OP-59 Revised

HW-3-291

PROJECT 9536

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Subject Memo Report SE-PC-#72

To Simon-Mackey-Smith

From A.H. Angerman

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MEMORANDUM REPORT - SE-PC-#72

CRYSTALLINE LANTHANUM FLUORIDE

(Continuation of experimental work reported in SE-PC-#44, File No. 3-2597)

Classification Cancelled (Change to DECLASSIFIED)

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SE-PC-#72 [redacted] DECLASSIFIED July 26, 1945

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CRYSTALLINE LANTHANUM FLUORIDE

I Introduction

During a study devoted to the improvement of the inherently poor centrifugation characteristics of gelatinous lanthanum fluoride, crystalline LaF_3 was developed. Fundamental data regarding its properties, preparation, and usefulness as a plutonium carrier were reported in SE-PC-#44, File No. S-2597. The work described herein is a continuation of the development and exploitation of crystalline lanthanum fluoride, the use of which offers a possible method of shortening and simplifying the plant process cycles at the cross-over with improved yields of product.

Detailed studies have been made as to methods of alkali lanthanum sulfate preparation, the evaluation thereof by means of sedimentation analyses, and the formation of fines during the metathesis of the double sulfate to the crystalline LaF_3. Results of plant tests are also reported.

II Summary and Conclusions

A Product losses in the plant E-3-#S effluents have been consistently lower when crystalline lanthanum fluoride was employed in the cross-over cycle. The improvement, however, was not sufficient to reduce the product precipitation step to a single precipitation-single centrifugation operation. Consistent waste losses well within specification limits are assured using a double precipitation-double centrifugation technique with crystalline LaF_3 in the first shot and gelatinous LaF_3 in the second shot. (See Table I).

B Sedimentation analyses indicate that the fraction of small particles present in the alkali lanthanum sulfate is negligible compared to the fraction of finely divided fluoride produced during conversion. The presence of hydrogen ion is responsible for the observed diminution in average particle size during the metathesis of the double sulfate to crystalline lanthanum fluoride. (See Figures I, II, and III).

C Carrying of Pu(IV) by externally prepared crystalline lanthanum fluoride is inferior to that prepared directly in process solution. This eliminates consideration of a process based on the use of externally prepared, uniformly sized lanthanum fluoride crystals.

D A superior type of sodium lanthanum sulfate has been developed, the preparation details of which are given in another report (SE-PC-#73). It possesses a uniformly large particle size and upon conversion to the fluoride exhibits less tendency toward the formation of "fines" (See Figure IV). Semi-Works tests indicate it to be better than the double sulfate employed in earlier plant trials.

E Crystalline lanthanum fluoride has been identified as the dihydrate of the formula $LaF_3 \cdot 2H_2O$.

III Experimental Details

A Plant Evaluation of Crystalline Lanthanum Fluoride

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When the plant was operating at full volume (October 5th, 1944 Flowsheet) in the cross-over, it was necessary to precipitate gelatinous lanthanum fluoride in three separate portions with a total of at least three centrifugations in the product precipitation step to insure adequate plutonium recovery. In recent plant runs, a 40% decrease in solution volume was achieved by process modifications prior to the cross-over step. This afforded an opportunity of increasing

the lanthanum fluoride concentration of the slurry without necessitating the use of additional lanthanum. Under these conditions a significant improvement was achieved in the separation of gelatinous lanthanum fluoride, but occasionally three centrifugations are still required to keep the product losses within specifications.

Crystalline lanthanum fluoride was evaluated in the plant in a total of six runs, three at full volume and three at the 60% volume, and employed both in the by-product and product cycles. Although this effected a marked decrease in centrifugation losses, it was not successful in achieving the desired goal, that of reducing the cycle to a single precipitation-single centrifugation operation. The lowest product loss after the first centrifugation (2.5%) was obtained by precipitating 50% of the total lanthanum as crystalline LaF_3 (to carry product) and the remaining 50% as gelatinous fluoride to aid in the removal of crystalline "fines". Both forms were separated by a single centrifugation. The data in Table I show that the use of a crystalline LaF_3 by-product, a crystalline LaF_3 first precipitation in the product cycle followed by centrifugation and a subsequent second shot of gelatinous LaF_3 decreased E-S-NS losses from approximately 1.5% to about 0.5% and only two centrifugations are required in the product cycle.

