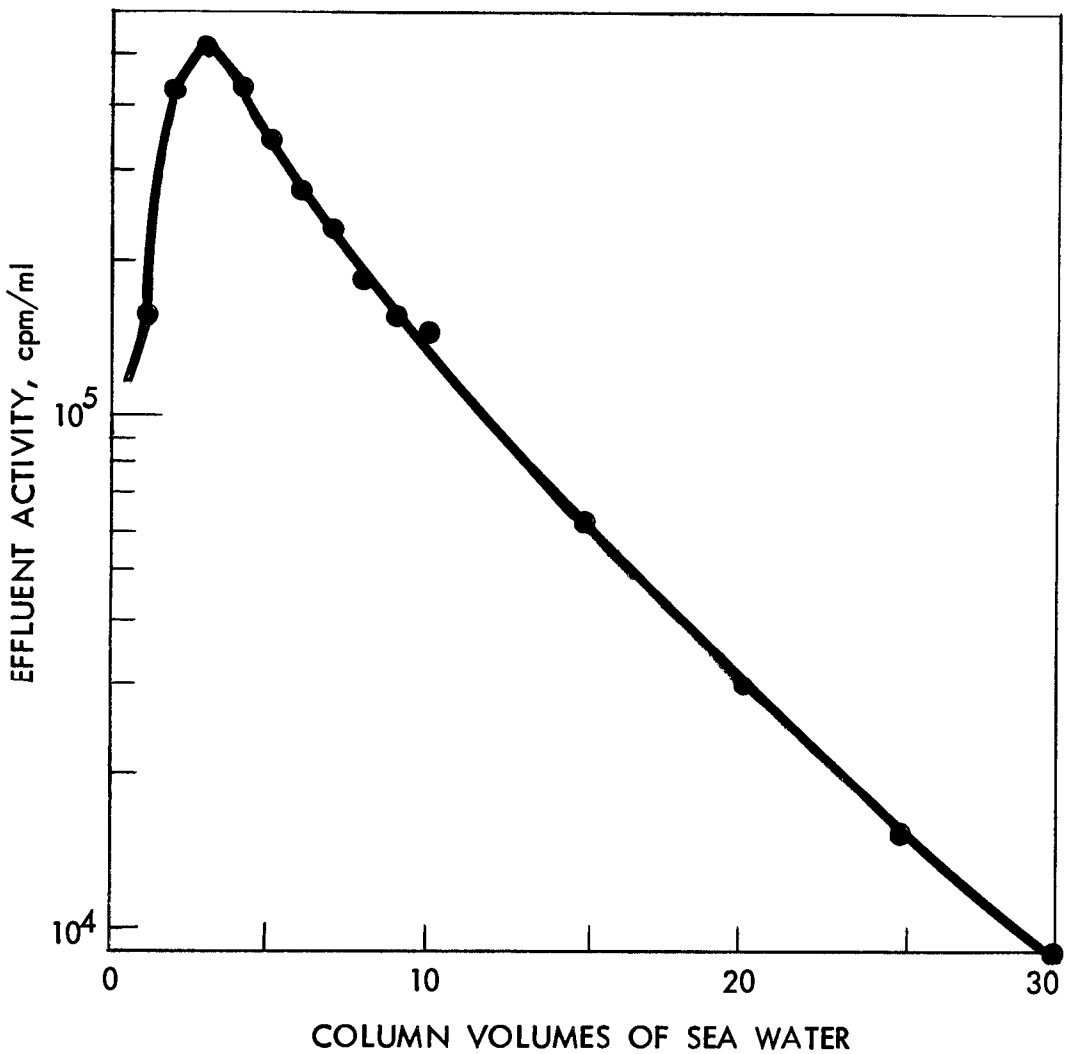

Fig. 2. APPR resin bed elution with sea water; 30 column volumes of sea water removed 61% of the activity originally on the resin.

