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HEAD-END TREATMENT OF LOW LEVEL WASTES PRIOR TO FOAM SEPARATION

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ABSTRACT

Calcium-magnesium precipitation apparatus was used to reduce the concentrations of these elements in ORNL tap water, used as a substitute for waste water of low level of radioactivity, prior to strontium removal by foam separation. With and without alkali and flocculator chambers and with a stirred sludge of ratio height to diameter equal to 1/1 to ~4/1, use of 5×10^{-3} M each of NaOH and Na_2CO_3 and 2 ppm Fe^{3+} reduced the dissolved Ca + Mg concentrations to 1-2 ppm as calcium. Simultaneously, a strontium DF of 20-200 was achieved, and, by adding Grundite clay in the proportion ~0.5 lb/1000 gal, a cesium DF of 10-40 was achieved.

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1.0 INTRODUCTION

One of the potential advantages of the foam separation process is the possibility that simultaneous flotation of solids in the foam will void the necessity of a filter, such as is now required when NaOH, Na_2CO_3, or phosphates are added to these solutions to precipitate calcium. The degree of supersaturation of water with respect to calcium carbonate and the rate of precipitation are important factors in water treatment plants. Thus, commercial units can reduce the $CaCO_3$ content to 15-30 ppm by the cold soda lime process[1]. This is not an equilibrium value; it is controlled by precipitation kinetics.

Since calcium interferes with the removal of strontium from low level wastes by the foam separation process, a number of experiments were performed to reduce its concentration to more desirable values[2], i.e., in the range of a few parts per million as Ca^{++}. The principals used to govern the course of these experiments were that the total $CaCO_3$ precipitated should be proportional to the mixing time, the concentration of seed crystals, the specific surface area of the crystals, and the difference between the concentration of $CaCO_3$ in the solution and its equilibrium value. A sludge column was used not only to act as a partial filter but also as a zone for more complete precipitation of the $CaCO_3$. Experiments described in this report were performed with ORNL tap water as a substitute for low level waste; studies with actual low level waste are now in progress.

The authors wish to thank C. T. Thompson who performed many of the experiments summarized in this report.

2.0 EXPERIMENTAL

During the course of these experiments the apparatus to precipitate calcium, as $CaCO_3$, and magnesium, as $Mg(OH)_2$, by the addition of Na_2CO_3 and/or NaOH and to aid in the flocculation of the precipitate by the addition of ferric ion evolved from that shown in Fig. 1 (but with no stirrer in the sludge column) to that shown in Fig. 2, which contains neither the alkali mixing chamber nor the ferric ion mixing chamber, i.e., the floc-

