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SUBJECT OR TITLE
STATUS OF THE FLUORIDE VOLATILITY PROCESSES

(Rough Draft)

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ABSTRACT

The properties of uranium, plutonium and fission product fluorides are compared with the properties of the respective nitrates. It is concluded that the greater solubility of the plutonium and fission product nitrates and their corresponding greater mobility make the nitrate process more practical on a tonnage scale. The various fluoride processes are described and evaluated.

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STATUS OF THE FLUORIDE VOLATILITY PROCESSES

INTRODUCTION

Hanford irradiated slugs have hitherto been separated into uranium, plutonium, and fission products by the use of nitric acid-water systems. They can also be so separated by use of volatile fluoride processes.

A meeting was held at K-25 on September 8 and 9, 1952, to discuss these processes. The minutes of this meeting are given in ORO-23517, "Report of Chlorine Trifluoride Separation Processes Conference", R. E. Leed and E. E. Sinclair, 9-26-52. The objectives of this report are (1) to compare the nitrate and fluoride systems, and (2) to describe the less well known fluoride systems.

SUMMARY

1. A comparison of processes involving nitrate systems and processes involving fluoride systems favors the nitrate system, because the soluble plutonium and fission product nitrates can be moved and processed in aqueous solution, whereas the insoluble, refractory plutonium and fission product fluorides must either be handled as solids or converted to nitrates and so processed.

2. The chemistry of the volatile fluoride processes is fairly well understood and demonstrated; the process can be made to work.

3. The engineering development of the processes is barely begun, and will be difficult and expensive. The biggest problems arise in getting the plutonium and fission products out of the dissolver, and in subsequent plutonium processing.

4. It is recommended that the effort of the Hanford Works be confined to following and evaluating the process developments at other sites.

DISCUSSION

A. Comparison of Fluoride and Nitrate Systems

Uranium has two compounds with properties rarely found in inorganic compounds. The nitrate is soluble in organic solvents, and may be purified by solvent extraction systems. The fluoride is volatile, and may be purified by distillation. Uranium is highly mobile in either of these systems.

Plutonium has organic soluble (IV and VI) nitrates, and an organic insoluble(III) nitrate. These plutonium oxidation states are easily converted from one to the other, and are all easily transported in aqueous solution. Thus, a solvent extraction system can be used for purifying uranium and plutonium together, and for separating them from each other, on a tonnage basis.

Plutonium has a volatile (VI) fluoride, and non-volatile (III and IV) fluorides. The volatile plutonium(VI) fluoride is not sufficiently stable to form the basis of a process, and the non-volatile fluorides are refractory, insoluble compounds. Since the plutonium fluorides have these unfavorable properties for processing, and are so difficult to move, no process for purifying plutonium based on fluoride systems has much promise.

The fission products form nitrates of varying organic solubility, and special treatment is needed to eliminate the more organic soluble ones in solvent extraction systems. Likewise, there are fission product fluorides of varying volatility, but distillation procedures are so effective that a single distillation with highly effective equipment completely purifies uranium from fission products. However, many of these fission product fluorides are insoluble, refractory compounds, and moving these creates grave difficulties.

These immobile fission product fluorides and the immobile plutonium compounds can be converted to soluble nitrates by treatment with aqueous aluminum nitrate solution, and these nitrates separated by solvent extraction techniques. Most of the work thus far completed on the volatile fluoride processes contemplates moving the fission products and plutonium as the nitrates.

With present know-how, these processes cannot be made safe and cannot give large productions per unit, and hence, are too expensive to complete with solvent extraction. Speculations have been made, and some work done on processes in which the plutonium and fission products are moved as a slurry. It does not

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suffice to merely transfer the plutonium and fission product fluorides by this slurrying technique; it is also necessary to cool the materials. The fission products from one ton of uranium slugs generate some three kilowatts of heat, and hence can never be isolated. Thus, a dual slurrying technique is necessary, the plutonium and fission product fluorides must first be removed from the dissolver by some medium relevant to dissolving, said medium being unstable toward water, and then transferred to a second medium stable to water in which the plutonium and fission product fluorides can be brought to the aqueous system. This proposal is described more fully in Section 2.22 of this report. The processes are compared in Table I.

