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CRYSTALLINE [illegible]

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Lanthanum fluoride as normally precipitated is a finely divided, amorphous, hydrated, flocculent mass which even under the electron microscope shows no definite crystalline structure, but rather a small, ill-defined mass less than 0.01 micron in size. In this form, the lanthanum fluoride is exceedingly difficult to remove quantitatively from plant solutions in the volumes in which it is formed. Filtrations are impractical, and continuous centrifugal separations are seldom more than 90% complete even at high angular velocities and low through-put rates. These above characteristics of flocculent lanthanum fluoride necessitate repeated centrifugations, increased operating complexity and undesirably long time cycles in the lanthanum fluoride product precipitation step of the crossover cycle ([illegible] Building).

The process advantages inherent in a crystalline lanthanum fluoride of [illegible] particle size have long been recognized and considerable experimental work [illegible] been carried out previously in various attempts to precipitate LaF$_3$ under [illegible] which would yield a material more easily separated from process solutions. [illegible] fugation. This report covers the initial phases of the development of a [illegible] lanthanum fluoride and the application of this material to the problem of [illegible] waste losses and decreasing tim[illegible] building).

1. A procedure has been deve[illegible] [illegible] fluoride of comparatively [illegible] a relatively insoluble, crysta[illegible] fluoride-containing solution.

The [illegible] lanthanum sul[illegible] solution of lanthanum ammonium [illegible] at elevated temperature follow[illegible] taining alkali lanthanum sulfa[illegible] structure as the parent compoun[illegible] in a slurry of alkali sulfate [illegible] showed that the resulting LaF$_3$ [illegible] and sulfate. There appears to [illegible] of the potassium salt in that [illegible] less fragile.

2. Complete carrying of Pu(IV[illegible] [illegible] by addition [illegible] solutions under normal process [illegible] a solution 1N in HNO$_3$ and 0.5N [illegible]

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DATE 9-7-60
For The Atomic Energy Commission
H B Carrell
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J E Savely 3-30-00
J Miller 4-7-00
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CRYSTALLINE LANTHANUM FLUORIDE

Introduction

Lanthanum fluoride as normally precipitated is a finely divided, amorphous, hydrated, flocculent mass which even under the electron microscope shows no definite crystalline structure, but rather a small, ill-defined mass less than 0.01 micron in size. In this form, the lanthanum fluoride is exceedingly difficult to remove quantitatively from plant solutions in the volumes in which it is formed. Filtrations are impractical, and continuous centrifugal separations are seldom more than 80% complete even at high angular velocities and low through-put rates. These above characteristics of flocculent lanthanum fluoride necessitate repeated centrifugations, increased operating complexity and undesirably long time cycles in the lanthanum fluoride product precipitation step of the crossover cycle (224 Building).

The process advantages inherent in a crystalline lanthanum fluoride of finite particle size have long been recognized and considerable experimental work has been carried out previously in various attempts to precipitate LaF_3 under conditions which would yield a material more easily separated from process solutions by centrifugation. This report covers the initial phases of the development of a crystalline lanthanum fluoride and the application of this material to the problem of reducing waste losses and decreasing time cycles in the plant concentration operations (224 Building).

Summary

1. A procedure has been developed for the preparation of a crystalline lanthanum fluoride of comparatively large particle size. This was accomplished by adding a relatively insoluble, crystalline lanthanum salt (alkali lanthanum sulfate) to a fluoride-containing solution.

The alkali lanthanum sulfate was prepared by adding a concentrated aqueous solution of lanthanum ammonium nitrate to a concentrated solution of alkali sulfate at elevated temperature followed by a short aging period. Conversion of this crystalline alkali lanthanum sulfate to LaF_3, which retained the same crystalline structure as the parent compound, was effected by adding the lanthanum double salt in a slurry of alkali sulfate to a process solution at least 0.5M in HF. Analyses showed that the resulting LaF_3 crystals were essentially free of alkali metal ion and sulfate. There appears to be some advantage in starting with the sodium instead of the potassium salt in that the crystalline LaF_3 derived therefrom appears to be less fragile.

