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DATE 3/23/50 [redacted] [redacted]

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SUBJECT OR TITLE

DRY FLUORIDE VOLATILIZATION PROCESS

TO
File

FROM
C. Groot

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RL ongill 4/28/99
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BY JW Jordan DATE 6/4/81
BY AE Barber DATE 6/10/81

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HW-28268

[redacted]

ROUGH DRAFT

March 23, 1950

TO: F. W. Albaugh

FROM: C. Groot

[redacted]

14 Pages [redacted]

I. INTRODUCTION

The Volatilization Process for separating an irradiated slug into uranium, plutonium and fission products is visualized as follows.

A. Fluorination of the slug with fluorine gas.

B. Separation of the fission products or their fluorides from UF_6 and PuF_6.

C. Separation of UF_6 from PuF_6.

D. Conversion of the UF_6 and PuF_6 to useful forms.

II. OBJECTIVES

The objective of this study was to evaluate, as far as could be done in a brief literature search, the probability of success of this process and to establish what research needed to be done to develop this process.(6) Particularly, this study was an attempt to evaluate how much of the fundamental data necessary for design (and for an accurate appraisal of the process) were at hand.

III. SUMMARY AND CONCLUSION

The probability of success of this project, from the point of view of producing pure uranium and plutonium at minimum cost, is small. The fluorination step presents severe control, heat transfer and closure problems, to which your ~~author~~ does not see even solutions that might work. The separation of the fission products from UF_6 should offer few real difficulties. No usable data could be found on the separation of UF_6 from PuF_6; data on the volatility of PuF_6 are insufficient to tell if it is more or less volatile than UF_6. The determination of the vapor pressure of PuF_6 would probably do more than any other experiment to [redacted]

[redacted]

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establish whether or not this process could ever be made to work. The conversion of UF_6 to PuF_6 to usable form should not present insoluble difficulties.

IV. DISCUSSION

A. Fluorination step.

The first step in the Volatilization Process is the conversion of the slug to UF_6, PuF_6, and the higher fluoride of the fission product elements. Experimental work on this subject is discussed(1) in K-548 "Fluorination of Uranium Pile Slugs with Elemental Fluorine" by L. A. Berry, G. H. Montillon and R. Van Winkle. In their first two runs the reaction got completely out of control, in one case melting copper cooling coils and in another melting the nickel tube. The reaction was brought under control by careful watch over temperature and flow rates, which might be difficult on a large scale. Their report reads in part "...the metal is rapidly converted to some intermediate fluoride which coats the surface and prevents further attack. The reaction then proceeds more slowly at a steady rate as this intermediate is converted to UF_6. The rate of conversion of the intermediate to UF_6 then becomes the controlling reaction. Increasing the temperature, slowly, increased the reaction rate as long as no point on the surface reaches the temperature of the melting point of the intermediate. When this occurs, the protective film of intermediate melts and flows away from the metal at this point. This continues to expose fresh metal to the fluorine. The metal at this point is very much above its activation temperature and reacts with the fluorine at an extremely high rate, which is accompanied by the liberation of tremendous quantities of heat at their localized area. This is substantiated by comparing the following heats of reaction:

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$$U + 2F_2 \longrightarrow UF_4$$

$$\Delta H = -3373 \text{ BTU per lb. of U}$$

$$UF_4 + F_2 \longrightarrow UF_6$$

$$\Delta H = -447 \text{ BTU per lb. of U}$$

This heat rapidly raises the surrounding areas of the slug surface to a temperature high enough to continue to melt the intermediate film, and the uncontrolled reaction soon spreads over the entire slug. The temperature continues to rise sharply, melting the slug and producing the final mass as observed with the first two slugs. The identity of the intermediate formed during the reactions is not known because it apparently is not stable at lower temperatures and analysis of the residue shows nothing but UF_4 and uranium. In all instances when the reaction got out of control, the average slug surface temperature always appeared to be lower than 1892°F., the melting point of UF_4. This temperature appeared to be in the range 1600°F. to 1700°F."

The reaction was initiated by heating the slug to 572°F., at which temperature the reaction started. The normal operating temperature is 1200-1400°, and the reaction gets out of hand at 1600°. This points up the difficult heat transfer and control problem. In order to give the maximum surface for the reaction, there must be a minimum amount of surface used for support and heat transfer, and hence substantially all heat transfer must be by radiation. The same radiating surface must be used for heating at the start of the run and cooling thereafter. There must be a lot of this radiating surface so that each slug may "see" nothing but cool wall. One cannot just dump a ton of slugs into a big tank and turn on the fluorine because in such a case the center slugs would "see" only hot slugs, would get hotter and hotter and finally melt. The heat transfer problem may be summed up as "Burning a cubic inch of uranium in fluorine gives three times as much heat as burning a cubic inch of coal in oxygen".

The closure problem lies in making a remotely operated, heat-proof and fluorine-proof, gas tight "door" to get the slugs into the reactor. This would have to stay gas tight for years though opened daily and subject to mechanical abuse as the slugs banged against it as they were put in the reactor.