B. Comparison of the Various Fluoride Systems

1. Gas Phase Fluorination

The direct fluorination of slugs is a difficult and dangerous operation[1]. A coating of a lower fluoride forms, and the reaction of this coating with fluorine to form uranium hexafluoride is rate determining. If a hot spot forms, the coating may melt, giving a very rapid reaction rate that melts the uranium and sometimes the apparatus. Heat transfer during fluorination is largely by radiation. This makes the reactor unit in this system the single slug. If one hot slug can "see" another hot slug, it will develop a hot spot. Hence, there must be controlled temperature partitions between the slugs, leading to impossibly complex equipment on a tonnage basis.

The plutonium will not stay put during the fluorination. It will neither all volatilize, nor all stay behind.[2] The plutonium moves as the plutonium(VI) fluoride.

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1) K-548 "Fluorination of Uranium Pile Slugs With Elemental Fluorine", by L. A. Barry, C. H. Montillon and R. Van Winkle, 12-30-49.

2) ORNL-980 "Dry Fluoride Process Status Report", R. K. Lauze, 3-27-51.

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TABLE I

COMPARISON OF AQUEOUS AND FLUORIDE SEPARATIONS PROCESSES

Aqueous Processes	Fluoride Processes
Plutonium moves as solution.	Plutonium moves as a solid.
Fission products move as solution.	Fission products move largely as solids.
Aqueous processes safer because:	Fluoride processes dangerous because:
1. Can operate below atmospheric pressure.	1. Must operate above 9 p.s.i.g. and some at 125 p.s.i.g.
2. Can operate down to 0°C .	2. Must operate above triple point of UF_6, 64°C.
3. Chemicals do not react with cooling water or steam.	3. Chemicals react explosively with water or steam.
4. Cold chemicals mostly harmless, some give surface burns. All harmless if neutralized.	4. Cold chemicals highly toxic even when neutralized. Give dangerous burns. Incendiary.
5. Vapor above process solution harmless.	5. Vapors attack metal, glass, concrete, and cause very high maintainance costs. Also highly toxic.
Processes demonstrated by $100,000,000 worth of experience.	$20,000,000 development program required.
Uranium produced in the form of uranyl nitrate, a useless form. Requires expensive processing to UF_6 .	Uranium produced in form of hexafluoride, a useful form.
Decontamination requires head or tail-end treatment for certain fission products.	No head or tail-end treatment needed for ClF_3 processes to decontaminate uranium. Probably none needed for BrF_3 process.
No single cycle process demonstrated. Lab results indicate single cycle may work.	Single cycle process demonstrated for ClF_3 process, for uranium stream.

Florine of Los Alamos showed at the meeting that plutonium(VI) fluoride is an endothermic compound: that 1% plutonium(VI) fluoride was in equilibrium with solid plutonium(?) fluoride at 600°C, and 0.01% at 100°C. Thus at the high temperatures used in gas phase fluorination, considerable, but not complete formation of volatile plutonium(VI) fluoride may be expected.

The fission products also divide between the gas phase and the reactor. As it stands, the process is not attractive, and there is no obvious way to improve it. There is little or no work being performed on this process.

2. Liquid Phase Fluorination

2.1 General Considerations

Liquid phase fluorination is much superior to gas phase fluorination. The heat transfer is much better, and thus the batch size can be increased up to the limits improved by critical mass consideration. Reactions proceed at much lower temperature. Plutonium and fission products are much better separated from the uranium hexafluoride, the low temperature and low fluorine activities keeping the plutonium in the non-volatile (III) state.