2. Complete carrying of Pu(IV) has been obtained with crystalline LaF_3 formed in the laboratory by addition of sodium lanthanum sulfate to product containing solutions under normal process conditions, that is, with 100mg La per 25mg Pu from a solution 1N in HNO_3 and 0.5N in HF.

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Losses in the product precipitation wastes in plant runs employing crystalline LaF_3 have been consistently lower than those runs with gelatinous LaF_3. Such losses as occur have probably been occasioned by "fines" which are formed during conversion of the sodium or potassium lanthanum sulfate to LaF_3, and not to incomplete carrying.

3. On the basis of data presented herein, the recommended procedure for the synthesis of crystalline sodium lanthanum sulfate involves addition, over a 30 minute period of a 40% lanthanum nitrate solution (sp.gr. 1.272) to an excess of 0.65M sodium sulfate solution at 75°C followed by digestion for an hour at 75°C. Good mechanical agitation is advantageous but does not appear to be critical. Excess sodium sulfate is employed to insure complete insolubility of the crystalline sodium lanthanum sulfate.

Further work is in progress on a study of variables involved in the preparation of the double salt and present data indicate that a salt of a somewhat larger and more uniform crystal size can be obtained from a different precipitation procedure. This work will be covered in a separate report.

4. Decontamination equal to - or better than - that obtained with gelatinous lanthanum fluoride has resulted from the use of crystalline LaF_3 in the cross-over by-product precipitation step.

5. As far as can be ascertained, crystalline LaF_3 is as easily metathesized as is the gelatinous LaF_3. Lanthanum hydroxide from crystalline LaF_3 is also crystalline.

Experimental Details

1. Preparation of Crystalline Lanthanum Fluoride

An attempt was made to synthesize potassium lanthanum fluoride with the expectation that this compound would be more crystalline in nature than ordinary lanthanum fluoride. For this purpose, the sparingly soluble crystalline double sulfate of potassium and lanthanum, ($La_2(SO_4)_3 \cdot 4\frac{1}{2} K_2SO_4 \cdot 2H_2O$)* was added to an aqueous solution of hydrofluoric acid. The resulting insoluble compound was far superior to ordinary lanthanum fluoride with respect to sedimentation velocity. Microscopical examination showed it to be crystalline in nature and indicated that its crystal habit was identical to that of the initial double sulfate.

The initial assumptions were that the compound was either the potassium lanthanum fluoride as anticipated or the original double sulfate covered with an impregnable film of lanthanum fluoride. Subsequent investigations, however, have shown that the compound: (1) consists primarily of lanthanum and fluorine, (2) is essentially free of potassium (or sodium), and (3) exhibits all the well known reactions of lanthanum fluoride such as solubility in zirconium nitrate solution, insolubility in dilute mineral acids, and conversion to the hydroxide upon treatment with strong alkali. The above experiments have adequately established the compound as a heretofore unknown crystalline modification of lanthanum fluoride.

The mechanism of the reaction:

Double sulfate** $\xrightarrow{HF}$ LaF_3 (crystalline) is unusual in that it represents a rapid solid-solid metathesis which preserves the crystallinity of the original system.

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* Seidell - "Solubilities of Inorganic and Metal Organic Compounds"

** Either sodium lanthanum sulfate or potassium lanthanum sulfate

Removal of alkali sulfate and water from the crystal lattice of the double sulfate does not alter the outward appearance of the crystal. Examination of the double sulfate crystals under polarized light has shown them to be anisotropic, probably hexagonal, but upon conversion to LaF_3 by treatment with HF, the crystals become isotropic. Samples of alkali lanthanum sulfate, the LaF_3 derived there-from, and the $La(OH)_3$ formed by alkaline metathesis of the crystalline LaF_3 were examined at Site C by X-ray spectrograph. All three were reported to be crystalline.