Unexpected difficulty was encountered in removing the crystalline fluorides from the centrifuge bowl. This problem was not observed in semi-works runs. Since the crystals do not possess adhesive properties, it is believed that the difficulty was due to inadequate suspension of the solid during the removal of slurry from the bowl. Harder packing of the precipitates in the plant than in the Semi-Works may also have been a factor in that centrifugations in the plant were at higher gravity (1800 G in the plant vs. 1000 G in the Semi-Works.) No apparent difficulties were reported during the subsequent KOH metathesis step.

The sodium lanthanum sulfate submitted for plant trial was prepared in the Semi-Works (321 Building) by adding a 40% aqueous solution of lanthanum ammonium nitrate to a 0.65 molar solution of sodium sulfate at 75°C over a period of 0.6 hours, followed by a digestion for 1 hour at 75°C. The final lanthanum concentration of the slurry was 15 grams per liter.

B Sedimentation Analyses of Double Sulfates and Crystalline Fluorides Derived Therefrom

In SE-PC-#44, File No. 3-2597, it was suggested that finely divided particles of double sulphate are responsible for the formation of a corresponding fine fraction of crystalline lanthanum fluoride, and that the "fines" so produced escape removal by centrifugation, resulting in excessive product losses.

It was therefore deemed of interest to determine the actual percentage of fine particles in a given double sulphate before and after conversion to crystalline lanthanum fluoride. A simple experimental technique was devised to determine particle size distribution. The principle involved was similar to the well-known sedimentation balance method save that the percentage of particles of a given size, settling over an interval of time was determined by measuring the relative volume of sedimented solids rather than the weight thereof. Sedimentation of a dilute slurry of the crystals was allowed to take place in a stoppered 2.6cm I.D. glass tube, 18 inches in length and the volume of settled particles measured at regular intervals by means of a millimeter scale placed adjacent to the tube. The slurry being tested was sufficiently dilute to produce free settling of individual particles. Sedimentation was allowed to continue until measurements showed no increase in volume, and individual values obtained during the sedimentation period were compared to this maximum value.

Table I

Plant Evaluation of Crystalline Lanthanum Fluoride

(All Centrifugations at 18000 with a slurry feed rate of 70lbs/min)

Run No.	By-Product Step: Procedure	Process Vol.	Beckman D.F.	Prod. Loss	Product Precipitation Step: Procedure	1st Cent'n. Loss	2nd Cent'n. Loss	3rd Cent'n. Loss	Final Loss
03-B3	1 Pptn. of gelatinous LaF_3 225 g/l	100%	13		3 separate Ppt'ns. of gelatinous LaF_3-33mg/l per shot. 70 lbs./minute centrifugation rate.	13	3.4	0.7	0.8
03-B4	1Pptn. of gelat nous LaF_3 - 225mg/l. 0.5N HF	100%	22		Same as 03-B3	17	3.7	0.98	0.9
03-B5	Same as 03-B-4	100%	15		Same as 03-B-3	12.5	2.3	1.2	--
03-B6	1 Pptn. of Cryst. LaF_3 - 225 mg/l.	100%	20	1.7	1 Pptn. of crystalline LaF_3 - 100mg/l waste reworked with gelatinous LaF_3	4.5	0.7	0.18	0.18
04-B1	Same as B6 above	100%	13.3	1.3	2 separate Pptn's. of Cryst. LaF_3 reworked with gelatinous LaF_3	6.5	2 9	3.0	0.24
04-B2	Same as B1	100%	14.4	1.0	1 Pptn. of Cryst. LaF_3 followed by 1 Pptn. of gelatinous LaF_3	5.3	1.0	0.6	--
04-B3	1 pptn. of gelatinous LaF_3 - 225mg/l	60%	16.4		2 Pptns. of gelatinous LaF_3-83mg/l each	7.2	1.0	0.6	--
04-B3A	Same as B3	60%	12.5		Same as B3	8.4	1.1	0.6	--
04-B4	Same as B3	60%	15.9		Same as B3	8.5	1.1	0.64	--
04-B5	Same as B3	60%	10		1 pptn. of cryst. LaF_3 reworked with gelatinous LaF_3.	5.9	0.98	0.75	0.98
04-B6	1 Pptn. of Cryst.LaF_3 225mg/l	60%	16		Same as B5	3.15	0.55	0.41	0.32
04-B7	Same as B6	60%	12.3		50% of total La Ppt'd. as Cryst. LaF_3, digested, remaining La Ppt'd. as gelatinous LaF_3. Cent'd. simultaneously.	2.54	1.8		1.6

The slope at any point on a given curve is a measure of the actual size of an individual particle or aggregate whereas the rate of change of the slope is a measure of particle size distribution.

