

indicates that the addition of UF_4 under normal operating conditions results only in a slight depression of the melting point of the mixed salt.

If dissolution were to be initiated in $LiF-NaF$, omitting the ZrF_4 from the barren salt, inconveniently high temperatures would be required. Hence, the barren salt charged for dissolution is 37.5-37.5-25 mole % $LiF-NaF-ZrF_4$. Dissolution results in a final concentration (exclusive of the UF_4 content) of 27.5-27.5-45 mole %. This change in composition is shown as a dissolution line on the phase diagram. As dissolution proceeds, the melting point of the salt rapidly drops from slightly above $600^\circ C$ to about $450^\circ C$, the result of adding more zirconium tetrafluoride to the melt as the zirconium in the alloy is converted to the tetrafluoride by the HF that is bubbled through the salt. [See reaction (1).] This reduction in melting point permits a reduction in operating temperature during dissolution and results in a salt whose melting point is close to the minimum melting point for all subsequent operations.

Volatilization of Uranium Hexafluoride

Having dissolved the uranium-zirconium alloy in the melt, uranium is removed by converting it to the volatile hexafluoride, using the reaction $UF_4 + F_2 \rightarrow UF_6$. The fluorine is merely bubbled through the melt. The uranium hexafluoride (UF_6), with its vapor pressure of 1 atmosphere at about $55^\circ C$, is volatilized, leaving more than 99% of the fission product activity behind. However, some of the fluorides have an even higher vapor pressure than UF_6 and thus are volatilized along with it. Other contaminants are carried in the gas stream in only trace quantities, but even traces are unacceptable. For example, the vapor pressure of ZrF_4 at the fluorination temperature ($500^\circ C$) is less than 1 mm of Hg, but even the small quantity of fission product zirconium which is evolved during fluorination would prohibit direct handling of the UF_6 . Hence, the UF_6 stream leaving the fluorinator must be purified, as described next.

Purification of the Uranium Hexafluoride

The purification of the uranium hexafluoride is done by sorption and desorption, as follows: The impure UF_6 stream from the fluorination step is passed first through a bed of sodium fluoride pellets held at $400^\circ C$. At $400^\circ C$, UF_6 is not sorbed, but the fluorides of some of the corrosion products (such as chromium) and some of the fission products (such as niobium and ruthenium) are sorbed to varying degrees by the NaF.

The partially purified UF_6 stream next enters a bed of NaF pellets held at $100^\circ C$. At this temperature, the UF_6 is sorbed by the NaF [4]. Some of the remaining contaminants, such as zirconium and molybdenum fluorides, are sorbed along with the UF_6 , while others, such as tellurium, pass through as a part of the waste stream. Thus, the UF_6 is collected and is fairly pure, but still not pure enough.

The sodium fluoride bed containing the UF_6 is then heated to $150^\circ C$ and held for two hours while fluorine is passed through the bed. Most of the molybdenum

hexafluoride is desorbed from the bed (and sent to waste), while only a negligible amount of uranium accompanies it and is lost, though it can be recovered if necessary. Very little UF_6 leaves at $150^\circ C$ because it is in the form of a fairly heat-stable complex of NaF and UF_6 , thus permitting it to remain behind while the molybdenum is being removed.

The sodium-uranium fluoride complex is completely dissociated at 1 atmosphere at $363^\circ C$ [4]. Hence, the next step involves heating the bed to $400^\circ C$ while "sweeping" the bed with fluorine to prevent reduction of the UF_6 to UF_5 . This treatment removed UF_6 , leaving behind contaminants such as ZrF_4 . The UF_6 product finally passes through a bed of magnesium fluoride pellets at $125^\circ C$ for preferential sorption of technetium and neptunium, while the UF_6 flows to a cold trap for final collection of the purified product.

DESCRIPTION OF THE VOLATILITY PILOT PLANT

As mentioned earlier, a pilot plant was built to recover the Aircraft Reactor Experiment fuel [1]. This pilot plant was subsequently modified to permit processing high-burnup, short-cooled U-Zr alloy fuel elements [5]. ("Cooling" the fuel is just another way of saying, "Let the short-living radioisotopes decay and thereby make the fuel element less radioactive.") The details of the reactions that take place in the components of the system (dissolver, sodium fluoride beds, etc.) were discussed earlier in "Process Chemistry." In the pilot plant, specialized vessels were designed for these reactions. Briefly, the major vessels through which the uranium passes from the fuel element carrier-charger to the product receiver (which is also the shipping cylinder) are, in order: dissolver, fluorinator, movable-bed absorber (NaF pellets), impurity trap (MgF_2 pellets), and product receiver (or cold traps). The pilot plant is described in more detail below.

