HW--24115

A Facsimile Report

DECLASSIFIED

HW-24115

UNITED STATES ATOMIC ENERGY COMMISSION

THE MECHANISM OF CARRYING Pu(III)
ON LANTHANUM FLUORIDE

A Thesis

By
Delbert Lloyd Ralphs

Declassified 2/1/56

DECLASSIFIED BY CG-NMP-2
SEPT. 2000 AND APPROVED
FOR PUBLIC RELEASE 7/1/03
NAME/DATE
NAME/DATE

April 15, 1952

Hanford Works ORG.   PNNL NSAT
Richland, Washington

Technical Information Service Extension, Oak Ridge, Tenn.

Photostat Price $ 9.30
Microfilm Price $

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

903   001

DECLASSIFIED

AN ABSTRACT OF THE THESIS OF

Delbert Lloyd Ralphs for the Master's Degree in Inorganic Chemistry

Date Thesis Presented -- April 1952

Title -- The Mechanism of Carrying Pu(III) on Lanthanum Fluoride

ABSTRACT APPROVED _

When trivalent plutonium is added to a hydrofluoric acid solution
containing a lanthanum fluoride slurry, the plutonium is quite completely
removed by the preformed lanthanum fluoride. If the lanthanum fluoride
is formed in the presence of the trivalent plutonium ions by coprecipi-
tating with hydrofluoric acid, the plutonium is similarly removed from
solution. The mechanism by which the plutonium is thus removed from
solution has never been elucidated but has been assumed to be either iso-
morphous replacement or adsorption. This thesis represents a study of
this problem.

The age of preformed lanthanum fluoride did not noticeably affect
the carrying efficiency. Also, the mode of addition of reagents did not
affect the carrying. With tracer concentrations of plutonium, equilib-
rium carrying on 0.35 mg. of LaF_3 in 0.5 ml. of solution was complete in
5 minutes; however, as the amount of lanthanum fluoride was considerably
reduced, a longer period of time was required to reach equilibrium.

With variable amounts of preformed lanthanum fluoride and 5 minute
contacting, trivalent plutonium carried as though the mechanism was ad-
sorption. The resulting curve could be interpreted according to the
Freundlich adsorption by the equation

$$x/n \frac{counts/minute}{mg.\ LaF_3} = 2665 \cdot C^{0.7464}$$

where C is the concentration in counts per minute per 0.5 ml. The same
curve could be described by the Langmuir type equation

$$x/n = \frac{874 \cdot C}{1 + 1.93 \cdot 10^{-5} \cdot C}$$

At the lower limit of adsorbate the adsorption curve had not leveled
off appreciably, indicating that saturation of the surface of the lantha-
num fluoride had not been reached. However, with the smaller amounts of
lanthanum fluoride equilibrium was reached too slowly, leading to the be-
lief that if adsorption took place on the surface of lanthanum fluoride,
there might be a secondary mechanism of incorporation into the crystals.

In approximating the amount of surface that would be covered if carrying was by surface adsorption, for an average particle size of 0.01 micron as determined by electron microscope, approximately 50 per cent was the maximum coverage, corresponding to 0.011 mg. of preformed lanthanum fluoride. Precipitated lanthanum fluoride, however, appears to have a larger particle size than 0.01 micron, or else it precipitates because the particles agglomerate. If the particles were larger than 0.01 micron, surface adsorption by a single layer would be unlikely.

Adsorption should be decreased by the presence of an excess of other high valence positive ions and increased by the presence of an excess of negative ions. As freshly precipitated lanthanum fluoride dissolves in dilute nitric acid and no trivalent positive ions can exist in appreciable amounts in a fluoride solution, it was necessary to use lanthanum fluoride which had been metathesized from $NaLa(SO_4)_2 \cdot H_2O$ with a sodium fluoride solution and oven-dried to make this test of adsorption. In a solution 0.02 M in nitric acid plutonium was sorbed more slowly if the solution was 0.02 M in La(III) than if it were only 0.001 M in La(III), or if no other tri positive ions were present, or if the solution was also 0.25 M in hydrofluoric acid. However, they all tended to complete carrying.

To investigate the isomorphous replacement mechanism to form mixed crystals, a series of hydrofluoric acid precipitations were made with different amounts of lanthanum, which was tagged with radioactive La^{140}, and plutonium. The proportions of both elements in the supernate* and precipitate were determined by counting. The value of D in the following equation was found to be reasonably constant and approximately 0.5.

$$\left(\frac{La^{+3}}{Pu^{+3}}\right) \text{ supernate } = D \left(\frac{LaF_3}{PuF_3}\right) \text{ precipitate}$$

Constancy in the value of D indicates formation of isomorphous mixed crystals.

From the experiments carried out in this work the conclusion is that coprecipitated lanthanum fluoride carries Pu(III) by the formation of isomorphous mixed crystals apparently in all proportions, the incorporation being very rapid just as the precipitate is formed. However, the data does not exclude the possibility of some change in the relative concentrations in the supernate and precipitate as recrystallization and perfection take place. With preformed lanthanum fluoride a rapid adsorption appears to take place followed by a slower incorporation of the plutonium into the crystals. In most cases of carrying tracer amounts of Pu(III) on preformed lanthanum fluoride carrying is completed quickly, probably due to surface adsorption, making any secondary mechanism unnoticed.

---

*Used throughout as a technical term to designate "supernatant liquid".

APPROVED:

_____
Professor of Chemistry

                In Charge of Major

_____
Head of Department of Chemistry

_____
Chairman of School Graduate Committee

_____
Dean of Graduate School

ACKNOWLEDGMENT

The author wishes to express his thanks to General Electric Company's School of Nuclear Engineering and the Analytical Unit for making this work possible, by coordinating with the Graduate School of the Oregon State College, supplying the means for doing the laboratory work and library research, and for the direction and guidance in the research and preparation of this thesis.

In particular, the author is grateful for the direction, suggestions, and criticism of the manuscript given by Doctors H. R. Schmidt, A. E. Bushoy, and G. B. Barton, of the Analytical Research groups.

The writer also wishes to acknowledge the help received in the form of several prepared solutions from the Standards Laboratory, also for the time saved him by having the counting room personnel do all of the A.S.V.P. and the majority of the A.B.P. and B.G.O. counting work for the high level plutonium and lanthanum mixed crystal experiments. This help was very important because it allowed the author to carry out the maximum number of experiments during the useful period of a short-lived radioactive isotope.

Thanks must also be given to the Pile Physics group for their willingness to do the special irradiation of the lanthanum in the pile.

The constants in the two adsorption equations were determined by W. C. Healy and R. F. Cell of the Statistics group.

TABLE OF CONTENTS

THE MECHANISM OF CARRYING Pu(III)

ON LANTHANUM FLUORIDE

INTRODUCTION

Analytical procedures for the determination of plutonium samples from the extraction and concentration plants utilize the carrying of the hydroxylamine-reduced trivalent plutonium by coprecipitation on lanthanum fluoride (17 pp. 5-8 and pp. 37-39). Most other plutonium procedures also take advantage of the efficient carrying on lanthanum fluoride.

From the similarity of Pu(III) and La(III) ions, isomorphous mixed crystals have been postulated as the likely mechanism for the carrying of Pu(III) on lanthanum fluoride (26 p. 10). However, with a fine gelatinous precipitate adsorption is a very common characteristic. Such a precipitate is capable of carrying non-isomorphous ions, and of course, similar ions might be attracted likewise. Lanthanum fluoride carries Pu(IV) very well which is the basis of the concentration steps of the plant process (12 p. 150 and pp. 703-719; and 6 pp. 9-10). The compound $2LaF_3 \cdot PuF_4$ was apparently produced when a precipitation was made with insufficient lanthanum to carry Pu(IV) completely (9 p. 31). Thus, there is a possibility Pu(IV) carries by compound formation. However, adsorption could be the mechanism because of the high valence charge and the speed with which the lanthanum fluoride takes up Pu(IV). A report has been made that Pu(III) is expected to be oxidized rather easily

by O_2 or HNO_3 in the presence of hydrofluoric acid due to the Pu(IV)
fluoride complex that is formed (19 p. 1). However, in Connor's report
they were able to keep PuF_3 reduced for over three days with the solu-
tion saturated with sulfur dioxide. Conversely, Zachariasen believes
$PuF_4 \cdot LaF_3$ is reduced to trivalent plutonium during the hydrofluoric acid
treatment (27 pp. 5-6).

Since the proposed experiments were carried out in the presence of
some hydroxylamine, the mechanism of oxidation and compound formation was
not considered possible. This conclusion was also confirmed by
K. M. Harmon who precipitated macro amounts of PuF_3, without indications
of oxidation, in 1 $\underline{M}$ nitric acid made 2-3 molar in hydrofluoric acid, if
the temperature was below 80°C. Also, he precipitated PuF_4 from hydro-
fluoric acid solution when tetravalent plutonium was the starting material
(14 pp. 6-8).

A better knowledge of the plutonium carrying process on lanthanum
fluoride was considered important in connection with new procedures to
be developed.

HISTORICAL

Plutonium Carrying

The first isolation (23 p. 367 and 22 paper 1.8 pp. 54-64) of syn-
thetic plutonium and the search for natural plutonium and neptunium in
pitchblend (22 paper 1.3 pp. 9-10) used rare earth fluorides as carriers.
Chiefly lanthanum has been used as the carrier for trivalent actinides.

Previous to plant operations reduced plutonium was reported to carry quantitatively on lanthanum fluoride in both nitric and hydrochloric acids of concentrations from 0.5 to 6 $\underline{M}$ and hydrofluoric acid, which was added last in "direct strike", of 1 to 6 $\underline{M}$. A system 1 $\underline{M}$ in nitric and 2 $\underline{M}$ in hydrofluoric acids with 5 minutes digestion and 5 minutes centrifugation with a lanthanum concentration of 0.05 to 0.20 mg. per ml. will give losses in the supernate* of less than one per cent. In the above report no mention was made of the reducing agent. In a subsequent report (17 pp. 19-30) a study of reducing agents was described. Hydroxylamine was considered the best. Previously, sulfur dioxide had been used. The previous experiments were very likely performed with a reduced stock solution of plutonium carrier which may have consisted of plutonium in both reduced valences. Mixed valence solutions easily occur unless conditions for a single state are properly kept, as can be seen from Figure 1 (5 p. 22).

FIGURE 1

FORMAL** OXIDATION-REDUCTION POTENTIALS
OF PLUTONIUM IN 1 $\underline{M}$ HNO$_3$ AT 25-30°C

Pu(III) $\xrightarrow{\text{-0.92 volts}}$ Pu(IV) $\xrightarrow{\text{-1.10 volts}}$ Pu(VI)

-1.04 volts
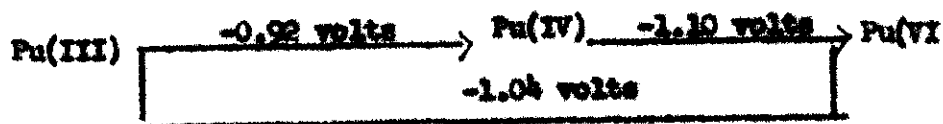
**Formal potential was defined as the measured cell potential
minus the calomel electrode potential when the concentration
of the reduced and oxidized form of plutonium are equal.

*Used throughout as a technical term to designate "supernatant liquid".

Theory of Carrying

Mechanisms of tracer carrying may in general be divided into two processes (3 pp. 49-59 or 3a pp. 104-41): (a) incorporation of the tracer into the crystal lattice of the precipitate, and (b) adsorption of the tracer on the surfaces of the precipitate during or after its formation.