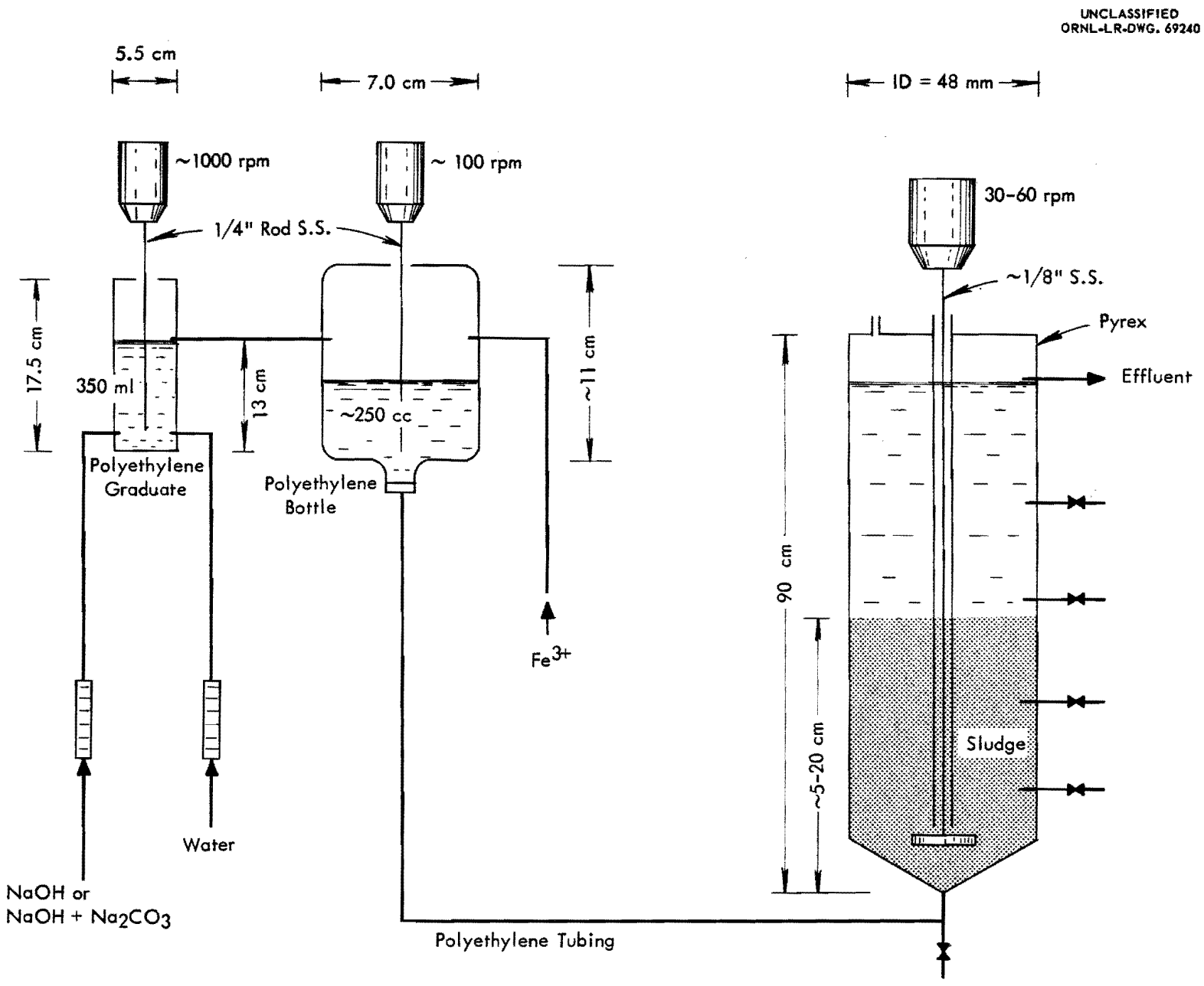

Fig. 1. Precipitation Unit with Alkali and Flocculator Chambers and Sludge Column.

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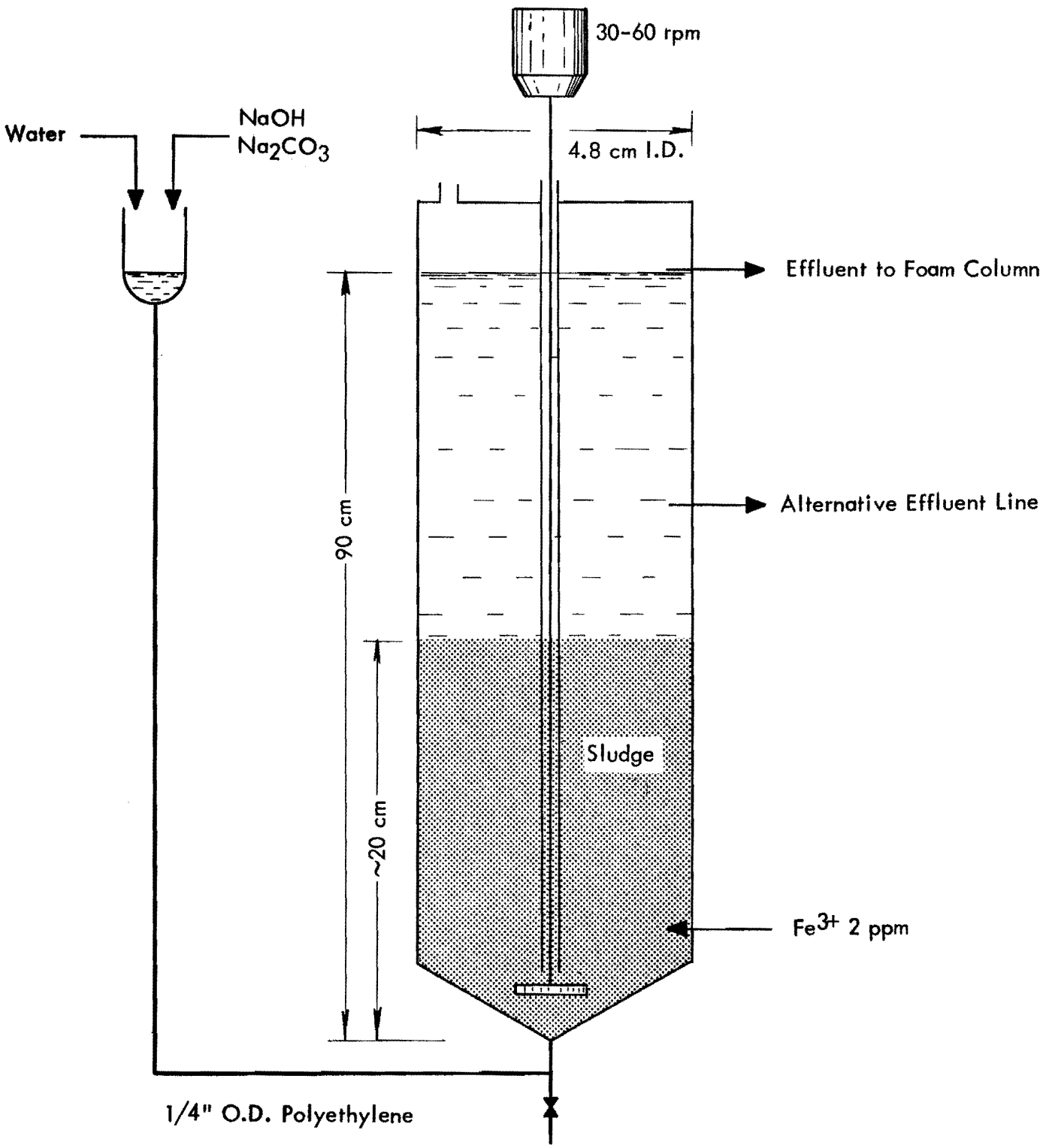