The crystalline LaF_3 can be formed directly in the process solution containing HF by addition of the alkali lanthanum sulfate, or the crystalline LaF_3 can be formed externally either by adding the double sulfate to a fluoride-containing solution or by adding fluoride to the slurry of the double salt in an alkali sulfate solution. This LaF_3 can then be added to the process solution. The first procedure is more convenient process-wise, the resulting LaF_3 carries product somewhat better than externally formed LaF_3, so consequently the first procedure has received most attention in the development study.

2. Preparation of Alkali-Lanthanum Double Sulfate

Initial investigations designed to establish the applicability of crystalline lanthanum fluoride to the present process were confined to the double sulfate of potassium and lanthanum. This compound varies in molar composition depending on the mode of preparation,[1] but in early experiments the compound employed was believed to be $La_2(SO_4)_3 \cdot 4\frac{1}{2}\,K_2SO_4 \cdot 2H_2O$. This was prepared by adding an aqueous 40% solution (sp.gr. 1.272) of lanthanum[2] ammonium nitrate to a 0.74M solution of potassium sulfate (at 75°C) over a period of 0.5 hour followed by a digestion period of one hour at 75°C. The final lanthanum concentration was 0.106M. The resulting well-defined equilateral hexagonal crystals were approximately 0.01mm. in diameter, and the crystals in suspension settled through 12 inches of slurry liquid in 5 minutes.

To insure quantitative precipitation of lanthanum in this preparation, it is important that reasonable precautions be observed to prevent accidental dilutions by water or acids. Double sulfates are insoluble only in the presence of excess neutral alkali sulfate, and it is accordingly necessary that the lanthanum salt solution contain no added nitric acid, an addition that is now made to plant solutions of the same salt. Any lanthanum that may remain dissolved in the supernatant of the alkali lanthanum sulfate will precipitate as gelatinous lanthanum fluoride when the slurry of the double salt is added to HF-containing process solution. The presence of gelatinous LaF_3 offsets to some extent the advantages of using crystalline LaF_3.

Sodium lanthanum sulfate crystallizes as a single definite compound, i.e. La_2SO_4 $Na_2SO_4 \cdot 2H_2O$,[1] regardless of the method employed. The present method of its preparation is identical with that of the potassium salt. Good mechanical agitation during the strike appears to be advantageous. Crystals prepared by this method are elongated hexagons (~0.01-0.02mm in length) and occasionally extensive twinning of crystals results in dendrite formation.

Upon conversion of the sodium double sulfate to lanthanum fluoride, one mole of sodium sulfate is released from the crystal lattice per mole of lanthanum sulfate, whereas 4.5 moles of potassium sulfate are released in the same reaction involving potassium lanthanum sulfate. This suggests that lanthanum fluoride crystals prepared from the sodium salt may be more compact, i.e. less "spongy" than lanthanum fluoride derived from the potassium salt, and therefore less subject to disintegration by violent impact such as mechanical agitation, and cavitation during jetting.

[1] Seidell - "Solubilities of Inorganic and Metal Organic Compounds."

[2] The lanthanum salt must be essentially free of other rare earth elements not precipitable by alkali sulfates.

In laboratory tests, crystalline lanthanum fluorides were subjected to moderate mechanical pressures. Upon microscopic examination, it was found that the lanthanum fluoride crystals from potassium lanthanum sulfate were readily crushed, whereas the lanthanum fluoride dendrites from the sodium double salt, althouth disintegrated somewhat by the mechanical action, retained their initial elongated hexagonal appearance. Although there is no conclusive evidence on which to state that one alkali lanthanum sulfate yields superior LaF_3 to that obtained from the other alkali double sulfate, most research has been confined to sodium lanthanum sulfate and the LaF_3 derived therefrom.

Recent laboratory tests strongly indicate that the LaF_3 "fines" are produced during the metathesis of the sodium lanthanum sulfate, and are not present in the parent salt. A description of these tests will be given in a subsequent report.