Isomorphous replacement is the more important process in the first category. Salts which will crystallize isomorphously in macro amounts because of similar valence, ionic radius, and crystal type will carry by isomorphous replacement if one component is present in a trace amount.

Isomorphous replacement follows one of two laws depending upon whether the precipitate and solution are in equilibrium, or the solution and only the surface layer of the crystal are in equilibrium.

The homogeneous distribution law of Henderson and Kroesk (3 p. 49 or 3a p. 106) is applicable when all of the precipitate is in equilibrium with the supernate with respect to the micro component. In essence, the homogeneous distribution law is:

$$\left(\frac{tracer}{carrier}\right) solid = D \left(\frac{tracer}{carrier}\right) solution$$

For values of D greater than unity, the precipitate is enriched in tracer. Homogeneous distribution is favored by stirring the precipitate and supernate for a long enough period after formation. Small crystals by rapid formation favor a homogeneous distribution.

The heterogeneous type of distribution law applies when the solution is in equilibrium with each layer of the crystal as it is formed, but in

which the recrystallization and solid diffusion effects are negligible.
The ions in the interior of the precipitate retain their relative posi-
tions after the crystal growth has covered them. This distribution re-
sults in a concentration of the trace component either in the center or
surface of the crystals, heterogeneously according to the law introduced
by Doerner and Hoskins (7 pp. 663-5 or 3a pp. 106-7 and 112-7). This
well known logrithmic distribution law is:

$$\log \frac{\text{total tracer}}{\text{tracer in solution}} = \lambda \log \frac{\text{total carrier}}{\text{carrier in solution}}$$

For values of λ greater than unity, the precipitate is enriched in the
tracer, which is concentrated in the center more than the outer layers
of the crystal. For values of λ less than unity, the solution is enriched
in the tracer, and the outer layers of the crystal are richer than the
interior. The heterogeneous distribution is unstable and in time tends
to change to a homogeneous state by a recrystallization process.

Sometimes a trace amount of an ion can enter a carrier crystal
seemingly isomorphously even though the crystal characteristics are dis-
similar, and they do not form mixed crystals when both components are
present in appreciable quantities. Radioautographs of both isomorphous
and anomalous mixed crystals show a continuous distribution of the radio
component (11 pp. 82 and 135). With anomalous mixed crystals the host
crystal has only a limited capacity for inclusion of the micro component.
The belief is that the micro component can modify its crystal habit to
conform with that of the host crystal. This is a case of very slight

solid phase solubility.

A characteristic of mixed crystal formation, both the isomorphous and the anomalous, is that they are little affected by external conditions, such as the type of lattice ion in excess, or the presence or absence of highly charged foreign ions.

Adsorption has two classes, namely surface and internal. Surface adsorption has been studied more extensively and is better understood.

There are two mathematical relationships applying to surface adsorption: (a) The classical, empirically derived equation of Freundlich (10 pp. 1196-7)

$$\frac{x}{m} = k \ C^n$$

where $\frac{x}{m}$ is the amount of adsorbate found per unit mass m of adsorbent, k and n are constants.

(b) The Langmuir equation (10 pp. 1196-1200), derived from a consideration of a partially continuous monomolecular film over the surface of the adsorbent, has the form $\frac{x}{m} = \frac{KC}{1+KC}$, where C is the concentration of the micro component in the supernate, and x is the amount of tracer adsorbed on m mass units of adsorbent. In these equations it is necessary to assume the surface to be proportional to the mass.

In internal adsorption it is believed that as the host crystal is formed, the tracer is tightly adsorbed to certain edges and lattice defects. As the crystal growth continues, the tracer is trapped. Internal adsorption, like surface adsorption, is usually characterized by a

reduction of the amount adsorbed in the presence of an excess of the lattice ion whose charge is of the same sign as the tracer or by the presence of other highly charged ions of the same sign. The distribution of the tracer as shown by radioautographs is not orderly like that in mixed crystals (11 pp. 126-130).

SOLUTIONS AND EQUIPMENT

Frequently Used Solutions

Nitric Acid 1.0 M. Baker and Adamson Reagent C.P. nitric acid was selected which was free from any brownish discoloration, since the presence of nitrite in dilute nitric acid will oxidize Pu(III) to Pu(IV) in the absence of hydroxylamine. This nitric acid was properly diluted with distilled water to make one liter of 4 $\underline{M}$ nitric acid, which was standardized as 3.92 $\underline{M}$. Several dilutions were made by taking 100 ml. of the stock solution and adding 292 ml. of distilled water to give a final concentration of exactly 1.0 $\underline{M}$.

The **concentrated hydrofluoric acid** was Baker and Adamson Reagent 48%. It was poured from its Polythene container to a hard rubber bottle and was dispensed with a dropper made from Teflon.

1 M nitric, 1 M hydrofluoric and wash solution was made by mixing 100 ml. of 3.92 $\underline{M}$ nitric acid, 14.5 ml. of concentrated hydrofluoric acid and diluting to 400 ml.

Lanthanum carrier 5 mg./ml. was prepared by the solutions laboratory (13 Code SL-1c) by weighing 31.18 grams of Eimer and Amend $La(NO_3)_3 \cdot 6H_2O$, dissolving in 200 ml. of 10 M nitric acid, and diluting to 2 liters.

The carrier concentration was checked by ignition of the precipitated lanthanum oxalate and weighing as La_2O_3.

Lanthanum carrier 0.5 mg./ml. was prepared by diluting one ml. of 5 mg./ml. lanthanum carrier to ten ml. with 1.0 $\underline{M}$ nitric acid.

Lanthanum tracer-carrier 0.5 mg./ml. tagged with La^{140} activity. There was available a rather old Ba^{140}-La^{140} activity that had been obtained from Oak Ridge for use in other experiments. The La^{140} activity was "milked" from the Ba^{140} and the considerable barium carrier that was present by adding an ice-cold solution of 5 ml. of Baker and Adamson Reagent C.P. hydrochloric acid and 25 ml. of Merck Reagent ether to several milliliters of the active solution, which caused the precipitation of barium as $BaCl_2 \cdot H_2O$ (16 pp. 19-21). After strong centrifugation for about 15 minutes in an International size I type SB Centrifuge in a 50 ml. pyrex tube, the supernate was removed with a transfer pipet and evaporated to dryness. The lanthanum activity along with the small amount of barium remaining was dissolved in about 6 ml. of water. A few crystals of sodium nitrate were dissolved in the solution to prevent emulsion formation while extracting. The pH was adjusted to 4.9 on a Beckman pH meter equipped with small glass and calomel electrodes. This solution was extracted with three 1 ml. portions of 0.5 $\underline{M}$ TTA (11 grams of thenoyltrifluoroacetone, which was obtained from the University of California, dissolved in 100 ml. of Merck Reagent benzene). The lanthanum was back extracted from the benzene solution of the TTA lanthanum complex into two 2 ml. portions of 1.0 $\underline{M}$ nitric acid (18 p. 11). One ml. of 5 mg./ml. lanthanum carrier was added to this active solution,

and then, the volume was made up to 10 ml. with 1.0 M nitric acid.

<u>High Activity, pile irradiated lanthanum tracer-carrier 0.51 mg./ml.</u>
A solution of 0.86 grams of La(NO$_3$)$_3$·6H$_2$O in 200 ml. of water with 1 ml.
of concentrated nitric was heated nearly to boiling, and dilute oxalic
acid solution was slowly added, while stirring, until a slight excess
was present. The lanthanum oxalate was aged over an hour and filtered
through a porcelain crucible, dried, and ignited to 600°C. A machined
aluminum capsule containing 0.0601 grams of this La$_2$O$_3$ was irradiated in
the X test hole of the 100-J pile for 45 minutes. The irradiated lantha-
num was dissolved with gentle warming in 1.0 M nitric acid and was diluted
to 100 ml. with more of the acid. This solution, when tested the next
day on the high pressure ionization recording instrument, had a gamma
activity equivalent to 24.4 microcuries of radium per ml. of solution.
Periodic checks with the same instrument over the period of a week and a
half showed that this active solution checked with the expected decay
curve of La^{140} (21 pp. 80-6).

<u>Plutonium solution I</u> was prepared by taking 50 microliters of an
approximately 15 gram/liter purified plutonium nitrate solution which
had been at the plant for several years and was known as the "Bureau of
Standards" plutonium. This was diluted to several milliliters with 1.0 M
nitric acid, and half a milliliter of 5 M hydroxylamine hydrochloride was
added, and several minutes allowed for reduction to the plus three valence
state. The reduction could be observed immediately by the appearance of
a blue color. Next, the remainder of 50 ml. of 1.0 M nitric acid was
added. The solution was thoroughly mixed before it was used. This

solution had 2276 c/m/microliter.

Plutonium solution II was made by adding approximately 0.1 ml. of a concentrated plant plutonium solution in nitric acid to several milliliters of 1.0 $\underline{M}$ nitric acid and reducing with 1.5 ml. of 5 $\underline{M}$ hydroxylamine hydrochloride and diluting to approximately 50 ml. with 1.0 $\underline{M}$ nitric acid. By radioassay this solution was $2.6 \cdot 10^{-3}$ $\underline{M}$ in plutonium.

20-32% Zapon was made by the solutions laboratory by adding 100-125 ml. of Zapon Aquanite "A" to 400 ml. of Zapon number 5 thinner; both are obtainable from the Zapon Division of Atlas Powder Company. A few crystals of methyl violet or some carbon black are mixed until it is suitably darkened (13 Code F1-2a). Zapon darkened each way was used.

Collodion 0.4 mg./ml. solution. A stock solution was analyzed for solids by evaporating 500 microliters on a weighed watch glass and weighing. The final solution was prepared by diluting a portion of stock solution with a mixture of equal parts of ether and alcohol to give a 0.4 mg./ml. solution (13 Code SC-17a). The final collodion was kept stoppered to prevent evaporation. This solution was supplied by the solutions laboratory.

Regularly Used Equipment and Instruments

An Eberbach and Sons' "Power-Stir" with variable speed electric motor equipped with a 20 mil platinum stirring wire was used for stirring all samples except those containing radioactive lanthanum.

For stirring the active samples and in the extraction of lanthanum activity, a rapid turning, air-driven wand stirrer with a two foot

handle was used. The stirring was done with a platinum wire.

An International clinical centrifuge equipped with a head and cone holders for 2 to 15 ml. centrifuge cones. Besides the commercially available 2 ml. cones and 50 ml. centrifuge tubes made of Pyrex and the 3 ml. Lusteroid cones, some approximately 2 ml. cones were made to order by the American Platinum Works. These were designed to fit inside the 3 ml. Lusteroid cones, without touching the bottom, for support during centrifugation.

Platinum discs of 22 mm. diameter and 2, 5, and 10 mil thickness were used for mounting the supernates and precipitates.

Disc carriers. Two kinds were used -- cardboard carriers with four depressions to hold the discs and a flap cover. For discs containing beta and gamma radiation, shielded disc carriers were used. These consisted of round stainless steel hollow tops and circularly grooved base to allow the two parts to fit together. The top has a circular opening tangent to its circumference. Thus, the top can be turned so this opening is over each disc individually shielding the hands from radiation from the other discs while the one is being removed for placing in the counting instrument. The base of the disc carrier fits in the shielded disc dryer. There are circular cardboard discs to fit the base of the carriers with pressed depressions for holding four platinum discs.

The shielded disc dryer consisted of a 6 inch diameter stainless steel cylinder, 10.5 inches high, on a square base. Just above the base there is a shelf that swings out, which supports the base of the shielded disc carrier while drying discs. In the top was mounted an infrared

heat lamp in a socket.

