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JUNE 19, 1946

MEMORANDUM REPORT - SE-PC-#52

STUDIES ON THE CENTRIFUGIBILITY OF LAF₃

INV.
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CLASSIFICATION CANCELLED
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 For The Atomic Energy Commission
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Introduction

At the time this work was undertaken, the highest single loss in the separations process was occurring in the LaF₃ product precipitation step of the crossover cycle. This step was one of the most time consuming operations in the process. It was, therefore, considered advisable to conduct a laboratory study on methods of improving the centrifugability of LaF₃ and especially to determine the effect of all possible chemical process variables on the centrifugability. It was also considered worthwhile to study the effect of plant process variables from the point of view of operational errors and uncalculated chemical effects (such as Ca⁺⁺ in process water) since in run T-5-02-B-2 losses in the LaF₃ product precipitation step dropped to an unprecedentedly low level for unaccountable reasons while in the next run, losses returned to the usual high level.

It is realized that this type of plant problem (centrifugability of precipitates) is one of the most difficult to study on a small scale in the laboratory. However, if the plant trouble could be eliminated by chemical means, and in particular if the pronounced and unexplained effect in T-5-02-B-2 was due to a chemical variable, laboratory experiments involving chemical variables should be of considerable help in guiding semi-works experiments and determining optimum plant solutions.

Summary and Conclusions

No very pronounced chemical effects on the centrifugability of LaF₃ were found in any case. The mild effects observed were insufficient to explain the particularly low losses observed in plant run T-5-02-B-2. Several variations from the standard procedure produced an improvement in the separation of LaF₃ as judged by controlled slow speed laboratory centrifugation. Variations producing some evidence of improvement were increased product concentration, increased lanthanum concentration, increased HF concentration, higher digestion temperatures, decreased agitation, decreased HNO₃ concentration, use of CeF₃ carrier in place of LaF₃, and decreased concentrations of the constituents of the solution from previous steps; namely, H₃PO₄, Cr(III), K(I), Na(I), and Mn(II) (when all these substances were decreased simultaneously).

Laboratory settling rate experiments on a thirty liter scale and two runs in the Cold Semi-Works (321 Building) corroborated the centrifugation improvement using a low acidity procedure during digestion and centrifugation of the LaF₃. The semi-works runs indicated approximately a factor of 2 decrease in waste loss.

The improvement given by increased concentration of La carrier in the lanthanum fluoride product precipitation step has been verified by plant runs beginning with the T-5-04 series. In these runs, the total amount of lanthanum used per process batch has been the same as in previous runs, but the lanthanum concentration has been increased by a factor of 1.7 as a result of reducing the process volumes in the crossover to 60% of their former level. Waste losses following this change have been lower by approximately a factor of 2 than before the change.

Laboratory centrifugation tests during and immediately after the plant LaF₃ centrifugation in run T-5-02-B-1 indicated at least part of the plant difficulty to be mechanical in nature, i.e. laboratory centrifugation of the plant LaF₃ slurry (E-1-F6) prior to plant centrifugation left a lower concentration of product in the supernatant than laboratory centrifugation of the waste (E-3-W5) following plant centrifugation. These results point toward the violent agitation of jetting and/or the shearing action upon introducing liquid into a continuous centrifuge as factors in determining the physical characteristics of LaF₃.

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In order to study the effects of process variables upon the centrifugability of LaF₃, it was necessary to compare the degree of separation of LaF₃ in a test where a given condition was varied from standard conditions with a control test in which standard conditions were employed, both tests being performed simultaneously under otherwise identical conditions.

The first step involved preparation of synthetic mixtures of the following general composition (flow-sheet LaF₃ product slurry) to be used in the control (standard) tests.

HNO ₃	0.95M
HF	0.57M
H ₃ PO ₄	0.06M
NaNO ₃	0.0015M
KNO ₃	0.0077M
Cr(NO ₃) ₃	0.0015M
Mn(NO ₃) ₂	0.0078M
H ₂ C ₂ O ₄	0.047M
La	(added as solution of La(NO ₃) ₃ ·2H ₂ O 100g/l (2-50g/l shots combined).
Pu	15g/l (approx. 150g/l level)