Since the size of the alkali double sulfate crystal determines largely the crystal size of the resulting LaF_3, appreciable research was centered on the determination of optimum conditions necessary for the production of a more uniform particle-sized double sulfate. A wide variety of methods has been tested to achieve this goal. Procedures tried to date and results therefrom are presented in Table I.

3. Carrying of Plutonium by Crystalline Lanthanum Fluoride

Numerous experimental results obtained in the laboratory and semi-works indicate that crystalline lanthanum fluoride is as efficient a carrier for Pu(IV) as the conventional type of lanthanum fluoride. In the experiments outlined below (Table II) the crystalline lanthanum fluoride was prepared by rapidly adding an alkali sulfate slurry of the double salt to a process solution containing Pu(IV), hydrofluoric acid (0.5M) and nitric acid (1M).

Table II

Carrying of Crystalline LaF_3

Data Obtained In	Scale	No. of Experiments	Type of Double Sulfate	Product Level*	La^{+3} Conc. mg/liter	Digestion Period At 35°C.	% Pu Carried
Laboratory	1 liter	3	K	1	225	1½ hours	99+
Laboratory	12 ml.	1	K	250	100	2 hours	98.9
Semi-Works	600 liters	6	K	Tracer	100	2 hours	98.3
Laboratory	10 ml.	1	Na	250	100	1 hour	99.2
Laboratory	10 ml.	1	Na	625	100	1 hour	92.3
Laboratory	10 ml.	1	Na	875	100	1 hour	61
Laboratory	10 ml.	1	Na	1330	100	1 hour	68
Semi-Works	600 -l.	1	Na	Tracer	200	2 hours	99.3
Semi-Works	600 -l.	10	Na	Tracer	100	2 hours	99.7
Semi-Works	600 -l.	6	Na	Tracer	50	2 hours	98.9
Plant	3000 gallons	1	Na	65[illegible]	100	2 hours	99+

* Grams of product per process batch - full process volumes of October 5 flowsheet assumed (*ca.* 10,000 liters).

Externally prepared crystalline lanthanum fluoride has been found to carry tracer product quantitatively, but the degree of carrying for a given digestion period falls off to some extent as "W" concentrations of product are approached.