Sedimentation analyses of a double sulphate similar to material submitted for plant evaluation, hereinafter referred to as "plant type double sulphate", were made before and after conversion to the crystalline fluoride. The curves presented in Graph I indicate that a marked production of fines occurs during conversion in 1N HNO_3-0.5M HF, that 50% of the double sulphate is converted to smaller particles and that the initial double sulphate is quite uniform in size. These data indicate that the fraction of small particles present initially in the double sulphate is negligible compared to the fraction of finely divided fluoride produced during conversion.

In order to determine the factor responsible for this degradation in particle size, portions of a plant type double sulphate were converted to the fluoride in the following systems: (1) 1M HNO_3-0.5M HF; (2) 0.5M HF and (3) 0.8M NaF; the media being progressively lower in total acidity. Conversion to the fluoride was easily followed by means of the polarizing microscope. The data plotted in Graph II show a definite improvement in sedimentation velocity and particle size distribution as the total acidity is decreased. This suggests that the hydronium ion present during conversion is responsible for the diminution in particle size. The deleterious effect of acid still obtains when crystalline LaF_3 is made in a neutral solution and then eventually added to an acid medium, for when crystalline lanthanum fluoride prepared by sodium fluoride conversion is introduced into a 1N HNO_3-0.5M HF medium, a marked change in particle size distribution results (See Graph III).

An improvement in particle size distribution, as determined by the smaller quantity of fines produced, was achieved by adding sodium fluoride converted lanthanum fluoride to a simulated process solution in which the total acidity was reduced by adding sodium hydroxide equivalent to the nitric acid therein. This procedure was found to be impractical, because upon neutralizing the process solution containing product equivalent to 250 grams per ton of metal, an insoluble gelatinous product compound, presumably sodium plutonous fluoride, precipitated.

Another procedure designed to eliminate the adverse effect of "fines" was investigated. A plant type double sulphate was converted to crystalline lanthanum fluoride in 1N HNO_3-0.5M HF and its sedimentation curve determined. The fluoride was resuspended and allowed to settle for the interval of time required for sedimentation of the first 50%. The solids remaining in suspension (fines) were decanted and a sedimentation curve redetermined on the coarse fraction remaining. Although this fractionation produced a superior settling fluoride, the effective surface area available for product adsorption and/or double fluoride formation was probably reduced, because the carrying of product from solutions containing the equivalent of 250 grams per ton of metal was only 17% after 2 hours of digestion.

A dried crystalline fluoride was found to be superior with respect to the absence of fines to that produced directly in solution but carrying again was found to be poor. Using tracer quantities of product, carrying by dried crystalline lanthanum fluoride was 0.0, 2.2, 38.7 and 51.7% after 1/2, 1, 1-1/2 and 2 hours of digestion. Further work on the application of externally prepared crystalline lanthanum fluoride was therefore discontinued.

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Although sedimentation experiments indicated that the plant type double sulphate is quite uniform in particle size, microscopical examinations have revealed that the crystals are very irregular in habit and growth. These irregularities, principally those of twinning and aggregation may be responsible for the non-uniformity of the crystalline lanthanum fluoride derived therefrom.

An extensive study of double sulphate precipitation variables was made by G.W.Sears (See SE-PC-173) and methods sought whereby a uniformly large particle sized double sulphates could be produced. Throughout this study, sedimentation curves were obtained for preparations of particular interest, and in most cases it was found that precipitates possessing a uniformity in crystal size and habit were superior to the plant type double sulphate. A typical comparison is shown in Graph IV.

C Semi-Works Evaluation of Sears' Improved Sodium Lanthanum Sulfate

Several samples of a uniformly large particle size sodium lanthanum sulphate were submitted to the 321 Semi-Works, to determine their efficacy in the product precipitation step of the crossover. The double sulfates were prepared by a preferred method described in another report (SE-PC-173).

The results in Table II indicate that the improved double sulphate is capable of reducing product losses by a factor of 2-3 and on this basis additional plant tests employing crystalline lanthanum fluoride may be justified.

