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Radioactive Waste

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PHYSICAL CHARACTERIZATION OF ACIDIC AND NEUTRALIZED SYNTHETIC FUEL REPROCESSING WASTE SOLUTIONS ON EVAPORATION AND CALCINATION

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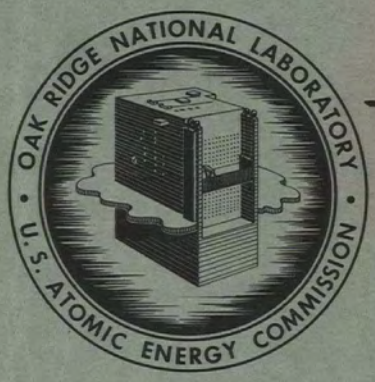

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CHEMICAL TECHNOLOGY DIVISION

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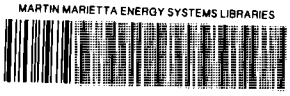

ABSTRACT

Five synthetic fuel reprocessing waste solutions have been subjected to physical and chemical treatments designed to reduce the volume and make the residue more suitable for storage or for further treatment prior to disposal.

Evaporation of acidic wastes to dryness gave solid residues with volumes of 6.8% (of original waste volume) for Purex, 24% for TBP-25, 15% for STR, 9.2% for Darex, and 3% for SIR. Condensates were approximately the volume of the original waste. Calcination of these dried residues at 900°C gave reductions in weight (referred to dry residue) of 43% for Purex, 58% for TBP-25, 34% for STR, 9% for Darex, and 74% for SIR.

Neutralization with NaOH gave slow-settling, poorly filterable precipitates. Precipitates from neutralization with $Ca(OH)_2$ settled more rapidly and could be filtered with less difficulty. None of the precipitates was considered suitable for commercial filtration equipment. A flocculating agent (IFA-313, Illinois Water Treatment Company) increased settling rates in some cases. Maximum settling rates were attained with SIR waste neutralized with $Ca(OH)_2$.

Unfiltered, neutralized wastes were evaporated to dryness and produced residues having volumes of 10% to 50% of original waste volume. Evaporation of the neutralized waste might be more desirable from the standpoint of reducing the volatility of certain fission products and reducing corrosion of equipment.

CONTENTS

1.0 INTRODUCTION

Since a variety of high-level wastes are produced as by-products of reactor-fuel reprocessing, a variety of physical and chemical treatments will probably be required to prepare them for disposal. Five simulated representative types of waste were chosen as subjects of a preliminary study of their behavior upon neutralization, filtration, evaporation to dryness, and calcination of the dry residues. So that investigators at different sites might work with comparable material, the wastes were synthesized following a manual[1] giving compositions and suggested preparation procedures (Tables I-III).

The five wastes chosen were:

1. Purex (a nitric acid waste from aluminum-jacketed uranium fuel).
2. TBP-25 (an aluminum nitrate--nitric acid waste from enriched uranium-aluminum alloy elements).
3. STR (Zr-F-Al-NO_3 waste).
4. Darex (stainless steel nitrates in nitric acid).
5. SIR (stainless steel nitrates in nitric and sulfuric acids).

Since the wastes were not derived from actual irradiated fuels, they do not contain fission products, nor do they contain the trace of organic residue resulting from solvent extraction. However, it is not believed that the conclusions of this report will be substantially affected by the presence of these materials. Further studies on actual waste solutions will be required before practical disposal methods based on this study can be developed.

As actual wastes (Fig. 1) may be stored in acidic or neutralized form (for the decay of short- or intermediate- lived fission products) the simulated wastes were treated in both forms: wastes were evaporated while acidic, or neutralized with NaOH or $Ca(OH)_2$ in attempts to form filterable precipitates. Nitric acid wastes (Purex) are currently neutralized with 50% NaOH; fission products are precipitated and scavenged, leaving a supernatant containing most of the cesium and nitrate of the original solution along with traces of strontium, the rare earths, americium, plutonium, and about 10% of the ruthenium.

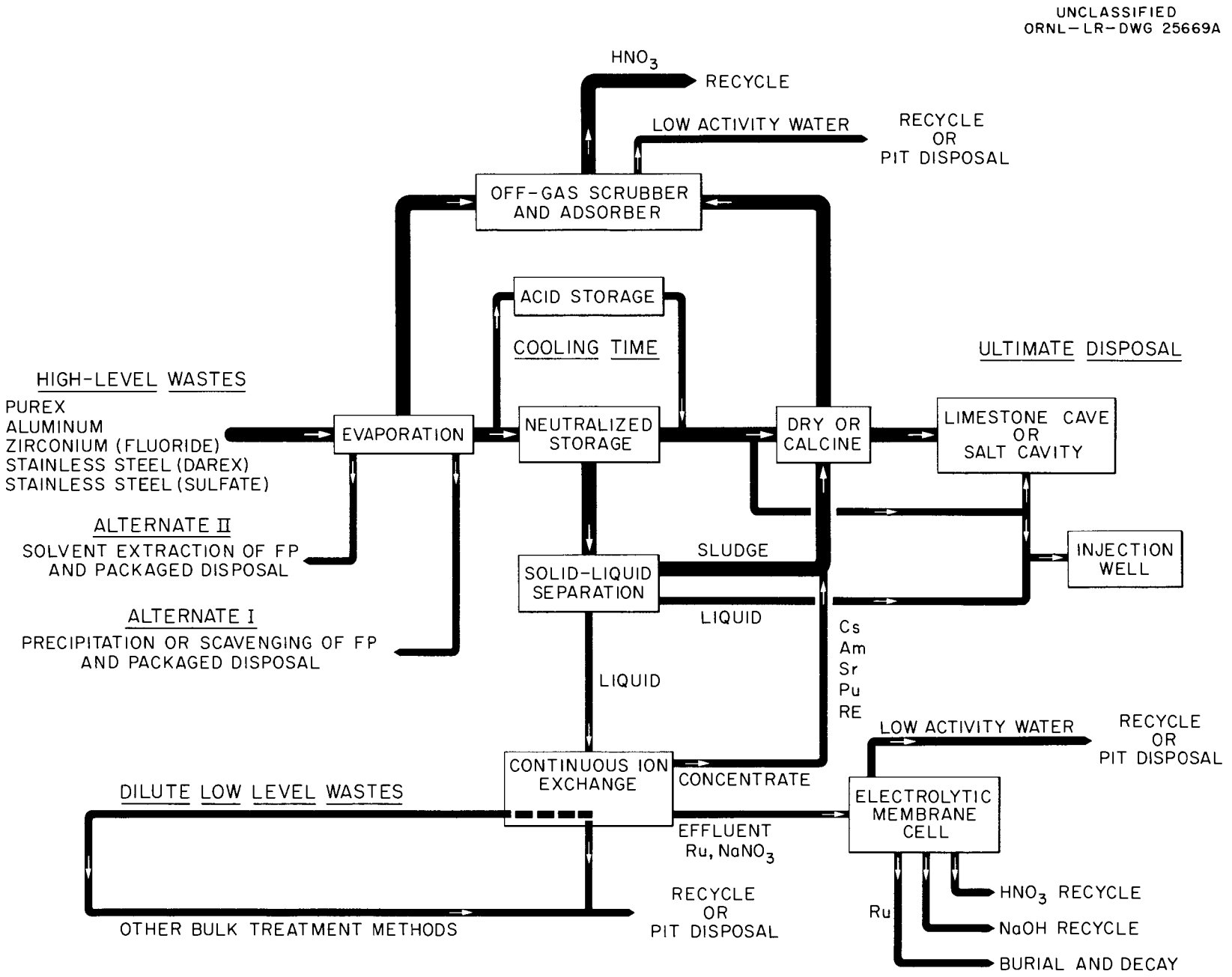

Fig. 1. Disposal of High-Level Fuel Reprocessing Waste Solutions. Area within the broken line is subject of characterization studies.