For handling cones which were active with gamma rays, __mechanical__ __hands__ with 1.5 foot handles were used. One had a straight ridged handle while the other was flexible.

__Alpha Simpson Proportional (A.S.P.) Counters__ have flowing methane filled chambers at atmospheric pressures. The disc to be counted for alpha particles has to be inserted into the stream of methane in the chamber by means of a sliding floor and a screw up pedestal. The chamber operates in the proportional region from 2200 to 2550 volts; for this region the voltage must be very constant. The A.S.P. has usually been used for 50,000 or fewer counts per minute. At 100,000 counts per minute, according to Simpson (24 pp. 5-6), the coincidence loss is 0.80%; however, at the time others were redetermining the coincidence correction. They suspected the value might be around 3 or 4%; however, their completed report gives the per cent coincidence correction as the product of counting rate in minutes and $1.175 \cdot 10^{-5}$. At 100,000 counts per minute coincidence is 1.2% and half that at 50,000 counts (8 pp. 1 and 6).

The geometry for a given voltage is determined by counting a standard disc of about 100,000 disintegrations per minute. The geometry is held between 50.35 and 50.65%. Because the activity of the standards was approximately 50,000 counts per minute, discs were not prepared at appreciably higher activity for counting on the A.S.P.

The A.S.P. will tolerate considerable beta without affecting the alpha count if the instrument is operated at the lower portion of the voltage range.

The Alpha Simpson Vacuum Proportional Counter (A.S.V.P.) is similar to the A.S.P., except the discs are at the bottom of an evacuated tube which fits under the chamber in place of the sliding floor and pedestal (24 p. 7). The value of the low geometry is determined by the per cent of the spherical area around the disc, which is in the form of a window to allow a few of the alpha particles to enter the methane chamber. The window is of mica mounted in brass. It separates the chamber proper containing flowing methane at atmospheric pressure from the vacuum column containing the disc of activity.

The Beta-Gamma Offner Counter (B.G.O.) measures the activity which has been placed on a small watch glass or disc of approximately 25 millimeters. The disc is mounted on either a cardboard or aluminum slide which fits into the grooves of any of the five shelves below the mica window Geiger-Müller tube with a resulting geometry of about 1 to 2% for beta. Gamma activity is counted by shielding the associated beta activity from the tube by placing an aluminum-lead shield in the uppermost shelf position. Gamma activity counts approximately 1% of beta activity and does not have any approach to absolute counting.

The tube and sample shelves are enclosed in a shielded lead "pig" to eliminate outside gamma and cosmic radiations and to protect the operator. The counts are recorded on a scaler circuit electronically.

The instrument is checked against a known standard and must operate at a constant voltage in the Geiger-Müller region. The dead time of the electronic circuit is appreciable; hence, there is an increasing positive coincidence correction as activities become greater.

EXPERIMENTAL PROCEDURE

The Carrying of Plutonium(III) on Preformed Lanthanum Fluoride by "Direct" Strike"

Experiments were conducted forming lanthanum fluoride from 0.25 mg. of La(III), as this is the amount used in the standard analytical method (17 p. 6-8) and because it is a compromise amount -- enough to carry efficiently, yet not enough to cause appreciable self-adsorption of alpha counts when mounted on 22 mm. platinum discs (4 Figure 8a). The latter consideration is of particular importance in determining the amount of carrying.

The volumes of liquid through these experiments were 500 microliters, as this is the amount that can be mounted on a 22 mm. platinum disc for counting.

The general procedure was as follows:

1. Place 250 microliters of 1.0 $\underline{N}$ HNO$_3$ in a 2 ml. centrifuge cone*.

2. Add 50 microliters of 5 mg./ml. standard lanthanum nitrate solution. This gave 0.25 mg. La(III) or 0.35 mg. lanthanum fluoride.

3. Next, these solutions were mixed and two drops of concentrated hydrofluoric acid were added. (ca. 50 microliters making the final solution 2.7 $\underline{N}$ in hydrofluoric acid.)

4. The slurry was stirred again and allowed to stand for varying times.

*For short periods of aging, Pyrex tubes were used throughout. For longer periods the lanthanum fluoride was formed in Lusteroid cones and transferred to Pyrex two minutes before the Pu(III) was added. This procedure was deemed necessary because hydrofluoric acid attacks Pyrex and plutonium adsorbs on Lusteroid.

5. The precipitate of lanthanum fluoride was stirred up briefly two minutes before the Pu(III) was added. If the slurry was formed in Lusteroid, it was transferred to a Pyrex cone by means of a micro transfer pipet.

6. After the aging period, 49.94 microliters of Pu(III) solution (113,800 counts per minute at 50.5% geometry) was added below the surface of the liquid and the pipet washed once with the solution in the cone. Next, the contents of the cone were briefly stirred and the pipet washed twice more with 50 microliters of 1.0 $\underline{N}$ HNO_3. With these additions the total volume is brought to 500 microliters. This required about one minute of the digestion time. The slurry was stirred at a moderate rate for the remainder of 2 1/2 minutes and was allowed to stand for a second 2 1/2 minutes. Next, the cones were centrifuged for 10 minutes at full speed.

7. The supernate was drawn off with a micro transfer pipet and mounted on a 22 mm. platinum disc that had been ringed with Zapon. The discs were dried under an infrared lamp. The precipitate was slurried briefly in a half ml. wash solution 1 $\underline{M}$ in nitric and hydrofluoric acids. This was centrifuged, and the supernate was mounted on a separate platinum disc.

(It has been observed that the precipitate of step 3 is flocculent and settles loosely on the bottom of the cone in less than two minutes as a flocculent mass, which, after it has been restirred, settles selectively according to particle size, there being a granular precipitate on the bottom while the solution is still milky. The lanthanum fluoride seems to lose its flocculent appearance with age and stirring. Lanthanum fluoride formed in a solution lacking nitric acid remains flocculent after being stirred.)

8. The lanthanum fluoride was slurried with three drops of 1.0 M HNO₃ and mounted on two platinum discs*. The cone was washed three or four times with two or three drops of 1.0 M HNO₃ by rapidly stirring with a platinum wire attached to an electric motor.

Because, after drying, there appeared to be a ring of material next to the Zapon due probably to the partial solution of lanthanum fluoride in the acid and redeposition with evaporation of the liquid, a drop of concentrated hydrofluoric acid was added to each disc and the contents stirred with a platinum wire. This was to produce an even coating of the activity over the disc for counting.

9. After evaporation the discs were waved through the top of a Bunsen flame until the Zapon was gently burned off and the disc heated to redness. After the discs were cool, one drop of 0.4 mg./ml. of collodion solution was added to each disc. The discs were then tilted until the collodion spread over the whole surface.

"Zero Time" Experiments

As a comparison with the preformed lanthanum fluoride carrying experiments, which of necessity had to be aged at least two minutes, several "zero time" precipitates were formed in which the plutonium was

---

*Two discs were used instead of one because the "Alpha Simpson Proportional" counter geometry is determined with an alpha source of about 50,000 c/m. The pair of discs had a count in excess of 110,000. To count one disc at this level would introduce a coincidence error that could not be corrected for at that time. (See discussion of Alpha Simpson Proportional Counters pp. 10-11.)

added before the hydrofluoric acid. Again, the contents were stirred for 2 1/2 minutes and allowed to stand for 2 1/2 minutes, then centrifuged for ten minutes. These data are listed in Tables I, II, and III, along with the results from the related experiments.

"Reverse Strike" Experiments

In these experiments the $La(NO_3)_3$ was added after the hydrofluoric acid. In this mode of addition the lanthanum fluoride was visible immediately, while when hydrofluoric acid was added last, the precipitate did not appear immediately. It has been reported (2 p. 5 and pp. 12-13) that lanthanum fluoride formed by reverse strike is more transparent and flocculent, settling in a larger volume of gelatinous precipitate than lanthanum fluoride formed by direct strike. Lanthanum fluoride formed by reverse strike was also reported to centrifuge more readily in the plant than the direct strike, but in the laboratory the reverse was found. It is recognized that the plutonium count in a supernate may be due to ions carried by very fine lanthanum fluoride, as well as in true solution, as either reduced or a trace of oxidized plutonium.

The data for the two modes of addition follow:

TABLE I

"DIRECT STRIKE" - HF ADDED LAST

Age of LaF$_3$	Time Aged in Pyrex	Per Cent of Count in	
		Supernate	1 M HNO$_3$-1 M HF Wash
* 0 min.	0	0.021%	0.057%
* 0	0	.070	.090
2	1'40"	.174	.094
2	2	.171	.126
5	2	.135	.121
5	5	.402	.257
5	5	.179	.101
10	2	.148	.116
10	10	.178	.185
16	2	.158	.115
20	2	.110	.062
30	2	.181	.126
65	2	.150	.122

*coprecipitated

TABLE II

"REVERSE STRIKE" - La(III) ADDED LAST

Age of LaF$_3$	Time Aged in Pyrex	Per Cent of Count in	
		Supernate	1 M HNO$_3$-1 M HF Wash
* 0 min.	0	0.455%	0.116%
0	0	.396	.134
2	2	.134	.139
5	5	.174	.130
11	2	.180	.122
26	2	.161	.083

*Coprecipitated

These values are graphed in Figures 2a and b. Similar experiments with Pu(IV) gave very nearly the same values, except on the reverse strike which gave low values like the two direct strikes for the "zero Time" experiments.

"Direct Strike" With Increased Concentration of Hydrofluoric Acid

Several experiments are summarized in Table III for precipitating solutions with 100 microliters of concentrated hydrofluoric acid (ca. 5.4 M HF). In these experiments 200 microliters of 1.0 M HNO$_3$ and 50 microliters of La(NO$_3$)$_3$ solution were added to a cone and stirred. Next, 100 microliters of concentrated hydrofluoric acid was added, and the contents of the tube were stirred and aged. Then, 49.94 microliters of Pu(III) solution and two pipet washes were added. This was stirred, and the pipet washes added during the first 2 1/2 minutes and were allowed to sit for the next 2 1/2 minutes and then centrifuged for 10 minutes, as in the previous experiments. The data of Table III are graphed on Figure 2c.