Table II

Semi-Works (321 Building) Evaluation of Crystalline LaF_3

Comparison of Losses in Runs Employing Different Types of Sodium Lanthanum Sulfate

Run No.	Type of Na-La Double Sulfate	Procedure	% of Prod. Associated with insoluble matter prior to addition of La salt	First Effluent Product Loss (%)	Second Effluent Product Loss (%)
LF-20	Plant	2-5Omg/l Ppt'ns. of La^{+3} as Cryst.LaF_3	10.6	16.4	8.0
LF-21	Plant	2-5Omg/l Ppt'ns. of La^{+3} as Cryst.LaF_3	0.0	15.5	8.9
LF-26	Plant	2-5Omg/l Ppt'ns. of La^{+3} as Cryst. LaF_3	19.7	24.4	13.1
LF-27	Plant	50mg of La^{+3} as Cryst. LaF_3 + 50mg of La^{+3} as gelatinous LaF_3 cent'd. together	52.2	14.3	8.8
LF-41	Improved	2-50mg/l Ppt'ns. of La^{+3} as Cryst.LaF_3	5.6	4.8	2.8
LF-44	Improved	2-50mg/l Ppt'ns. of La^{+3} as Cryst.LaF_3	26.8	7.8	6.7
LF-46	Improved	50mg/l La^{+3} as Cryst.LaF_3 + 50mg/l La^{+3} as gelatinous LaF_3 Cent'd. simultaneously	4.4	12.4	7.6

In the above tests, tracer quantities of product were employed and centrifugations made at 1000G with a throughput rate equivalent to 70lbs./min.

D. Miscellaneous Data of Theoretical Interest

1) Specific Gravities of Solid Salts - The specific gravities of sodium lanthanum sulphate, potassium lanthanum sulphate and crystalline lanthanum fluorides derived therefrom were determined pycnometrically using butyl alcohol as the immersion liquid. For comparative purposes the specific gravities of sodium, potassium and lanthanum sulphates are included in the following table.

$La_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$	3.17-3.24
$La_2(SO_4)_3 \cdot 4\frac{1}{2}\ K_2SO_4 \cdot 2H_2O$	3.09-3.18
$LaF_3 \cdot 2H_2O$ from $La_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$	3.10
$LaF_3 \cdot 2H_2O$ from $La_2(SO_4)_3 \cdot 4\frac{1}{2}\ K_2SO_4 \cdot 2H_2O$	4.02-4.07
Gelatinous LaF_3	4.7
Na_2SO_4	2.69
K_2SO_4	2.66
$La_2(SO_4)_3$	3.60

2) Specific Gravity of Aqueous Lanthanum Ammonium Nitrate Solutions at 25°C

% $La(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$	Specific Gravity
39.4	1.268
32.0	1.203
28.4	1.174
24.3	1.144
18.2	1.102
15.4	1.083
11.8	1.059
9.5	1.046
6.5	1.029

3) Other Crystalline Rare Earth Fluorides

Crystalline neodymium fluorides were prepared by treating rubidium-neodymium, potassium-neodymium and sodium-neodymium double phosphates with hydrofluoric acid. In each case a pseudomorphic change similar to that occuring during lanthanum fluoride conversion was observed, i.e., a change in crystal structure from anisotropic to isotropic, accompanied by no change in the outward appearance of the crystal. Crystalline lanthanum fluoride was prepared from rubidium lanthanum sulphate in a similar manner.

4) Formula of Crystalline Lanthanum Fluoride

Two 6.63 gram samples of $La_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$ were treated with hydrofluoric acid and the resulting crystalline lanthanum fluorides filtered, washed with acetone, dried at 100°C for ½ hour, cooled and weighed. 4.08 and 4.05 grams respectively of lanthanum fluoride were obtained, representing an average weight ratio of 1.63. The theoretical weight ratio: $\frac{La_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O}{2LaF_3}$ is 1.90 and that for $\frac{La_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O}{2(LaF_3 \cdot 2H_2O)}$ is 1.60.

Since the experimentally determined ratio, considered accurate within ± 2%, differs from the ratio required by the formula LaF_3 by 14% and deviates 2% from the ratio required by the formula $LaF_3 \cdot 2H_2O$, it appears that the latter structure is correct.

Upon heating a portion of a dried fluoride in a glass tube, condensation of water was observed on the upper part of the tube. The theoretical water content of $LaF_3 \cdot 2H_2O$ is 15.6%; a dried crystalline fluoride gave a 13% loss on ignition.