Table I. Composition of "Standard" Synthetic Wastes[1]

Ionic Components (M)	Purex			TBP-25 (Aluminum)	STR (Zirconium Fluoride)	Darex ($SS-UO_2$)	SIR ($SS-UO_2$-Mg U)
	Original	Evaporated Concentrate	Neutralized Concentrate				
Volume	1280 $\frac{gal}{ton\ U}$	125 gal/ton U	132 gal/ton U	0.22 to 0.11 gal/g U-235	2500 gal	0.5 gal/g U-235	0.35 gal/g U-235
Sp. G.	1.01	1.3	1.18	1.29	1.216	1.28	1.09
H^+	1.0	7.0	0	0.5	2.14	2.94	3.52
Al^{+++}				1.6	0.75	0.123	
Na^+	Trace	0.3	5.3				
Fe^{+++}	Trace	0.5	0.034	0.002		0.68	0.066
NH_4^+				0.05			
Hg^{++}				0.01			
Zr^{4+}					0.55		
Sn^{++}					0.012		
Cr^{++}					0.016	0.16	0.018
Ni^{++}						0.075	0.008
Mn^+							0.001
Mg^{++}							0.017
Cl^-						30 ppm	
F^-					3.00		
NO_3^-	1.0	7.3	7.1	5.5	3.59	6.1	2.8
SO_4^{--}	0.03	0.75	0.10	0.02			0.51
OH^-			5.0				

[1]From CF-58-4-45 Manual for the Preparation of Simulated Fuel Reprocessing Waste Solutions, W. J. Lacy

Table II Materials for Preparation of Synthetic Wastes

Basis: 1 Liter Synthesized Waste

Ingredients	Purex	TBP-25 (Aluminum Nitrate)	STR (Zirconium Fluoride)	Darex ($SS-UO_2$)	SIR ($SS-UO_2-MgO$)
$Fe(NO_3)_3 \cdot 9\ H_2O$	202 g			275 g	28 g
Na_2SO_4	21.3 g				
H_2SO_4	35.5 ml, 18 M				28 ml, 18 M
HNO_3	353 ml, 15.6 M	33 ml, 15.6 M	83 ml, 15.6 M	189 ml, 15.6 M	131 ml, 15.6 M
$Al(NO_3)_3 \cdot 9\ H_2O$		600 g	273 g	46.1 g	
$Fe_2(SO_4)_3 \cdot X\ H_2O$		0.8 g			
$(NH_4)_2\ SO_4$		2.64 g			
$Hg\ (NO_3)_2$		3.25 g			
NH_4NO_3		2.4 g			
$Zr\ (OH)_4 \cdot 12\ H_2O$			206 g		
$Cr\ (NO_3)_3 \cdot 9\ H_2O$			6.4 g	64 g	13 g
Sn (mossy)			1.43 g		
HF			107 ml, 28 M		
$Ni\ (NO_3)_2 \cdot 6\ H_2O$				19.8 g	2.3 g
$Mg\ (NO_3)_2 \cdot 6\ H_2O$					4.4 g
HCl				1 ml, 1 M	
$Mn\ (NO_3)_2 \cdot 6\ H_2O$					0.119

Table III. Evaporation of Acidic Waste

Original Volume evaporated 250 ml

Evaporated by boiling at 1 atm.

Waste Type	Percent of Original volume at which soln. is saturated at boiling point	Still Temp. Range (°C)	Solid Residue			Condensate Volume (ml)	Remarks
			Weight (g)	Volume (ml)	% original Waste Volume		
Purex	40	106°->150°	26.8	17	6.8	241	
TBP-25 (Aluminum Nitrate)	~ 24	109-160	47.0	60	24	232	Syrupy liquid which solidified on cooling
STR (Zirconium-Fluoride)	~ 50	108-165	38.1	38	15.2	236	Crystals did not form immediately
Darex ($SS-UO_2$)	40	106-170	23.0	23	9.3	257*	Crystals formed
SIR ($SS-UO_2-MgO$)	7	105-150	6.6	8	3.2	245	Glassy solid formed without crystallization

*Probably due to experimental error

The concentrate compositions as given in Table 1 represent, in most cases, a concentrated solvent extraction raffinate to which may be added other streams. These compositions are believed to be most representative of waste composition which may be expected, although subject to change as improvements in separations technology continue to be made. A brief description of each process follows:

A. Purex Process: Tri-butyl-phosphate solvent in an inert diluent is contacted with a solution of uranium and fission products dissolved in nitric acid. This process is used for the processing of irradiated natural uranium. By far the largest volume of waste now being produced is from the Purex process.

B. TBP-25 Process: This process is designed to recover enriched uranium from irradiated uranium-aluminum alloy fuel elements. The fuel elements are dissolved in nitric acid using a mercuric nitrate catalyst to give a solution of aluminum nitrate and uranyl nitrate. The extraction solvent is TBP in an inert diluent. The waste is primarily aluminum nitrate plus fission products.

C. STR (Zirconium-Fluoride) Process: Several reactor designs (including the Nautilus, or STR) use zirconium or a zirconium alloy as a cladding material and as an alloying agent in the fuel elements. Zirconium is very resistant to dissolution by nitric or sulfuric acid, but has been found to be attacked by hydrofluoric acid. Following hydrofluoric acid dissolution, chromate is added to oxidize the uranium to U(VI) and aluminum added to complex the free fluoride. After the addition of nitric acid, the uranium is recovered by TBP extraction.

D. Darex Process: Dilute aqua regia is used to dissolve stainless steel-constituted fuels. After removal of chloride ion down to about 30 ppm by nitric acid-stripping, the uranium (and plutonium, if present) is recovered by TBP extraction.

E. SIR Process: The SIR element is fabricated of a sintered UO_2-MgO core with stainless steel cladding. The stainless steel is dissolved in boiling 4-6 M H_2SO_4, followed by the addition of nitric acid to dissolve the core. The mixed nitrate-sulfate solution is subjected to solvent extraction with TBP.

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2.0 PROCESSING OF ACIDIC WASTES

2.1 Evaporation

Each of the five standard acidic wastes (Table 1) was evaporated to dryness under test conditions. The apparatus consisted of a 500-ml reaction flask, an electric mantle heater, and a water-cooled condenser. After evaporating 250 ml of the waste to a dry residue, the volume of condensate and the volume and weight of solid residue remaining in the flask were measured (Table III). Following evaporation to dryness, the residue was subjected to calcination from 3 to 64 hr at temperatures to 900°C (Table IV). Figure 2 shows the loss in weight of the dry residues as a function of calcination temperature.

Purex. In the evaporation of the Purex waste, crystals precipitated when the volume of the sample reached 40% of the original volume at approximately boiling temperatures. The solid residue weighed 26.8 g, had a bulk volume of 17 ml, a bulk density of 1.6 g/ml and occupied 6.8% of the original sample volume. Condensate volume was 241 ml, 96.5% of the sample volume. The evaporation was carried out without bumping or spattering and the solid residue was removed from the flask without difficulty. This behavior indicates that commercial evaporation and drying equipment can probably be used to reduce this waste to a dry solid.

When the dry residue was calcined in steps up to 900°C (Table IV), the weight dropped to 57% of that of the dried residue. Nitrate content appeared to remain about constant up to 600°C (1.4 to 2.5% of the residue) but decreased to 0.74% at 900°C.

TBP-25. The yield of solid residue after evaporation was much greater for the TBP-25 waste than for any of the other types. Sixty ml of solids (24% of original waste volume) weighing 47 grams remained in the flask. The condensate volume was 232 ml, 93% of the original waste volume. There was no precipitation of crystals as concentration proceeded. Instead, the solution became viscous and solidified upon cooling. Solidification became apparent when solution volume was reduced to about 25% of the original.

Calcination of the evaporation residue reduced it to 42% of the evaporation residue weight. Nitrate content of the solid dropped from 23.8% to 5.8% after calcination at 900°C.

Table IV. Calcination of Residues from Acid Evaporation

Waste Type	Calcination Temp (°C)	Time (hr)	Weight (g)		Calcined Weight, (% of Original)	NO_3 (% of residue)
			Sample Before Calcination	Sample After Calcination		
Purex	200°	3	1.00	1.00	100	10.42
	300	3	1.00	1.00	100	--
	400	16.5	1.00	1.00	100	1.36
	500	4.75	1.00	0.97	97	--
	600	3	1.00	0.76	76	2.54
	700	64	1.00	0.59	59	--
	800	4	1.00	0.57	57	--
	900	3.75	1.00	0.57	57	0.74
Darex ($SS+-UO_2$)	200	3	1.00	1.00	100	6.51
	300	3	1.00	0.98	98	--
	400	16.5	1.00	0.93	93	3.91
	500	4.75	1.00	0.92	92	--
	600	3.00	1.00	0.90	90	3.08
	700	64	1.00	0.92	92	--
	800	4	1.00	0.91	91	--
	900	3.75	1.00	0.91	91	4.77
STR (Zr-F)	200	3	1.00	0.99	99	8.43
	300	3	1.00	0.97	97	--
	400	16.5	1.00	0.90	90	8.90
	500	4.75	1.00	0.88	88	--
	600	3	1.00	0.77	77	8.99
	700	64	1.00	0.69	69	--
	800	4	1.00	0.68	68	--
	900	3.75	1.00	0.66	66	6.20
TBP-25 ($Al(NO_3)_3$)	200	5	1.77	1.33	75	23.8
	300	16	1.55	0.89	37.5	12.8
	400	4	1.68	0.83	49.5	--
	500	3.5	2.12	1.06	50	--
	600	64	1.36	0.60	44.1	--
	700	2.5	1.50	1.68	45.3	--
	800	2.5	1.28	0.60	47.0	--
	900	2.5	1.36	0.57	42.0	5.79
SIR ($SS-UO_2$-MgO)	200	3	0.47	0.40	85.1	--
	300	2.75	0.47	0.37	78.7	--
	400	64.0	0.47	0.36	76.6	--
	500	3.75	0.47	0.34	72.3	--
	600	3.75	0.47	0.23	48.9	--
	700	16.0	0.47	0.13	27.6	--
	800	4	0.47	0.12	25.5	--

STR. In the evaporation of a 250-ml sample of STR waste, there was no apparent attack of hydrofluoric acid on the glass. In determination of the point at which crystallization first occurred, a 50-ml sample was evaporated to 26% of original volume without the formation of crystals at near boiling temperatures. However, on dilution to 50% of original volume, white crystals were formed which did not redissolve at boiling. Evaporation of the 250-ml sample to dryness gave 38 ml (15% of the original volume) of a solid residue weighing 38 g. Condensate volume was 236 ml, 95% of that of the original waste.