LaF₃ product precipitation was made by adding La solution after adding the Pu to the solution. The solutions in all cases had the same composition and treatment with the exception of the variable under consideration. Normally, three "variable" tests and one control test were simultaneously centrifuged for 3 minutes at 270 R.C.F*. The waste losses were then measured and the results of these three tests were compared only with the simultaneously run control. The particular time and R.C.F. employed in these experiments was such as to result in waste losses for the control of 15-20% which approximates losses occurring in the plant after one centrifugation at the time these experiments were undertaken (T-5-02 and T-5-02 series). Controls run under identical conditions on different dates turned out to be very reproducible - ± 2.2% maximum deviation in waste loss. The results are shown in tables in the form of improvement factors or ratios of waste loss in controls to waste loss in the "variable" test. Thus, an "improvement factor" of less than 1 is obviously a higher waste loss in the "variable" test than in the control. The results do not necessarily represent quantitatively the decrease in waste loss to be expected in actual operation of the particular procedure, but are intended to show the tendency of the chemical variables to improve or impair the centrifugability of LaF₃.

Table I shows the effect of various possible impurities upon the centrifugability of LaF₃. Hydraulic centrifuge oil was tested for possible deleterious effect because of the possibility of its getting into plant solutions from the centrifuges. The effect of Ca⁺⁺ was tested since process water (used prior to the use of condensed steam beginning about Run T-5-02-B-3) contains the same order of magnitude of Ca(II) concentration as the La carrier concentration in the LaF₃ product precipitation step. The effect of K₂SiF₆ was tested because of its low solubility and the possible Si impurities in process reagents and process water.

Table II shows the effect of some of the ordinary process variables on the centrifugability of LaF₃ and is more or less self-explanatory.

* Relative centrifugal force or gravities.

Table I

Effect of Miscellaneous Variables on the Centrifugability of LaF₃

Variables	Improvement Factor
Hydraulic centrifuge oil added -0.01%	1.0, 1.5
Hydraulic centrifuge oil added -0.1%	1.2
Hydraulic centrifuge oil added -1.0%	1.2
K ₂ SiF ₆ co-precipitated, 0.01M K ⁺ , 0.01M SiF ₆ ⁼	1.0, 1.1
K ₂ SiF ₆ co-precipitated, 0.01M K ⁺ , 0.1M SiF ₆ ⁼	1.0, 0.9
K ₂ SiF ₆ co-precipitated, 0.1M K ⁺ , 0.1M SiF ₆ ⁼	1.2, 1.2
K ₂ SiF ₆ co-precipitated, 0.5M K ⁺ , 0.1M SiF ₆ ⁼	1.5
Ca ⁺⁺ added, Ca/La mole ratio = 0.5	1.1
Ca ⁺⁺ added, Ca/La mole ratio = 1.0	1.1
Ca ⁺⁺ added, Ca/La mole ratio = 2.0	1.0

Table II

Effect of Process Variables on Centrifugability of LaF₃

Variable	Improvement Factor
Pu concentration at 10g/T level	0.7
Pu concentration at 30g/T level	0.9
Pu concentration at 60g/T level	1.0
Digestion temperature 55°C (25°C for control)	1.0
Digestion temperature 50°C	1.1
Digestion temperature 75°C	1.7
Ce(III) carrier 100mg/l (no La)	1.4
Increase La to 250mg/l	1.4
Increase HF to 2N	1.3
Eliminate H ₃ PO ₄ , Na ⁺ , K ⁺ , Cr ⁺⁺⁺ , Mn ⁺⁺ , H ₂ C ₂ O ₄	1.2
Increase H ₃ PO ₄ , K ⁺ , Na ⁺ , Mn ⁺⁺ , Cr ⁺⁺⁺ by factor of ~5	0.7
No agitation after mixing reagents	1.3
Violent agitation	0.8
Violent agitation followed by settling period	0.8
Add 0.5M HF - no HF	1.8
Add 0.5M KF - no HF	0.8
0.5M HNO ₃ , 0.1M H ₂ C ₂ O ₄ , 1N HF, 200mg/l La ⁺⁺⁺ , 0.5M K ⁺	1.9
0.5M HNO ₃ , 0.1M H ₂ C ₂ O ₄ , 1N HF, 200mg/l Ce ⁺⁺⁺ , 0.5M K ⁺	2.4
0.1M HNO ₃ , 0.1M H ₂ C ₂ O ₄ , 2N HF, 200mg/l La ⁺⁺⁺ , 1M K ⁺	1.5
No HNO ₃	1.2
0.1N HNO ₃	1.1, 1.1
0.5N HNO ₃	1.1
1.5N HNO ₃	0.8
2.0N HNO ₃	0.6
3.0N HNO ₃	0.5
Addition of 0.1M K ₂ C ₂ O ₄	1.5
Addition of 0.5M K ₂ C ₂ O ₄	2.0
0.5M K ⁺ (as KNO ₃)	1.0
0.5M K ⁺ (as KNO ₃) 0.1N HNO ₃	1.2

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From the data in Tables I and II, the following qualitative conclusions may be drawn.