TABLE III

"DIRECT STRIKE" - INCREASED HF, ADDED LAST

| Age of LaF$_3$ | Time Aged in Pyrex | Per Cent of Count in | |
		Supernate	1 M HNO$_3$-1 M HF Wash
0 min.	0 min.	0.047%	0.067%
2	2	.218	.189
5	2	.142	.105
6	3	.252	.149
19	2	.171	.105

Variable Stirring Time in Contacting Pu(III) with Lanthanum Fluoride Formed in 2.7 M HF Solution and in 1.0 M HNO$_3$-2.7 M HF Solution

Lanthanum fluoride was formed in 2.7 M HF, but with the absence of nitric acid, by adding 250 microliters of H$_2$O to a 2 ml. Pyrex centrifuge

cone; adding 2 drops (50 microliters concentrated HF); stirring, adding 50 microliters of 5 mg./ml. La(III) solution, and stirring. The lanthanum fluoride was centrifuged about 2 minutes, and the supernate was removed. The hydrofluoric acid was added before the La(III) because it had been observed that a precipitate of lanthanum fluoride was visible immediately by this mode of addition, while it was slow to appear if the hydrofluoric was added last. At this time it was expected that aging was a large factor in the carrying efficiency, and it was desirable to keep the precipitate in contact with ions for the shortest time possible to keep the precipitate "new". Before the precipitate was contacted with Pu(III), 300 microliters of 1 part concentrated hydrofluoric in 5 parts of 1.0 $\underline{M}$ HNO_3 were added above the lanthanum fluoride. Next, 49.94 microliters of Pu(III) solution and three pipet washes of 1.0 $\underline{M}$ HNO_3 were added, making a 300 microliters solution 1 $\underline{M}$ HNO_3-2.7 $\underline{M}$ HF, containing 113,800 alpha counts per minute of Pu, this being the same composition of a supernate as that used in the variable aged precipitates. A series of experiments was also run according to the general procedure on pages 20-22, except the aging time was held to three or four minutes, and the time of stirring varied from 15 seconds to 9 minutes. The data from these two series are found in Table IV.
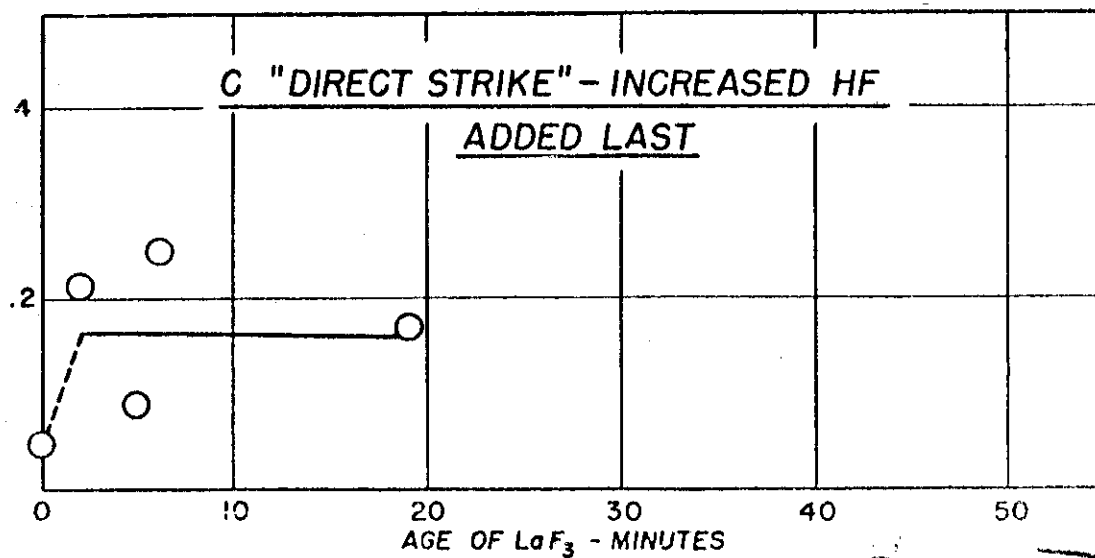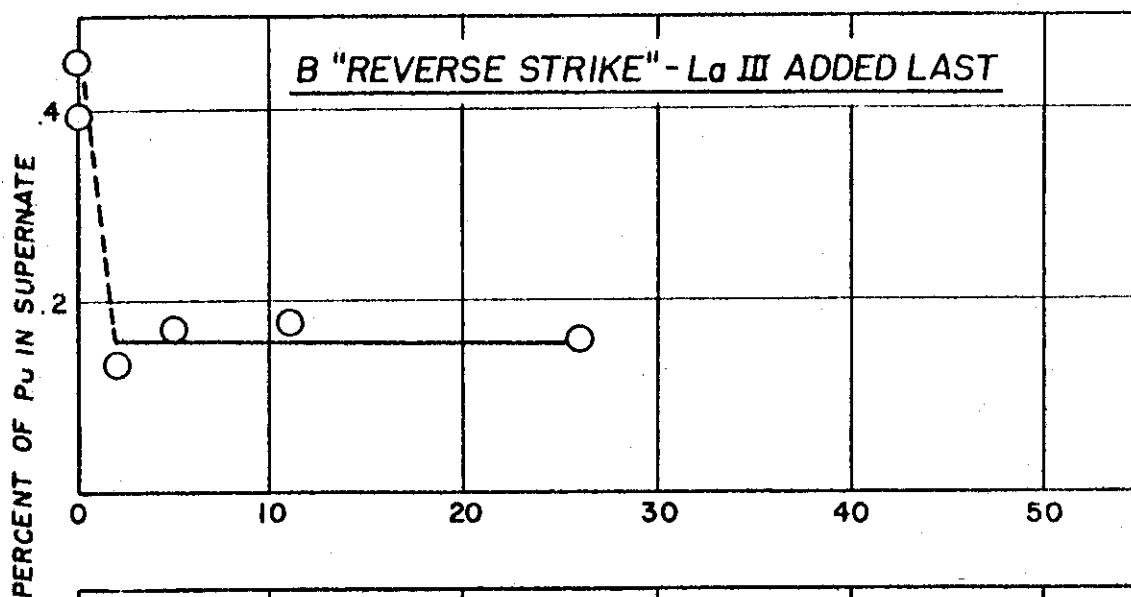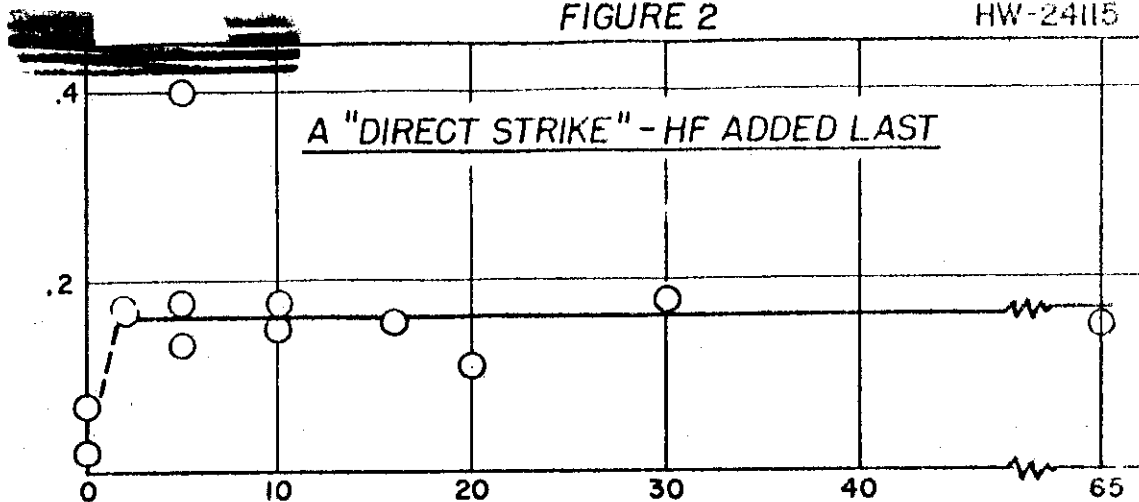
FIGURE 2
27
HW-24115

A "DIRECT STRIKE" - HF ADDED LAST

B "REVERSE STRIKE" - La III ADDED LAST

C "DIRECT STRIKE" - INCREASED HF
ADDED LAST

PERCENT OF Pu IN SUPERNATE

AGE OF LaF$_3$ - MINUTES

SEC 027

TABLE IV

VARIABLE TIMES OF STIRRING IN
CONTACTING Pu(III) WITH PREFORMED LaF$_3$

Contact Time	c/m in Supernate and % of total in Supernate			
	LaF$_3$ formed in 1 M HNO$_3$ 2.7 M HF (HF last)		LaF$_3$ formed in 2.7 M HF (La(III) added last)	
15"	7,985 c/m	7.02%	{34,351 c/m {24,616	{30.20% {21.64
30"	6,818	6.08	14,967	13.16
45"	5,110	4.49	4,033	3.55
1'	{4,860 {3,884	4.27 3.41	2,078	1.83
1"15"	1,572	1.38	3,825	3.36
1'30"	{2,300 {1,193	2.02 1.05	1,345	1.18
2'	933	0.82		
2'30"	{968 {1,148	0.85 1.01	1,102	0.97
3'	512	0.45		
5'	516	0.45	905	0.80
9'	253	0.22		
10'			275	0.24
15'			322	0.28

Except for stirring times of 30 seconds or less, which is hardly

long enough to completely slurry the precipitate and remove the water

film, the lanthanum fluoride formed in the presence and absence of nitric

acid picked up Pu(III) ions from solution at approximately the same rate.

These data are plotted in Figure 3.

Variable Amounts of Fresh Preformed Lanthanum Fluoride

From the previous data it appears that the sorption* of Pu(III) ions

by freshly prepared lanthanum fluoride is at equilibrium after five minutes.

A series of sorption experiments were run in Pyrex according to the

general procedure described on pages 20-22, except the amount of La(III)

*For definition of sorption see Glasstone (10 p. 1194).

FIGURE 3
VARIABLE TIMES OF STIRRING
IN CONTACTING Pu III WITH
PREFORMED LaF₃

○ LaF₃ FORMED IN 1 M HNO₃
2.7 N HF (HF LAST)

◯ LaF₃ FORMED IN 2.7 M HF
(La III ADDED LAST)
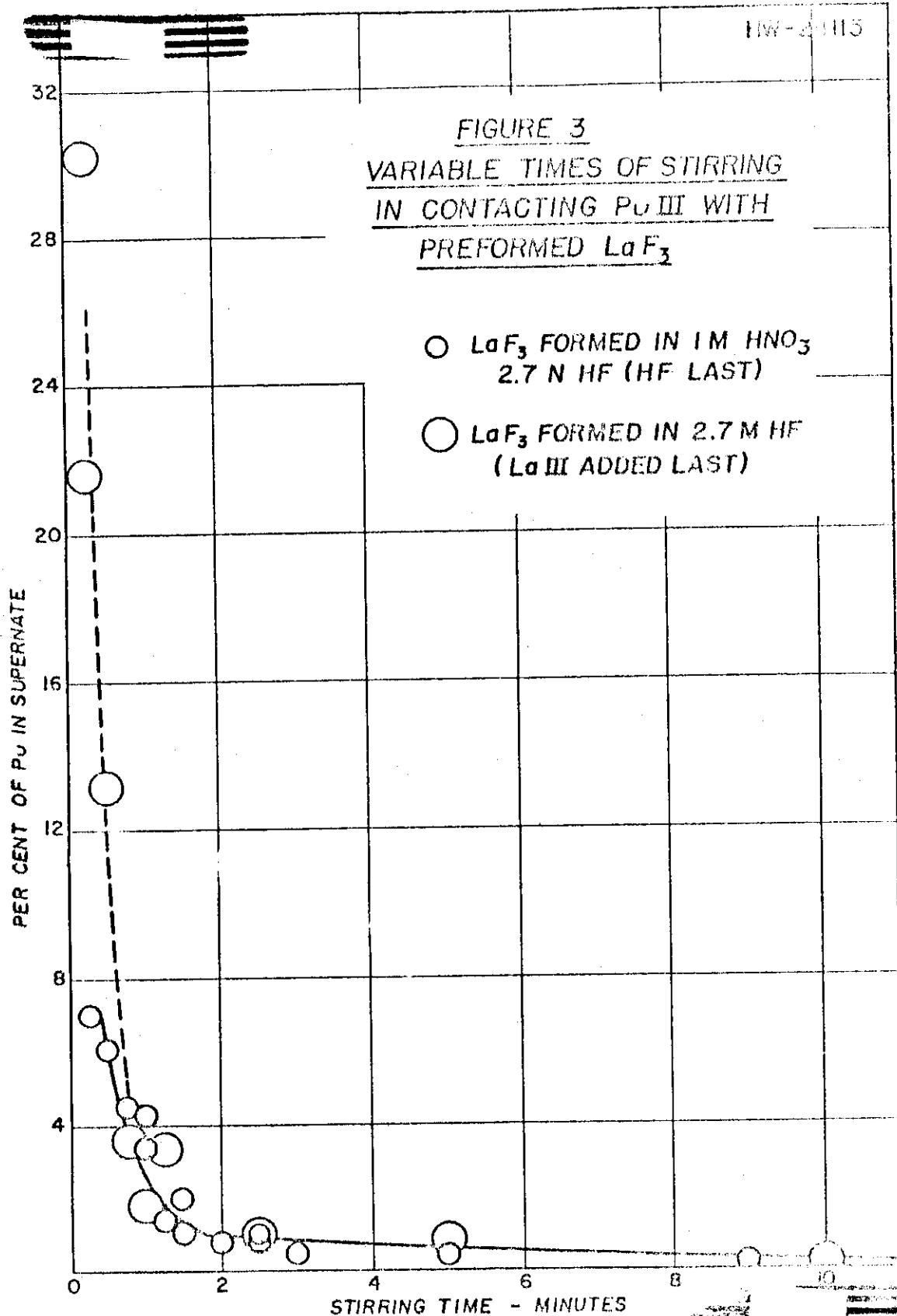
was varied by using a number of different sized pipets and a 0.5 mg./ml. La(III) solution as well as the 5 mg./ml. solution used previously. These mixtures were each stirred for five minutes; however, some were repeated and stirred 2, 1 1/2, and 1 minutes. The data appear in Tables V and VI, and are plotted in Figures 4, 5, 6, and 6a.