When calcined, this waste had a total weight loss of 66%. The nitrate content did not show a significant variation (9.0 to 6.2%) and was not accounted for by weight loss on calcination.

Darex. When Darex waste was evaporated, crystals formed at 40% of the original volume. With evaporation of 250 ml to dryness, 23 ml (9.2% of the original volume) of a solid residue weighing 23 g was formed. The volume of condensate collected was 257 ml. This apparent volume increase is probably due to experimental error. No difficulty was experienced in removing the cake from the flask.

This residue had the least loss in weight on calcination of the five materials evaluated, only 9% of original. The variation in nitrate content was from 3.1 to 6.5%. The nitrate variation did not correspond to weight loss.

SIR. When SIR waste was evaporated to 7% of the original volume, a glassy, non-crystalline solid was formed. Eight ml (3% of the original volume) of final solid residue remained and weighed 6.6 grams. Condensate volume was 245 ml. No difficulty was encountered in the evaporation.

A calcined sample of this waste lost weight down to 25.5% of the original when calcined to 900°C. This was the greatest weight loss on calcination for any of the residues. There was not sufficient sample available to secure nitrate analyses.

3.0 NEUTRALIZATION OF ACIDIC WASTES

Each of the five types of waste investigated was neutralized (after dilution) with both sodium hydroxide solution and with dry calcium hydroxide under varied conditions in an effort to produce a precipitate, which would carry most of the fission products and which could be readily separated from the supernatant. The supernatant could then receive further treatment. In general, filtration characteristics were poor. Settling rates, expressed

in mm/min, varied over an extremely wide range. The following general statements may be made regarding the five types of waste, based on data in Table V.

1. Precipitates from Purex, TBP-25, and Darex wastes settled very slowly.

2. SIR wastes gave precipitates which settled most rapidly. The STR wastes had an intermediate settling rate. The SIR precipitate settling rate was up to a factor of 20 faster than the rates for Purex, TBP-25, and Darex wastes.

3. Precipitates from $Ca(OH)_2$ neutralization settled more rapidly than those from NaOH neutralization.

4. Addition of the flocculating agent IFA-313 (Illinois Water Treatment Company) increased the settling rate except in the case of neutralized TBP-25 waste, where settling rates were too low to detect a difference (Section 4.1).

5. In every case filtration rates on fritted glass or sintered stainless steel disks were prohibitively low.

3.1 Experimental Procedure

Two reagents, sodium hydroxide and dry calcium hydroxide, were used in neutralization experiments. Exploratory tests were made to determine the effect of dilution on the settling and filtration rates of neutralized waste. Because of the voluminous precipitates formed on neutralization, the concentration chosen was 10% standard waste solution and 90% water for most tests (Table V).

All neutralizations were carried out with continuous agitation by a magnetic stirrer. Electrodes of a Beckman pH meter were immersed in the solution and addition of neutralizing reagent continued to a pH of approximately 8.5. Neutralizations of some concentrated wastes went to pH values greater than 9.0 due to difficulty in maintaining thorough mixing in the more viscous slurries. A flocculating agent (IFA-313, Illinois Water Treatment Company) was added in some neutralizations in an effort to determine its gross effect on settling rate. Detailed tests of the effectiveness of the IFA-313 are presented in Table VI.

Table V. Neutralization of Reactor Fuel Reprocessing Wastes

Waste Type	Composition: Waste	Composition: Dilution H_2O	Neutralizing Agent	pH	Flocculation Agent, IFA-313 (ml/liter)	Cumulative Average Settling Rates (mm/min): Elapsed Time (min) 5	10	20	40	Terminal[a]	Filtration Characteristics
Purex	50	50	NaOH	8.8	None	0	0	0.09	0.10	0.16 (135)	Poor-slimy precipitate
	50	50	$Ca(OH)_2$	8.65	None	0	0	0	0	0.06 (150)	Poor
	35	65	NaOH	8.72	None	0.36	-	0.23	0.26	0.31 (135)	Poor-slimy precipitate
	35	65	$Ca(OH)_2$	8.5	None	0	0	0.07	-	0.07 (150)	Poor-improving
	20	80	NaOH	9.28	None	1.45	-	1.73	1.82	0.76 (135)	Poor-slimy precipitate
	20	80	$Ca(OH)_2$	9.7	None	-	-	0.36	-	0.59 (150)	Better-cake more granular
	10	90	NaOH	9.3	None	3.64	-	3.73	2.91	0.88 (135)	Poor-slimy precipitate
	10	90	$Ca(OH)_2$	8.8	None	-	-	1.24	-	0.80 (150)	Good-slowing with increased cake thickness
Darex (SS+-UO_2)	10	90	NaOH	8.45	0.63	0.36	0.55	0.55	0.68	0.57 (140)	Slow filtering
	10	90	NaOH	8.65	None	0.36	0.46	0.46	0.5	0.57 (140)	Very slow filtering
	10	90	$Ca(OH)_2$	8.41	0.5	2.55	4.55	3.82	2.51	0.83 (140)	More rapid than NaOH neutralized
	10	90	$Ca(OH)_2$	8.50	None	2.36	2.73	2.73	2.32	0.87 (140)	
SIR(SS-UO_2-MgO)	10	90	NaOH	8.51	0.42	17.5	11.5	6.37	3.64	0.98 (150)	Slow filtering, small cake volume
	10	90	NaOH	8.79	None	0.73	4.81	4.73	2.96	0.93 (150)	Slow filtering, small cake volume
	10	90	$Ca(OH)_2$	8.45	0.5	29.9	15.5	7.96	4.00	2.42 (150)	More rapid than NaOH neutralized
	10	90	$Ca(OH)_2$	8.50	None	20.0	14.2	7.65	3.96	1.07 (150)	More rapid than NaOH neutralized
TBP-25 (Al-NO_3)	10	90	NaOH	8.5	1.5	0	0	0.09	0.08	0.08 (105)	Will not filter
	10	90	NaOH	8.5	None	0	0	0.09	0.08	0.05 (105)	Will not filter
	10	90	$Ca(OH)_2$	8.42	2.72	0	0.18	0.18	0.24	0.33 (105)	Will not filter
	10	90	$Ca(OH)_2$	8.45	None	0	0.36	0.27	0.36	0.33 (105)	Will not filter
STR(Zr-F)	10	90	NaOH	8.45	1.89	0.55	0.55	0.64	1.46	1.03 (90)	Slow filtering
	10	90	NaOH	8.5	None	5.46	4.91	4.82	3.05	1.48 (90)	Slow filtering
	10	90	$Ca(OH)_2$	8.45	2.78	5.10	4.82	4.64	2.78	1.36 (90)	Better filtering than NaOH Neutralized
	10	90	$Ca(OH)_2$	8.52	None	2.18	1.82	2.00	1.86	1.23 (90)	Better filtering than NaOH Neutralized

[a] numbers in parentheses indicate total settling times.