Table III

Effect of Chemical and Process Variations on Centrifugability of LaF₃

Evaluation of Effect of Changing Conditions		
Improved Centrifugability	No Definite Effect	Impaired Centrifugability
higher Pa concentrations	presence of hydraulic (centrifuge) oil in solution	increased concentration of H ₃ PO ₄ , Na ⁺ , K ⁺ , Cr ⁺⁺⁺ , Mn ⁺⁺
higher digestion temperatures		
higher La concentration	presence of Ca ⁺⁺	violent agitation
higher HF concentration	addition of KF instead of HF	high HNO ₃ concentration
absence of H ₃ PO ₄ , Na ⁺ , K ⁺ , Cr ⁺⁺⁺ , Mn ⁺⁺		
mild agitation		
low HNO ₃ concentration		
addition of K ₂ C ₂ O ₄ instead of H ₂ C ₂ O ₄		
CeF ₃ instead of LaF ₃ carrier		
co-precipitation of K ₂ SiF ₆		
increased F ⁻ concentration with low acidity		

A series of experiments on a 50 liter scale were performed in the laboratory to determine settling rates of LaF₃ under various conditions. The data are presented below in Table IV expressed as % LaF₃ remaining suspended after a given time interval. An interesting fact noted in connection with these experiments was that although samples were carefully taken from various levels from 1/2 inch to 12 inches (top of solution) in the tank, no definite gradation or concentration of activity toward the bottom could be detected until the actual settled precipitate on the bottom was reached. This phenomenon has not been adequately accounted for, but may possibly depend upon convection currents keeping the finely divided particles uniformly suspended throughout the supernatant until coagulation or agglomeration occurs after which the larger particles settle out very rapidly or separate only when the bottom of the tank is contacted. It was thought that if the precipitate were composed of larger particles than the suspended material, upon reagitiation of a settled precipitate, the settling rate would be much faster than was originally the case. However, as is shown below, the opposite result was encountered. If the settled precipitate does exist as larger agglomerates than the suspended material, it is very easily broken up by agitation to its former finely divided state.

Neutralization of the solution with KOH or K₂CrO₄ seems to give an initial increased settling rate, although the improvement is not as readily apparent after longer periods of settling.

* Based on measurement of product remaining in supernatant.

Table IV

Settling of LaF₃*

Expt. No.	1		2		3		4		5		6		7		8	
	Regular Pptn. Conditions	Ppt. from Expt. No. 1 Reagitated	Ppt. from Expt. No. 2 reagitated and solidly reduced to 0.1N with NOH	MF used in place of HF	Ppt. from Expt. No. 4 Reagitated	O ₂ S ⁺ K ₂ C ₂ O ₄ used in place of H ₂ C ₂ O ₄	All L ₂ added at once	Slow Strike La added over 1 1/2 hrs.								
1	60	95	28	50	91	40	68	94								
2	18	44	16	31	52	22	29	55								
4	--	19	9	--	24	14	18	20								
5 to 6	--	12	7	--	16	11	15	--								
19 to 23	4	--	--	4	4	3	4	6								

* The numbers tabulated are based on analysis of solution for product and expressed as % of product (added originally) in an aliquot of the same size. As noted in the text, the amount of product found in the supernatant at any time was independent of the depth at which the aliquot for analysis was taken.

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Semi-Works

Two tests, (LF-31, 32 and EM-22,23) were made by the S21 Semi-Works of the partial NaOH neutralization procedure to test its effectiveness under actual operating conditions in reducing LaF₃ waste losses. The conditions employed in the Semi-Works were based on experimental work from two sources: (1) previous unreported laboratory work by E. F. Faris in which it was demonstrated that partial neutralization gave improvement by a factor of ~2* and (2) the experimental work presented in this report which indicated an improvement at low acidities. The total amount of NaOH added was 1.2 moles per 1-mole of HNO₃. This was added after the first 50mg/l La strike has been made. The reduced acidity slurry was then digested and centrifuged and a second La strike was made which was also digested and centrifuged in the normal manner. The semi-works waste losses are not of the same magnitude as the plant losses, so it is the comparison between the control run made under standard conditions of acidity and the runs in which the acidity was reduced which is of interest rather than the absolute losses. Pu at tracer concentrations was used in the runs to measure losses. The number of experiments of this type is too few to attach quantitative significance to the differences in factors observed.