Flowsheet

The pilot plant flowsheet is shown in Fig. 2. Although construction materials (primarily nickel and nickel alloys) and design details are not included, this schematic diagram does show the shapes and relative elevations of all major vessels.

Dissolution System—Fuel elements are lowered into the small (5-in. diameter) bottom section of the dissolver. Molten barren salt is added until the fuel elements are completely submerged. Anhydrous HF is then circulated through the system for 16 to 24 hours, converting the zirconium and uranium to the tetrafluorides. Dissolver off-gas, containing hydrogen, unreacted HF, and inert gas used for purges, entrains 300 to 500 grams of submicron-size particles per run. These particles are about evenly divided between salt and unfluorinated metal. They are highly radioactive and if allowed to remain in the gas stream would quickly plug the first valve they reach. Several methods of removal, such as filtration, were tried. The problem was reduced but not eliminated until the scrubbing system shown in the flowsheet was installed. The off-gas from the dissolver first enters the flash cooler, into

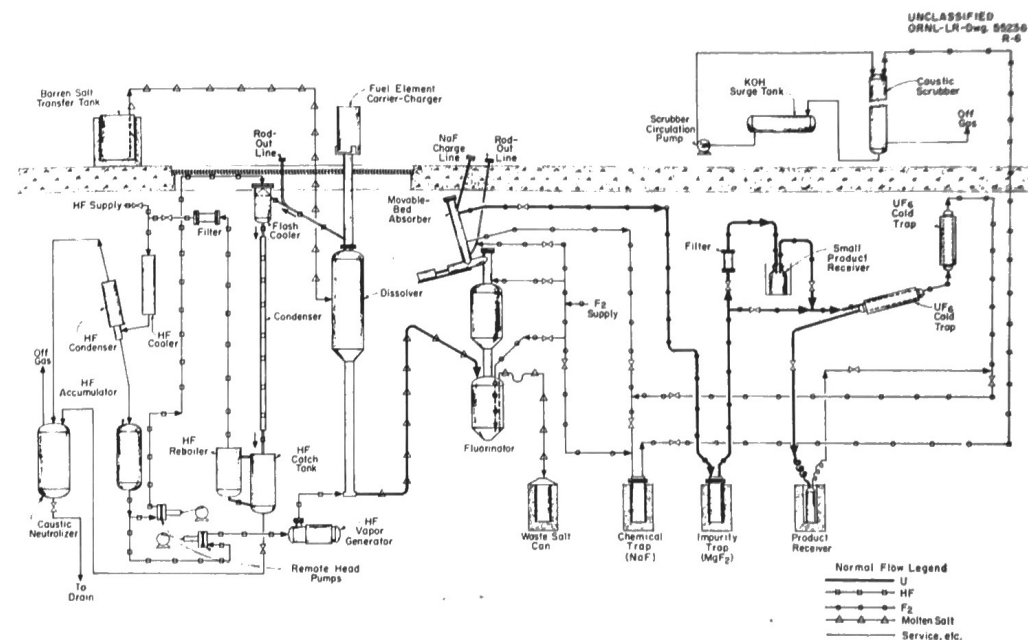


Fig. 2. Schematic Diagram of Volatility Pilot Plant.

which liquid HF is being pumped. The gas stream is cooled to $20^\circ C$ by vaporization of part of the liquid HF. The remaining liquid supplies a washing action. Additional scrubbing is achieved as HF is liquefied in the condenser. The particles settle in the bottom of the catch tank, and HF is vaporized in the reboiler for recirculation to the dissolver. Any water resulting from hydrofluorination of oxides is also retained in the catch tank. At the end of the run, the impurities are flushed out by draining the HF from the catch tank to the caustic neutralizer.

The off-gas leaving the HF reboiler passes through a filter used principally to determine the effectiveness of the scrubbing system. The HF is condensed and recirculated as a liquid to the flash cooler and to the HF vapor generator (which supplies HF to the dissolver). Noncondensibles in the off-gas stream are bubbled through potassium hydroxide solution to remove traces of HF before entering the main off-gas line.