Table VI. Effect of a Flocculating Agent (IFA-313) on Settling Rates-Neutralized Synthetic Waste

Waste Type	Waste Dilution (ml)	H_2O	Neutralizing Agent	pH	IFA-313 (ml/l)	Cumulative Average Settling Rates (mm/min) Elapsed Time (min) 5	10	15	20	25	30	35	40	45	50	55	60	70	75	>75
Purex	50	450	33% NaOH	8.74	0	0.55	0.55		0.73				0.68						0.61	
"	"	"	"	"	0.13	0.55	0.55		0.73				0.64						0.59	
"	"	"	"	"	0.3	0.36	0.45		0.73				0.68						0.66	
"	"	"	"	"	0.8	0.55	0.55		0.77				0.75						0.73	
"	"	"	"	"	1.6	0.36	0.55		0.73				0.68						0.64	
"	"	"	"	"	2.5	0.55	0.55		0.73				0.66						0.56	
"	10	90	"	8.5	2.8	1.56	1.41		1.40				1.25					1.07		0.66(130)*
"	"	"	"	10.1	5.5	3.75	4.1		3.82				2.42					1.47		0.82(130)
"	50	450	$Ca(OH)_2$	9.35	0	0.94	1.56		1.56				1.60					1.41		1.05(100)
"	"	"	"	"	0.22	1.25	1.72		1.87				1.83					1.47		1.05(100)
"	"	"	"	"	0.5	1.56	1.87		2.03				1.95					1.47		1.09
"	"	"	"	"	0.9	1.85	2.18		2.34				2.11					1.47		1.09
"	"	"	"	"	1.7	3.13	3.44		3.28				2.34					1.52		1.11
"	"	"	"	"	3.3	4.4	5.63		4.22				2.50					1.56		1.12
Darex (SS-UQ)2 55 +	100	900	33% NaOH	8.5	0	0.36	0.36			0.29			0.27					0.29		0.28
"	"	"	"	"	0.12	0.36	0.36			0.29			0.27					0.29		0.28
"	"	"	"	"	0.42	0	-			0.18			0.20					0.26		0.25
"	"	"	"	"	0.95	0.73	0.45			0.36			0.30					0.29		0.28
"	"	"	"	"	2.3	0.73	0.45			0.33			0.30					0.30		0.29
"	"	"	"	"	5.6	0.36	0.36			0.29			0.27					0.31		0.30
"	50	450	$Ca(OH)_2$	8.45	0	1.28	1.55			1.68						1.39				0.85(115)
"	"	"	"	"	0.12	1.46	1.73			1.82						1.52				0.87
"	"	"	"	"	0.27	1.46	1.82			1.97						1.57				0.87
"	"	"	"	"	0.47	1.46	2.0			2.14						1.61				0.89
"	"	"	"	"	1.4	1.46	2.0			2.33						1.59				0.87
"	"	"	"	"	5.1	3.28			3.0						1.46					0.70(110)
"	10	90	"	8.3	5.6	1.46	1.64	1.70			1.58			1.23			1.00			0.73(90)
"	10	90	"	8.2	5.6	0.73	0.91	0.97			1.21			1.13			1.08			0.95(90)

Table VI. (Continued)

Waste Type	Waste Dilution (ml) Waste	H_2O	Neutralizing Agent	pH	IFA-313 (ml/l)	Cumulative Average Settling Rates (mm/min) Elapsed Time (min) 5	10	15	20	25	30	35	40	45	50	55	60	70	75	>75
SIR	50	450	33% NaOH	9.55	0	0.95	0.78		0.94					2.08					1.42	
(SS-UO_2-MgO)	"	"	"	"	0.12	0.63	0.78		0.94					1.98					1.40	
"	"	"	"		0.25	0.95	1.25		3.44					2.12					1.44	
"	"	"	"	"	0.54	1.25	2.34		3.75					2.22					1.46	
"	"	"	"	"	1.3	0.95	0.94		0.94					1.04					0.98	
"	"	"	"	"	2.4	1.87	3.13		2.97					2.02					1.42	
"	"	"	"	"	3.9	1.56	1.72		1.72					1.60					1.25	
"	"	"	"	"	6.3	1.25	2.5		2.66					1.95					1.40	
"	"	"	$Ca(OH)_2$	8.5	0	14.4	11.2		6.3				3.24							1.01(130)
"	"	"	"	"	0.12	19.4	11.9		6.4				3.28							1.02
"	"	"	"	"	0.27	20.6	11.9		6.4				3.28							1.02
"	"	"	"	"	0.58	22.2	12.2		6.4				3.35							1.03
"	"	"	"	"	1.3	22.5	12.2		6.4				3.28							1.01
"	"	"	"	"	2.2	22.8	12.2		6.4				3.24							1.01
"	"	"	"	"	3.9	22.5	12.2		6.3				3.24							1.00
"	"	"	"	"	6.0	24.0	13.0		6.6				3.28							1.02
STR (Zr-F)	50	450	33% NaOH	8.52	0	0	0.16		0.16				0.20				0.16			0.17(120)
"	"	"	"	"	0.11	0	0.16		0.16				0.20				0.18			0.18
"	"	"	"	"	0.23	0	0.16		0.16				0.16				0.16			0.17
"	"	"	"	"	0.56	0	0.16		0.16				0.20				0.18			0.17
"	"	"	"	"	0.83	0	0		0.16				0.16				0.16			0.17
"	"	"	"	"	1.6	0	0.16	0	0.16				0.16				0.18			0.18
"	"	"	"	"	2.7	0	0.16		0.16				0.16				0.21			0.21
"	"	"	"	"	5.4	0	0.31		0.31				0.39				0.36			0.22

Table VI. (Continued)

Waste Type	Waste Dilution (ml) Waste	H_2O	Neutralizing Agent	pH	IFA-313 (ml/l)	Cumulative Average Settling Rates (mm/min) Elapsed Time (min) 5	10	15	20	25	30	35	40	45	50	55	60	70	75	>75
"	50	450	$Ca(OH)_2$	8.45	0	2.81	2.81		2.82				2.38				1.72			0.68(165)
"	"	"	"	"	0.11	2.81	3.12		2.97				2.42				1.72			0.68
"	"	"	"	"	0.23	4.37	4.06		3.60				2.46				1.74			0.68
"	"	"	"	"	0.56	4.37	4.06		3.75				2.50				1.77			0.69
"	"	"	"	"	0.83	6.87	5.62		4.53				2.54				1.77			0.68
"	"	"	"	"	1.6	8.45	6.87		4.45				2.50				1.74			0.68
"	"	"	"	"	2.7	6.87	6.56		4.38				2.46				1.72			0.66
"	"	"	"	"	5.4	1.88	2.03		2.03				1.64				1.40			0.66

* Numbers in parentheses indicate total settling time.

Filtrations of the neutralization precipitate were carried out on fine fritted glass disks except for large volume neutralizations which were filtered on sintered stainless steel. In all cases the filtration rates were very low. In some cases the filtration began at a good rate, but the pores of the filter very quickly became plugged. In every case it was found that $Ca(OH)_2$-neutralized material was more readily filtered than the NaOH-neutralized. Only the aluminum hydroxide gel from TBP-25 waste was completely unfilterable. The zirconium-fluoride (STR) waste gave the most readily-filtered precipitate. In view of the difficulty of filtering these precipitates, additional development will be required to establish the feasibility of handling the precipitates on conventional filtration equipment under radioactive conditions.

Experiments on Purex waste were carried out in attempting to improve the characteristics of the precipitated solids by neutralization at elevated temperatures and by using both direct and reverse strike techniques. Temperatures up to boiling had no effect on the physical properties of the precipitate. The method of addition of reagents also had no effect.

4.0 EFFECT OF CONCENTRATION OF FLOCCULATING AGENT IFA-313

After the neutralization and filtration tests (Table V), which included a rough evaluation of the effect of IFA-313, more detailed tests were made to determine the effect of increasing concentrations of IFA-313 on settling rates (Table VI). Known amounts of IFA-313 were added to a batch of neutralized, diluted waste, and a sample removed for settling following each addition. Plots of settling rate versus elapsed time for each of the waste types after both NaOH and $Ca(OH)_2$ neutralizations are shown in Figures 2-8.

Settling rates were determined in graduated cylinders from the rate of fall of the solid-liquid interface, computed as millimeters per minute. Most of the rates are shown for 5-min, 10-min, and 20-min periods.