TABLE V

VARIABLE AMOUNTS OF FRESH PREFORMED LaF$_3$ AND STIRRED CONTACT TIME

LaF$_3$ mg.	Contact Time,			
	1 min.	1 1/2 min.	2 min.	5 min.
0.011				35.01
.018				23.09
.035				10.72
.071				3.55
.11	5.83	4.18	3.64	3.12
.14				1.38
.18	5.94	3.84	1.90	0.93
.21				0.95
.35	3.41 / 4.27	1.05 / 2.02	0.82	0.45
.71	1.89	1.43	0.34	0.34
.88		0.43		
1.06	1.58	0.17		0.15
1.4	1.66	0.20	0.31	

TABLE VI

ADSORPTION DATA AFTER 5 MIN. STIRRING ON VARIABLE AMOUNTS OF FRESH PREFORMED LaF₃

LaF₃, mg.	"C" c/m in 0.5 ml. supernate	Log "C"	c/m in LaF₃ 113,800-"C"	$\left(\frac{x}{m}\right)$ c/m/mg.LaF₃	Log $\frac{x}{m}$
0.011	39,844	4.6004	73,960	6.71×10^6	6.8967
.018	26,280	4.4196	87,520	4.88	6.6884
.035	12,200	4.0864	101,600	2.885	6.4602
.071	4,044	3.6068	109,760	1.555	6.1917
.11	3,550	3.5502	110,250	1.003	6.0013
.14	1,574	3.1970	112,230	0.802	5.9042
.18	1,058	3.0245	112,740	0.627	5.7973
.21	1,082	3.0342	112,720	.536	5.7292
.35	516	2.7126	113,280	.322	5.5079
.71	387	2.5877	113,410	.161	5.2068
1.06	172	2.2355	113,630	.107	5.0294

An analysis of these data according to the Freundlich equation, $x/m = K C^n$, where x/m is plutonium adsorbed by lanthanum fluoride in c/m/mg, K and n are constants found to be 2665 and 0.7464, respectively, and "C" is concentration of plutonium in the supernate in c/m per 0.5 ml.

Using the same data and fitting a Langmuir type of equation, $x/m = \frac{k_1 C}{1+k_2 C}$, to it, k_1 and k_2 were found to be 294 and $1.93 \cdot 10^{-5}$, respectively.

The two empirical curves are drawn on Figure 6, and the lower portion is shown expanded on Figure 6a. The experimental points are plotted on each figure.

Carrying on Oven-Dried Lanthanum Fluoride Prepared by Metathesis of NaLa(SO₄)₂·H₂O

Experiments were attempted to study the carrying of Pu(III) on freshly precipitated lanthanum fluoride in the presence of an excess of

HW·24115

FIGURE 4
VARIABLE AMOUNTS OF FRESH
PREFORMED LaF_3 AND
STIRRING TIME
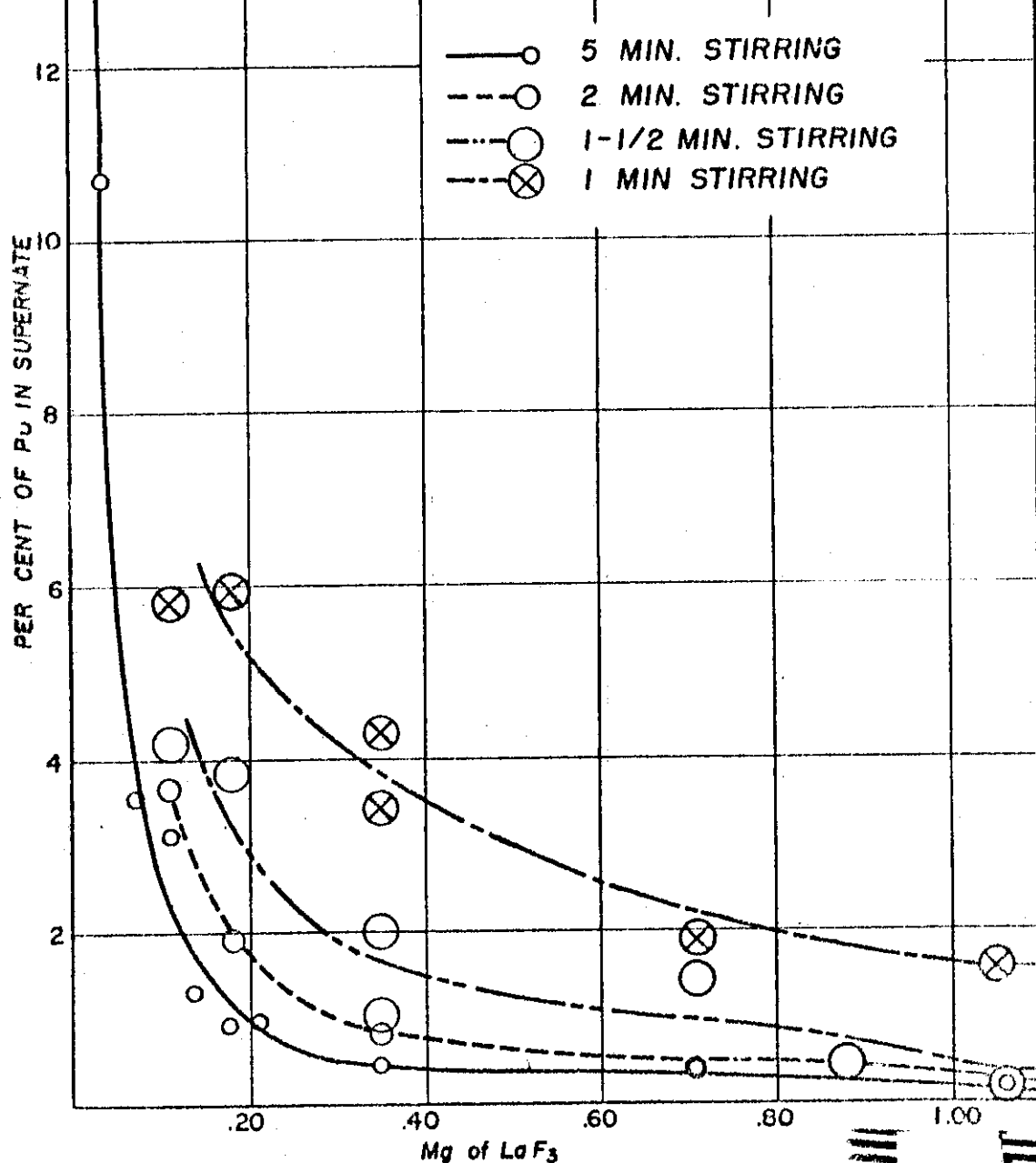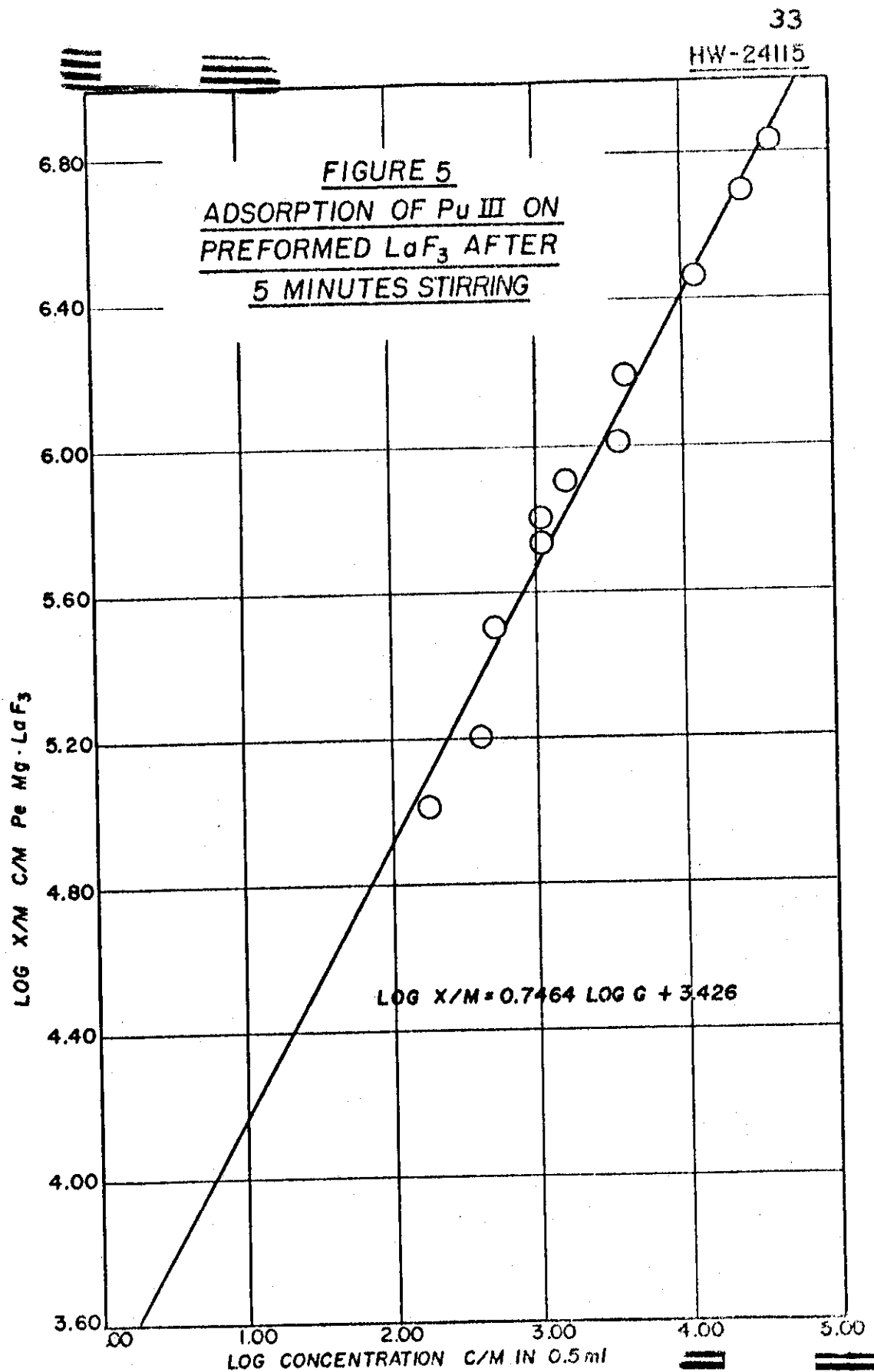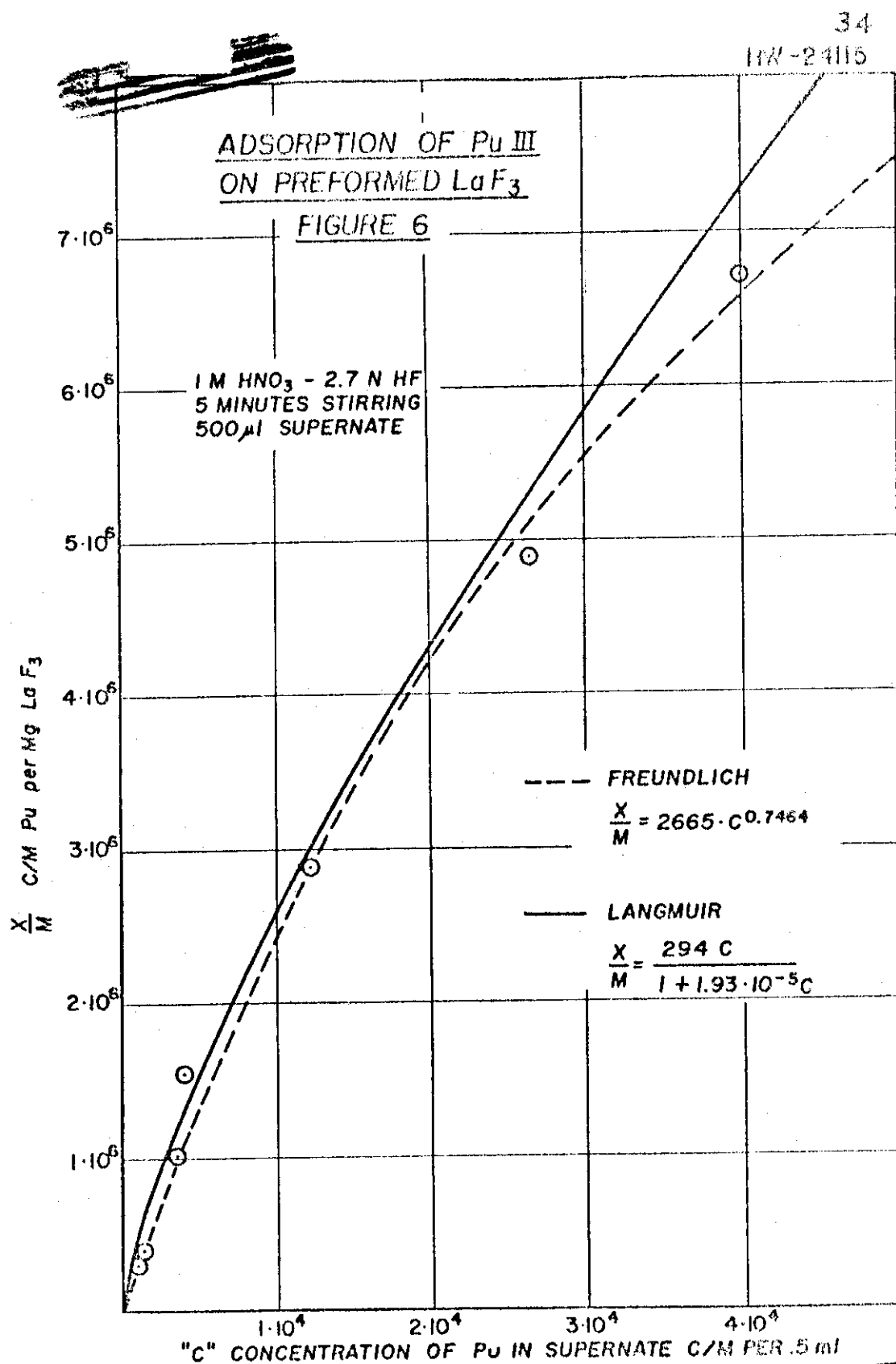
5 MIN. STIRRING
2 MIN. STIRRING
1-1/2 MIN. STIRRING
1 MIN STIRRING

