CHEMICAL PROCESSING TECHNIQUES AND HISTORY FOR MOLTEN-SALT REACTORS

January 6, 2015

Flibe Energy, Inc.
PO Box 5952
Huntsville, Alabama, USA
(256) 679-9985
info@flibe-energy.com

Contents

Chemical Processing Techniques and History for Molten-Salt Reactors

Kirk F. Sorensen

January 6, 2015

1 Introduction

Molten-salt reactors are a class of reactors for which chemical processing and reactor design have been intertwined from their conception. One could even make the case that the existence of fluorination as a chemical separation process was one of the earliest motivations to investigate molten-salt reactors and to consider how the thorium fuel cycle might be implemented in them.

Fluorination, as a chemical separation technique, was originally considered during the Manhattan Project by Dr. Glenn Seaborg as a way to separate uranium from plutonium, a task for which it was not particularly well-suited. Fluorination was much better suited to the task of separating uranium from thorium, and even more so if both the uranium and thorium existed as fluoride salts dissolved in other fluoride salts. So one should not be surprised to find the thorium fuel cycle associated so early with molten-salt reactors.

Molten-salt reactors were originally developed at Oak Ridge National Laboratory (ORNL) from 1951 to 1976. They use liquid fluoride fuel forms that are much more robust against a loss of coolant. They are also often associated with the use of thorium as a nuclear fuel rather than on the consumption of the small amount of uranium-235 in natural uranium. Work on molten-salt reactor at ORNL was undertaken as part of their Molten-Salt Reactor Program (MSRP). One of the most significant of the achievements by the MSRP was the construction and operation of a demonstration molten-salt reactor called the Molten-Salt Reactor Experiment (MSRE).

The MSRP at ORNL also put forward concepts for modular molten-salt reactors for electrical generation in 1966 and 1967 that would generate 250 MW of electricity each. These concepts were later modified into a single large reactor that would alone generate 1000 MW of electricity. There were several technological reasons why the MSRP moved from smaller to larger reactors.

Work on molten-salt reactors at ORNL ended in 1973 when funding was diverted to a greater priority of the Atomic Energy Commission: liquid-metal fast-breeder reactors (LMFBR). Funding was reinstated in 1974 for a year, then cancelled again. Very little research or development on molten-salt reactors has taken place since then.

Beginning in 2006, Kirk Sorensen (then at NASA) began to promote a modern variant of the molten-salt reactor called the liquid-fluoride thorium reactor (LFTR). Sorensen continued to promote this design after he left NASA to join Teledyne Brown Engineering in 2010 and then started his own company, Flibe Energy, in 2011.

Since its inception, Flibe Energy has worked to design a new kind of modular molten-salt reactor that addresses the concerns raised by the MSRP during their research efforts. The incentive for this effort is an expectation that the chemical reprocessing system that the reactor would use could be greatly simplified over what the MSRP had anticipated in their work. The challenge has been to conceive of a reactor core design that will keep the two main fluid streams of the reactor (fissile and fertile-bearing salts) separate from one another while allowing neutronic communication. Flibe envisions a modular LFTR that would generate electricity at high efficiency and with enhanced safety features over present pressurized-water reactors. The basis of this claim has been the research that was conducted at the Oak Ridge National Laboratory.

This report was generated to provide historical background to the use of various chemical separation processed in molten-salt reactors.

2 Early Fluid-Fueled Reactors (1945-1950)

Even before the molten-salt reactor concept was conceived, a great deal of thought had been directed towards the idea of a nuclear reactor whose fuel was in a liquid rather than a solid form. This idea was considered much more in the main stream of thought in the later days of the Manhattan Program because the central goal of a nuclear reactor then was not to generate electrical energy, but to generate plutonium that could be chemically isolated from its uranium parent. They went so far as to sketch their ideas out in a May 1945 report which included a graphic of what they thought such a reactor might look like, shown in Figure 1.

With a fluid rather than a solid fuel, it was reasoned that chemical processes could be greatly simplified and that there would be no associated need for new fuel fabrication. Solutions of uranyl nitrate or uranyl sulfate in light or heavy water were the first liquid fuels that were considered. Eugene Wigner and his protege Alvin Weinberg were among their chief proponents in the Metallurgical Laboratory division of the Manhattan Project, which was located at the University of Chicago. Shortly before the end of the war, both men were transferred to the Clinton Laboratories near Oak Ridge, Tennessee, which would later come to be called Oak Ridge National Laboratory.