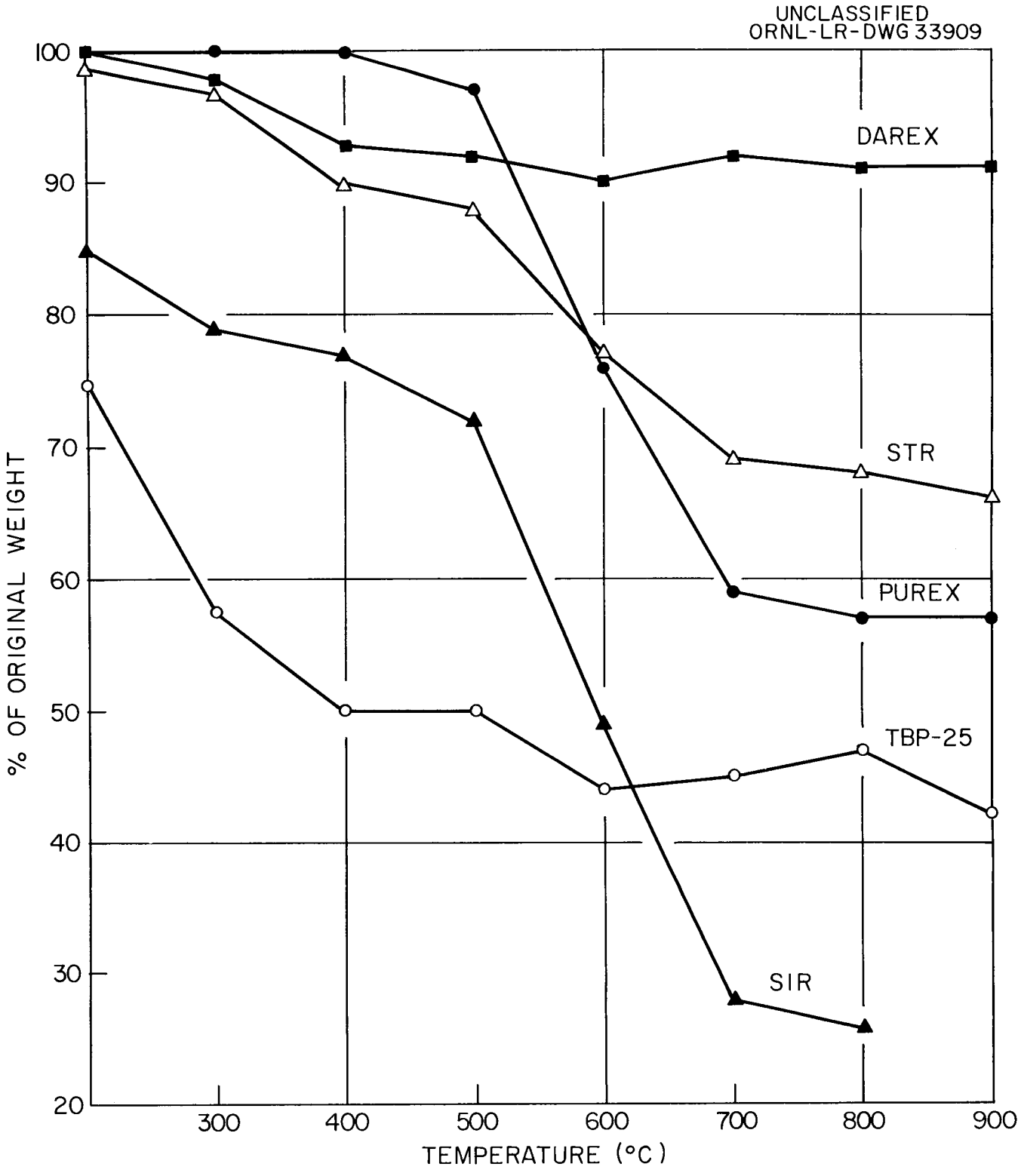

Fig. 2. Loss in Weight by Calcination of Acid Evaporation Residues.

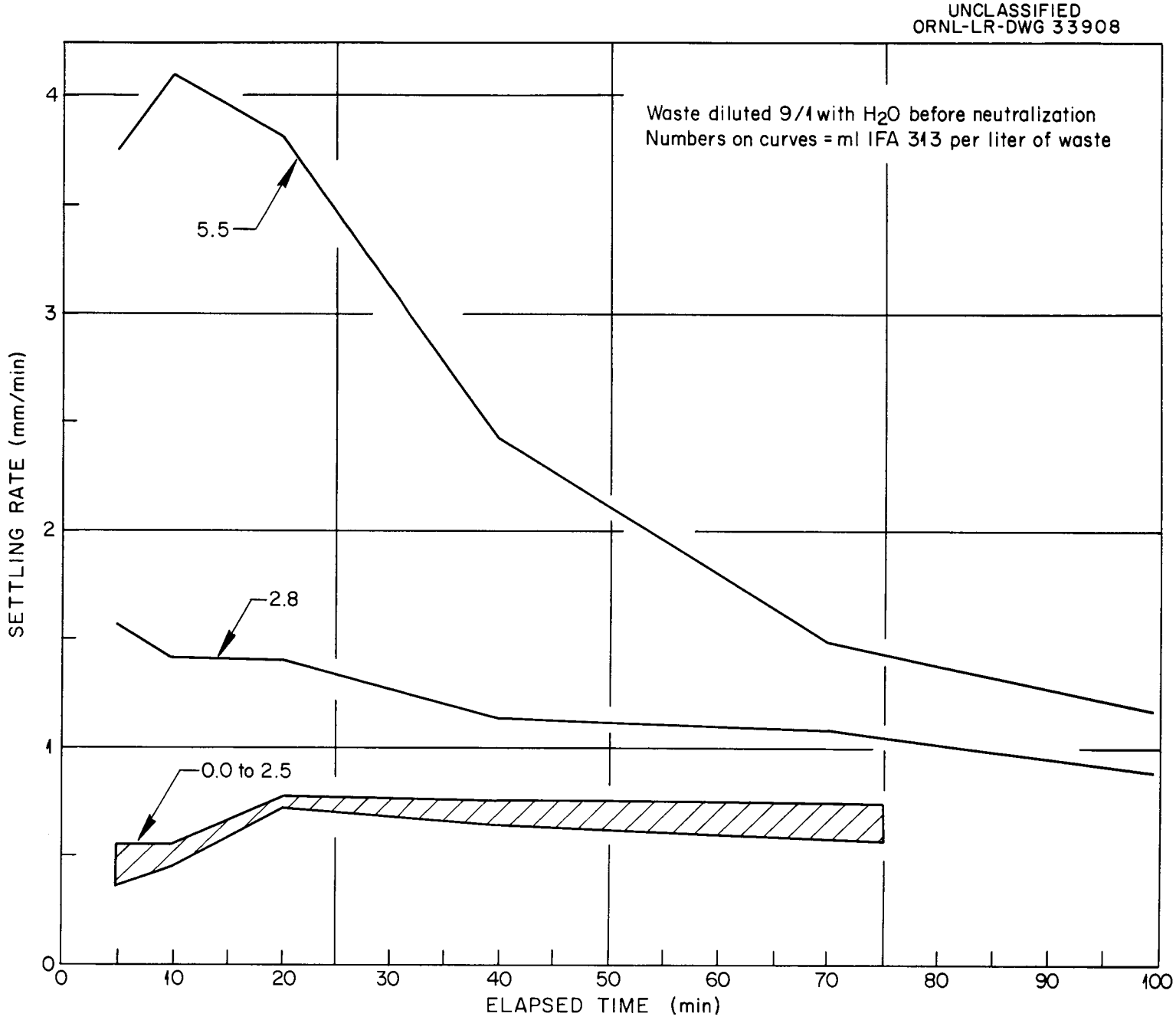

Fig. 3. Effect of IFA 313 on Settling Rates of NaOH-Neutralized Purex Waste.