There is one disadvantage of the liquid phase system; namely, the systems so far tested must be operated under pressure to get reasonable reaction rates. To get enough fluorine in the liquid phase, the volatile interhalogens, bromine trifluoride and chlorine trifluoride, have been used. Bromine trifluoride is the least volatile of the interhalogens and chlorine trifluoride is the cheapest.

2.2 Chlorine Trifluoride Process (CTF Process)

2.21 Batch Process

The Chlorine Trifluoride Batch Process is adequately described and discussed in K-519[3] and HW-24054[4]. The dissolver cycle consists

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3) K-519, "Pilot Plant Studies of the Recovery and Decontamination of Hanford Irradiated Uranium by the Chlorine Trifluoride (CTF) Process" R. A. Gustison 6-18-52.

4) HW-24054, "Fluoride Volatility Process" [illegible] Group, [illegible]-52

of jacket removal, dissolving of the slugs in hydrogen fluoride-chlorine trifluoride mixture, distillation of uranium hexafluoride and the solvent, and dissolving out the plutonium trifluoride with an aluminum nitrate solution.

This cycle is excessively long. Even at 125 p.s.i.g. and 80°C on the dissolving step, the probable time cycle is about 48 hours. The size of the charge is limited by critical mass considerations to about one-half ton of uranium; thus a single dissolver can handle only a quarter ton per day and 40 dissolvers are required for a ten ton per day plant. Also, there is excessive hazard of mixing water and chlorine trifluoride through defective valves. In the present state of the art, it is unsafe to pipe water and chlorine trifluoride to the same vessel, for the valves will in time leak or fail entirely. Hence, the dissolving step is too expensive and not safe enough for use at the Hanford Works until considerable more development work can be performed.

In consideration of the processing of the uranium stream only, the process looks more attractive. In the last run described in K-519, the product from the first distillation was distilled in a 50 theoretical plate column at 7.5 to 1 reflux to product ratio. This step was highly successful, with recovery of 99+% and purity meeting K-25 specifications.

The decontamination achieved through this double distillation, which included vapor filtration, was about 10^7. This is the most effective separation ever obtained by a single type of separation, and it could probably be done on a "once through a single column" basis. This separation is much cheaper and more effective than any precipitation or solvent extraction process so far studied.

2.22 Continuous Chlorine Trifluoride Processes

The low unit productivity and danger of explosion from mixing chlorine trifluoride and aqueous solutions can be alleviated by a continuous process, such as that proposed by R. A. Gustison of K-25 and described in ORO-23517, Figures 7, 8 and 9. In this flowsheet, the dissolver does nothing but dissolve slugs. This has the advantage that aqueous solutions and chlorine trifluoride cannot mix because they will not be piped to the same vessel. Also, since the dissolver is to be fed continuously, the dissolver will always be full, and not be wasting its time dissolving the remnants of a charge. These changes increase dissolvers capacity to about one ton per day per dissolver.

The jackets are removed by standard Hanford techniques, dried, and transferred intermittantly but frequently through a lock into the dissolver. The dissolver will operate at 80°C and 125 p.s.i.g., with a solvent consisting of 0.3 moles chlorine trifluoride per mole hydrogen fluoride. The hydrogen fluoride is a good moderater, hence nuclear safety is obtained by keeping the column down to six inched I.D. The by-product chlorine monofluoride gas is regenerated to chlorine trifluoride with fluorine, the inert gasses going to a gaseous waste disposal system.

The plutonium and non-volatile fission products are to be removed from the dissolver continuously as a suspension in a uranium hexafluoride-chlorine trifluoride-hydrogen fluoride mixture. This suspension is to be distilled, removing the fluorinating mixture overhead. It is then to be redistilled, removing pure uranium hexafluoride overhead. In order to maintain the mobility of the plutonium and fission product fluorides, a fluorocarbon vehicle is to be introduced in the redistillation section, as in extractive distillation. The suspension in the fluorocarbon is to be stripped with an aluminum nitrate solution putting the plutonium and most of the fission into aqueous solution. The plutonium can then be recovered by Purex techniques.