At ORNL, Wigner and Weinberg continued their research into fluid-fueled reactors and obtained support and funding from the Atomic Energy Commission to build a proof-of-principle "aqueous homogeneous reactor" at ORNL. This first reactor was called the Homogeneous Reactor Experiment (HRE) and achieved criticality on April 15, 1952[1]. Full power was achieved almost a year later on February 24, 1953 when the reactor generated 1000 kilowatts of thermal power, from which 150 kW of electrical energy was generated[2]. The HRE was the second nuclear reactor (after the EBR-1 in Idaho) to generate significant amounts of electrical energy. This event came a month before the prototype reactor for the *Nautilus* submarine (the Mark I reactor) achieved criticality (on March 30) and several months before the *Nautilus* prototype reached full power on May 31[3]. It is interesting to note that the first two reactors built in the US that generated electrical power were both demonstrations of breeder reactor technology rather than light-water reactors.

The aqueous homogeneous reactor had been envisioned by Wigner and Weinberg since 1945 as a way to create a breeder reactor in the thermal-neutron spectrum using thorium as the fertile material and uranium-233 as the fuel.[4] But there were significant challenges associated with any attempt to create a thorium breeder using aqueous fuels. One of the most fundamental was the simple fact that a suitably aqueous form of thorium did not exist. Thus aqueous thorium breeders had to rely on a suspension or slurry of thorium dioxide in water to form the breeding blanket of the reactor. Thorium dioxide was a challenging material to chemically process and despite being in a suspension or slurry, it still had to be chemically broken down in order for the bred uranium-233 to be extracted. This basic problem reduced the attractiveness of the fluid-fueled reactor concept by eliminating one of its key advantages—the fact that the fuel or blanket should be able to be chemically processed in the form in which it was used in the reactor.

---

[1] ORNL-1282

[2] ORNL-1516

[3] *Nuclear Navy*, page 184

[4] MUC-EPW-134: Preliminary Calculations on a Breeder with Circulating Uranium, May 17, 1945