2.2 Formation of Resin-in-concrete Blocks

Ion-exchange resins can be concreted with ordinary Portland cement, the resin serving as an aggregate material in place of sand or gravel. The best concrete blocks for sea disposal were prepared by slurrying 2 volumes of Portland cement with 1 volume of the resin in enough water, usually 1 volume, to make a workable mud. The mixture was allowed to set up in a polyethylene bottle. After hardening, the resulting concrete block was cut out of the plastic and allowed to air-dry for several weeks. The density was 1.6 g/cm^3. The block was extremely hard and resistant to mechanical shock (deliberate fracture with a hammer). Breaking the block showed the resin beads homogeneously dispersed. Other blocks prepared in this way showed no tendency to fissure or crack even after several months of soaking in simulated sea water. The above properties were pronounced in blocks that were cooled while setting up.

A block formed similarly from 1 volume of the mixed resin and 1 volume of Portland cement slurried with excess water showed extreme hardness and resistance to mechanical shock, had the resin beads homogeneously dispersed, and had a density of 1.4 g/cm^3, which is sufficient to ensure deposition of the block on the ocean floor. However, when allowed to soak in simulated sea water the block showed minute cracks, which indicate that it would probably rupture when exposed to pressure in the depths of the ocean.

Blocks prepared similarly but in which a concrete additive, Daraweld, a synthetic latex emulsion, was substituted for part of the water in an attempt to improve the waterproof qualities of the concrete were somewhat more elastic than the ordinary cement block and thus harder to fracture. However, when exposed to simulated sea water for a short time, the additive leached from the block and deposited on the block and leaching vessel and the block became very brittle. After several months the block crumbled completely (Fig. 3).

2.3 Leaching of Activity from Concreted Resins

Leaching experiments with concrete blocks indicated that concreting of contaminated resins is a satisfactory method of treating contaminated resins prior to discharge to the ocean. Two concrete blocks, one containing 10 mc and the other 20 mc of mixed fission products sorbed on mixed resins, were prepared by the first method described in Sect. 2.2. The block containing 10 mc of activity was twice the size of the block containing 20 mc. The blocks retained more than 99.5% of their activities in $\sim$2500 and $\sim$1000 hr respective leaching with simulated sea water (Table 2, Fig. 4a).