Plant Off-Gas System—The main off-gas line collects all off-gas from the plant, including the noncondensibles discussed above, off-gas from the fluorination system, off-gas from the purification system, and cell-ventilation air. The main off-gas system includes an auxiliary scrubber (not shown) to protect the filters at the off-gas stack from accidental releases of fluorine or hydrogen fluoride.

Fluorination System—After dissolution of the fuel alloy is complete, the salt is transferred to the fluorinator.

Bubbling fluorine through the salt for two hours results in uranium being removed as the volatile compound, UF_6 . The waste salt remaining is subsequently transferred to a waste can where it is allowed to freeze. The can is then buried in concrete. Thus the high-activity waste from the process is permanently disposed of in a relatively small volume, a prime virtue of the volatility process.

UF_6 Purification System—The UF_6 stream leaving the fluorinator enters the movable-bed absorber, a vessel that combines the functions of three sodium fluoride beds used during early pilot plant work. Pellets in the lower portion of the absorber are held at $400^\circ C$. During fluorination and molybdenum stripping, the waste-gas stream leaves the absorber through the outlet near the middle of the vessel. During these two stages of operation, the pellets just below the outlet are held at 100 and $150^\circ C$, respectively.

For desorption, the entire bed is heated to $400^\circ C$, and the product stream is carried out through the line near the top of the absorber. After desorption is complete, the NaF pellets at the bottom of the bed are discharged into the waste salt in the fluorinator, and fresh pellets are charged to the top of the bed.

The UF_6 stream leaving the absorber goes through the impurity trap, which contains magnesium fluoride pellets. Removal of technetium and neptunium fluorides from a stream of uranium hexafluoride by magnesium fluoride was pioneered at the Paducah Gaseous Diffusion Plant, and the design of the impurity

trap was based on development work at Paducah. The product stream is filtered to remove fines resulting from the powdering of the pellets. The filter consists of nickel mesh followed by a porous, sintered nickel plate.

Product Recovery System—For the relatively small quantities of uranium (less than a kilogram) in the current fuel charges, a small product receiver was installed in the system. This small metal bottle, immersed in dry ice—trichlorethylene, acts as a cold trap and also permits removal of the product for analysis after each run. At the end of a series of runs, product collected in these small receivers can be transferred to the larger UF₆ cold traps and then to a shipping cylinder (shown as the product receiver at the bottom of the flowsheet).

Chemical Trap System—All off-gas from the fluorination system, the UF₆ purification system, and the product recovery system goes through a chemical trap, which is a bed of NaF pellets at room temperature. This trap removes any trace quantities of UF₆ before the off-gas is discharged to the caustic scrubber.

Interesting Design Features

Some of the design features of the Volatility Pilot Plant are of interest in that they represent techniques not in general use but holding a potential for widespread application. The features discussed below are: heating of salt-transfer lines, "valves" for salt-transfer lines, and control of leakage through the flanges.

Autoresistance Heating—Salt-transfer lines are made of metal that has a relatively low electrical conductivity, such as Inconel. The transfer line is then made a part of a low-potential, high-current circuit (e.g., 7v, 135 amp). Thus the pipe line also becomes the heating element and does not require cumbersome external heaters.

Freeze Valves—Conventional valves for molten salt service which are both cheap and reliable are non-existent. This problem was solved in the Volatility Pilot Plant by deliberately including a nondraining low point in the salt-transfer lines. After a transfer is complete, the small quantity of salt remaining at the low point is allowed to freeze, effectively plugging the line. To open the "valve", the line is heated until the salt melts.

Flange Buffer System—Ring-joint flanges are used in process gas lines. Ring-joint flanges are joined by a ring (usually a soft metal such as copper) which fits into a groove in each flange face. The ring keeps the flange faces separated, so that tightening the bolts seals the joint by compressing the ring between the flanges. The ring is thicker than the width of the groove, so that it does not reach the bottom of either groove. The two lines of ring contact at the sides of each groove form the seal. Inside each groove, between these contact lines, is a "dead" space, sealed from the process fluids and the atmosphere. A connection is made from this dead space to a manifold system, and pressurized inert gas is maintained in the groove. By drilling a hole through the ring to connect

both grooves of a flange pair, a gas buffer is maintained on the entire joint by a single connection. In the event that a leak develops, the leakage is inert gas rather than process gas escaping or moist air leaking in. In addition, with proper manifolding and measurement, the flange pair that is leaking can be identified and the rate of leakage can be measured.

