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TRIP REPORT - FEBRUARY 6-13, 1961

by

B. M. Johnson, Jr. - E. E. Voiland

Chemical Research and Development
Hanford Laboratories Operation

March 3, 1961

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HANFORD ATOMIC PRODUCTS OPERATION
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TRIP REPORT - FEBRUARY 6-13, 1961

by

B. M. Johnson, Jr. - E. E. Voiland

During the period the Argonne National Laboratory, Oak Ridge National Laboratory, University of Virginia, General Electric GEL, and General Electric APED laboratories were visited. The primary purpose of the trip was to obtain information on the chemistry and technology of plutonium hexafluoride and to become acquainted with new developments in gas centrifugation.

ARGONNE NATIONAL LABORATORY
PuF_6 Chemistry - R. Vogel, J. Fisher, L. Trevorrow

The chemical development work on PuF_6 at Argonne is under the direction of Jack Fisher and is being done by a group of three scientific personnel and four technicians. The work deals primarily with the stability of PuF_6 and the unique problems associated with its storage, handling, and transport.

Perhaps their most important result to date is establishment of the following rate law governing the decomposition of PuF_6:

$$\frac{-dp}{dt} = k_1 p + k_o a$$

where k_1 is the rate constant for the homogeneous gas phase decomposition. k_o is the constant for the heterogeneous reaction which varies with the temperature and the nature of the surface and "a" is the surface-to-volume ratio of the container. It was found that k_o increased with increasing PuF_4 deposited. With smooth reactor walls, k_o reached a steady state value, whereas in vessels packed with nickel wool, no such steady state condition was found during the duration of the experiment apparently because of inability to saturate the surface.

Recent experiments have led to the following values for these constants in a smooth-walled reaction vessel of 100 cm^2 surface and a surface to volume ratio of 0.86 cm^{-1}.

Temperature °C	k_1 (min^{-1})	$k_o a^*$
30 (calc.)	1.0×10^{-7}	4.6×10^{-5}
75 (calc.)	7.6×10^{-6}	1.5×10^{-3}
140	7.2×10^{-4}	5.6×10^{-2}
161	25×10^{-4}	11.2×10^{-2}
173	42×10^{-4}	24.4×10^{-2}
E_{act}	20 kcal/mole	16 kcal/mole

* k_o is in units of cm Hg-cm-min^{-1}

They believe that extrapolation of these values to the temperatures of interest (30-80 C) can be used to provide approximate decomposition rates. Such a calculation indicates the rate of decomposition at 75 C and 1000 mm pressure is about nine times the gas phase decomposition rate due to alpha radiation (0.35 percent per day). At 30°C and 100 mm the calculated rate is less than twice the alpha decomposition rate. The rate in the condensed phase is about 2 percent per day.

The equilibrium constants for the reaction

$$PuF_4 + F_2 \rightleftharpoons PuF_6$$

were re-determined over the temperature range 100 to 600°C and were found to be in agreement with Florin[1] at the higher temperatures but at lower temperatures were considerably high and coincided with an extrapolation of the high temperature data. The standard free energy change is expressed by the following expression:

$$\Delta F_o = 6.09 \times 10^3 + 1.26\ T(^oK)\ \text{cal/mole}.$$

The experimentally determined values of $k_p = P_{PuF_6}/P_{F_2}$ are as follows:

T°C =	100	300	400	500	600
k_p =	0.0005	0.0027	0.005	0.01	0.017

Plutonium hexafluoride is normally prepared by passage of fluorine over PuF_4 contained in a nickel boat at 550 C. At lower temperatures, the equilibrium is less favorable and at higher temperature corrosion becomes a problem. Direct fluorination of PuO_2 can also be done. The reaction is presumed to go rapidly to a PuF_4 intermediate and more slowly to PuF_6. The rate of the latter reaction was estimated at 85 mg PuF_4/cm^2hr, quite low in comparison with the values reported for fluorination of Rocky Flats and Los Alamos PuF_4, 420 and 650 mg PuF_4/cm^2hr respectively.