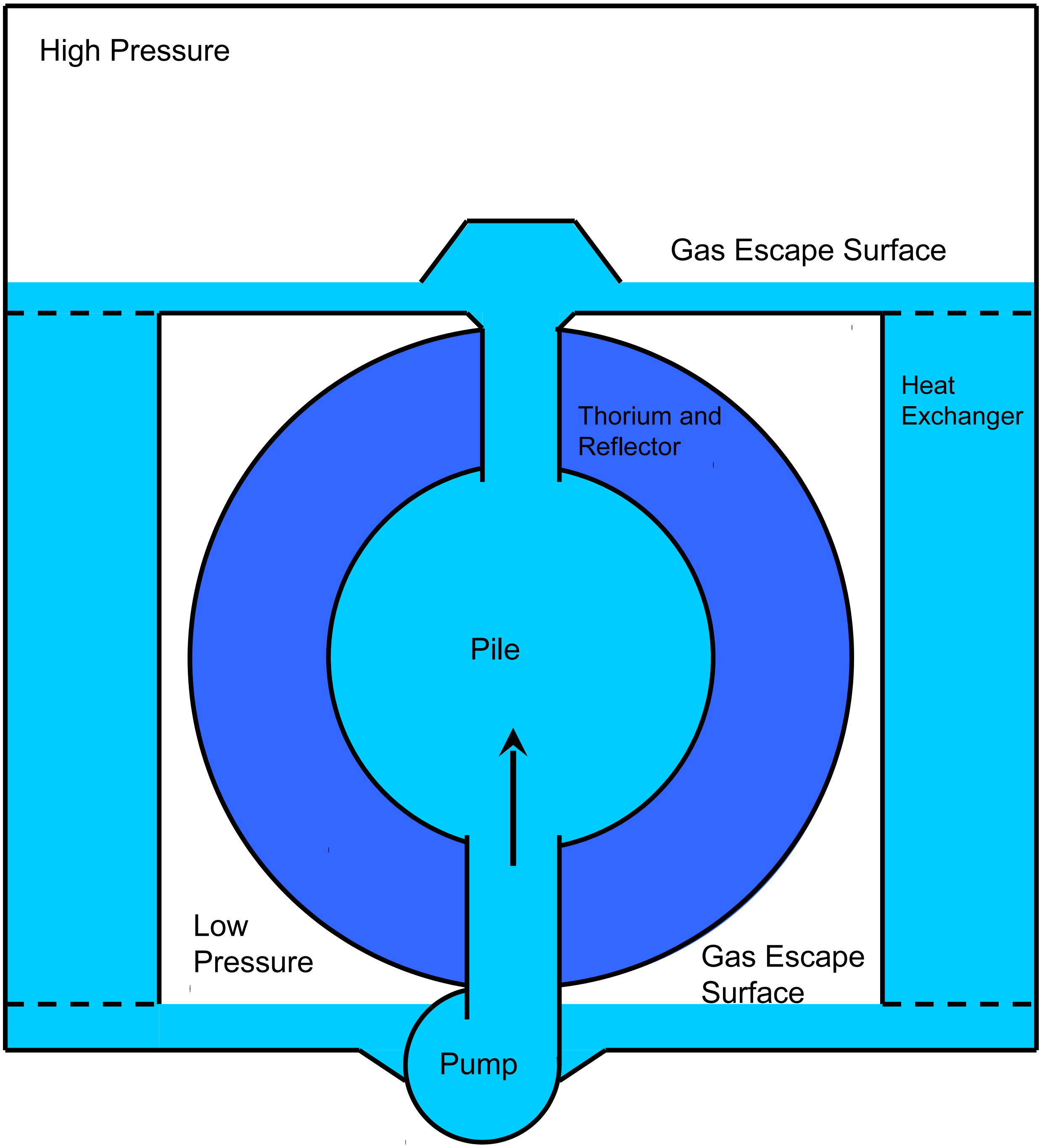

Figure 1: A recent adaptation of the thorium breeder reactor concept described in the Wigner-Weinberg report of May 17, 1945. The original caption states: "The degassing method is only illustrative."

Aqueous forms of uranium existed, but they also had several chemical challenges. Uranyl sulfate was favored for use in the reactor but uranyl nitrate was a better chemical form for processing. The prospect of converting all the uranyl sulfate to uranyl nitrate for processing was not particularly appealing when considering a future chemical processing system for a thorium breeder reactor.

Aqueous reactors had a significant advantage in the fact that the same water that carried the nuclear fuel was an excellent neutron moderator, but this advantage was balanced by the fundamental disadvantage of high-pressure operation. For a reactor intended to produce power, the requirement for high pressure was unavoidable. Designers were trying to make the aqueous homogeneous thorium breeder reactor work, but were also looking out for something better and simpler. A superior approach came from an unexpected direction.