PER CENT OF Pu IN SUPERNATE

Mg of LaF_3

900 032

FIGURE 5
ADSORPTION OF Pu III ON
PREFORMED LaF_3 AFTER
5 MINUTES STIRRING

$$LOG \ X/M = 0.7464 \ LOG \ C + 3.426$$

LOG X/M C/M Pe Mg·LaF_3

LOG CONCENTRATION C/M IN 0.5 ml

34

HW-24115

ADSORPTION OF Pu III
ON PREFORMED LaF₃
FIGURE 6

1 M HNO₃ - 2.7 N HF
5 MINUTES STIRRING
500 μl SUPERNATE

- - - FREUNDLICH

$$\frac{X}{M} = 2665 \cdot C^{0.7464}$$

LANGMUIR

$$\frac{X}{M} = \frac{294\ C}{1 + 1.93 \cdot 10^{-5}\ C}$$

$\frac{X}{M}$ C/M Pu per Mg LaF₃

"C" CONCENTRATION OF Pu IN SUPERNATE C/M PER .5 ml

9○○
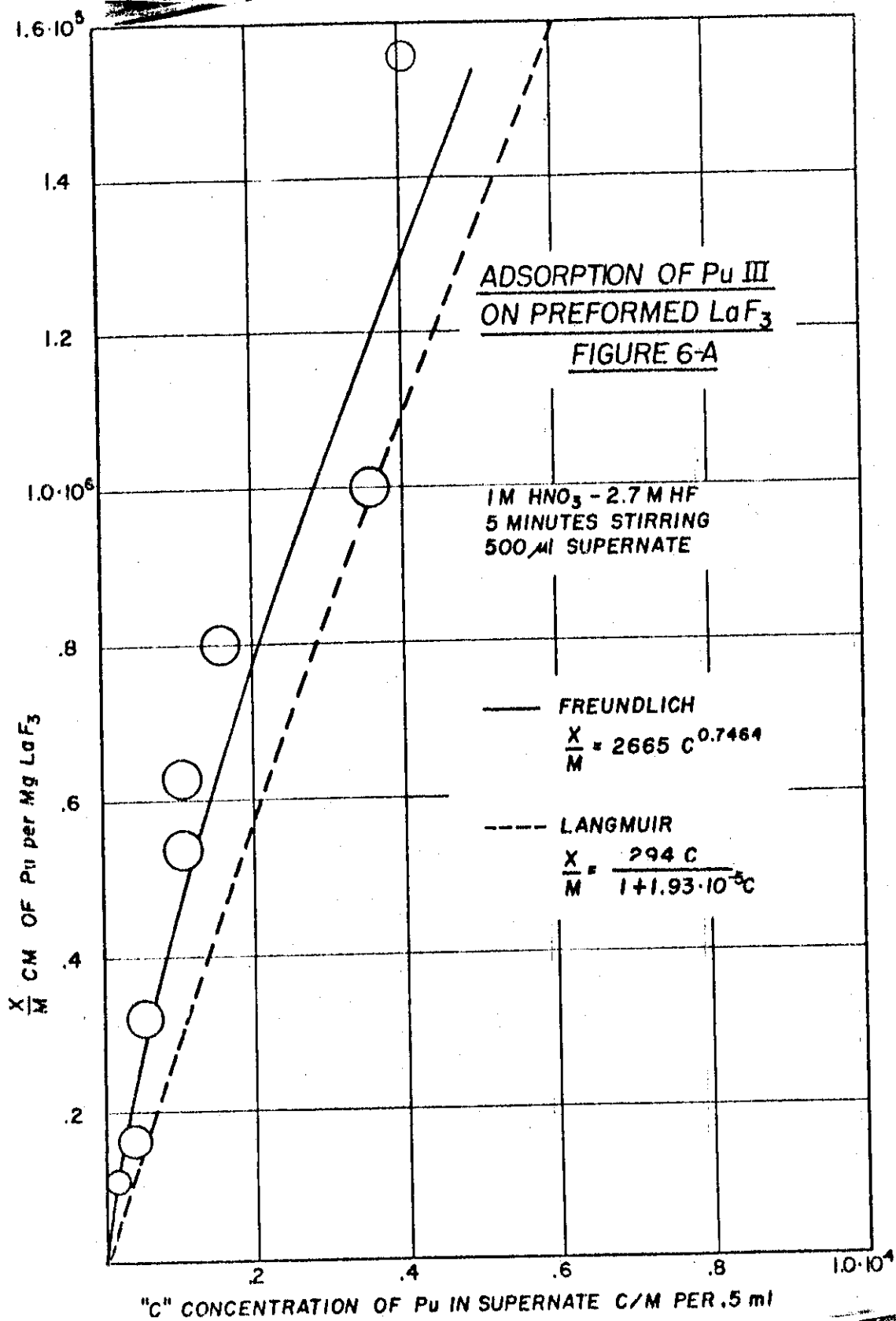
lanthanum ions by making the precipitation, centrifuging, and removing the supernate; then washing with a dilute acid lanthanum solution, followed by slurrying up in a solution containing the excess La(III) ions. It was observed that 1.6 mg. of lanthanum fluoride dissolved in two 500 microliter washes 0.001 $\underline{M}$ La(III) and 0.009 $\underline{M}$ HNO_3.

Previously for the purpose of x-ray study, some $NaLa(SO_4)_2 \cdot H_2O$ had been prepared, and a portion of this had been metathesized to LaF_3 (21 pp. 87-93). This lanthanum fluoride more or less kept its original larger particles size such that it did not peptize to a colloid in the absence of an appreciable ionic strength in the surrounding aqueous solution but had the characteristic lanthanum fluoride x-ray diffraction pattern (20 pp. 272-291)*. Testing this dried, metathesized lanthanum fluoride showed that it was quite difficultly soluble in dilute nitric acid, as ten ml. of 0.01 $\underline{M}$ HNO_3 which had contacted the lanthanum fluoride had to be concentrated to a fourth of a ml. to give a faintly visible precipitate with hydrofluoric acid.

The $NaLa(SO_4) \cdot H_2O$ was sieved through a #60 Tyler equivalent mesh sieve (250 micron openings), and the portion that was retained on a #100 Tyler equivalent mesh sieve (149 micron openings) was metathesized in platinum with two portions of 1 $\underline{M}$ sodium fluoride, then the precipitate was washed several times with distilled water by decantation and transferred to a 50 ml. Lusteroid cone and centrifuged, and the water drawn

---

*See Card 3-1021 of the American Society for Testing Materials, Alphabetical and Grouped Numerical Index of X-Ray Diffraction Data, 1950, 441 pages and a Card Index File.

off the precipitate. The lanthanum fluoride was removed to the platinum crucible and dried at 105°C. The particles crumbled very easily and passed the #60 sieve practically completely, and over 80% was retained on a #140 sieve (105 micron openings).

This latter material was weighed into the following described 10 ml. glass stoppered flasks, and 5 ml. of solution with 2,188,000 c/m of Pu(III) was added to each, making the different solutions listed in Table VII. These were shaken on a variable speed mechanical shaker. The shaker was stopped periodically, and 50 microliters of the supernate were removed and mounted on a platinum disc and counted on the A.S.P. At the beginning the lanthanum fluoride was allowed to settle momentarily before the sample was removed; however, as the results were noted to be rather erratic at the approximately 18 hour sampling, the flasks were lightly centrifuged in an International clinical centrifuge equipped with a head and holders for 50 ml. centrifuge tubes.