F. Decontamination ~~xxx~~ step.

1. Non-volatile fluorides

   The fluorides of strontium, yttrium, zirconium, barium, lanthanum, cerium and the rare earths are essentially non-volatile and would be expected to be found on the walls of the reactor.

2. Non-condensible

   Xenon would not be expected to be condensed, ~~xxx~~ especially since the reactor would be run below atmospheric pressure, and the UF_6 would freeze up in the condenser.

3. Light ends

   The light ends would be tellurium hexafluoride and iodine heptafluoride. Iodine heptafluoride is the higher boiling, and hence the column must be designed for the UF_6-IF_7 separation. In order to keep the UF_6 from freezing (F.P. 64.5) we will run the column at 100°C. and 3200 mm pressure.

   The vapor pressure of iodine heptafluoride is given by the expression(3) $\log p = 8.6604 - 1602.6/T$ for the range 210 to 273°K. If we extend this equation to 373°K, $p = 23{,}120$ mm, and $\alpha = \frac{23{,}120}{3200} = 7.23$.

We require a decontamination factor of 10^7, but the mole fraction of UF_6 in the feed is essentially unity hence the equation

$$n + 1 = \frac{\log\left(\frac{xA}{xB}\right)\left(\frac{yB}{yA}\right)}{\log}$$

gives

$$n + 1 = \frac{\log 10^7}{\log 7.23} = \frac{7}{0.86} = 8.1.$$

We will thus need a minimum of eight theoretical plates, (plus one for the pot) below the feed.

If we operate the condenser at 70°C., to prevent freezing, we cannot condense anything richer in IF, than 0.21 mole fraction. Since the mole fraction of iodine (active plus inactive) is about 3.4×10^{-6} in the feed, the minimum number of plates above the feed is

$$n = \frac{\log\left(\frac{0.21}{3.4 \times 10^{-6}}\right)\left(\frac{1.0}{0.79}\right)}{\log 7.23}$$

$$= 5.7.$$

We will thus need a minimum of six theoretical plates above the feed.

4. Heavy ends

The volatile fluorides boiling above UF_6 are RuF_5 (B.P. 313°C.)(5), CbF_5 (B.P. 225°C.), TeF_4 (B.P. 97°C.) and IF_5 (B.P. 97°C.). Perhaps we will remove all the tellurium and iodine as the hexa- and hepta-fluorides in the light ends column; in that case only a few plates would be needed for the heavy ends column. If we must design for TeF_4 and IF_5, we will have an α value around 4.00, and require around 20 plates for separation.

5. Over-all

The decontamination step should work very well with two big "ifs". The first "if" deals with the valence states of tellurium and iodine. If they are removed in the light ends column as TeF_6 and IF_7, the decontamination is not difficult. If they pass through the first column as TeF_4 or IF_5, and in the boiler of the second column undergo the reactions

$$TeF_4 + UF_6 \longrightarrow TeF_6\uparrow + UF_4\downarrow$$

or

$$IF_5 + UF_6 \longrightarrow IF_7\uparrow + UF_4\downarrow$$

we will get poor decontamination with respect to these products.

The other big "if" is plate efficiency. In a normal column the condensation of a little heavy component and the vaporation of a small amount of light component bring the liquid and vapor to equilibrium. In these columns with high α's and almost infinitesimal concentration gradients in the liquid, diffusion in the liquid will be slow, and may result in low plate efficiencies. For design purposes I would allow a plate efficiency of 20% of that to be expected on a more normal system. This still leaves the columns of reasonable, though hardly desirable, size.

C. Separation of UF_6 from PuF_6

Nothing is known about the realtive volatilities of UF_6 and PuF_6, except that they are of the same order of magnitude. Brewer et al[4] reviewed the published work on the volatility of PuF_6 and finally concluded that they might as well use the accurately known values for UF_6. An experiment which would determine the relative volatility of PuF_6 with respect to UF_6 would do more than any other experiment to evaluate this process. A. Florin is said to be working on this at Los Alamos, but no reports have been received here on this.

D. Conversion of UF_6 and PuF_6 to Useful Form

1. UF_6

   UF_6 in highly purified form is a valuable form of uranium and could be fed into the K-25 process with further treatment.

2. PuF_6

   PuF_6, if separable from UF_6, should not be unreasonably difficult to convert to PuF_4 and then to the metal, by techniques now used for uranium.

V. REFERENCES

1. K-548 "Fluorination of Uranium Pile Slugs with Elemental Fluorine". L. A. Berry, G. H. Montillon and R. Van Winkle.
2. Hanford Works Technical Manual Section C, p. 120.
3. Chem. Abstracts 25:655 Iodine Heptafluoride. Otto Ruff and Rudolf Keim. Z. anorg. allgem. Chem. 193, 176-86 (1930).

