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THE SEPARATION OF PLUTONIUM ISOTOPES

INTRODUCTION

This report summarizes the results of a brief literature survey made to determine the chemical feasibility of preparing a fluid plutonium compound for isotope separation. The range of interest covers compounds useful in processes such as the Calutron, thermal diffusion, gaseous diffusion, centrifugation, etc.

Plutonium-240 is formed by action of neutrons on plutonium-239, and hence the relative amount of 240 increases linearly with the exposure of the uranium. The 240 content of the plutonium can be controlled by 1) the present technique of limiting pile exposures and recycling the uranium, 2) "burning out" the 240 by transmutation, or 3) removing the plutonium-240 from the 239, the subject of this report. The process sought would reduce the 240 content of the plutonium to 1% or less, losing not more than 1% of the 239.

The separation of plutonium isotopes has been previously reviewed in an interesting document WASH-100.

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SUMMARY AND CONCLUSION

The separation of plutonium-239 and plutonium-240 is likely to be difficult due to the small difference in mass. The ratio $\frac{\Delta m}{m}$ (.004) is so small as to indicate that differences in reaction and diffusion rates, as well as equilibrium constants, will be minute if measurable at all.

The compounds most likely to be useful are 1) the hexafluoride, useful in a centrifuge system but not stable enough for a gaseous diffusion system; 2) the nitrate, potentially useful in a solvent extraction or solid-liquid exchange system; and 3) the trichloride, useful in a Calutron system. No other known compounds appear useful at present.

The Hanford Atomic Products Operation could immediately apply skilled manpower and know-how upon the solvent extraction system. Envisaged is a long scrub section employing high reflux and a large number of stages. The degree of separation obtainable is unknown.

DISCUSSION

A. Plutonium Hexafluoride

1. History

In November, 1942, it was already established that (2)

a. "The higher fluoride of element 94 is unstable in the absence of fluorine. It slowly decomposes to PuF_4....."

b. "The higher fluoride of element 94 has a vapor pressure roughly of the same order of magnitude as UF_6."

Further experiments at Chicago (3, 4) confirmed this, and experiments at Ames (5) showed that "the higher fluoride has a negative heat of formation and is stable only at high temperatures in an atmosphere of F_2....." This volatile plutonium has also been observed at Oak Ridge (6) and Los Alamos (7, 8).

2. Preparation

Since plutonium hexafluoride is unstable at room temperature, it must be made at high temperatures and cooled rapidly to a temperature so low that its rate of decomposition is low. The apparatus described by Florin (8) is a convenient method for doing this on a laboratory scale.

In the words of the author (8), "The reactor assembly consists of a vertical brass tube, 5" high and 1 1/2" diameter, with a brass bottom silver soldered in place and a Teflon gasketed brass cap held on by six screws threaded into a flange on the reactor. Inside the reactor is a small resistance furnace consisting of 10 turns of 24 gauge nickel wire wound in a helical groove on a calcium fluoride tube 1" high, 5/8" O.D., and 13/32" I.D. A nickel crucible, 1 1/4" high, 3/8" O.D., and 0.035" wall thickness, fits inside the furnace and is used to hold the material to be fluorinated. A suitable size charge is 0.5 g. of plutonium tetrafluoride.

"During a fluorination run the reactor is immersed in a dry ice-trichloroethylene bath, fluorine is admitted to a pressure of one atmosphere, and the furnace is heated electrically to a temperature of about 700°. The cold walls and hot furnace presumably give rise to strong convection currents which provide circulation of the fluorine over the plutonium tetrafluoride in the crucible. The plutonium hexafluoride formed in the fluorination reaction is condensed out on the cold reactor wall, so that the reaction keeps going on a single charge of fluorine plus small amounts to compensate for that used up in the reaction. A production rate of approximately 40 milligrams of plutonium hexafluoride per hour has been realized in practice.

"To reach a temperature of 700°[C]in the crucible, it is necessary to have the nickel wire furnace at a temperature considerably higher than 700°. At this higher temperature the nickel wire is corroded by fluorine at an appreciable rate, and it was found necessary to replace the furnace after 15 hours' use. Somewhat heavier nickel wire than is now being used would no doubt extend the life of the furnace..........To date approximately 1 g. of plutonium hexafluoride has been prepared in this reactor........"

The corrosion difficulties referred to might be reduced by making the crucible the heating element, either by induction furnace techniques (with the coil inside the shell), or by using it as a resistance element in a high ampere, low voltage circuit.

3. Properties (8)

The triple point of plutonium hexafluoride is 50.7°C and 511 mm. The normal boiling point is 62.3°C, and the heat of vaporization 7.4 K cal. The vapor pressure of the solid is 17.3 mm. at 0°.

Plutonium hexafluoride decomposes by three mechanisms. One is a radiation induced decomposition, occurring at the rate of 1.3% per day (8) and is independent of temperature. Another is a dissociation according to the equation

$$(1) \quad PuF_6 \longrightarrow PuF_4 + F_2.$$

The rate is too slow to be measured at 50°C but is essentially complete in 15 minutes at 80°C. Finally, there is rapid fluorination of water vapor or any surface that can be fluorinated.