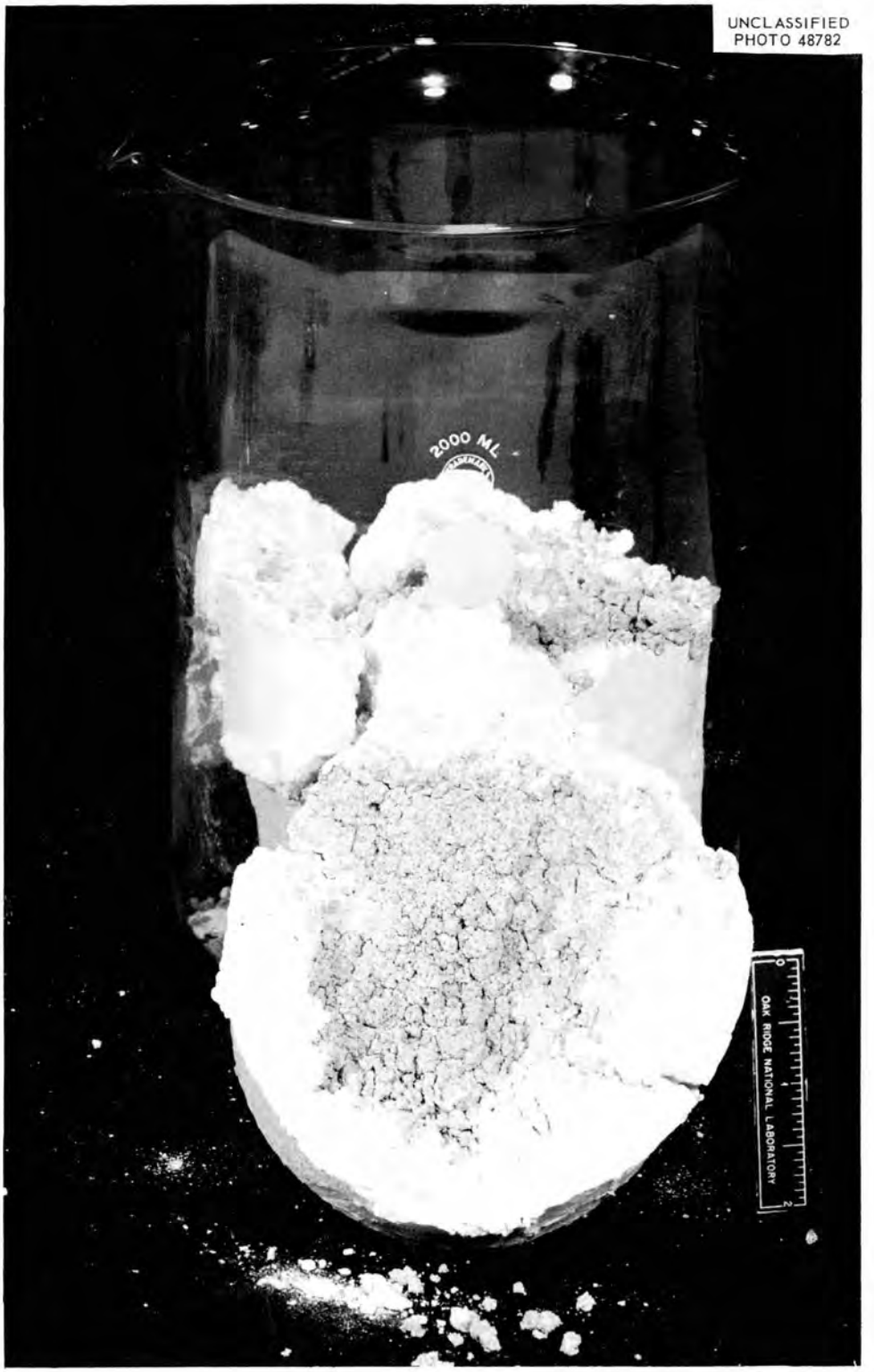

Fig. 3. Ion exchange resin embedded in concrete (50% cement, 25% resin, 12% water and 13% Daraweld) after 3 months exposure to simulated sea water.

Table 2. Leaching by Simulated Sea Water of Gross Gamma Activity from Ion-exchange Resin Embedded in Concrete

Resin: 50% strong acid cation-exchange resin and 50% strong base anion-exchange resin

Concrete: 50% Portland cement, 25% mixed resin, 25% water

Sample No.	Time Leached, hr	Volume of Sea Water, ml	Gross Gamma Activity (above 40 kev) Effluent Sample, cpm/ml	Total Leached cpm	Total Leached %[a]
10 mc of mixed fission products in block					
Background	0	3000	338	0	0
2	2	2980	469	3.90×10^5	0.069
3	20	2960	651	9.26×10^5	0.165
4	44	2940	731	1.16×10^6	0.207
5	74.5	2920	802	1.35×10^6	0.241
6	186.5	2900	939	1.74×10^6	0.311
7	240	2880	950	1.76×10^6	0.314
8	529	2860	1050	2.04×10^6	0.364
9	693	2840	1082	2.11×10^6	0.377
10	1532	2820	1208	2.45×10^6	0.438
11	1893	2800	1212	2.45×10^6	0.438
13	2540	2760	1230	2.46×10^6	0.439
Fresh simulated sea water added					
14	66	3000	374	1.08×10^5	0.019
15	138	2980	412	2.20×10^5	0.039
20 mc of mixed fission products in block					
Background	0	3000	463	0	0
2	0.67	2980	732	8.02×10^5	0.023
3	30	2960	3055	7.67×10^6	0.224
4	54	2940	3784	9.67×10^6	0.284
5	126	2920	4936	1.31×10^7	0.382
6	168	2900	5246	1.39×10^7	0.405
7	483	2880	6651	1.78×10^7	0.519
8	795	2860	7161	1.92×10^7	0.560
9	966	2840	7296	1.94×10^7	0.566

[a] Based on 5.6×10^8 cpm gross gamma activity present for 10-mc block and on 3.43×10^9 cpm for 20-mc block.