It is seen that an improvement factor of about 1.5 resulted after the first centrifugation and about 2 after the second centrifugation.

Table VSemi-Works Waste Losses in LaF₃ Centrifugation Using Partial Neutralization Procedure

Run	Conditions	% waste loss after 1st shot centrifugation	% waste loss after 2nd shot centrifugation
LF-31	Control	53.5	38.6
LF-32	NaOH partial neutralization	42.9	14.3
EM-22,23	NaOH partial neutralization	35.4	21.5

Laboratory Centrifugation Tests on Plant Run T-5-02-B-1

In the LaF₃ product precipitation step of plant run T-5-02-B-1, samples were taken continuously during the course of the run which were tested extensively in the laboratory with respect to the centrifugability of the precipitate. The tests were performed at the same time the run was being carried out in Cell E, 224-T Building. In all cases tests were made by laboratory centrifugation of samples for 5 minutes at the maximum speed of a clinical centrifuge and subsequent Pu analysis of supernatant and precipitate in less than 45 minutes after the samples were drawn. The data obtained are summarized in Table VI below. Most of the results shown represent the average of duplicate tests.

The results in the table show 72% efficiency in product removal by the first plant centrifugation and 68% efficiency in removal of the remaining product by the second shot centrifugation. This resulted in a 7% plant waste loss at this point. The results obtained upon laboratory centrifugation show marked differences in the

* In one experiment by E.F. Faris, the acidity was reduced to 0.25N with KOH after precipitation of LaF₃, in which case the improvement factor with respect to a control experiment employing usual acidity was 5.1. When the acidity was reduced to 0.25N by the addition of KOH before the precipitation of LaF₃, the improvement factor was 1.6. A factor of 5.1 was obtained when the acidity was reduced with NaOH instead of KOH, after the precipitation of LaF₃. The number of experiments of this type is too few to attach quantitative significance to the differences in factors observed.

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Table VI*

Centrifugation Tests During LaFg Product Precipitation Step of Run T-5-02-B-1

Sample	Total Analysis As Received	% in Lab. Centr. Supernatant	% in Lab. Centr. Precipitate	Comment
D-5-06 E-1-PS-1	83.5%	0.5%		Product slurry just before plant centrifugation (0.24% found not reduced)
E-3-WS-1	20.7	3.0	13.5	1st 5% of plant effluent
E-3-WS-2	20.3	2.8	18.2	1st 25% of plant effluent
E-3-WS-3	27.3	4.2	16.9	1st 50% of plant effluent
E-3-WS-4	22.2	5.5	16.1	1st 75% of plant effluent
E-3-WS-5	23.9	3.0	20.4	1st 100% of plant effluent before skim
E-3-WS-6	23.9	2.6	20.8	1st 100% of plant effluent after skim
E-3-PS-2	22.6	0.4	23.4	Product slurry just before 2nd centrifugation
E-3-WS-7	7.4	0.6	6.8	1st 25% of effluent
E-3-WS-8	7.1	0.7	6.4	1st 50% of effluent
E-3-WS-9	7.1	0.7	6.4	1st 75% of effluent
E-3-WS-10	7.6	1.2	7.3	1st 100% of effluent before skim
E-3-WS-11	6.7	0.6	6.4	1st 100% of effluent after skim
E-3-WS-12	7.1	0.3	6.4	1st 100% of effluent after ENO ₂ wash of Ppt.

* All percentages shown are based on 8-1-K assay for this run.

properties of the precipitate before and after plant centrifugation, particularly after the first shot of LaFg. Although the waste loss upon laboratory centrifugation of the plant product slurry before plant centrifugation was 0.6%, it could not be reduced to less than 2.5 to 5.5% on laboratory centrifugation of the 1st plant effluent. The effect was not so noticeable during the second centrifugation because all losses were lower. It is believed that the most probable explanation for this is that LaFg is de-flocculated by the vigorous operations of jetting or shearing action in the plant centrifuge to a form which is not easily separated even by high speed batch laboratory centrifugation.

The table shows no significant difference in waste loss at any point during centrifugation or before or after the skimming and washing operations.

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The experimental work covered in the report was done by W. J. Knox and R.P.S.Black. The results are recorded in H.E.W. notebooks 184-T and 180-T.

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