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Trip Report - Volatile Fluoride Processes

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TRIP REPORT

VOLATILE FLUORIDE PROCESSES

June 4-5, 1963

O. F. Hill

The author visited Oak Ridge National Laboratory on June 4, 1963, and Argonne National Laboratory on June 5, 1963, to discuss the status and plans for development of volatile fluoride processes. Specific emphasis was placed on the status of process development relating to the processing of plutonium containing fuels. These processes may have specific and unique application to the Plutonium Utilization Program, since they have high potential for short cooled, close-coupled, high decontamination application, not only for the recovery of uranium, but also for the recovery of plutonium.

SUMMARY

Both the ORNL and ANL processes are potentially applicable to the recovery of both uranium and plutonium from irradiated fuels. The ORNL process (volatilization from fused salt) has been demonstrated on highly irradiated fuel, but development with plutonium has barely been started. The ANL process (volatilization from an inert fluidized bed) has not been demonstrated on other than tracer level fission product content, but the process chemistry of plutonium is more advanced. The two processes are compared briefly in Table I.

Evaluation of fluorine volatility processes must be included in our process studies to determine incentives for process development and demonstration for plutonium recycle. The work at Brookhaven National Laboratory, including the Nitrofluor Process, should also be considered in this evaluation.

Steve Lawroski indicated a willingness on the part of ANL to enter into a cooperative demonstration program, should this be our desire.

Oak Ridge National Laboratory

Discussions were held with George I. Cathers and Sid Mann on the process development of the ORNL Process. The chemistry and process development of the uranium removal is well advanced, and has been demonstrated on highly irradiated, enriched uranium fuels in pilot plant equipment.

The pilot plant is sized to handle 50-55 liters of fused salt per batch, containing up to 3.5 kg of uranium. Heating is done by auto-resistance techniques and valving is accomplished by freeze-valves. Design must account for high expansion (about 30%) of the salt on melting. Major equipment problems have been associated with the off-gas and entrainment of fused salt. This has been solved in part by crude techniques to add new salt at the top which separates out entrained salt, and when necessary, clear off-gas lines with a "plumber's snake".

Plutonium hexafluoride has been recovered in laboratory experiments with good material balances and good recovery (cf. ORNL-3298). However, removal rates are low, with half-times of 3-5 hours. Some improvement is possible by increasing

the fluorine pressure. Variations planned for study include the study of different fluorinating agents (e.g., ClF_3, BrF_5) and a "radiant-heat spray fluorinator", using the fluorine gas as the continuous phase (vice the fused salt as the continuous phase). It is believed that the reaction is equilibrium controlled (ANL has found 100 moles fluorine required to form one mole of PuF_6 at 500° C). The author suggested trial of a metal salt catalyst, e.g., AgF_2, in the fused salt.

Ted Gens discussed briefly the work he is beginning on the processing of plutonium containing fuels using the volatile chloride ($PuCl_4$).

Argonne National Laboratory

Discussions were held with Dick Vogel, Al Jonke, and Jack Fisher.

Two pilot plants are under construction for studying the volatile fluoride processes with low irradiated materials. These are

(1) Unit for processing zirconium-based enriched uranium fuels. This unit is nearing completion and operation should begin soon.

(2) Approximately a 20 feet by 24 feet glove box, behind shielding, for processing UO_2-PuO_2 fuels. Equipment is being installed and it is expected that the unit will be ready for operation around the end of the year.

The fluorinator is a three-inch diameter unit with capability of processing up to a 10 kg uranium batch. In addition to this engineering scale unit, there is a one and one-half inches diameter fluidized bed unit installed in a glove box. This laboratory unit is to be used to study the kinetics of the fluorination of Pu from UO_2-PuO_2 fuel materials (not irradiated).

For about six months, personnel at K-25 (Oak Ridge) have been making some evaluations comparing solvent extraction processes to fluoride volatility processes for application to Rover fuels. The study is incomplete but it appears that the fluoride volatility processes may be cheaper for this particular fuel. Additional evaluations are being made on other fuels and comparing the fluoride processes. Vogel is confident the fluoride processes, and the ANL process in particular, will fare well. It is anticipated that K-25 will do cold semiworks engineering development studies on the process. This will include studies on gas pumps, compressors and fluidized bed phenomena, drawing on their past experience and background.

Although elevated temperatures are required for the fluorination (500° C is planned for the ANL process) and large excess of fluorine is necessary (at 500° C 100 moles of fluorine is needed per mole of PuF_6 formed) the PuF_6 once formed is quite stable at temperatures below about 150° C. Process design then requires rapid cooling of the process off-gas to catch the PuF_6 without decomposition. However, some PuF_6 does decompose to PuF_4 because of alpha decay energy and the design must provide for periodic recovery of PuF_4 from the system by heating in the presence of fluorine.

ANL plans to separate and purify the UF_6 and PuF_6 by selective distillation. It is also proposed to convert mixed UF_6-PuF_6 to UO_2-PuO_2 with a fluidized bed converter using the process developed by ANL for conversion of UF_6 to UO_2. This has not yet been demonstrated with UF_6 containing PuF_6, however.