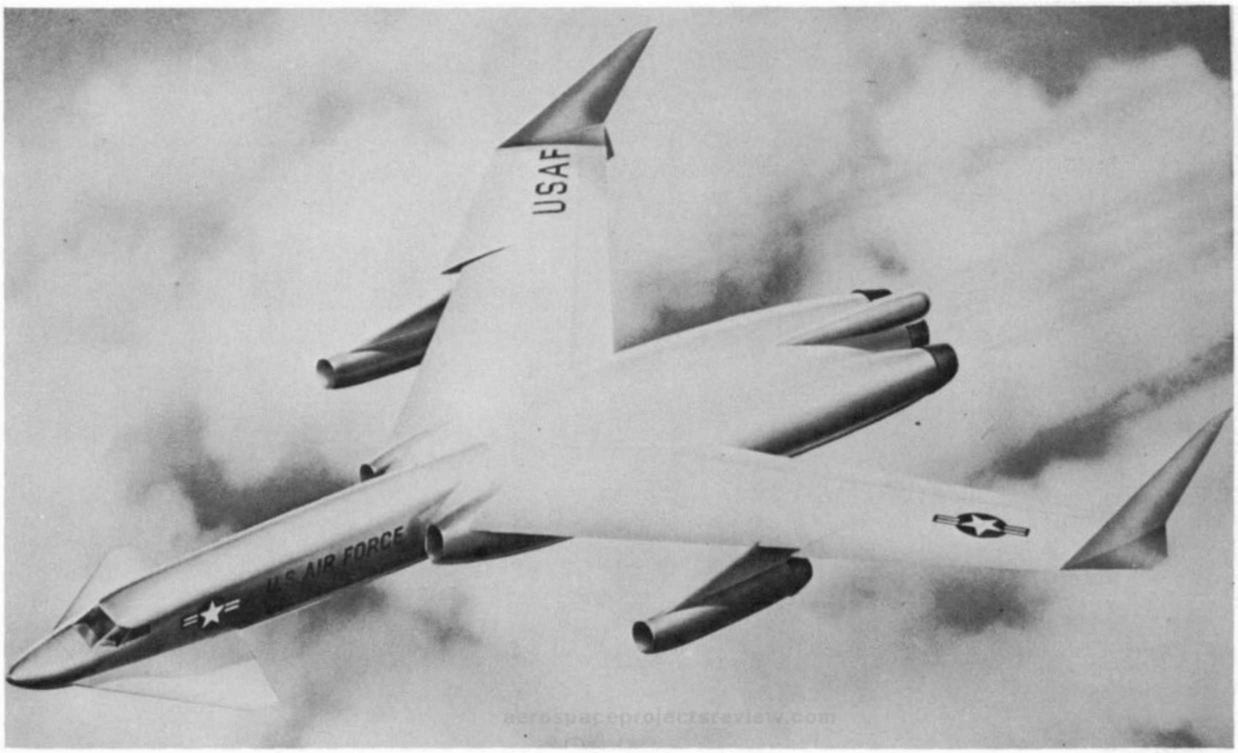

Figure 2: An artist's rendition of one of Convair's nuclear-powered aircraft concepts for the Aircraft Nuclear Program.

3 Aircraft Nuclear Program (1948-1960)

The Aircraft Nuclear Program (ANP) was created and administered by the US Air Force from 1948 to 1960. ORNL was the Atomic Energy Commission's lead laboratory for the ANP, but most of the funds were expended in industrial efforts with General Electric, Convair, and Pratt and Whitney. The reactors initially considered for the ANP used solid nuclear fuel cooled by either liquid metals or high-pressure gases. But the drive towards high power density and simplified operation led several researchers at ORNL to consider the merits of fluoride salt mixtures at temperatures above their melting point. Thus was born the molten-salt reactor, which came to be one of the most promising ideas in the ANP. Despite its promise, the molten-salt reactor was always a rather small fraction of the larger ANP effort, on the order of 20%. The program is noted, however, because its stringent requirements on size, power density, and operational simplicity drove the molten-salt reactor concept into existence. It is unlikely that the molten-salt reactor would have ever been developed under evolution from previous ideas.

There were uncertainties surrounding the molten-salt reactor concept that could only be resolved through the construction and basic operation of a simple proof-of-principle experiment. Therefore, a simplified reactor experiment was built using materials and approaches that had previously been intended for another reactor concept. It was called the Aircraft Reactor Experiment and first achieved criticality on November 3, 1954 and operated until November 12, at which point it had achieved its design objectives.

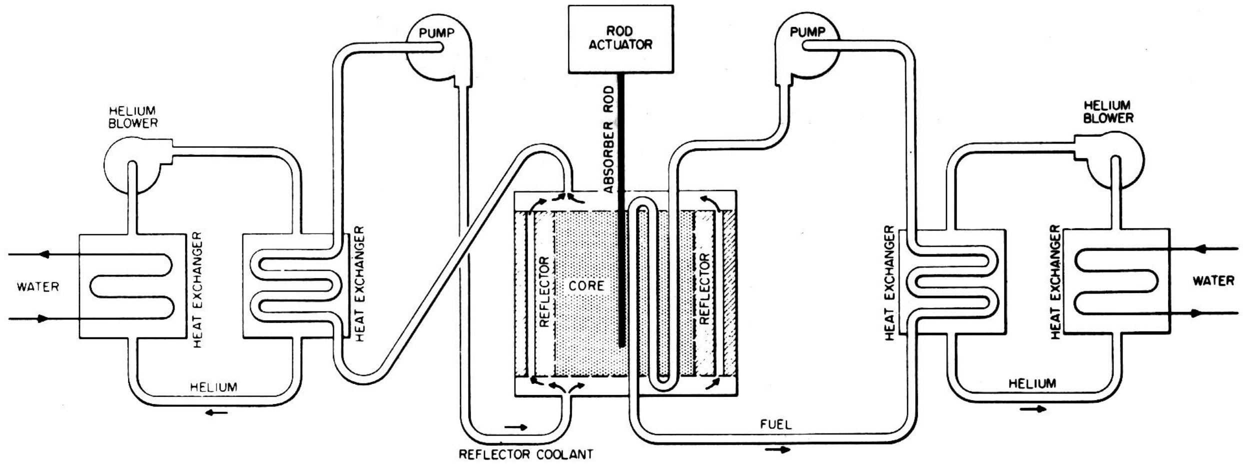

Figure 3: Flow diagram of the Aircraft Reactor Experiment, the first molten-salt reactor.