Fig. 2. Precipitation unit - sludge column only.

culator chamber. Solutions were added at the indicated locations by use of finger pumps. Feed solution was ORNL tap water, Table 1, to which tracer quantities of Sr-85 and, in some experiments, Cs-137 had been added.

Table 1. Analyses of ORNL Tap Water

Component	Concentration ppm	Concentration 10^4 M, moles/liter
HCO_3^-	100	16.5
$CO_3^=$	0.5	
OH^-	-	
Cl^-	1.5	
Ca^{++}	27	6.7
Mg^{++}	7	2.9
$Fe^{2+} + Fe^{3+}$	0.5	
Na^+	7	3.4
pH	7.7	

Retention times in the alkali chamber and flocculator were 30 and 20 min, respectively; retention time in the sludge bed, usually of ~5-in. height, was ~35 min. Corresponding retention times in the Scavenging-Ion Exchange pilot plant were 18 sec, 30 min, and 3 hr, respectively[4]. A water column of 29-in. height was maintained above the sludge bed, thereby increasing the retention time in the sludge column to ~2-1/2 hrs. However, the agreement of analyses for Ca, Mg, and Sr in solution 4 inches above the top of the bed and 29 inches above the top of the bed for run 147 indicated that the extra height of water had no effect on the results, thereby showing it was not needed.

Flow rates in most of the experiments were 10.5 ml/min, Table 1, corresponding to 0.58 $ml/min^{-1} \cdot cm^{-2}$, or 8.5 gal $ft^{-2} \cdot hr^{-1}$, in the sludge column. In experiment 139 the flow rates were 11 and 33 ml/min. Corresponding flow rates in the Scavenging-Ion Exchange pilot plant were 10 gal/min, corresponding to 14.3 gal $ft^{-2} \cdot hr^{-1}$ in the sludge bed, i.e., clarifier.

Although calcium, magnesium, and strontium removal was the primary aim of these experiments, Grundite clay was added to the flocculator in experiment 137 (Table 2) to determine the extent of cesium removal by this clay since it was retained in the sludge column. The Grundite was added approximately every 12 hours in 0.5 g quantities; the resulting average concentrations was ~0.5 lb/1000 gal of water.

In experiment 147, the solution, plus any contained solids, were passed through a column of Decalso of dimensions 0.85 cm^2 cross section and 10.5 cm high, corresponding to a volume of 9 cm^3 and a flow rate of 7.5 gal ft^{-3} min^{-1}. This may be compared with 2.5 gal ft^{-3} min^{-1} flow rate in the pilot plant. Both strontium and cesium decontamination and column capacity were measured in this experiment to provide an additional measure of the quality of the sludge column effluent.