From the data in Table VII one can readily see that lanthanum fluoride will remove Pu(III) ions from the solution both when there is an excess of fluoride and when there is an excess of lanthanum ions to interfere with the plain adsorption of Pu(III) by competing strongly for the potential-determining ion positions. However, the fact that the presence of lanthanum ions does slow down the carrying by the preformed metathesized lanthanum fluoride, particularly at the higher concentration, does give an indication that the initial step of the expected isomorphous replacement is surface adsorption through a Helmhotz double layer (10 pp. 1220-2).

The fact that Pu(III) carries well under all of the conditions strongly supports the contention that it becomes incorporated into the crystal. The more rapid carrying with the stronger acid is expected after the solution has become saturated with La^{+3} and F^- ions, because recrystallization is taking place faster. Before the solution becomes saturated, there is very little carrying of Pu(III) into the crystal because all of the surfaces are losing ions to the solution. In the presence of excess fluoride (hydrofluoric acid) the acidity is increased but slightly, but the surface of the lanthanum fluoride undoubtedly is negative due to adsorbed fluoride ions. This negative surface attracts the Pu(III) ions, and the fluoride forms a precipitant.

Such complete carrying with lanthanum fluoride that has a relatively small amount of surface also is an indication that the mechanism is not simple adsorption.

TABLE VII

CARRYING WITH METATHESIZED LaF$_3$

Flask W (wax lined), 0.0213 g. LaF$_3$, 0.02 M $AlNO_3$-0.25 M AlF

Time, hrs.	c/m/50 ul.	x/m c/m/mg.LaF$_3$	% sorbed
0.167	16,640	2.46·10^4	24.0
1.	13,114	4.11	40.0
1.67	3,584	8.59	83.6
2.4	10,425	5.33	52.4
18.5	4,556	8.13	79.2
26	60	10.25	99.7
50	9	10.26	99.96

Flask I, 0.0204 g. LaF$_3$, 0.02 M HNO_3

0.167	7,063	7.34·10^4	67.7
1.	8,929	6.41	59.2
2.	8,973	6.38	59.0
18.5	3,423	9.14	84.4
26	375	10.15	98.3
50	462	10.11	97.9
74	96	10.79	99.56

Flask II, 0.0266 g. LaF$_3$, 0.001 M La(III), 0.02 M $AlNO_3$

0.2	9,195	4.77·10^4	58.0
1.	7,874	5.26	64.0
2.	9,418	4.68	57.0
18.5	7,287	5.49	66.7
26	5,041	6.32	77.0
50	4,699	6.46	78.5
74	1,429	7.68	93.5

Flask III, 0.0207 g. LaF$_3$, 0.02 M La(III), 0.02 M $AlNO_3$

0.167	21,772	0.052·10^4	0.5
1.1	21,095	.38	3.6
2.	20,303	.81	7.2
18.5	19,359	1.22	11.5
26	18,351	1.71	16.1
50	15,150	3.25	30.8
74	4,786	8.67	78.1
164	5,275	8.02	75.9

Flask IV, 0.0239 g. LaF$_3$, 1 M $AlNO_3$

0.167	20,374	0.63·10^4	6.9
.9	20,783	.46	5.0
2.	5,003	7.04	77.1
18.5	877	8.77	96.0
26	138	9.08	99.37
50	98	9.10	99.55

Coprecipitation of PuF3 With Tagged LaF3

To study the relationship of both components in mixed fluoride crystals, it is necessary to determine the $\frac{La^{+3}\ solution}{LaF_3\ crystal}$ relationship in the precipitations. First, the lanthanum tracer-carrier 0.5 mg./ml. prepared from Oak Ridge Ba^{140}-La^{140} activity was used.*

The lanthanum and plutonium were coprecipitated in a direct strike of 2.7 N hydrofluoric acid, 0.5 ml. volume and 5 minutes stirring. Table VIII contains the amounts of lanthanum and plutonium used and the beta counts of La^{140} and the alpha counts of the plutonium for both the precipitate and the supernate.

TABLE VIII

MIXED CRYSTAL EXPERIMENTS WITH TAGGED LaF3

	c/m Pu		c/m La^{140}		$D = \dfrac{\frac{La^{+3}}{Pu^{+3}}\ soln.}{\frac{La^{+3}}{Pu^{+3}}\ solid}$
LaF, mg.	Total Pu	Pu^{+3} Supernate	LaF$_3$ Precipitate	La^{+3} Supernate	
0.035	113,800	495	1,800	6	0.77
.071	"	245	3,535	9	1.16
.14	"	96	7,060	8	1.34
.21	"	202	10,335	24	1.31
.28	"	64	14,317	10	1.24
.21	341,500	274	7,152	7.5	1.31
.14	569,000	715	4,765	6.5	1.09
.071	854,000	1,197	2,401	3.5	.97

Average D = 1.1

As the values of D were uncertain due to the very low beta activity in the supernate and as it was desirable to investigate the mixed crystal

*Its preparation has been described on page 14.

relationship with the amount of plutonium of the same order of magnitude as the lanthanum, experiments were carried out using the higher activity plutonium and lanthanum solutions.

These experiments were carried out by adding different amounts of the pile-irradiated lanthanum tracer-carrier, plutonium solution II, and 1.0 $\underline{N}$ nitric acid solutions to make 500 microliters after the 50 microliters of concentrated hydrofluoric acid, which was added last to make the precipitation. These tubes of slurry were stirred up and readings made on them with the high pressure ionization chamber*.

The supernates and precipitates were each mounted on platinum discs and dried for counting. It was found the gamma count in the supernate was too low for a good count, and the beta activity of the precipitate was too high for the BGO to record. However, it was possible to count the beta activity of the supernate on the second shelf and count the gamma activity of the precipitate on the second shelf through a lead and aluminum gamma sandwich which adsorbed the beta particles. To determine the relationship between beta and gamma counts of La^{140} mounted on platinum, a 1/40 dilution was made on the active solution, and four platinum discs were mounted with 200 microliters of this dilution. These discs

---

*These readings of the gamma activity from the solution could not be used for comparative purposes because similar readings on the supernate alone were too low to be detected with accuracy. However, the readings did show that the activity decayed with a forty-hour half life indicating that the La^{140} activity was not noticeably radioactively contaminated.

were counted 5 minutes each for beta activity and for two 10 minute periods
for gamma activity. The corrected counts are shown in Table IX. The ratio
was shown to be 1 gamma count equals 91.9 beta counts.

TABLE IX

COMPARATIVE BETA AND GAMMA COUNTING ACTIVITY
WITH PLATINUM BACKING

Count Corrected for Background of 18

Disc	Beta Counts	1st γ count	2nd γ count
1	2942	31	32
2	2948	30	32
3	2956	30	35
4	2914	33	11
Avg.	2940		32

After the lanthanum activity on the sample discs had decayed, the
same discs were counted for alpha activity. The supernates were counted
for five or more minutes in an ASP. The precipitates were counted for
10 minutes on an ASVP. In the latter case, the disintegrations per
minute can be converted to counts per minute comparable to the ASP read-
ings by multiplying by the average geometry, 0.505.

Some of the precipitate discs could not be counted for plutonium
because some of the plutonium was rubbed off by the cardboard carriers.
The alpha count for these were calculated by multiplying the volume of
plutonium solution used by $0.505 \times 8.1 \times 10^4$ d/microliter.

The D for the equation $\left(\dfrac{La^{+3}}{Pu^{+3}}\right)_{super.} = D \left(\dfrac{La^{+3}}{Pu^{+3}}\right)_{solid}$

was solved by the equation $D = \left(\dfrac{La^{+3}\ \beta\ c/m}{Pu^{+3}\ \alpha\ c/m}\right)_{super.} \cdot \left(\dfrac{0.505 \cdot Pu^{+3}\ \alpha\ c/m}{91.9 \cdot La^{+3}\ \gamma\ c/m}\right)_{solid}$

Table I lists the experimental values and the calculated values of

D which are of the same range of magnitude as those derived with low

concentration of Pu(III) and low La^{140} activities.

TABLE I

SECOND MIXED CRYSTAL EXPERIMENTS

LaF$_3$ mg.	Plutonium c/m Precip.	c/m Super.	La^{140} γc/m Precip.	βc/m Super.	D
0.036	4,141,000	38,253	3030	810	0.24
.036	7,974,000	47,267	2014	310	.14
.036	15,636,000	34,375	1985	297	.37
.036	23,726,000	76,967	1924	860	.76
.072	4,086,000	12,457	2733	655	.43
.072	24,381,000	39,947	1913	150	.26
.072	8,196,000	22,650	1911	165	.17
.072	8.1·10^4·200*	26,351	1889	164	.29
.144	8.1·10^4·50*	9,250	2386	486	.49
.144	8.1·10^4·200*	19,020	2406	445	.86
.144	8.1·10^4·100*	9,952	2235	239	.48
.216	8.1·10^4·50*	4,100	3378	272	.44
.216	7,913,000	8,192	3263	384	.63
.29	8.1·10^4·50*	3,008	4290	447	.77
.072**	8.1·10^4·300*	44,273	1062	119	.34
.29**	8.1·10^4·50*	5,813	4248	894	.80

Mean D = 0.5

*Plutonium values calculated from the volume of solution used.
**Experiments were carried out in 3 ml. Lusteroid cones.

The action of hydrofluoric acid on the Pyrex glass is an undesirable

condition. A concentration of 1 M H$_2$SiF$_6$ has been used as a method of

partial separation of lanthanide from actinide rare earths (22 pp. 1344-6).

The fluosilicic acid produced in a short period is of no significance;

however, as the contact with glass in the case of the data on Table IV

was about half an hour, two experiments were carried out in Lusteroid to

eliminate the fluosilicate. As the results are comparable, it is believed that the effect is smaller than other errors in the series of experiments.

DISCUSSION

In conducting the experimental work with this problem, there were several conditions somewhat peculiar to the elements involved in the research which considerably restricted the course of pursuit, namely, (1) the cost and contamination hazards of working with plutonium along with counting as the most convenient method of detection limited the working amounts of this element to the micro scale; (2) the necessity of maintaining an acid media to prevent plutonium from hydrolyzing and adsorbing to a great extent on the glass required an excess of fluoride ion to be present in all cases, except when dried lanthanum fluoride was used, as precipitated lanthanum fluoride would have dissolved or peptized. The excess of precipitating agent made impossible the use of excess lanthanum or other high valent positive ions to suppress an adsorption of Pu(III) on lanthanum fluoride because they would either be precipitated or form complexes with the fluoride. The presence of hydrofluoric acid limited the time that an experiment could be carried out in Pyrex glass without depleting the fluoride and forming fluorosilicic acid.

Within the short time lanthanum fluoride was formed before contacting with the Pu(III), there appeared to be little change in carrying ability due to aging via reduction of surface and perfection of crystals. Plutonium so contacted with preformed lanthanum fluoride appeared to

observe both equations for adsorption. At the lower limit of adsorbent
the Langmuir equation appeared to represent the data best. However, as
it is doubtful if the amount of surface remains proportional to the amount
of precipitate when they are formed at considerably different lanthanum
concentrations, these adsorption equations appear less valid.