Table I

Preparation of $La_2(SO_4)_3 \cdot Na_2SO_4 \cdot 2H_2O$

Reaction Strike	Concentration (Molarity)	Slurry Volume in ml.	Temperature	Rate and Method of Addition	Agitation and Digestion	Crystal Description
1. $La_2(SO_4)_3$ to Na_2SO_4	La*** = 0.157 *Na_2SO_4 = 0.4	200	70°C	Very rapid in one shot	Moderate Digested 1-hr.	Small and bipyramidal prisms 3-10 μ. Largely loose clusters.
2. $La_2(SO_4)_3$ to Na_2SO_4	La = 0.157 Na_2SO_4 = 0.6	200	70°C	Very rapid in one shot	Moderate Digested 1-hr.	Few bipyramidal prisms 2-3μ in length. Largely open clusters.
3. **LL to Na_2SO_4	La = 0.157 Na_2SO_4 = 0.8	200	70°C	Very rapid in one shot	Moderate Digested 1-hr.	Bipyramidal prisms 1-1.5μ in length. Very few clusters.
4. **LL to Na_2SO_4	La = 0.915 Na_2SO_4 = 0.37	30200	70-75	3.575-1.in 30 min.(3%/min.)	Moderate Digested 1-hr.	Few prisms 5-20 μ in length. Solid aggregates to 40 μ in diameter.
5. **LL to Na_2SO_4	La = 0.915 Na_2SO_4 = 0.2	300	70-75	35ml. in 10min. (10%/min.)	Moderate Digested 1-hr.	Few prisms 5-12 μ in length. Largely aggregated.
6 **LL to Na_2SO_4	La = 0.915 Na_2SO_4 = 0.37	300	70-75	35ml. in 10min. (10%/min.)	Moderate Digested 1-hr.	Few prisms 10-15 μ in length. Largely aggregated.
7. Na_2SO_4 to LL	La = 0.141 Na_2SO_4 = 0.37	300	75°C	100ml.Na_2SO_4 in 10min.(10%/min.)	Moderate Digested 1-hr.	Few small pieces about 1μ in length. Almost all in aggregates.
8. Na_2SO_4 to LL	La = 0.225 Na_2SO_4 = 0.37	300	75°C	100ml.Na_2SO_4 in 2-hrs.(0.83%/min.)	Moderate Digested 1-hr.	Single prisms 15-30 μ in length. Partly aggregated.
9. Na_2SO_4 and LL Simultaneously	La = 0.328 *Na_2SO_4 = 0.37	300	24°C	Total in 20 min.	Rapid Digested 1-hr.	Very fine crystals <1μ in diameter. Partly aggregated.
10. NaOH to LL + H_2SO_4	La = 0.144 Na_2SO_4 = 0.37	300	75°C	75ml. in 1-hr. (1.7%/min.)	Moderate Digested 1-hr.	Very few prisms 2-50 μ in length. Largely chunky aggregates.
11. NaOH to LL + H_2SO_4	La = 0.144 Na_2SO_4 = 0.37	300	24°C	75ml. in 1-hr. (1.7%/min.)	Moderate Digested 1-hr.	Few prisms 2-50μ in length. Largely chunky aggregates to 150 μ.
12. $(NH_4)_2SO_4$ to LL + $NaNO_3$	La = 0.09 Na_2SO_4 = 0.37	500	75°C	Added dropwise	Moderate No digestion	Irregular Bipyramids 8-15 μ. Many fines and large clusters.

* Na_2SO_4 concentration in all cases represents concentration in final slurry

** LL represents $La(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$ produced by the Lindsay Light Co.

*** La concentration represents concentration of La solution prior to strike

Table I (Cont'd)

Reaction Strike	Concentration (Molarity)		Slurry Volume in ml.	Temper-ature	Rate and Method of Addition	Agitation and Digestion	Crystal Description
13. LL to NaOH H_2SO_4 to $La(OH)_3$	La NaOH H_2SO_4 Na_2SO_4	=0.24 =2.17 =3 =0.4	500	80°C	Slow stream Total La=5g. 75% in slow stream 25% dropwise	Very vigorous No digestion Very vigorous No digestion	Crystals started to form at 81-82% neutralized. Prism length = 8-15 μ. Many fines but no large aggregates.
14. LL to NaOH H_2SO_4 to $La(OH)_3$	La NaOH H_2SO_4 Na_2SO_4	=0.526 =1.81 =3 =0.2	500	80°C	Slow stream Total La= 5g. 75% in slow stream 25% in 1-rapid shot	Vigorous No digestion Vigorous No digestion	Prisms to 10μ in length. Many fines in large aggregates.
15. LL to NaOH H_2SO_4 to $La(OH)_3$	La NaOH H_2SO_4 Na_2SO_4	=0.225 =2.09 =3 =0.4	500	80°C	One rapid shot Total La=5g. 75% in slow stream 25% dropwise	Very vigorous 15min. digestion Very vigorous No digestion	Prisms 4-8μ in length Small clusters from twinning. Little, if any fines.
16. NaOH to LL H_2SO_4 to $La(OH)_3$	La NaOH H_2SO_4 Na_2SO_4	=0.115 =5 =3 =0.4	500	80°C	One rapid shot Total La=5g. 75% in slow stream 25% dropwise	Very vigorous 15min. digestion Very vigorous No digestion	Prisms about 6μ in length Largely in small clusters due to twinning. Very few fines.
17. LL to NaOH H_2SO_4 to $La(OH)_3$	La NaOH H_2SO_4 Na_2SO_4	=0.225 =2.14 =3 =0.42	30,000	80°C	One rapid shot Total La=300g. 75% at 1.5 l/min. 25% subsurface over 15 min.	Very vigorous 10min. digestion Very vigorous 45min. digestion	Prisms 10-14μ in length Very few visible fines, but crystals largely as small clusters or aggregates.
18. LL to NaOH H_2SO_4 to $La(OH)_3$	La NaOH H_2SO_4=75%=3,25%=15 Na_2SO_4	=0.231 =2.0 =0.35	30,000	80°C	One rapid shot Total La=300g. 75% in slow stream. 25% subsurface over 40 min.	Very vigorous 15min. digestion Very vigorous 45min. digestion	Almost all crystals are hexagonal prisms 25 μ in length, either single or twinned. No visible crystals less than 5μ in length.
19. LL to NaOH H_2SO_4 to $La(OH)_3$	La NaOH H_2SO_4 Na_2SO_4	=0.225 =2.85 =3 = 0.6	600	80°C	One rapid shot Total La=5g. 75% in slow stream. 25% very slow & subsurface	Very vigorous 15min. digestion Very vigorous No digestion	Prisms 8-16μ in length. Very clean from fines. Nearly all single or simply twinned.