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4. CN-3300 "The Higher Fluorides of Plutonium" Leo Brewer, Leroy A Bromley, Paul W. Gilles and Norman L. Lofgren. October 10, 1945.
5. K-294 "The Preparation of Ruthenium Pentafluoride and the Determination of Its Melting Point and Vapor Pressure. H. A. Bernhardt, R. L. Farrar, Jr., R. S. Gustison and S. S. Kirslis.
6. This may have been done already in KDD-84 "Preliminary Survey of Dry Fluoride Separation Processes" R. P. Levey, Jr., Memo No 17, May 2, 1949, which was not on this site.

HW--8-88

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March 12, 1951

TO: R. H. Beaton

FROM: C. Groot

The following problem came up on my recent trip to Los Alamos and because it requires an immediate answer, is submitted separately from my trip report.

The extraction columns to be used in their slag and crucible recovery system are 6" I.D. by 20 ft. long with 16 ft. packed with half-inch Raschig rings. They hope to get four theoretical stages from these columns at a nominal flow rate of 10 g.p.h. This stage height of 4 feet seemed to me impossible so I proposed that our engineering group be requested to predict the stage height in these columns. The problem may be formalized as:

Given: Six inch I.D. column with 16 feet packed with 1/2 inch Raschig rings. Fifteen per cent T.B.P. (Purex) system, E_a^o about 15. Concentration 1 to 0.0001 g/l.

To find: (1) What will be the stage height at 10 g.p.h. (2) What rate will give the minimum stage heights. (3) What is this minimum stage height.

Answer: (Informal communication from E. Merrill)

(1) Ten to fifteen feet

(2) Stage height not a function of rate

(3) Ten to fifteen feet

The answer to the problem should be checked, that it may represent an official opinion of the Separations Technology Division, and transmitted forthwith to Mr. Wayne Hazen, D. P. West, Los Alamos.

cc: ~~RB~~ Richards - FW Woodfield
OF Hill - FJ Leitz
WH Reas - C Groot

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CHLORINE TRIFLUORIDE SEPARATION PROCESS CONFERENCE

September 8 and 9, 1952

Conference Room, K-1005, K-25 Area

Probable Attendance

Division of Production

C. H. Fisher
J. M. Wardrop

Division of Research

Thomas H. Johnson
S. G. English
G. M. Kavanagh

Division of Reactor Development

D. Duffey

American Cyanamid Company

F. Allen Hall
H. A. Ohlgren

Argonne National Laboratory

J. J. Katz
C. E. Stevenson
R. C. Vogel

Brookhaven National Laboratory

O. E. Dwyer
L. G. Stang

Carbide and Carbon Chemicals Company

C. E. Ce[illegible]r
W. B. Hu[illegible]

[redacted]

[redacted]

K-25 Area

A. P. Huber
F. W. Hurd
E. J. Barber
H. A. Bernhardt
R. A. Gustison
R. H. Lafferty
D. M. Lang
W. J. Wilcox

ORNL Area

C. E. Larson
F. R. Bruce
F. L. Culler
J. R. Flannary
D. L. Foster
R. E. Leuze
E. O. Nurmi
F. L. Steahly
W. E. Unger

Y-12 Area

L. B. Emlet

E. I. du Pont de Nemours & Company

J. E. Cole
L. Peery

General Electric Company

Hanford Site

O. H. Greager
C. Groot
G. Watt

KAPL Site

A. Ahmann
J. Marsden

[illegible]

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Los Alamos Scientific Laboratory

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A. E. Florin
E. R. Jette

Chicago Operations Office

J. Burelbach

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R. E. Leed

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Agenda for

Chlorine Trifluoride Separation Process Conference

September 8 and 9, 1952

Conference Room, K-1005, K-25 Area

Monday, September 8

Morning Session, 10:00

10:00 Welcome of Visitors to K-25 and Introduction of Dr. George M. Kavanagh as Program Chairman - Dr. F. W. Hurd (K-25)

10:10 Introduction - Dr. George M. Kavanagh (AEC)

10:20 Background Discussion on Fluorination Work - Dr. E. J. Barber (K-25)

11:30 Chlorine Trifluoride Process Developments at K-25 - Mr. R. A. Gustison (K-

12:45 Lunch

Afternoon Session

1:45 Visit to K-25 Batch Pilot Plant

2:15 Preliminary Design of Pilot Plants - Mr. R. A. Gustison (K-25)

- A. Batch Pilot Plant
- B. Continuous Pilot Plant
- C. Semi Continuous Pilot Plant

3:45 Plutonium Recovery - Mr. J. R. Flannary (ORNL)

4:15 Comparison of Chlorine Trifluoride Process with Purex - Mr. R. E. Leuze (ORNL)

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Tuesday, September 9

Morning Session

9:00 Development Program Required on the Chlorine Trifluoride Process - Mr. W. E. Unger (ORNL)

10:15 Conclusions - Mr. R. A. Gustison (K-25)

10:30 Discussion of the Scope and Location of Future Development of the Process (Round table discussion led by Dr. George M. Kavanagh)

12:45 Lunch

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