Other Fluoride Volatility Work

Other studies being undertaken on fluoride volatility work include fluidized bed studies at Brookhaven National Laboratory. BNL is also investigating the Nitrofluor Process which involves dissolution in nitric oxide-hydrogen fluoride media. Under some conditions the product ($NOUF_6$) can be made volatile and later decomposed to UF_4. The paths of fission products and plutonium are not yet known.

In Europe, extensive studies are being carried out at C.E.N., Mol, Belgium (in fact, Al Florin of LASL, and one of the pioneers in PuF_6 chemistry, is on assignment there). The French are building three pilot plants to study volatile fluoride processing.

The Sol-Gel Process

At Floyd Culler's request, the status of the development of the Sol-Gel Process was discussed with R. G. Wymer, O. C. Dean and J. P. McBride. The process for preparing ThO_2-UO_2 fuel particles for use in vibratory compaction fabrication methods is in advanced stages of development. A pilot plant, called the Kilorod Facility, is in operation to prepare about 1200 fuel rods for test in a Brookhaven reactor. This facility was described by C. C. Haws, Jr.

The process has been described in detail in ORNL-3385, the "Fuels Cycle Annual". Thermofax copies of schematic flowsheets were given the author and these are available to interested persons. ThO_2 sol preparation is brought about by steam denitration of thorium nitrate solution. Uranyl nitrate solution is added to the sol and ammonia added to fix the uranium on the ThO_2 as UO_3. The sol is evaporated to prepare a gel which is then calcined and reduced in argon-hydrogen to form a dense UO_2-ThO_2 suitable, after sizing, for vibratory compaction. Only two particle sizes are being used by the ORNL people for vibratory compaction, 6-16 mesh and -200 mesh.

Work is underway and optimism is high on preparing UC_2-ThC_2 spheres by the Sol-Gel Process. A high-surface carbon is added to the UO_3-ThO_2 sol to make a UO_3-ThO_2-C sol. This sol is dehydrated in a spray column using a CCl_4-isopropyl alcohol mixture. The oxide-carbon spheres are heated to make the UC_2-ThC_2 spheres.

Work has been initiated on preparing UO_2 sol. This is preliminary to the longer range objective of preparing mixed UO_2-PuO_2 sols and gels. McBride is confident that if he can prepare the UO_2 sol, he will be able to incorporate PuO_2 into it. So far his work has shown him that he probably can make a UO_2 sol, but there are several critical problems. He prepares a uranium(IV) nitrate solution using the Italian platinized catalyst method with urea to stabilize the solution. He hopes to prepare (and some exploratory experiments indicate it is possible) the UO_2 by the use of air-free ammonium hydroxide under an inert atmosphere (argon) followed by rapid centrifugation to produce a gel suitable for calcining to a dense oxide.

Major advantages for the Sol-Gel Process seen by its investigators are its simplicity and ease of obtaining uniform uranium to thorium ratios (and presumably in obtaining uniform plutonium to uranium ratios if the development for the latter material is successful).

The development of this process should be followed by Hanford Laboratory scientists and engineers since successful development of the Sol-Gel Process for UO_2-PuO_2 fuel material would be a definite competitor to other methods of preparing UO_2-PuO_2 fuel particles; i.e., high energy compaction, salt-cycle electrodeposition, and the ANL fluidized bed conversion of mixed UF_6-PuF_6 to mixed UO_2-PuO_2.

TABLE I

COMPARISON OF ORNL AND ANL
FLUORIDE VOLATILITY PROCESSES

COMPARISON	ORNL PROCESS	ANL PROCESS
Fluorination Medium	Fused fluoride salt.	Inert fluidized bed
Temperature	600° C	500° C
Material of Construction	INOR-8 (Pilot Plant) Nickel (Laboratory)	Nickel
Corrosion	High (1 mil/day).	Good ($\leq$ 0.2 mil/day)
Decladding	Dissolve Zircaloy in fused salt. Fate of other claddings not established.	Oxidative decladding (AI) has been proposed. Adaptable to any metal cladding.
Product Traps	NaF Sorption beds.	Cold traps
Purification of Product	Selective sorption.	Selective distillation
PuF_6 Volatility	Demonstrated slow from fused salt (half-times of 3 - 5 hours).	Demonstrated good on batch processes.
Status of Pilot Plant Demonstration	Demonstrated in "hot" pilot plant for fully enriched (UF_6 only). PuF_6 studies performed only on small, laboratory scale.	Two pilot plants under construction: (1) Zr-base enriched U fuels. Near completion. Studies to start soon. (2) UO_2-PuO_2 fuels. Under construction. Studies should start late this year or early next.
Waste Disposal	Package the fused salt.	Not determined, but potential for smaller volumes.
Entrainment	Some difficulty with deposition and plugging by entrained, fused salt.	No problems observed.