3.0 RESULTS

Solution effluent from the sludge column in all experiments, Table 1, would probably be very suitable for high strontium decontamination and large volume reduction by foam separation. In experimental sequence, addition of NaOH solution to the alkali chamber to a level of 10^{-2} M and ferric nitrate to a level of 2 ppm in the flocculator and using an unagitated sludge column reduced the total Ca + Mg content from ~43.5 to ~4 ppm* (90% removal) of which ~2 ppm was dissolved and ~2 ppm existed as suspended solids. The associated strontium DF was ~4. Replacing the 10^{-2} M NaOH by 5×10^{-3} M NaOH + 5×10^{-3} M Na_2CO_3 yielded similar results with respect to Ca and Mg removal but increased the overall strontium DF to ~20.

Agitation of the sludge at the rate of 30-60 rpm produced further improvement when alkali mixing and flocculator chambers were still in use (runs 133, 137). Physically the static sludge column exhibited channelling throughout its full ~5 in. of height whereas the upper, relatively static half, of the agitated sludge column did not show channelling. In addition, larger particles plus much of the strontium activity (Fig. 3) settled to the bottom of the sludge column when agitation was employed. The effluent solution contained only ~1 ppm of dissolved Ca + Mg and

* This and all other values are as calcium.

Table 2. Performance of Precipitator Apparatus

Run No.	Feed Flow Rate ml/min	Alkali Chamber Conc. x 10^3 mole/liter NaOH	Alkali Chamber Conc. x 10^3 mole/liter Na_2CO_3	Alkali Chamber pH	Floc Chamber Fe^{+3} Conc, ppm	Effluent from Sludge Column, Except as Noted: Sample Time from start, hr	Concentrations as ppm Ca: Ca in Soln	Ca as Solid	Mg in Soln	Ca + Mg in Soln	Ca + Mg as Solid	Sr DF: Soln + contained Solids	Sr DF: Soln Only	Cs DF: Soln + contained Solids	Cs DF: Soln Only	Effluent from Decalso Column: Column Vols	Overall DF Sr	Overall DF Cs
111	10.5	10	None	11.7	2.							9						
126	10.5	10	None	11.7	2.	24	1.5	0.8	0	1.4	2.75	3.9						
						25.5	1.5	0.5	0.4	1.9	1.6	4.1						
						27.5	1.5	0.2	-	-	-	4.1						
131	10.5	5	5	11.2-11.3	2.	22						22	22					
						23						19	24					
						24						21	28					
						25						22	65					
						26	1.4	1.2	1.4	2.8	4.7	22	65					
						27	1.6	1.0	0.6	2.2	2.3	26	65					
						28	1.7	0.7	0.4	2.1	3.4	27	62					
133	10.5	5	5	11.2-11.3	2.	27						11.7	17.7					
						30						14.6	15.7					
						32						13.1	22					
						52	Sludge Agitation Initiated and Continued through all Subsequent Experiments											
						56	0.7	0.1	0.45	1.15	0.65	18.8	22					
						57	0.7	0.2	0.35	1.0	1.1	25.0	25.4					
						73	0.65	0.1	0.2	0.8	0.1	19	21					
						74	0.6	0.1	0.45	1.05	0.1							
137	10.5	5	5	11.2-11.3	2.	6	0.65	0	-	0.68	0	460		360		~0.5 g Grundite added at ~12 hr intervals.		
						7	0.5	-	-	-	-							
						22						74	96	36.5	43			
						30	0.63	0	-	-	-							
						47						36	38	11.2	10			
						52	0.50	0	0.1	0.6	0.3	35	40	9	8.5			
139		5	5	11.2-11.3					Feed									
							29.0		14.5	43.5								
							Effluent from Alkali Chamber											
	11.0				2.	48	4.3		8.1	12.4	30 min. retention time							
						51	4.6		5.4	10.0								
	33.0				0.7	53	7.5		10.0	17.5	10 min. retention time							
							Effluent from Flocculator											
	11.0				2.	48	4.0		3.0	7.0	20 min. retention time							
						51	3.9		3.5	7.4								
	33.0				0.7	53	6.4		11.1	17.5	7 min. retention time							
							Effluent from Sludge Column											
	11.0				2.0	48	0.8		0.2	1.0	35 min. retention time							
						51	0.75		0.5	1.25								
	33.0				0.7	53	1.0		-	-	12 min. retention time							
							Alkali and Flocculator Chambers Eliminated (Fig. 2)											
147	10.5	5	5	11.3-11.4	1	6	0.45		1.25	1.7	0.15	211	190	11	13.5			
						26	-		-	1.4	0.3	162	150	-	-	1300	>16,700	1000
						30.5	-		-	1.5	0.1	-	-	-	-			
						49	-		-	-	-	163	220	1.55	1.48	2500	14,000	600
						55	0.60		0.6	1.2	0.13	125	161	-	-	3000	7,000	245
						72	-		-	-	-	165	280	1.22	1.21	4000	9,800	225
						96	0.75		0.4	1.17	0.2	122	[illegible]	1.16	1.18	5400	11,900	38
						120	-		-	-	-	121	194	1.16	1.18	6700	16,700	7.3
						125	0.65		0.5	1.17	0.2	126	204	1.15	1.12	7000	8,300	5.9
							Equilibrium Data (Batch Contacting)											
		5	5	11.29 Final		48	0.55			2.0			93					
						72	0.60			1.4			103					