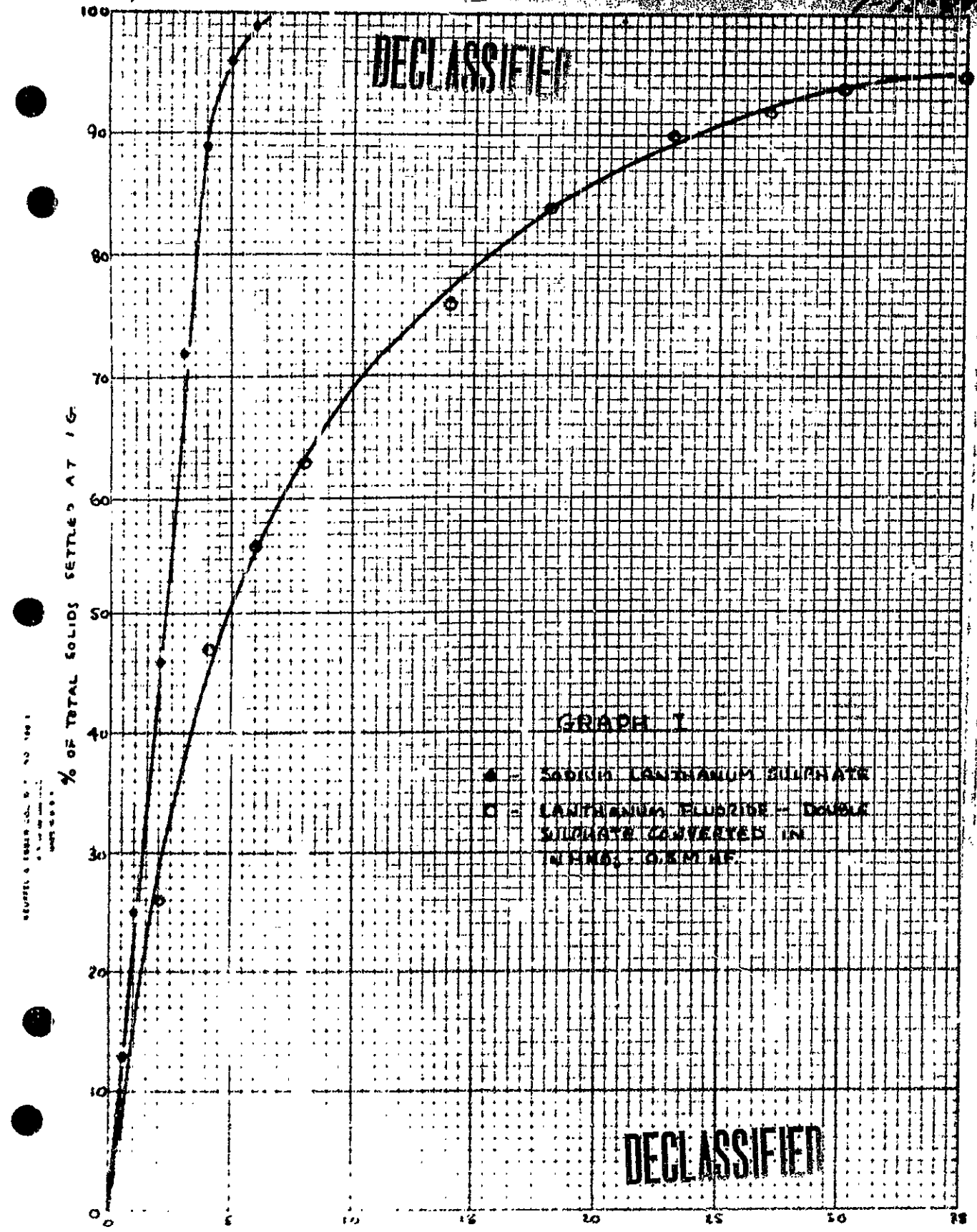
Results reported herein are recorded in:
HEW-149-T, pages 155-187
HEW-419-T, pages 1-6