An approximation of the surface of lanthanum fluoride, as compared
to the surface required for the amount of plutonium carried, if by a
surface adsorption, can be made by first taking the size of the particles
as 0.01 micron (1 p. 1) and considering them as spheres. The density of
lanthanum fluoride should be approximately 6.2 calculated from the density
of PuF_3, which is 9.3 (28 p. 11), neglecting the small differences in
crystal constants. Now, ignoring the actual space relationship of the
ions, and calculating as though the whole surface of the lanthanum fluoride
were covered with potential determining fluoride ions in a hexagonal close
pack arrangement, and taking the fluoride ionic radius as 1.33 Angstrom
units (15 p. 2628), which is larger than either La(III) or Pu(III) --
given as 1.04 and 1.01 Angstroms, respectively (25 p. 7) -- and assuming
that one plutonium can be bonded to every three fluoride ions, there are
a possible $5.8 \cdot 10^{15}$ Pu(III) ions adsorbed on 0.011 mg. of LaF_3 and
$5.6 \cdot 10^{17}$ ions on 1.06 mg. Calculations of the number of plutonium atoms
carried from the values of x in Table VI yield $2.7 \cdot 10^{15}$ and $4.1 \cdot 10^{15}$ atoms
carried on the two quantities of lanthanum fluoride. This corresponds to
47 and 0.7% of the surface covered.

The assumptions made in the calculations were such as to give large surface, and the close pack of the fluoride ions in the calculation assumes very close arrangement of the Pu(III) ions.

The colloidal range is considered 0.001 to 0.1 micron; hence the lanthanum fluoride particles are in the colloidal range if the electron microscope figure of 0.01 microns is accurate, and LaF_3 particles settle and are visible due only to agglomeration of the particles. This is reasonable since in washing precipitated lanthanum fluoride in distilled water, a large portion becomes colloidal as soon as the ionic strength is lowered. It is difficult to postulate how an agglomeration of fine particles affects the effective surface for adsorption. If the average size of the particles were 0.1 micron, there would be a five-fold excess of plutonium over total surface in the case of 0.011 mg. of lanthanum fluoride.

Adsorption cannot be considered the only mechanism taking place because of the fact that when the amount of adsorbent is greatly reduced, equilibrium is achieved much too slowly. If the supernate count for 0.035 and 0.071 mg. of lanthanum fluoride from Table VI are compared with those for co-precipitated PuF_3 and LaF_3 in Table VIII for the same amount of carrier, it can be seen that equilibrium has not been reached for the preformed lanthanum fluoride.

To further show that total sorption equilibrium had not been reached on the lanthanum fluoride, 113,800 c/m of Pu(III) was contacted in a platinum cone with 0.018 mg. of lanthanum fluoride for 17 minutes, 1 hour,

and 2 1/2 hours. The supernates contained 15.96, 5.05, and 1.61 per cents of the plutonium, respectively. This is to be compared with 23.09 per cent of the plutonium in the supernate for five minutes contact in Table V. For 0.035 mg. of co-precipitated lanthanum fluoride, in Table VIII, there was 0.44 per cent of the plutonium in the supernate.

In the experiments with tagged lanthanum tracer, of necessity, as explained above, the co-precipitation had to be made by rapid precipitation with a great excess of hydrofluoric acid. Bonner and Kahn (3 p. 54 or 3a p. 115) say of rapid precipitations after addition of the precipitating agent, "The degree of local supersaturation caused by addition of a precipitating agent is so erratic that a quantitative study of the type of tracer distribution is not practical. However, when isomorphous replacement is possible, carrying by precipitates formed in the presence of the tracer is known to be very reliable......"

Even though the rapid precipitations do not conform to either of the isomorphous distribution laws, one might expect such a fine and gelatinous precipitate to come to an equilibrium between solution and the entire precipitate by re-solution processes and thus conform to the homogeneous distribution law. Since from previously shown data the carrying on preformed lanthanum fluoride is essentially equal in five minutes to the carrying by co-precipitated lanthanum fluoride, provided the amount of lanthanum fluoride is not reduced much below 0.35 mg. in 0.5 ml. solution, it might be expected that the solution and precipitate have approached a homogeneous distribution state, especially in the experiments

using pile irradiated tracer-carrier because these were held for approximately one half hour. However, they were not stirred continually as gamma measurements were taken. The values of D are in fair agreement and indicate that PuF_3 might be more soluble than LaF_3.

From the evidence foregoing in this paper it is concluded that Pu(III) carries by isomorphous replacement in an erratic manner with co-precipitated lanthanum fluoride, which can be aged and stirred until the homogeneous distribution state is fairly accurately represented. The mechanism of carrying on preformed lanthanum fluoride, however, is first that of rapid adsorption on the surface, followed by a slower redistribution through the crystal by re-solution through the capillary film of solution around the particles. For plant process and analytical purposes the tracer concentration is so low that the second step in the carrying on a preformed precipitate does not need to take place to any appreciable degree. For the ordinary tracer concentration of Pu(III) the initial adsorption on the preformed lanthanum fluoride might be adequate to carry effectively nearly all of the plutonium and be practically as effective as co-precipitated lanthanum fluoride.

SUMMARY

This and previous work show that Pu(III) will carry quite well on co-precipitated and preformed gelatinous lanthanum fluoride, and given enough time will be carried quite readily with coarse, oven-dried lanthanum

fluoride that has been metathesized from $NaLa(SO_4)_2 \cdot H_2O$. With the dried lanthanum fluoride it was possible to demonstrate that an excess of La(III) ions retarded the initial adsorption of Pu(III) but did not prevent carrying of Pu(III) by incorporation in the crystal. Stronger acid (1 $\underline{M}$ HNO_3) and the presence of excess fluoride ion favored the more rapid incorporation of Pu(III) in the crystal lattice of lanthanum fluoride.

The carrying of Pu(III) on preformed precipitated lanthanum fluoride appeared to follow nicely both the Freundlich and Langmuir equations; however, carrying was so complete that the investigation could not be carried to the point where the adsorbent was saturated. Further, it was shown with diminishing amounts of lanthanum fluoride that equilibrium was reached more slowly. Hence, it was concluded that carrying on preformed lanthanum fluoride precipitates is initiated by an adsorption mechanism and that incorporation into the crystals follows by re-solution through the liquid film that wets the particles, the final state being isomorphous mixed crystals.

In co-precipitation of Pu(III) and La(III) with hydrofluoric acid, homogeneous mixed crystals appear to form with stirring. The value of D in the Henderson and Kracek equation is approximately 0.5, indicating that PuF_3 might be more soluble than LaF_3.

BIBLIOGRAPHY

(1) Angerman, Albert M., Crystalline Lanthanum Fluoride. HW-3-2597, Hanford Works Memo Report, June, 1945. 11 p.

(2) Balthis, Joseph Hendrickson, and Sutton, Joseph Bartlett, The Flocculation of Lanthanum Fluoride. CN-2010 (Final Report), Metallurgical Project, Clinton Laboratories, Separations Development Divisions. November, 1944, 27 p.

(3) Bonner, Norman Andrew, and Kahn, Milton, Some Aspects of the Behavior of Carrier-Free Tracers I. Nucleonics 8 No. 2, 46-59 (1951).

(3a) Wahl, Arthur C., and Bonner, Norman Andrew (Editors), Radioactivity Applied to Chemistry, John Wiley and Sons, Inc., New York, 1951, 604 p.

(4) Clifford, Alan Frank, and Koshland, D. E., Jr., et.al., Development of Radiochemical Analytical Procedures for Plutonium - (1) Synthetic Solutions. CN-2040, Metallurgical Project, Chemistry Division Progress Report. September, 1944. 35 p.

(5) Connick, Robert Elwell, Oxidation States, Potentials, Equilibria, and Oxidation-Reduction Reactions of Plutonium. CC-3869, Metallurgical Project, Department of Chemistry, University of California, May, 1948. 135 p.

(6) Cunningham, Bunis Bell, V Summary of Plutonium Carrying Agents. N-2205, June, 1946. 42 p.

(7) Doerner, Henry Alfred, and Hoskins, William M., Co-precipitation of Radium and Barium Sulfates. Journal of the American Chemical Society 47, 662-75 (1925).

(8) Fisk, Philip Burrell, and Buckingham, John Stevens, Coincidence Loss in Alpha Simpson Proportional Counting Instruments. HW-20485, Hanford Works, March, 1951. 7 p.

(9) Franck, James, Seaborg, Glenn Theodore, and Willard, John Ela, Production and Extraction of Plutonium. CN-813 Report for Month Ending July 17, 1943. 33 p.

(10) Glasstone, Samuel. Textbook of Physical Chemistry, 2nd Edition. D. Van Nostrand Company, New York, 1946, 1320 p.

(11) Hahn, Otto, Applied Radiochemistry, Cornell University Press, Ithaca, New York, 1936. 278 p.

(12) Hanford Operations Manual, Section C, HW-10473.

(13) Hanford Works Laboratory Manual - Laboratory Reagents Section.

(14) Hill, Orville Farrow, and Leits, Fred John, Jr., Quarterly Report, Janu -March, 1951. HW-20863, Chemical Research Section, Hanford Works   fied Document, April 16, 1951.

(15) Hodgman, Charles David (Editor) Handbook of Chemistry and Physics. Thirtieth Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1947. 2686 p.

(16) Hume, David Newton, and Glendenin, Laurence Elgin. A Manual of the Radiochemical Determination of Fission Product Activities. CN-2815 (Final Report) Second Edition. Metallurgical Project, Chemistry Division, June 1945. 74 p.

(17) Koshland, D. E., Jr., Development of Radiochemical Analytical Procedures for Plutonium, (2) Recommendations for a Standard Procedure

and Tests in Uranyl Solutions. CN-2041, Metallurgical Project, Chemistry Division Progress Report. January 1945. 39 p.

(18) Latimer, Wendell Mitchell. University of California Radiation Laboratory Progress Report, Chemical Section, Part D. September 1947, 12 p.

(19) O'Connor, Paul. Basic Chemistry of Plutonium. CN-1764, Chemical Research Report for the Month Ending July 1, 1944. 17 p.

(20) Oftedal, Ivar. The Crystal Structure of Tysonite and Some Artificial Lanthanide Fluorides. Z. Physik. Chem. 5, 272-91 (1929) Abstract C.A. 24, 537 (1930).

(21) Ralphs, Delbert Lloyd, Hanford Works Laboratory Notes, HW-2648-T, 152 p.

(22) Seaborg, Glenn Theodore; Katz, Joseph, J., and Manning, Winston Marvel (Editors). The Transuranic Elements. National Nuclear Energy Series, Division IV, Volume 14B. McGraw Hill, 1949. 859 p.

(23) Seaborg, Glenn Theodore; Wahl, Arthur Charles, and Kennedy, Joseph William. A New Element: Radioactive Element 94 from Deutrons on Uranium. Physical Review 69, 367 (1946).

(24) Simpson, John Alexander, Jr., Manual for the Proportional Alpha Counter. CP-1817 (Declassified) Instrument Section, Argonne National Laboratory, Chicago, Illinois, May 1945. 15 p.

(25) Zachariasen, Fredrik William Houlder. The Crystal Chemistry of Fluorides of Thorium, Uranium, Neptunium, and Plutonium. MDDC-1151,

U.S. Atomic Energy Commission Technical Information Division, Oak

Ridge Directed Operations, Oak Ridge, Tennessee, June 1947, 8 p.

(26) Zachariasen, Fredrik William Houlder. On the Size of the Plutonium

Atom. CK-1493, Metallurgical Project, General Physics Research.

April 1944. 11 p.

(27) Zachariasen, Fredrik William Houlder. General Physics Research.

X-Ray Diffraction Section. CN-1733, Report for Month Ending May 25,

1944, Part II. 6 p.

(28) Zachariasen, Fredrik William Houlder. X-Ray Diffraction Results

for Uranium and Plutonium Compounds. CK-1367, Metallurgical Project,

General Physics Research, February 1944. 16 p.