Purification of PuF_6 from HF, F_2, and CF_4 is accomplished by evacuation of the higher components at -78°C.

Vapor pressure data for PuF_6 has been published.[2]

The PuF_4 produced by thermal decomposition is considerably more dense ($\rho = 4.2$) than that produced by radiation decomposition ($\rho = 0.3$). It was observed that PuF_4 formed at low temperature was finer in particle size and was thought to be chemically more reactive.

Recently, data have been obtained on the gamma and neutron emission from samples of PuF_4 contained in polyethylene bottles. Neutron flux was studied as a function of PuF_4 mass. Representative values at 10 cm are approximately:

Sample Size	Flux n/cm^{-2} sec
77 g	80
220 g	320

(1) J. I. N. C., 2, 368 (1956).

(2) J. I. N. C., 11, 104 (1959).

Currently the PuF_6 work is being performed in 2 gloved hoods. These hoods consist of 3 modular sections which are approximately 3 1/2'x 3 1/2'x 5' high. A novel feature of these boxes is the method of attaching the glass panels through the use of an extruded rubber molding used in installation of airplane windows. The details of these boxes are covered in Paper No. 42-3 of the Eighth Hot Laboratory and Equipment Conference.

The cost of a double module box installed was estimated at $37 to $42 per cubic foot for glass and coated carbon steel construction.

The equipment used in the handling of PuF_6 is prefluorinated nickel. Techniques used at Oak Ridge in the handling of UF_6 have been adapted for use in this work. Information on storing and distributing fluorine gas was obtained, as well as on low-head pumping of these highly reactive gases.

Direct Reduction of Oxide - R. Steuneburg

Considerable work has been done on the reduction of UO_2 using Zn-5% Mg and using a flux consisting of 47.5 m/o $MgCl_2$-47.5 m/o MCl-5 m/o MgF_2. The rate of reduction varied with M, decreasing in the series LiCl> NaCl> KCl> RbCl. The extent of reduction was thought to be essentially complete in all cases. The same order with increasing rate was observed in the alkaline earths but with $SrCl_2$ and $BaCl_2$, reduction was incomplete. There was a difference of opinion as to whether this phenomenon was due to a displaced equilibrium or grossly inferior kinetics.

Only one PuO_2 reduction has been done with Zn-5 w/o Mg and the 47.5 w/o $MgCl_2$-47.5 w/o $CaCl_2$-5 w/o MgF_2 system. Reduction was essentially complete in 30 minutes, resulting in a 0.54 w/o Pu alloy.

Steunenberg believes as much as 15 w/o MgO can be accommodated (as a slurry) by the flux and that metal 5 w/o in Pu can be prepared at high yield. A temperature of 675 to 800 C for UO_2 has been found to be acceptable.

OAK RIDGE GASEOUS DIFFUSION PLANT

Centrifuge - G. A. Garrett, and W. E. McMahon ORGO

Because of the unsettled nature of the classification of gas centrifuge work and some uncertainty as to Hanford's interests, only access to centrifuge technology on an unclassified basis was permitted. This covers work up to and through the studies of G. Zippe of the University of Virginia (most of which appears in unclassified reports and journal articles). No access to current investigations was permitted, although there apparently has not been a great deal in the way of tangible results accomplished.

The cost figures of K1368 are high and on the basis of the Zippe centrifuge concept, have been revised downward. Garrett could not give us the revised figures but stated that the costs were not reduced by a whole order of magnitude.

On the basis of calculations, the separative capacity was found to increase less rapidly with increasing velocity than predicted by the fourth power dependency term of the expression. The reason for this was

not made completely clear but was apparently due to changes in flow pattern occurring when the high centrifugal field forced the material to the periphery. Garrett did not believe that center feeding was intrinsically responsible for the low efficiency of the Zippe design; in fact, center feeding eliminates the "circular flow" problem associated with the dual exit and entry ports of earlier designs.