L.SQUIRES, CHIEF SUPERVISOR
SEP.ENG.DIV.-200 AREAS TECHt
B.F.PARIS, SENIOR SUPERVISOR

A.H. Angerman

A.H.Angerman

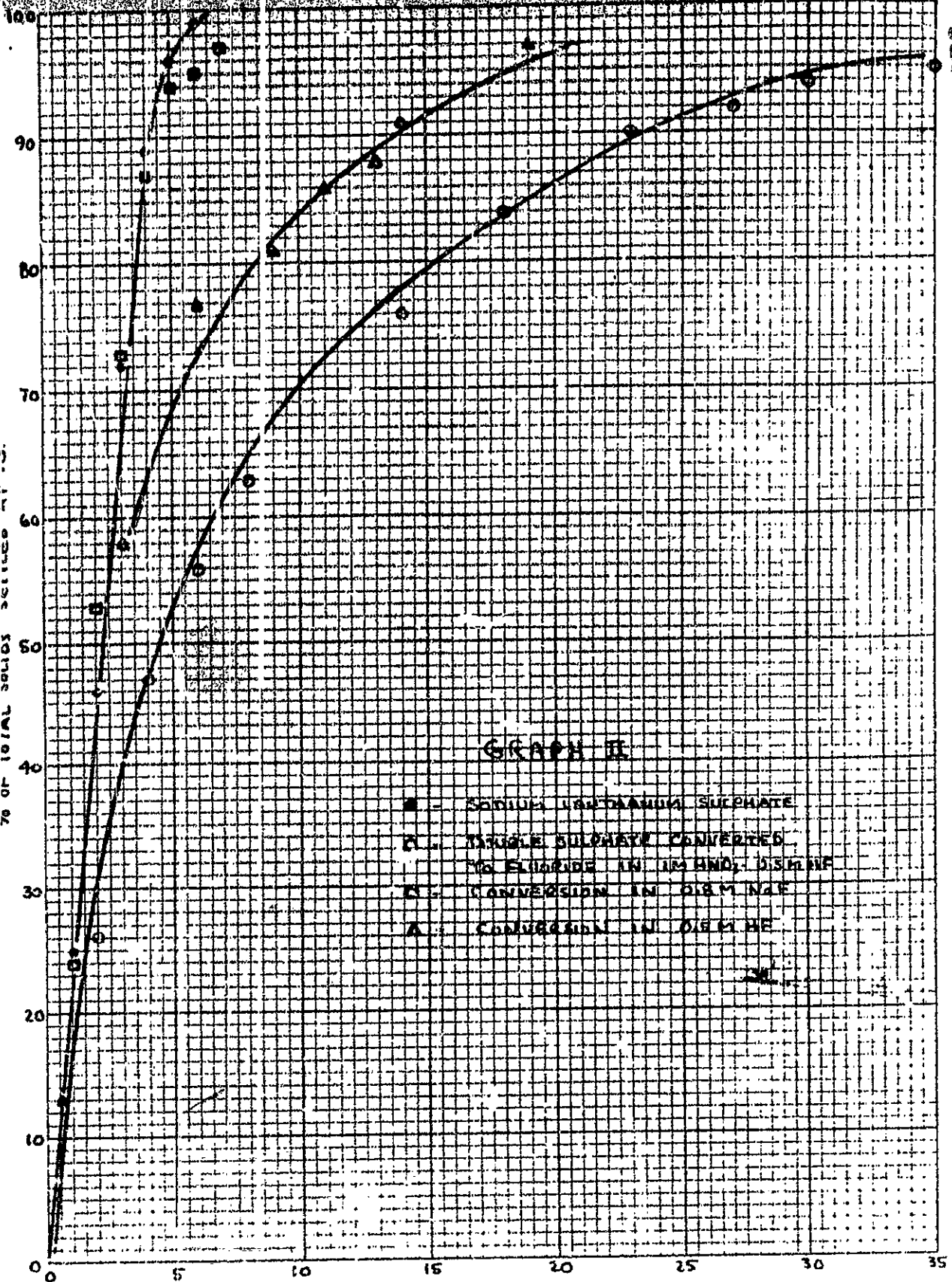
AHA:jd



GRAPH I

● = SODIUM LANTHANUM SULPHATE

□ = LANTHANUM FLUORIDE -- DOUBLE SULPHATE CONVERTED IN NH_4NO_3 - 0.5M HF.



GRAPH II

● - SODIUM URANYL SULPHATE

B. - INSOLUBLE SULPHATE CONVERTED TO FLUORIDE IN 1M HNO_3 DISMINF

B. - CONVERSION IN DISMINF

A. - CONVERSION IN DISMINF