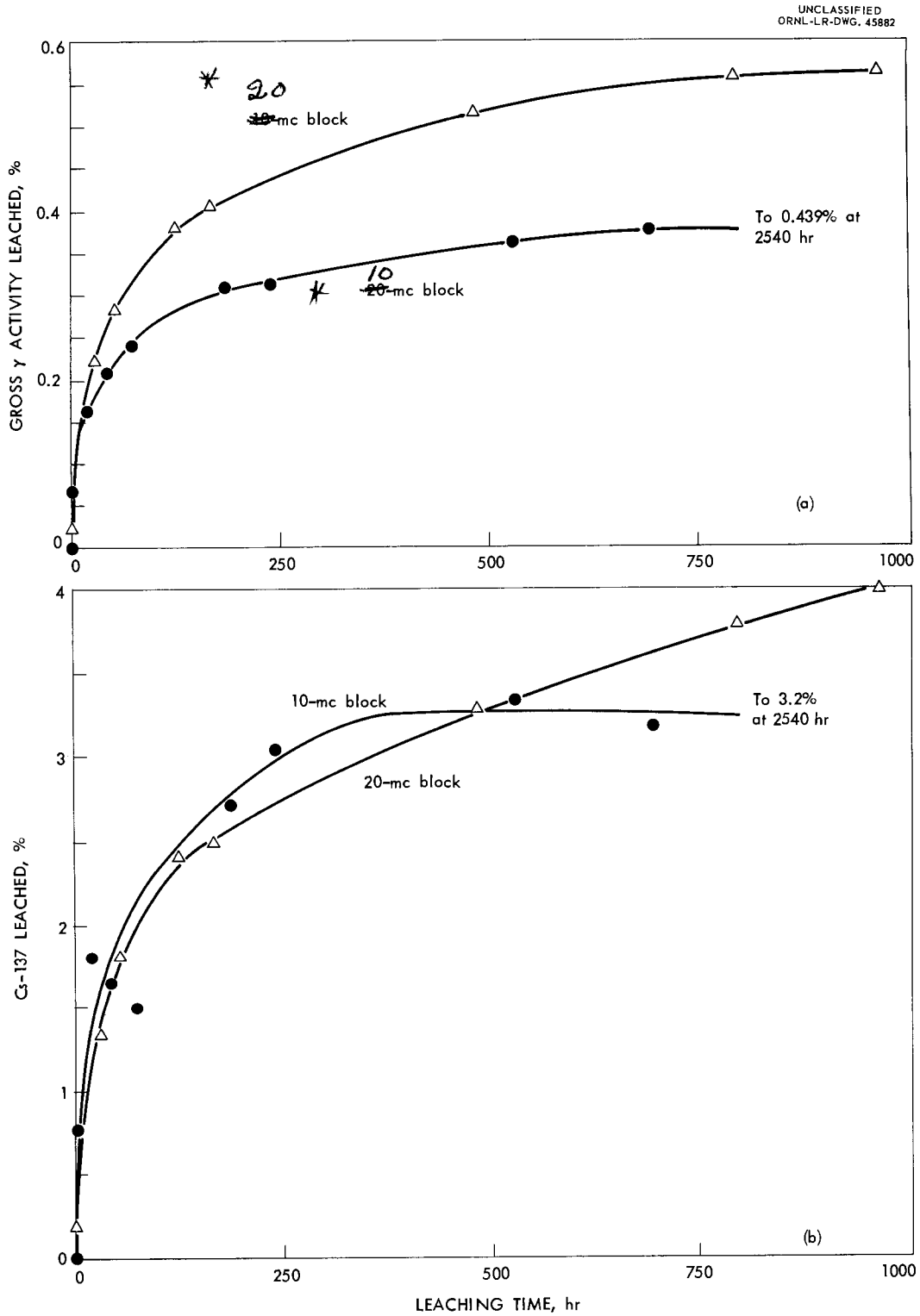

Fig. 4. Leaching of (a) gross gamma activity and (b) Cs^{137} embedded in concrete by simulated sea water. Conditions given in Tables 2 and 3.