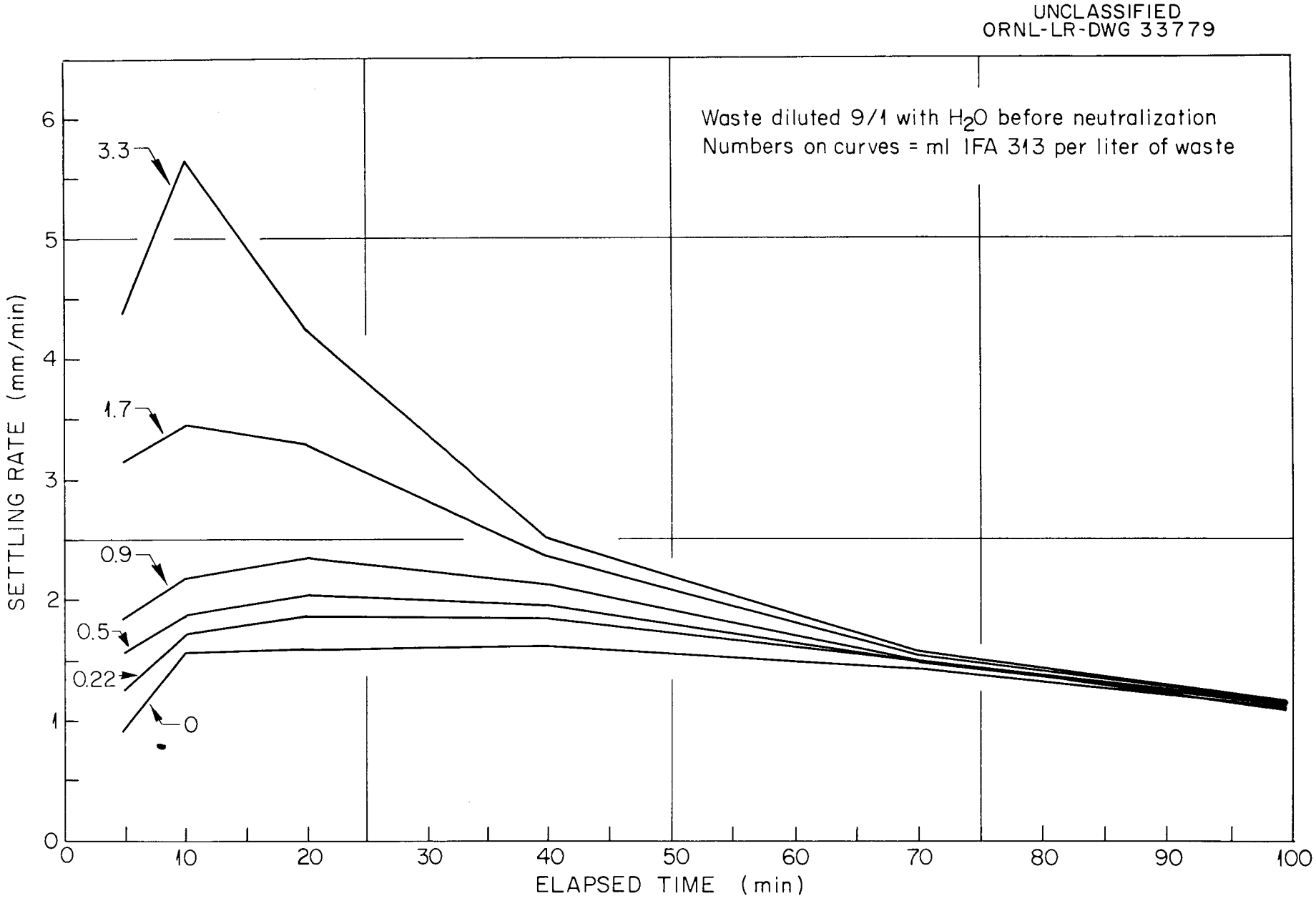

Fig. 4. Effect of IFA 313 on Settling Rates of $Ca(OH)_2$-Neutralized Purex Waste.

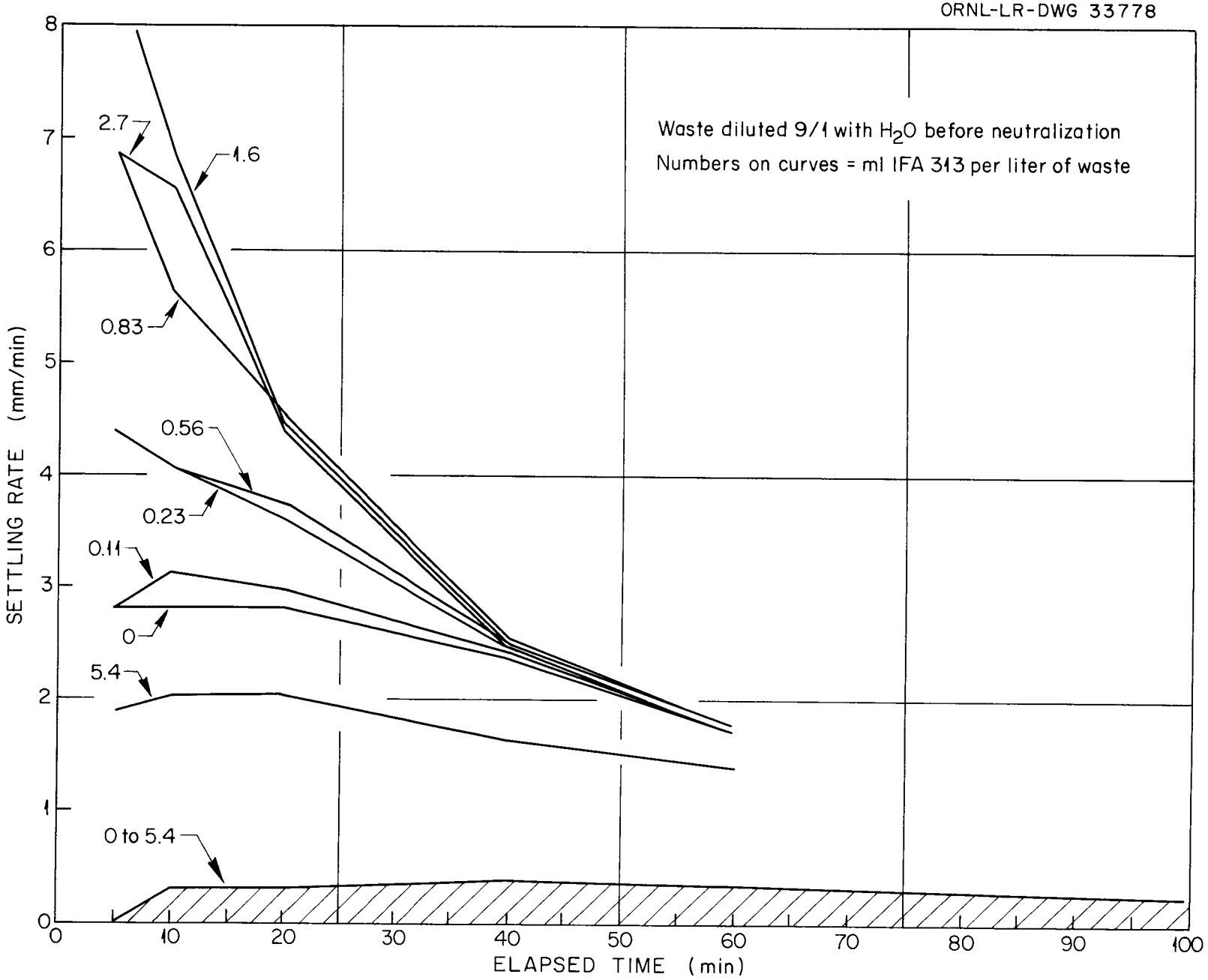

Fig. 5. Effect of IFA 313 on Settling Rates of $Ca(OH)_2$-Neutralized STR Waste.

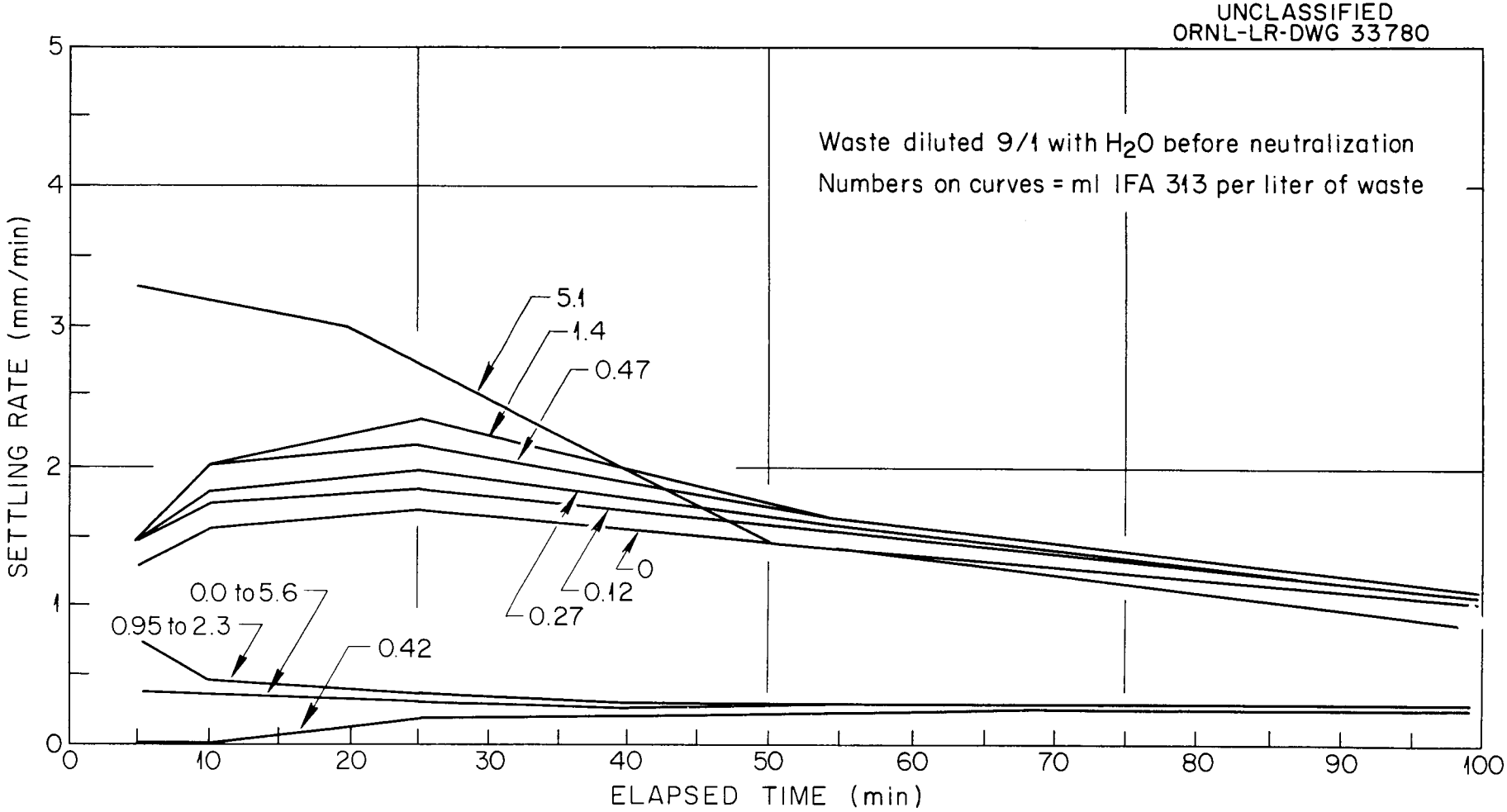

Fig. 6. Effect of IFA 313 on Settling Rates of Neutralized Darex Waste.