Since the ARE was intended simply to demonstrate that molten-salt reactors could operate at high temperatures and with acceptable chemical and nuclear stability, there was no meaningful provision made to process the fuel salt, which was a mixture of sodium fluoride, zirconium fluoride, and uranium fluoride ($NaF\text{-}ZrF_4\text{-}UF_4$). The automatic removal of noble gases (including xenon-135) was noted during its operation, and it was also shown to have very stable nuclear operation. Chemical stability was adequate for the design lifetime of the intended aircraft reactor (~100 hr) but more information would be needed before a longer-lived experiment could be contemplated.

After its succesful operation, the ARE was disassembled and various components were examined to assess their performance under operating conditions. Beryllium oxide (BeO) had been used as the neutron moderator material in the ARE. It was known to be chemically incompatibly with the fluoride salt mixture used in the reactor, therefore the salt was kept segregated from the moderator in Inconel tubes. Liquid sodium was circulated through the interior of the ARE to cool the BeO moderator blocks, but chemical reactions between the sodium and BeO had damaged the moderator. Furthermore, the Inconel tubes through which the salt circulated were corroded by the salt and absorbed more neutrons than was desirable.

Graphite was an alternative moderator that promised better performance than beryllium oxide. It appeared to be chemically compatible with the salt, meaning that no metallic fuel channels would be necessary if graphite were used. Small chemical and in-capsule experiments were done with samples of various fuel salt formulations and graphite, and the results were promising.

The ANP itself suffered through a series of fits and starts, always searching for strong military support and a clear mission. The Atomic Energy Commission became increasingly reluctant to commit limited resources to the program in the absence of a compelling military requirement, and the development of intercontinental ballistic missiles (ICBMs) as well as in-air refueling for long-range bombers eroded the justification for the nuclear aircraft. ORNL leadership could sense that the program would not last much longer.

4 Molten-Salt Reactor Experiment (1961-1969)

Alvin Weinberg, director of the ORNL, felt that the technology of molten-salt reactors that had been developed for the aircraft reactor program had far more promise for civilian electrical power applications. Therefore, in 1957, ORNL laboratory management created a Molten-Salt Reactor Program (MSRP) that began working towards the objective of electrical power generation.

With long-term operation of the reactor now in consideration, much more attention was directed towards a suitable fuel processing approach and a longer-lived core design. High core power density was no longer so important, nor was there an extreme drive towards compact sizes.

MSRP leadership became aware of a funding opportunity through the AEC for demonstrators of innovative reactor concepts and they decided to put the graphite-moderated molten-salt reactor concept forward for consideration. The AEC was receptive to their proposal and thus began the design and construction of the second molten-salt reactor, far more advanced than its predecessor. The Molten-Salt Reactor Experiment (MSRE) was originally intended to demonstrate the chemical and nuclear compatibility of the key materials needed for a power-generating reactor:

1. the high-nickel-content alloy that had been developed to be compatible with fluoride salts, known at ORNL as INOR-8 but also by its trade name Hastelloy N,
2. unclad graphite as a moderator and structural material,
3. a fuel salt consisting of lithium fluoride, beryllium fluoride, and uranium or thorium tetrafluorides.

Because of funding limitations, the MSRE was envisioned as a test of only the core region of the desired reactor system. The thorium-bearing "blanket" was excluded from the design and the reactor was not intended to chemically remove fission products during operation.

Construction of the MSRE was initiated in 1961 and essentially completed in 1964. The reactor vessel was loaded with the basic salt combination (LiF-BeF_2) and then uranium tetrafluoride was added in batches until the reactor was brought to criticality. This was first achieved on June 1, 1965. Low-power testing continued throughout that year and then the reactor's power was raised in January 1966. Some problems were encountered from a lubricant leak, but full power was achieved in May 1966.

Operation was interrupted when one of two cooling fans failed in July 1966, but this inadvertently demonstrated the safety and reliability of the reactor, as the reactor dropped in power 50% without any operator intervention. The cooling fan was repaired and the reactor began demonstrating sustained operations at high power in December 1966 through May 1967. After shutdown to replace samples and test instrumentation, the reactor restarted and ran again at high power consistently through late March 1968.