This proposal is only in the idea stage and, thus, has not been tested. Among the chemical and engineering problems to be solved are: (1) design of the locking and transfer mechanism for the transfer of dejacketed slugs to the chlorine trifluoride dissolver; (2) continuously adding fluorine to [illegible]

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the reactor at 125 p.s.i.g., (3) design of an economical gaseous waste disposal system, (4) feasibility of transferring a slurry of solid fluorides in uranium hexafluoride or in a fluorocarbon, (5) transfer of the suspended fluorides from the hexafluoride to the fluorocarbon, (6) design of liquid level control and pressure reducing systems for this system, (7) stripping the slurry of insolubles from the fluorocarbon with aqueous aluminum nitrate and (8) the solvent extraction properties of the resulting aluminum nitrate solution.

At this meeting, the work proposed for the next year on the CTF Process is largely paper work such as lay out and economic studies. These may answer the question "If it works, will it pay?", but not "Will it work?" These studies are intended mainly to determine if pilot plant work is justified.

2.3 Bromine Trifluoride Process

2.31 Laboratory Work

The literature background for this process has been well reviewed.[5] The laboratory work[5] has shown (1) that any desired rate of dissolution may be obtained by use of temperature and pressure, or bromine or antimony pentafluoride catalysts and (2) that at high rates, appreciable quantities of plutonium are made volatile. The best compromise may be the conditions of run 20, 140°C and 44 p.s.i.g., under which conditions the volatile plutonium was below economic recovery (<u>ca.</u> 0.05%). Dissolving time under these conditions was about 26 hours.

Decontamination has not been proven. The best run, 21, had a product of 0.08 mv/gram gamma activity, compared to 0.07 mv/gram in natural

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5) ANL-4709, "The Organic Fluoride Volatility Process Status of December 31, 1951", H. H. Hyman and J. J. Katz, 2-10-52.

uranium and 0.21 mv/gram allowed. However, this feed for this run was only one per cent of Hanford level, so the required decontamination factor has not yet been obtained. Also, the distillation was poor in other ways; only 22% of the uranium in the feed was in the product, and this product was only 65% uranium hexafluoride.

The chief radiochemical impurity in this system is tellurium. Tellurium can be removed, at least in a synthetic system.[6] The chief gross contaminant in the product uranium hexafluoride is bromine pentafluoride (b.p. 42°C). Supercooled liquid uranium hexafluoride has a vapor pressure of one atmosphere at 52°C, so it may be seen that the separation is not easy.

2.32 Scale-Up Problem

The problem in scaling up the Bromine Trifluoride Process is mainly the problem of getting the plutonium and fission products out of the dissolver, away from bromine trifluoride, and into aqueous solution. The solutions so far proposed are:

(1) Dissolve the plutonium trifluoride in bromine trifluoride. This fails on low solubility, i.e., 0.003 to 0.03 g/l for plutonium trifluoride and less for some fission products.

(2) Convert the plutonium trifluoride to volatile plutonium hexafluoride. This fails because of low stability of plutonium hexafluoride and because it does not remove the fission product from the reactor.

(3) Remove the plutonium and fission products as a slurry in bromine trifluoride, distill off the bromine trifluoride using a disposable can for a boiler, and transfer this can to an aqueous dissolver. This has

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6) BNL-174 "A Continuous Flow Pilot Plant For The Separations of Bromine-Fluorine Compounds and Light And Fission Products Fluorides From Uranium Hexafluoride", W. R. Page, March 1952.

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not been tested but has the problems of (a) slurrying the plutonium and fission products, (b) getting enough heat transfer surface in a small can, (c) contamination control during transfer, and (d) heat generated by the fission products.

(4) Double slurry technique as proposed for the Continuous Chlorine Trifluoride Process, with the same problems as that process.

None of these techniques have been demonstrated to be satisfactory, and none appear to your author to be likely to be satisfactory. A continuous dissolver is under design at Brookhaven, and a decision on this problem may be reached from that work.

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