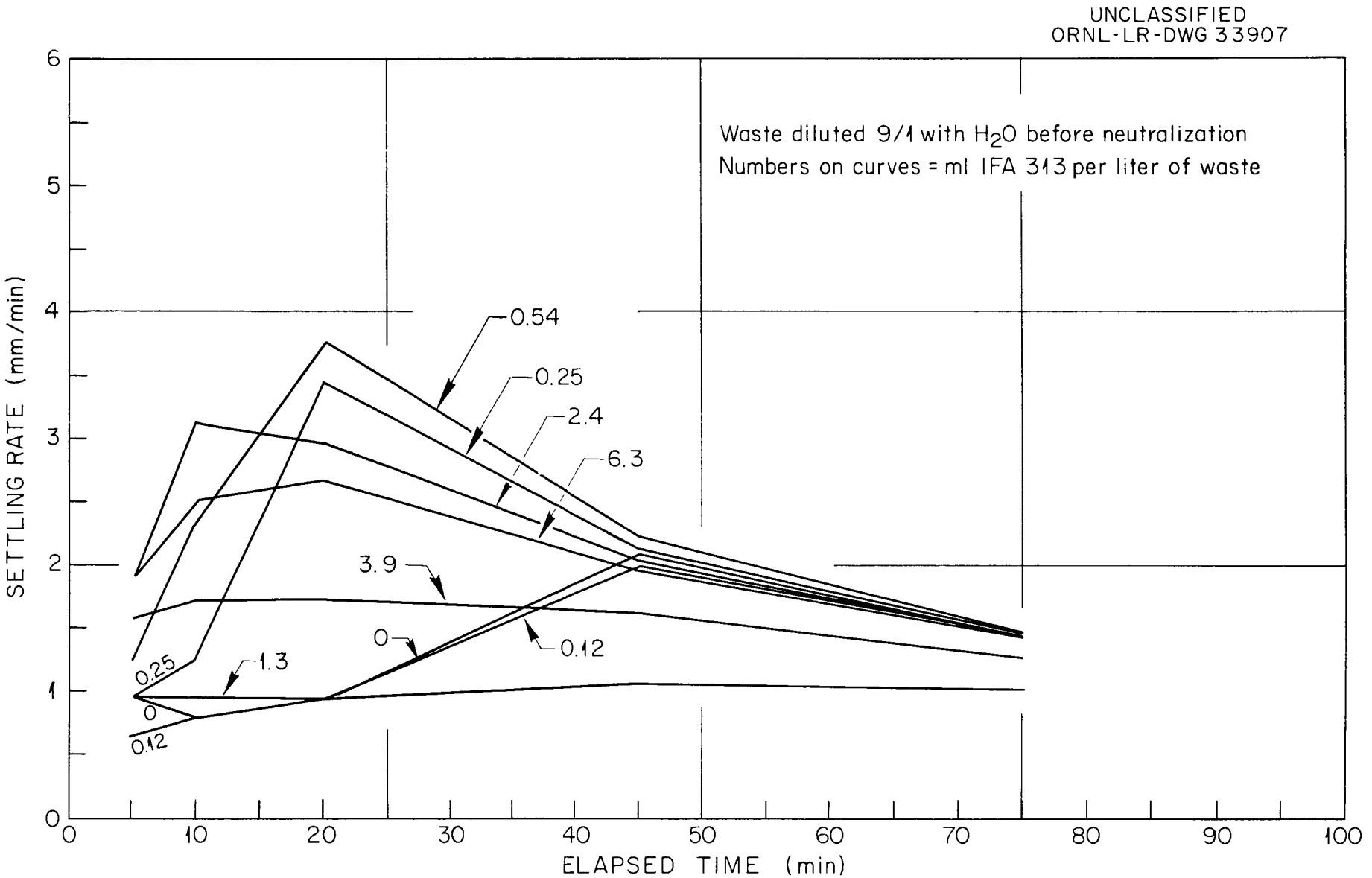

Fig. 7. Effect of IFA 313 on Settling Rates of NaOH-Neutralized SIR Waste.

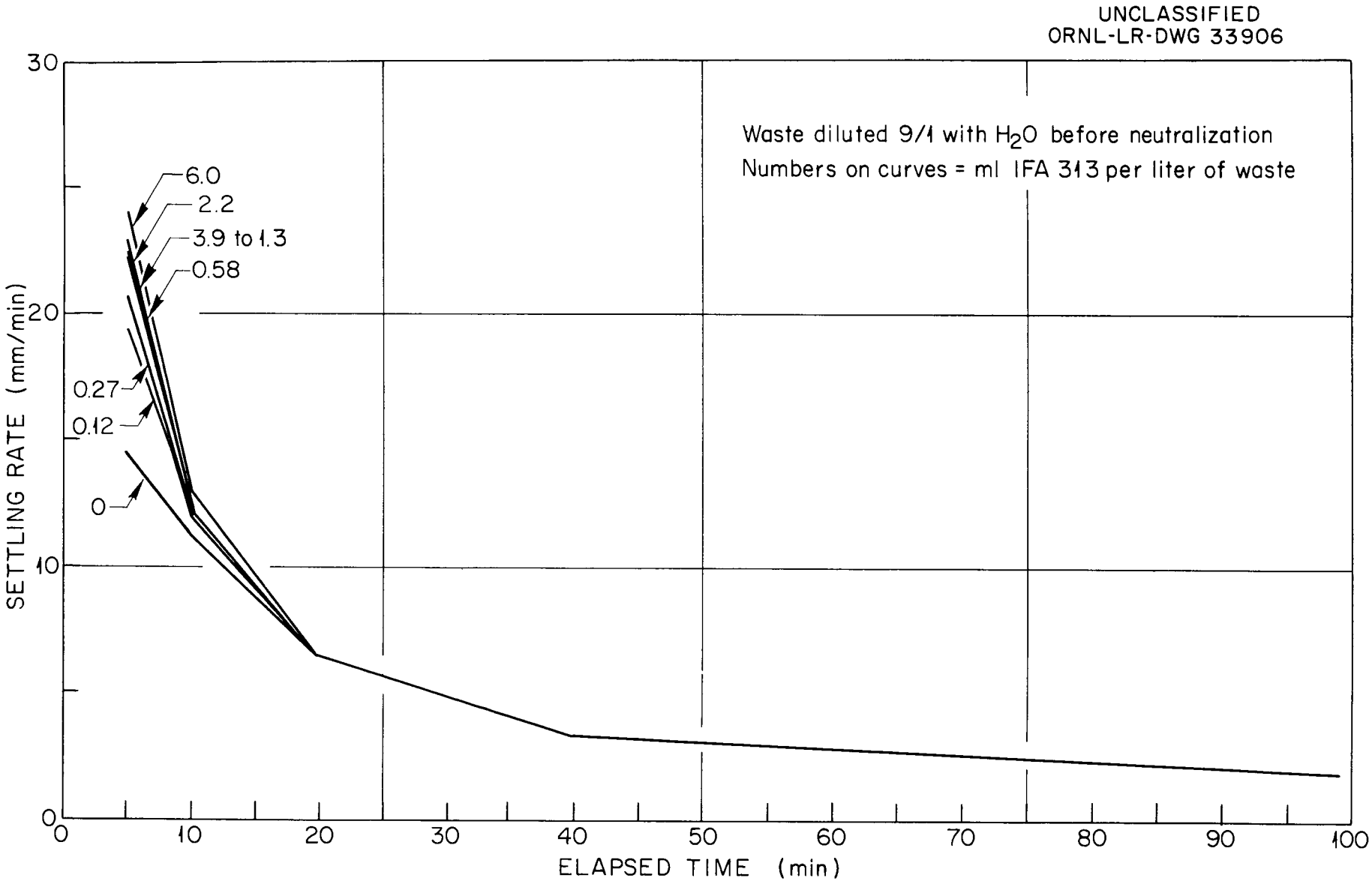

Fig. 8. Effect of IFA 313 on Settling Rates of $Ca(OH)_2$-Neutralized SIR Waste.

4.1 Results of IFA-313 Addition Tests

Purex. The threshold of significant effect of IFA-313 for NaOH-neutralized Purex waste was 2.8 ml of flocculating agent per liter of diluted (1:9) waste. At all concentrations below this level, there was no apparent effect (Table VII, Fig. 3). The maximum settling rate for 5.5-ml/liter addition was approximately 4.1 mm/min compared with about 1.5 mm/min for 2.8 ml/liter and about 0.75 mm/min for concentration up to 2.5 ml/liter. Maximum rate was at 10 min for 5.5-ml/liter concentration and 20 min for low concentrations.