At this point, the tremendous versatility of liquid fluoride fuel was demonstrated as all of the uranium in the reactor was chemically removed by fluorination of UF_4 to gaseous UF_6. A new inventory of uranium fuel was added to the reactor, but it did not come from natural uranium. It was uranium-233, the fissile result of neutron bombardment of thorium and the fuel that would be used in future thorium-fuel-cycle machines.

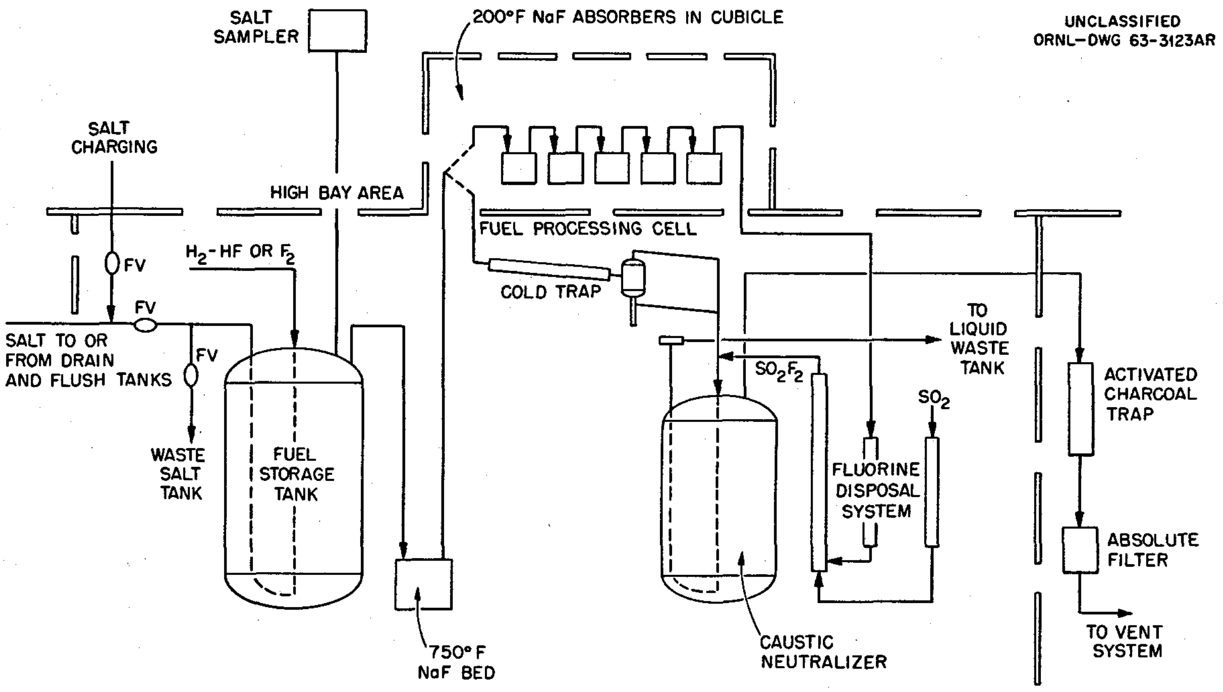

Figure 4: MSRE chemical processing flow diagram.

On October 8, 1968, the discoverer of ^{233}U and chairman of the Atomic Energy Commission, Dr. Glenn Seaborg, came to ORNL to take the MSRE to criticality on ^{233}U fuel. The MSRE was the first reactor ever to operate on ^{233}U. More long-duration power runs were undertaken and a variety of parameters were checked and rechecked to calibrate the use of ^{233}U fuel relative to enriched uranium fuel.

One of the last experiments undertaken in the MSRE was to demonstrate the use of plutonium fuel in the reactor. Small amounts of ^{239}Pu were added in November 1969 in order to maintain the reactivity of the reactor and the test was very successful. Thus the MSRE became the first and only reactor to operate with the three fissile fuels: ^{235}U, ^{233}U, and ^{239}Pu. In December 1969, having completed its research program and under pressure from Milton Shaw, head of the Reactor Division of the AEC, the MSRE shut down for the last time to allow its staff to go home and celebrate the Christmas holiday.

During and after its operation the MSRE demonstrated several important features that would be needed in a future molten-salt reactor.

- Batch fluorination of fuel salt to remove uranium as gaseous UF_6.
- On-line refueling of a molten-salt reactor using both uranium and plutonium.
- Distillation of a portion of the fuel salt from which uranium had been removed.