With respect to the separation of plutonium isotopes, Garrett was of the opinion that "if you had a centrifuge, that would be the way to do it (separate isotopes)". He felt that there is little reason to believe a practical centrifuge is immediately in sight. OR is building a small assembly of centrifuges for cascade studies, but the number was withheld.

Another facet of the centrifuge program is a theoretical hydrodynamic study of the flow problem which has recently been initiated under the direction of Prof. Onsager of Yale University. It was not clear whether this effort was under Oak Ridge jurisdiction or was a completely separate phase of the centrifuge program.

OAK RIDGE NATIONAL LABORATORY
Fluoride Volatility - G. Cathers

Oak Ridge National Laboratory has no direct interest in PuF_6 and has no research program involving its chemistry. Their work is aimed at the processing of naval reactor cores and involves only highly enriched uranium bearing fuels.

The process is essentially that previously described. It consists of conversion of the uranium and zirconium of the fuel element to fluoride salts in a sodium fluoride-lithium fluoride melt by the action of HF, removal as UF_6 by reaction with fluorine, and purification by absorption-desorption steps with NaF beds. The principal effort is on engineering development, materials development and pilot plant testing. The most serious problem is apparently the carry-over of submicron sized particles of metals (Ni, Cr, Fe) produced by the reducing action of zirconium in the dissolution step. Inor 8 gives hope of being an adequate material but further corrosion testing with BMI is scheduled.

Oak Ridge plans no work aimed at application of the Fluoride Volatility Process toward Pu recovery. They have done very limited small-scale studies from which they learned (1) that Pu is volatilized from the dissolution bath, and (2) that PuF_6 is adsorbed by lithium fluoride beds under conditions that UF_6 is not. They indicated that they would rely on Argonne's work for any information related to the transport of PuF_6.

Their future work is aimed at (1) application of FVP to $BeO-UO_2$ and ZrO_2-UO_2 materials, and (2) application to the fused salt single-region ThF_4 bearing reactor.

UNIVERSITY OF VIRGINIA
Centrifuge - J. W. Beams, A. P. Kuhlthau, R. A. Lowry - U.V., - W. E. McMahon ORO

Discussions at the University of Virginia were also on an unclassified basis. These were primarily on the topics of flow conditions and efficiency of the various centrifuge designs. No specific reasons were given for the seemingly inherent low efficiency of the Zippe design (approximately 30%) as compared

with the Groth machines (about 80% efficient) but it was their opinion that the scoop arrangement was responsible, as the result of introducing disturbances in the flow pattern. Kuhlthau commented that the Zippe machine was not the "latest word" in machine design but that Zippe had very cleverly incorporated a number of previously recognized concepts into a single design. He believed that these same concepts could be applied to other designs which would retain the advantages of simplicity and low power consumption but would have greater efficiency.

A better appreciation for the behavior of a third component gas, e.g. fluorine, in the centrifuge was obtained and it was pointed out that the Germans believed it was beneficial to add a foreign gas to the system to stabilize the flow pattern. Consequently, it is felt that if it should prove to be advantageous to have fluorine present with the PuF_6 in the centrifuge, this would not be detrimental to the isotope separation.

The program at the University of Virginia includes three staff members and about five graduate students from the schools of mechanical and aeronautical engineering and the school of physics. Professor Beams is no longer formally associated with the program, but does take an active interest and provides consultation to the group. They were sorry not to be in a position to show us their work but they were enthusiastic and appeared optimistic of the potential for progress in this field.

General Engineering Laboratory - A. Carson and D. Munster

GEL became involved in the centrifuge program as the result of an AEC request that Karl Cohen of APED evaluate the centrifuge situation. Both General Electric and Union Carbide were asked to submit proposals for a program of centrifuge development. The G. E. program was divided into five general areas:

(a) Testing of a machine capable of 350 meters/sec. peripheral velocity with an emphasis on maximizing its efficiency.