Increased additions of flocculating agent to $Ca(OH)_2$ neutralized Purex waste gave increased settling rates. With no additions the maximum rate was 1.6 mm/min while 3.3 ml/liter gave a maximum settling rate of 5.6 mm/min (Fig. 4). Additions of 3.3 and 1.7 ml/liter gave maximum rates at 10 min while lower additions reached a maximum at times up to 40 min.

STR. When this waste was neutralized with NaOH, no significant effect of the flocculating agent on settling rates (Fig. 5) was apparent. For additions up to 5.4 ml/liter, settling rates were at a maximum of about 0.4 mm/min.

Use of the same IFA-313/waste volume ratios with $Ca(OH)_2$ neutralized STR waste produced a marked increase in settling rates (Fig. 5). The precipitate in a neutralized waste without IFA-313 settled at a maximum rate of about 2.8 mm/min while with 0.23 ml/l of additive per liter of waste, 8.45 mm/min. When the amount of flocculating agent was increased to 2.7 ml/liter, the rate dropped to 6.85 mm/min, and at 5.4 ml/liter the maximum rate was 2.0 mm/min.

Darex. No significant effect on the settling rate of NaOH-neutralized Darex waste was observed for IFA-313 additions up to 5.6 ml per liter. All rates were less than 0.75 mm/min (Fig. 6).

Settling rates of $Ca(OH)_2$-neutralized waste increased with the amount of flocculating agent added. Maximum settling rate was 3.25 mm/min at five minutes settling time with the addition of 5.1 ml/liter (Fig. 6).

SIR. The effect of the flocculating agent on the settling time for NaOH-neutralized waste is not clear. Maximum measured rates of 3.75 and 3.45 mm/min were observed after 20 min settling for 0.54 and 0.25 ml/liter, respectively (Fig. 7). Rates of 3.15 and 2.65 mm/min were observed for IFA-313 concentrations of 2.4 and

Table VII. Evaporation of Neutralized Wastes Without Filtration

250 ml evaporated by boiling at 1 atm.

Waste	Dilution		Neutralization		Final Still	Condensate		Solid Residue	
	Waste (ml)	Water (ml)	Agent	pH	Temp (°C)	Vol (ml)	pH	(ml)	(% of Waste)
Purex	25	225	33% NaOH	10	>150	260	6.1	14	56
"	197*	--	30% NaOH	8.45	--	309 **	3.0	71	36
"	25	225	$Ca(OH)_2$	8.65	>150	255	5.1	12	48
Darex ($SS-UO_2$)	25	225	10% NaOH	8.7	>250	252	-	4	16
"	25	225	$Ca(OH)_2$	8.7	>150	250	2.9	5	20
SIR ($SS+-UO_2-MgO$)	25	225	30% NaOH	9.5	>170	253	2.8	1	4
"	25	225	$Ca(OH)_2$	8.6	-	254	3.5	2	8
STR (Zr-F)	25	225	33% NaOH	8.9	>200	260	3.5	5	20
"	25	225	$Ca(OH)_2$	8.45	>106	253	3.1	5	20
TBP-25 ($AlNO_3$)	25	225	25% NaOH	8.55	>165	288	7.4	4	16
"	25	225	$Ca(OH)_2$	8.9	-	259	9.5	8	32

*Not diluted

** Volume discrepancy is due to dilution in neutralization.

6.3 ml/liter, respectively. In general it may be said that undetermined factors other than flocculating-agent concentration were controlling the settling rates.

For $Ca(OH)_2$-neutralized SIR waste, however, maximum settling rates were observed at 5 min after start and dropped rapidly (Fig. 8). The rate at the start of settling may have been much higher. The addition of only 0.12 ml of IFA-313 per liter of diluted waste increased the settling rate from 14.5 mm/min for an addition to 19.5 mm/min. The increase of IFA-313 concentration to 6.0 ml/liter gave a settling rate of 24 mm/min. After 20 min settling all concentrations were settling at essentially the same rate. The settling rates for $Ca(OH)_2$-neutralized SIR waste were the maximum observed.

General Conclusions. Certain general conclusions may be drawn with regard to the effect of IFA-313.

1. IFA-313 is not universally effective in improving settling rates.

2. $Ca(OH)_2$ neutralized slurries are more likely to be improved than NaOH.

3. Settling rates tend to approach a common value with time.

5.0 TREATMENT OF NEUTRALIZED WASTE

If volume reduction is desired following neutralization, an evaporation procedure may be carried out on neutralized slurry, or, if a solids-liquid separation is affected by filtration or centrifugation, the resulting supernatant may be evaporated. Both of these procedures were investigated.

5.1 Evaporation of Unfiltered Neutralized Waste

Each of the five types of waste was neutralized with NaOH and with $Ca(OH)_2$, and the resulting slurry evaporated to dryness. The equipment employed (reaction flask, mantle heater, and water cooled condenser) was similar to that used for the acidic evaporations. An additional feature of the equipment was a magnetic stirrer used to prevent bumping in the reaction flask. All neutralizations were of 1 part waste diluted with 9 parts water except for one NaOH neutralization of undiluted Purex waste. Neutralizations were carried to pH of 8.5-10.0.

The results of the evaporations are shown in Table VIII. The volume of solid residue is roughly proportional to the solids concentration of the waste, that is, the concentrated Purex waste gave a larger residue than the more dilute stainless steel waste. Diluted Purex waste, neutralized and evaporated to dryness, resulted in a residue occupying approximately 50% of the original waste volume. Undiluted NaOH-neutralized Purex waste (a single test) yielded a residue of 36% of the original volume. Residues from neutralized, evaporated waste were 16 and 32% for NaOH and $Ca(OH)_2$, respectively. The reason for the wide variation in volume between diluted and undiluted Purex waste and between NaOH- and $Ca(OH)_2$-neutralized aluminum waste is not apparent.

Residue from neutralized and evaporated STR waste was 20% of original waste volume for either NaOH or $Ca(OH)_2$. Darex neutralized and evaporated waste residues were 16% for NaOH and 20% for $Ca(OH)_2$. The difference (1 ml in 5) is not considered significant. For the SIR type waste the residue is very small, 4 and 8% of the original waste volume for NaOH and $Ca(OH)_2$, respectively. Considering the difficulty of measuring these small volumes by indirect means (it was impossible to remove the dried residue from the flask), it is doubtful that the difference between 1 ml and 2 ml is significant.

The pH of condensates from the neutralized evaporations range from 2.8 to 6.1 except for that from the TBP-25 waste, which was 7.4 and 9.5 for NaOH and $Ca(OH)_2$ neutralization, respectively. This indicates greater breakdown of nitrates to nitrogen oxides in the acids originally stronger in HNO_3.

5.2 Evaporation of Filtrates from Neutralization

A series of evaporations were made on filtrates from neutralizations of the synthetic wastes. These evaporations were carried out in equipment identical to that used previously in evaporation of un-neutralized waste and of neutralized waste without separation of liquid and solids. The solution was not agitated, and no difficulty was encountered with bumping or spattering. However, it was found to be impossible to remove the dry crystalline material from the reaction flask by mechanical means. Therefore, the residue was dissolved in a minimum volume of water and poured into an evaporating dish for evaporation to dryness. The salt could be more readily scraped from the evaporating disk than from the interior of a reaction flask.

Table VIII. Evaporation of Supernatant from Neutralization of Synthetic Wastes

Waste								
	Composition		Neutralizing		Liquid Volumes (ml)		Residue Volume	
Type	Waste (ml)	H_2O (ml)	Agent	pH	Supernatant	Cond.	(ml)	% of Orig Waste
Purex	25	225	25% NaOH	8.5	282	275	16	64
"	25	250	$Ca(OH)_2$	8.45	250	246	15	60
Darex ($SS-UO_2$)	10	90	1 M NaOH	8.45	114	110	5	50
"	10	90	$Ca(OH)_2$	8.41	108	104	5	50
SIR ($SS-UO_2-MgO$)	10	90	1 M NaOH	8.51	122	113	5	50
"	10	90	$Ca(OH)_2$	8.45	109	102	3	30
STR (Zr-F)	10	90	1 M NaOH	8.5	110	109	2.5	25
"	10	90	$Ca(OH)_2$	8.52	88	84	3	30

The data for all these evaporation tests are given in Table VIII.

The crystalline residues, sodium nitrate or calcium nitrate, in addition to fluoride salts in the case of STR waste, had volumes of 25 to 64% of the original waste volumes. The salts tended to be deliquescent, particularly those from $Ca(OH)_2$ neutralization. Again the relative volumes, residue to original, are greater with more concentrated wastes, such as Purex, than with more dilute wastes, such as STR.

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