Table I (Cont'd)

Reaction Strike	Concentration (Molarity)	Slurry Volume in ml.	Temperature	Rate and Method or Addition	Agitation and Digestion	Crystal Description
20 LL to NaOH H_2SO_4 to $La(OH)_3$	La =0.225 NaOH =2.14 H_2SO_4 =3 Na_2SO_4 =0.42	500	80°C	One rapid shot Total La=5g. 75% in slow stream. 25% very slow and subsurface	Very vigorous No digestion Very vigorous No digestion	Prisms 8-16 µ in length. Very clean from fines. Nearly all single or simply twinned.
21 LL to NaOH H_2SO_4 to $La(OH)_3$	La =0.40 NaOH =2.25 H_2SO_4 =3 Na_2SO_4 =0.4	500	80°C	One rapid shot Total La=7.5g. 75% in slow stream. 25% subsurface over 3 min.	Very vigorous 15min. digestion Very vigorous No digestion	Large clusters of fines showing insufficient mixing of La and OH^-.
22 LL to NaOH H_2SO_4 to $La(OH)_3$	La =0.288 NaOH =2.23 H_2SO_4 =3 Na_2SO_4 =0.4	500	80°C	One rapid shot Total La=6.25g. 75% in slow stream. 25% subsurface over 3 min.	Very vigorous 10min. digestion Very vigorous No digestion	Prisms 10-15µ in length. Considerable complex twinning but no visible fines.
23 LL to NaOH $La(OH)_3$ to H_2SO_4	La =0.24 NaOH =2.9 H_2SO_4 =1.5 Na_2SO_4 =0.4	500	80°C	One rapid shot Total La=5g. Added over one min.	Very vigorous No digestion Very vigorous No digestion	Bipyramidal crystals lemon yellow in color and 2-40µ in length. Very few fines and no large clusters.
24 LL to NaOH $La(OH)_3$ to H_2SO_4	La =0.24 NaOH =3.62 H_2SO_4 =1.23 Na_2SO_4 =0.4	500	80°C	One rapid shot Total La=5g. Added over 4 min.	Very vigorous No digestion Very vigorous No digestion	Yellow bypyramidal crystals 1-75µ in length. Some fines and slight tendency to form aggregates.

3-25

4. Effect of HF and HNO_3 Concentrations during Conversion of the Double Sulfate to Crystalline Lanthanum Fluoride

The same weight of sodium lanthanum sulfate was added to each of the following solutions with good agitation.