The equilibrium for the reaction (1) lies far to the right. Figures quoted (9) are that "1% plutonium(VI) fluoride [in fluorine] was in equilibrium with solid plutonium(?) fluoride at 600°C and 0.01% at 100°C".

4. Isotopic Separations

Plutonium hexafluoride is probably not sufficiently stable to use in a gaseous diffusion plant. With the very large number of stages and high reflux ratio, the residence time might well be a few months, during which time a large fraction of the hexafluoride might have decomposed. The products of this decomposition would tend to plug the barriers.

It might be better to employ a series of centrifuges. The separation per stage might be as much as 1.018 (23), and it is possible to get several stages in one centrifuge. Hence, a few hundred centrifuges in series might do the job. Centrifuges have their own problem; maintenance will be high, and occasionally a corrosion-weakened centrifuge will explode.

Plutonium hexafluoride has not been considered for use in a Calutron. Apparently, ionization efficiency is poor, and there are difficulties in trapping the volatile material.

B. Plutonium IV Nitrate

Plutonium IV nitrate has never been isolated as such, but its aqueous solution is probably the most convenient form in which to handle plutonium. It is highly soluble both in aqueous and some organic solutions. It is quite stable.

The separations process could be either an electromigration or a solvent extraction process. The electromigration process is not favored, because plutonium IV exists in several species, and the process would separate species rather than isotopes. Also, the experience with uranium (11) is discouraging.

The solvent extraction system is visualized as an overgrown Recuplex (10) process, operating in a very long, pump-mix mixer-settler bank. It would use tributyl phosphate as a solvent. There is no evidence to show what separation per stage might be obtained. The effect over a large number of stages could be tested with reasonable effort, and increasing the number of stages is easy.

The advantages of a solvent extraction system are the advantages of the present gaseous diffusion operation, smooth automatic transfer of material between stages, low mechanical stresses, and ease in making sure that the material "stays put". Also, there need be no feed preparation step; the plutonium will already be in the form of nitrate. The disadvantages come largely from the small separation to be expected per stage, which may lead to a high reflux ratio. This may require high thruputs on each stage. The permissible holdup on each stage is limited by critical mass consideration, especially since the solvents are good neutron moderators. This could easily require parallel lines to accommodate the thruput of the Hanford Atomic Products Operation.

C. Plutonium Trichloride

Plutonium trichloride is a high melting solid (m.p. 760°C)(12), and has a low vapor pressure. For the solid

$$\log_{10} p_{mm} = 12.726 - \frac{15,910}{T}$$

where T is in degrees Kelvin. Thus, it will have a vapor pressure of 10^{-4} mm. at 677°C. It is of interest in this report, because it is the compound selected for use in the Calutron (13, 14).

It is difficult to find much information on Calutron operation on this site. The most extensive information came in conversation with Dr. Kinderman and Dr. Bennett. In the Calutron process, as operated in 1944, UCl_4 was used as the feed material.

It was volatilized and ionized in a special furnace to a single (or possibly double) charged uranium ion (U+ or U++). These ions went through a slit and through a large tube to collector plates. Feed was charged at about 500 grams per batch, and it took about 10 days to run off a batch. Not more than 10% of the charge hit the collector plate. Apparently, many kinds of ions were formed, and only one kind could get to the collector plates. The other kinds deposited on the walls of the tube, in a mixture of metal, oxides, oxychlorides, lower chlorides, and probable other compounds. This mixture had to be dissolved, scraped, or brushed off the walls of the tube, and chemically reprocessed. There was a tremendous amount of hand labor in loading the units, operating each unit, disassembling the unit, cleaning the unit, and reassembling it vacuum tight. The prospect of doing this hand work with plutonium is unattractive.

The Oak Ridge National Laboratory Electromagnetic Research Division (13) was preparing to separate plutonium isotopes on a gram scale in 1951 (14) and 1952 (15). The present state of this work is unknown. Separation of extremely small quantities of the isotopes for analytical purposes has been done at Argonne (16, 17).

D. Other Compounds

An effort was made to find other compounds which might be useful in an isotope separations process. A study of CN-3551 (18) showed that the acetonylacetonate was slightly volatile (1 mm. at 170°C), but it is not believed that a successful process could be based on this, especially in view of the poor results obtained on uranium pentaethoxide and uranium pentapropoxide (19). There was some hope that trimethylplutonium might be made and that it would be volatile, analogous to the reported triethylscandium and triethylyttrium (2). However, further search (21, 22) cast grave doubt on the work sited above, and it is doubtful if plutonium trimethyl can be made. It is doubtful if compounds much better for isotope separation than the hexafluoride, nitrate, and chloride exist.

EXPERIENCE WITH URANIUM ISOTOPES

Considerable work at Columbia on gas-liquid, liquid-liquid, gas-solid, liquid-solid systems was performed (24). No satisfactory system was found. Workers at Y-12 were able to demonstrate slight enrichment by exchange between a two-phase system of aqueous tetravalent uranium and an organic complex, and by exchange between U^{+4}, UO_2^{+2} ionic species. A separation factor of 1.001 was reported (25). A bibliography of project literature on separations methods has appeared (26).

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