* See errata

Table 3. Leaching by Simulated Sea Water of Cs-137 Activity from Ion-exchange Resin Embedded in Concrete

Resin: 50% strong-acid cation-exchange resin and 50% strong-base anion-exchange resin

Concrete: 50% Portland cement, 25% mixed resin, 25% water

Sample No.	Time Leached, hr	Vol. of Sea Water, ml	Cs-137 Activity (662 ± 10 kev) Effluent Sample, cpm/ml	Total Leached cpm	Total Leached %[a]
10 mc of mixed fission products in block					
Background	0	3000	5	0	0
2	2	2980	16	3.28×10^4	0.77
3	20	2960	31	7.70×10^4	1.80
4	44	2940	29	7.06×10^4	1.65
5	74.5	2920	27	6.42×10^4	1.50
6	186.5	2900	45	1.16×10^5	2.71
7	240	2880	50	1.30×10^5	3.04
8	529	2860	55	1.43×10^5	3.34
9	693	2840	53	1.36×10^5	3.18
10	1532	2820	57	1.47×10^5	3.43
11	1893	2800	56	1.43×10^5	3.34
13	2540	2760	54	1.35×10^5	3.15
14	66	3000	6	3.00×10^3	0.07
15	138	2980	9	1.19×10^4	0.28
20 mc of mixed fission products in block					
Background	0	3000	3.6	0	0
2	0.67	2980	22	5.96×10^4	0.18
3	30	2960	153	4.41×10^5	1.34
4	54	2940	206	5.94×10^5	1.81
5	126	2920	274	7.88×10^5	2.40
6	168	2900	284	8.12×10^5	2.48
7	483	2880	380	1.08×10^6	3.29
8	795	2860	442	1.25×10^6	3.81
9	966	2840	468	1.32×10^6	4.02

[a] Based on 4.28×10^6 cpm total Cs-137 gamma activity present in 10-mc block and 3.28×10^7 cpm in 20-mc block.

Fig. 5. Simulated sea-water leaching baths.

In the first experiment (10-mc block), the sea water solution was removed after 2540 hr and replaced with fresh solution to see if equilibrium had been established. More activity was leached from the block by the fresh solution, but a factor of 10 less than that leached by the original solution in a corresponding length of time. This lower rate of leaching indicated that greater than 99% of the total activity would remain fixed in the concrete indefinitely under the experimental conditions. A gamma-ray energy scan of the sea water samples showed a predominant peak at 660 ± 10 kev, which was attributed to Cs-137. Determination of the percentage of Cs-137 leached showed 3-4% in 2500 hr (Table 3, Fig. 4b). The data indicate that greater than 95% of the cesium activity will remain fixed in the concrete. Results were similar with the 20-mc block; the slightly higher percentage of activity leached can be explained by the larger amount of activity embedded in a smaller volume of concrete.

The leaching experiments were performed in a series of continuously stirred baths (Fig. 5). Each container was charged with 3 liters of simulated sea water containing all the constituents of true sea water[5] that are normally present in concentrations greater than 100 ppm: 0.55 M Cl^-, 0.47 M Na^+, 0.05 M Mg^{++}, 0.03 M $SO_4^=$, 0.01 M Ca^{++}, and 0.01 M K^+. The blocks, which had air-dried for 2 days after setting up for 2 days, were placed in the continuously stirred simulated-sea-water leaching baths.

2.4 Shipboard Disposal of Resins

The concreting operation aboard ship would involve sluicing the resins from the demineralizers into a drum, adjusting the volume of water, adding the appropriate amount of cement, mixing, sealing the drum, and dumping to the ocean. The rolling motion of the drum while settling in the ocean would probably give satisfactory mixing and the ocean would provide the cooling which is desirable in producing a very high integrity concrete block. The laboratory experiments were made at room temperature, under atmospheric pressure and with vigorous stirring. The conditions of temperature and agitation were probably more stringent than would be encountered in the depths of the ocean; thus less leaching of activity would be expected. The effect of pressure in the depths of the ocean which could conceivably fracture the drum and concrete block needs further evaluation.

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