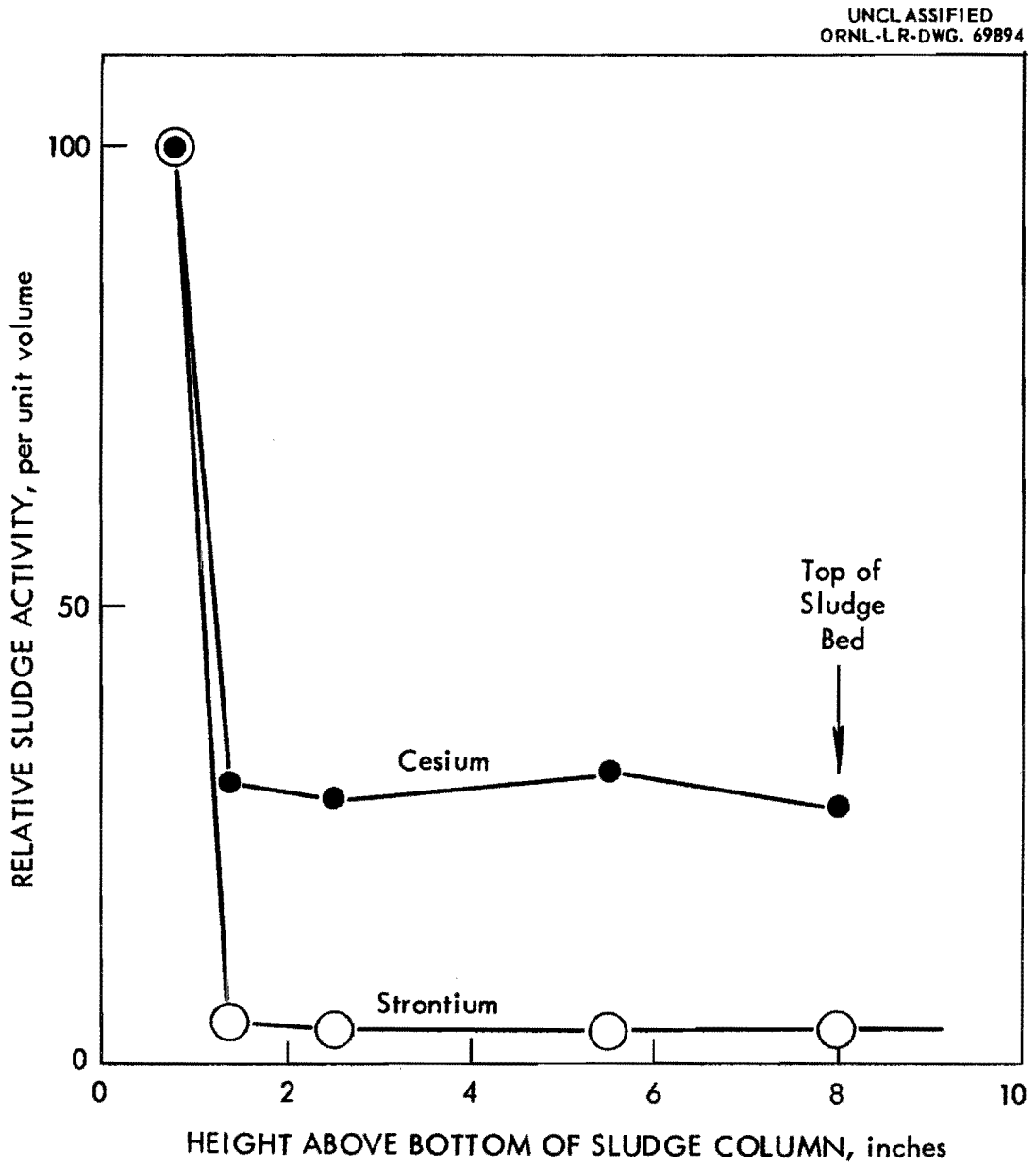

Fig. 3. Distribution of cesium and strontium in the sludge bed.