RESULTS OF PILOT PLANT OPERATIONS

A pilot-plant-scale uranium-zirconium alloy program was successfully completed. The two primary objectives, demonstration of continued operability and achievement of adequate decontamination from fission products, were reached. Reactor fuel cooled as short a time as six months was processed; some of the decontamination factors achieved are the highest that have ever been reported for a single-cycle radiochemical process.

In radiochemical processing, the degree of purification is often expressed as a decontamination factor, or DF, which is defined as the ratio of any particular activity in the feed to the corresponding activity in the product. Thus, a strontium-90 DF of 100 would mean that 1% of the original Sr⁹⁰ accompanied the product, and a cesium-137 DF of 5 x 10⁴ would mean that purification from Cs¹³⁷ was 99.998% complete. In each of the last four runs in the Volatility Pilot Plant, decontamination factors for some of the less volatile fission products were greater than 10¹⁰.

ADVANTAGES AND FUTURE PROSPECTS OF THE PROCESS

Volatility Pilot Plant operations have confirmed that two of the advantages of the ORNL volatility process, compared with conventional aqueous processes, are: Significantly lower volumes of high-activity wastes are produced, and extremely good decontamination is achieved.

Laboratory studies showed that this molten-salt fluoride-volatility process is applicable to other enriched-uranium fuels such as oxide fuels and aluminum alloy fuels. Hence, the next pilot plant program will be to study the processing of such fuels. Meanwhile, the feasibility of recovering uranium from highly enriched uranium-zirconium alloy fuels by this method has been demonstrated, with excellent results.

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LITERATURE CITED

- W. H. Carr, 1960. Volatility processing of the ARE fuel. *Chemical Engineering Symposium Series* 56, No. 28: 57-61.
- G. I. Cathers, W. H. Carr, R. B. Lindauer, R. P. Milford, and M. E. Whatley, 1961. Recovery of uranium from highly irradiated reactor fuel by a fused salt-fluoride volatility process. *Progress in Nuclear Energy Series III*, Vol.

- 3—Process Chemistry. Pergamon Press, London [Geneva Conference Paper (1958) P/535], pp. 307-318.
- G. I. Cathers, R. L. Jolley, and E. C. Moncrief, 1962. Laboratory-scale demonstration of the fused salt volatility process. *Nuclear Sci. and Eng.* 13: 391-397.
- G. I. Cathers, M. R. Bennett, and R. L. Jolley, 1958. UF₆-3NaF complex formation and decomposition. *Ind. and Eng. Chem.* 50: 1709-1710.
- R. P. Milford, S. Mann, J. B. Ruch, and W. H. Carr, 1961. Recovering uranium submarine reactor fuels. *Ind. and Eng. Chem.* 53: 357-362.
- R. E. Thoma [ed.], 1959. Phase Diagrams of Nuclear Reactor Materials, ORNL-2548. Oak Ridge National Laboratory, Oak Ridge, Tennessee, pp. 60-61.

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NEWS OF TENNESSEE SCIENCE

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following a week's journey from Longview, Tex., where it was fabricated. It was unloaded onto a low-boy trailer and transported to the ORINS Medical Division.

In addition to ensuring that the steel, concrete, and surrounding olive ore have low radioactivity levels, all construction materials within six feet of the counting chamber have been tested for background content. Those materials showing a background too high for this use have been rejected and other less active materials have been substituted.

When the completed facility is in operation, patients will lie in a horizontal sling and be transported into the counting chamber through a door in the front wall. A heavy steel door will be closed, and the counting procedure will begin. Gamma rays emitted by radioactive materials in the patient's body will be detected by eight large scintillation crystals arranged above and below the supporting sling.

Conceptual design of the whole-body counter was begun by Dr. Marshall Bruer, former chairman of the Institute's Medical Division, and actual design of the facility was carried out by Dr. Douglas A. Ross, a former member of the Division now at Oak Ridge National Laboratory, and A. C. Morris, Jr., associate scientist with the Medical Division. The design was done by the Medical Division in cooperation with the Engineering Division of the AEC Oak Ridge Operations over the past five years.

The fifteenth annual Fisk University Infrared Spectroscopy and Gas Chromatography Institute will be held August 11-15, 1964, at Fisk University, Nashville, Tennessee.

The sessions on basic gas chromatography and the fundamentals in infrared spectroscopy will be conducted during the same five-day period. The lectures for the two programs will be so arranged that persons enrolled in either program may, if they so desire, audit the general lectures of the other program without extra charge. A second infrared session is scheduled for August 17-21. Announcement of the sessions and other information are given on the inside back cover of this magazine.