(1) 1N - HNO_3 - No HF
(2) 1N - HNO_3 - 0.1M in HF
(3) 1N - HNO_3 - 0.2M in HF
(4) 1N - HNO_3 - 0.5M in HF
(5) 1N - HNO_3 - 1.0M in HF

After a thirty minute digestion, it was found that complete dissolution of the double sulfate was effected in (1), and hydrofluoric acid added thereto precipitated amorphous lanthanum fluoride; (2) consisted primarily of the amorphous type of lanthanum fluoride; in (3) ca. 75% of the precipitate was crystalline and 25% amorphous; (4) and (5) were essentially free of the amorphous variety. The experiments were repeated, again varying the hydrofluoric acid concentration from 0.1M to 1.0M with similar results.

To determine the effect of nitric acid concentrations, equal quantities of sodium lanthanum sulphate were added to each of the following solutions with good agitation.

(1) 1M HNO_3 - 0.1M HF
(2) no nitric-0.1M HF
(3) 1M HNO_3 - 2.7M HF
(4) no nitric-2.7M HF

(1) consisted chiefly of the amorphous form whereas essentially all of the precipitate in (2) was crystalline in nature. The precipitates in (3) and (4) were both crystalline, but (4) was slightly superior with respect to sedimentation velocity.

Two opposing mechanisms are evident. Nitric acid has an adverse effect in that it causes dissolution of the double sulphate, and in the absence of sufficient hydrofluoric acid, the lanthanum ions so liberated precipitate as amorphous lanthanum fluoride. At higher hydrofluoric acid concentrations, however, the reaction; double sulphate $\xrightarrow{HF}$ crystalline LaF_3 predominates, i.e., the rate of this reaction exceeds the rate of double sulphate dissolution in nitric acid. Optimum conditions for crystalline lanthanum fluoride formation are therefore a low nitric acid concentration and a high hydrofluoric acid concentration during conversion. It is accordingly essential that the 1M nitric acid process solution be at least 0.5M in hydrofluoric acid.

Following a lanthanum fluoride by-product precipitation, the effluent therefrom becomes less than 0.5M in hydrofluoric acid due to dilution by cake washes, and steam jetting. It appears desirable and even essential that this solution be readjusted to 0.5M in hydrofluoric acid.

Crystalline lanthanum fluoride once formed from a solution at least 0.5M in hydrofluoric acid does not revert to the amorphous modification when placed in a hydrofluoric acid-free system. Other than the possibility of dissolving crystalline lanthanum fluoride in strong acid and reprecipitating by adding fluoride ions, no method of converting crystalline lanthanum fluoride to the amorphous modification has been observed. All laboratory tests have failed.

3-2

5. Effect of Agitation Rate on the Conversion of the Alkali Lanthamm Sulfate to Crystalline Lanthamm Fluoride

A number of laboratory experiments have indicated that the rate of agitation of the process solution during addition of double sulfate slurry is not critical. No measureable difference in sedimentation velocity of resulting crystalline LaF_3 precipitates was detectable when they were prepared using feeble, moderate, or violent mechanical agitation. Some agitation is desirable, however, to avoid local exhaustion of hydrofluoric acid.

6. Effect of Double Sulphate Addition Rate on the Formation of Crystalline Lanthamm Fluoride

Laboratory results have indicated that the rate of double sulphate addition to the process solution is not critical, provided reasonable mechanical agitation is employed to suspend the solid. The sedimentation velocity of precipitates prepared by rapid and slow strikes was identical.

7. Metathesis of Crystalline Lanthamm Fluoride

The behavior of crystalline lanthanum fluoride during KOH metathesis is identical to the amorphous form. Laboratory, semi-works, and plant results indicate that no difficulties are likely to arise at this point in the process. Lanthanum hydroxide derived from the crystalline fluoride is more granular in nature and X-ray analyses of the material have revealed a definite crystalline structure, heretofore undetectable in lanthanum hydroxide derived from amorphous LaF_3 or by precipitation from basic solution.

8. Semi-Works Evaluation of Crystalline Lanthanum Fluoride

Data obtained from semi-works runs employing plutonium tracer cannot be interpreted directly in terms of plant performance at higher levels of product. However, the semi-works tests have shown that no major mechanical difficulties can be anticipated either in the preparation of double sulfates or in subsequent processing.