~0.2 ppm Ca + Mg as solids, corresponding to ~97% removal of these elements. Corresponding strontium DF was 20-40.

Analyses of the solid-free solutions from the alkali and flocculator chambers at two different flow rates, 11 and 33 ml/min, showed that a considerable portion of dissolved Ca and Mg was actually being precipitated in the sludge column, and essentially no precipitation of calcium in the flocculator, thereby suggesting that these two chambers could be eliminated and that NaOH, Na_2CO_3, and ferric ion could all be added to the bottom of the sludge column, Fig. 2. The inefficiency of calcium and magnesium precipitation in the flocculator can probably be traced to the formation of ferric hydroxide. As a flocculator it coats $CaCO_3$ and $Mg(OH)_2$ crystals, coagulates these into larger units, and thereby reduces the area on which dissolved $CaCO_3$ and $Mg(OH)_2$ can be deposited.

In a 5 day run without alkali or flocculator chambers, the dissolved Ca + Mg was reduced to ~1.2 ppm, i.e., not much higher than when alkali and flocculator chambers were in use, the suspended solids content remained at ~0.2 ppm, and the strontium DF actually increased to 100-200. This increase in DF is probably partly due to an effective increase in the solids content in the sludge column, due to its not being deposited on alkali and flocculator chamber walls, and partly to the existence of conditions more favorable to the formation of a high concentration of small crystals in which strontium can be occluded.

The closeness of the composition of the solution from the sludge column of these experiments to equilibrium values was checked by performing two batch experiments in which tap water was made 5×10^{-3} M each in NaOH and Na_2CO_3, agitated for 48 and 72 hours, filtered, and the solution then analyzed for Ca and Ca + Mg. The resulting data, i.e., 0.55 and 0.60 ppm dissolved Ca and 2.0 and 1.4 ppm dissolved Ca + Mg, indicate that equilibrium was approached quite closely in most of the dynamic experiments of this report.

Two auxiliary experiments were performed to effect some removal of cesium in addition to strontium. In the first, run 137, Grundite clay was added to the alkali chamber in ~0.5 g quantities at ~12 hr intervals

during this 2 day run. The average Grundite concentration was thus ~0.5 lb/1000 gal. Although this was a non-steady state system, Cs DF generally in excess of 10 was achieved. In the second experiment, the solution plus contained solids effluent from the sludge column was passed through a column of the cheap ion exchange mineral Decalso, which might preferably be discarded rather than regenerated. After 4000 column volumes of sludge column effluent had been passed through this column, the overall cesium DF, due primarily to the Decalso and not to the sludge column, was still 200. Cesium breakthrough to a 1% level occurred at ~5000 column volumes and 10% breakthrough at ~6500 column volumes. Simultaneously the strontium DF was further increased by a factor of ~50 from ~2×10^2 to ~1×10^4.

4.0 CONCLUSIONS

It may be concluded from the experiments of this report that the calcium and magnesium concentrations of ORNL tap water can readily be reduced to the 1-2 ppm as calcium range, corresponding to ~96% removal of these elements, by precipitation with 5×10^{-3} M each of NaOH and Na_2CO_3 and coagulation with 1 or 2 ppm Fe^{+3} in a single, stirred sludge column. The resulting solution, containing only ~0.2 ppm Ca + Mg as solids should be very suitable for further large decontamination with respect to strontium with any of 6-8 foaming agents[3] whose characteristics have been partially evaluated or by ion exchange. In addition to precipitating Ca and Mg, strontium DF's in the range 20-200 and cesium DF's in the range 10-40 were achieved.

One of the most important features of this work was use of a stirred sludge blanket of large, i.e., ~4/1, height to diameter ratio. Although the principal stirring occurred in the lower half of the blanket, wherein settling of larger particles was facilitated, the gentle movement in the upper half eliminated channelling, thereby producing better precipitation and filtration. Use of this single unit, i.e., without separate alkali and flocculator chambers, apparently provided better and more crystalline surface area on which $CaCO_3$ and $Mg(OH)_2$ could deposit.

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