(b) Operation of 25 to 30 units in a cascade.

(c) Theoretical hydrodynamic studies of the flow pattern within a centrifuge.

(d) Development of an advanced machine operating at a speed of about 450 m/s and having high efficiency and throughput.

(e) Program of advanced applied mechanics to develop materials, bearings, etc.

The AEC supervision of the centrifuge work was subsequently shifted from the division of research to the division of production at which time the AEC decided to divide the work into three headings:

(a) Cascade development using an existing design for the centrifuge.

(b) Theoretical hydrodynamic studies.

(c) Advanced machine design.

Area one was allocated to the development group at the Oak Ridge Gaseous Diffusion Plant, while area two was placed under the leadership of Professor Onsager of Yale, as previously noted. It was decided that the Commission should ask for competitive bids on the third phase rather than handing the work to G. E. Consequently, G. E., along with five other companies, is resubmitting a proposal to the commission for this third phase of the program. The AEC will probably review these proposals within the next several months.

The group at GEL has had no experience with actual centrifuges but had made an exhaustive study of their design and operating characteristics in order to be able to evaluate their potential for isotope separation.

Atomic Power Equipment Department, San Jose - Karl Cohen

Discussions with Karl Cohen dealt primarily with the feasibility of Pu isotope separation by centrifugation. Along these latter lines several points were of interest. He felt that with real concerted effort there was real reason to be optimistic that a suitable centrifuge could be developed that would be relatively efficient,(e.g., 60-75%) easily maintained, (Zippe has run machines at 400m/s peripheral speed for 11,000 hours continuous) and sufficiently efficient to bring the cost of uranium separative work in relative competition with that from the gaseous diffusion plant. Feasibility studies for Pu isotope separation should probably be based upon a supercritical machine which would maximize the separative capacity per unit, thereby minimizing the required handling of PuF_6 between units and the total hold-up in the system. Because of the extremely low tolerance on eccentricity of the rotors of any such machine, it was his opinion that any scheme for removing PuF_4, formed by the decomposition of PuF_6, from the system would have to involve doing the job with the rotor in place, i.e., without removing it from its casing. He felt that a major contribution Hanford could make to a program of centrifuge development for Pu isotopes would be along these lines of decontaminating spinning equipment. He expressed the opinion that "you will not know if Pu isotope separation is feasible until you run PuF_6 in centrifuges."

In arriving at an estimate of the required installation to do the job, he indicated that allowing 20% more units than required by theoretical calculations would be adequate to take care of squaring off effects (non-ideal cascade), unequal separations in parallel units, and the other non-ideal conditions that inevitably occur in an actual installation.

Centrifuges of the short bowl (subcritical) design spinning at 500 m/s and long bowl (supercritical) machines spinning at 450 m/s were suggested as being quite feasible in the relatively near future if the program is subjected to intensive engineering development.

Impressions

The writers have gained the following impressions as the result of these contacts. It should be stressed that these are only impressions, some of which are gained more from the enthusiasm, attitude, and reactions of the people with whom they talked than by concrete facts.

(1) While the stability of PuF_6 leaves much to be desired, at the low temperatures and relatively low pressures at which a centrifuge process would operate, it does not appear to be out of the question at this time and warrants further study to determine if the clean-up cycles, equipment requirements and containment limitations are within the realm of feasibility.

(2) With vigorous engineering development, it is conceivable that within several years a long bowl machine (supercritical) of relatively high efficiency (e.g. 65%) operating at 400-450 m/s peripheral speed will be developed which can be run for long periods of time essentially free of maintenance.

(3) For a cost basis one can assume that a cascade composed of such units operating with the uranium system will be less than a factor of three times as expensive, per unit separative work, as the gaseous diffusion approach.

EE Voiland and BM Johnson, Jr.: pct