The following general conclusions and observations have been extracted from the semi-works experimental data:

a) The use of crystalline LaF_3 (one precipitation at 100mg La/liter, one centrifugation) reduced product losses by a factor of 2 to 3 over use of amorphous LaF_3 under identical conditions. In one plant trial, the loss was decreased by a factor of 3.

b) Separation of crystalline fluoride from process solutions by centrifugation is more complete than for the amorphous modification. In 18 single centrifugations, the recovery of crystalline fluoride averaged 96%, whereas under similar conditions, the recovery of amorphous LaF_3 averaged 85%.

c) Product losses are due primarily to small amounts of finely divided particles of lanthanum fluoride which escape removal by centrifugation. In runs in which a by-product precipitation was made, the product losses in the semi-works averaged 33% in contrast to an average loss of 14% when the by-product step was omitted. This increased loss is undoubtedly due to the lanthamm fluoride "fines" which were not removed during the by-product centrifugation, and which picked up product immediately upon reduction of the solution prior to the product precipitation. All centrifugations were at 1000G with a through-put rate equivalent to 110 lbs./minute in the plant.

d) Similar product losses are sustained using either elutriated or non-elutriated double sulphates.

e) Passage of the crystalline fluoride through steam jets apparently has only a minor effect on yield losses during a subsequent centrifugation. In one experiment, the crystalline fluoride slurry was passed through a steam jet 10 times with no appreciable effect on centrifugation losses. Also, transfer of the slurry from precipitator to the centrifuge by means of a rubber tube pump did not decrease product losses.

f) Experiments in which plutonium tracer was employed were not comparable to results obtainable at higher levels of product. Upon reducing the by-product effluent with oxalic acid in the semi-works, 98% of the product was carried by fines, in both crystalline and amorphous LaF_3 runs, which escaped the by-product centrifugation step. In one plant run, employing crystalline LaF_3 in both the by-product and product steps, at 65GT level only 20% of the product was carried by these "fines". In the semi-works, the ratio of lanthanum loss to product loss averaged 1 to 7, whereas in one plant run under comparable conditions, this ratio was 1 to 1.

g) Due to differences in product centrifugation, in equipment, angular velocities employed during centrifugation, and through-put rate, semi-works product losses were much greater than plant effluent losses. Using the same double sulfate, the plant loss, after one shot, was 4.6% compared to a 32.4% loss obtained by the Semi-Works.

9. Use of Crystalline Lanthanum Fluoride in the Cross-over By-Product Precipitation Step

Laboratory experiments using various fission element tracers and simulated process solutions have shown that a single precipitation (225mg La/liter) and a single centrifugation of crystalline fluoride was essentially as effective in removing the tracer element as two precipitations totaling 225mg La/liter (two centrifugations) of the amorphous lanthanum fluoride. Pertinent data are tabulated below.

Gamma Decontamination Factors*

Tracer Element	One Precipitation of Crystalline LaF_3(225mg La/l)	Two Precipitations of Amorphous LaF_3(total 225mg La/l) - two Centrifugations
La-Ba	32	46
Zr-Cb	2.2	2.6

* Experimental work by J.A.Swartout - H.E.W. notebook 166-Y

In one plant run, a single precipitation of crystalline lanthanum fluoride resulted in decontamination comparable to that obtained in runs in which either one or two precipitations of amorphous lanthanum fluoride of the same total amount of La were made.

10. Other Crystalline Rare Earth Fluorides

The process described herein for the preparation of crystalline lanthanum fluoride can be expanded to the synthesis of crystalline fluorides of other rare earth elements, particularly those of the cerium group in the rare earth separation scheme. Their crystalline fluorides can be prepared through the use of their corresponding alkali double sulfates. Individual crystals of cerous fluoride, for example, have been prepared with crystal sizes as large as 0.25-0.5mm. in diameter.

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