Fundamentally, the MSRE showed that the materials used in the reactor (fluoride salt, graphite, and Hastelloy-N) were chemically compatible with one another even under high temperatures and neutron and gamma-ray fluxes. It also demonstrated that the reactor could be kept working for a sustained period of time, a challenge that had bedeviled earlier efforts with HRE-1 and HRE-2.

4.1 Batch Fluorination of Fuel Salt

After operating for slightly more that one equivalent full-power year with enriched (33%) uranium fuel, the MSRE was shut down on March 26, 1968 in order that the uranium might be removed and replaced with ^{233}U, which was representative of the fuel that future thorium reactors would be using. The fuel salt was processed in six runs. First it was cooled to within 50°F of its liquidus temperature (850-875°F) before sparging with fluorine was initiated. After the UF_4 was converted to UF_5, volatilization of UF_6 began. The gas stream passed through a NaF bed held at 750°F for removal of some of the volatile fluorides of metals such as Nb, Ru, and Sb. The decontaminated UF_6 then passed through a series of NaF absorbers, held at 200°F, where the UF_6 and some corrosion product MoF_6 were absorbed. The UF_6 volatilization and absorption were followed by mass flowmeters at the inlet and the outlet of the series of absorbers and by the heat of absorption in each absorber. Fluorination was stopped before any uranium reached the final absorber in order to prevent any loss of uranium to the aqueous scrubber. The scrubber was charged with 1300 liters of 2 M KOH-0.33 M KI; 0.2 M $K_2B_4O_7$ was added as a nuclear poison. The scrubber solution was replaced before 50% of the KOH had been consumed; the fluorine being fed to the scrubber was diluted to less than 50% with helium. The mist filter removed hydrated oxides of molybdenum from the scrubber exit gas stream, and the soda-lime trap prevented traces of fluorine from reaching the charcoal traps. Any radioactive iodine not removed by the scrubber was removed by the charcoal traps.

When fluorination was complete, the temperature was increased to 1200°F to reduce the corrosion product fluorides. The NiF_2 was reduced by hydrogen sparging, while the FeF_2 and CrF_2 were reduced by the addition of zirconium metal. The reduced metals were removed by filtration through an Inconel fibrous metal filter before the carrier salt was returned to the reactor drain tank.

All the equipment, except the absorbers, was located in shielded cells in the reactor building; the absorbers were in a sealed cubicle in the operating area. A shielded salt sampler for taking dip samples after fluorination and reduction was also located in the operating area.

After correction for uranium daughter activity, gross beta and gamma decontamination factors (DF's) of 1.2×10^9 and 8.6×10^8, respectively, were calculated. The gamma DF would have been higher if some metallic ^{95}Nb had not been blown into the line and flowmeter filter upstream of the absorber at the end of the salt transfer from the drain tank. This was the only radioactive material found in a measurable amount on the absorbers. Of the 400 mCi of ^{129}I calculated to still remain in the salt, 74% was found in the scrubber solution from the first two runs. None was detected in the charcoal traps. The 560 g of plutonium in the salt remained there during the fluorination.

Corrosion of the Hastelloy N processing tank was somewhat less extensive than expected from previous pilot-plant fluorinations but still significant. The corrosion rate, calculated from the increase in the Ni, Fe, and Cr contents of the salt, averaged approximately 0.1 mil/hr. About 10 kg of reduced metals was produced. Nickel analyses of the filtered salt showed that the reduction and the filtration of nickel were complete. Because of unreliable iron analyses, chromium analysis was used to determine the end of reduction. It was expected that iron would be reduced before the chromium. From subsequent reactor operations, however, it appeared that the concentrations of residual FeF_2 and residual CrF_2 were equal (35 ppm) since there was a rapid increase in chromium concentration from 34 to 67 ppm at the start of reactor operations.

4.2 Fuel Salt Distillation Experiment

Low-pressure distillation of the MSRE carrier salt was to be attempted in an experiment using a 48-liter batch of fluorinated fuel salt from the reactor. The experiment began with a nonradioactive phase that involved distilling six 48-liter batches of MSRE fuel carrier salt (four of which contained 0.1 to 0.3 mole% NdF_3). During these runs, vaporization rates were measured, and samples of the condensate were taken to assess the effect of concentration polarization and entrainment on operation of the equipment.

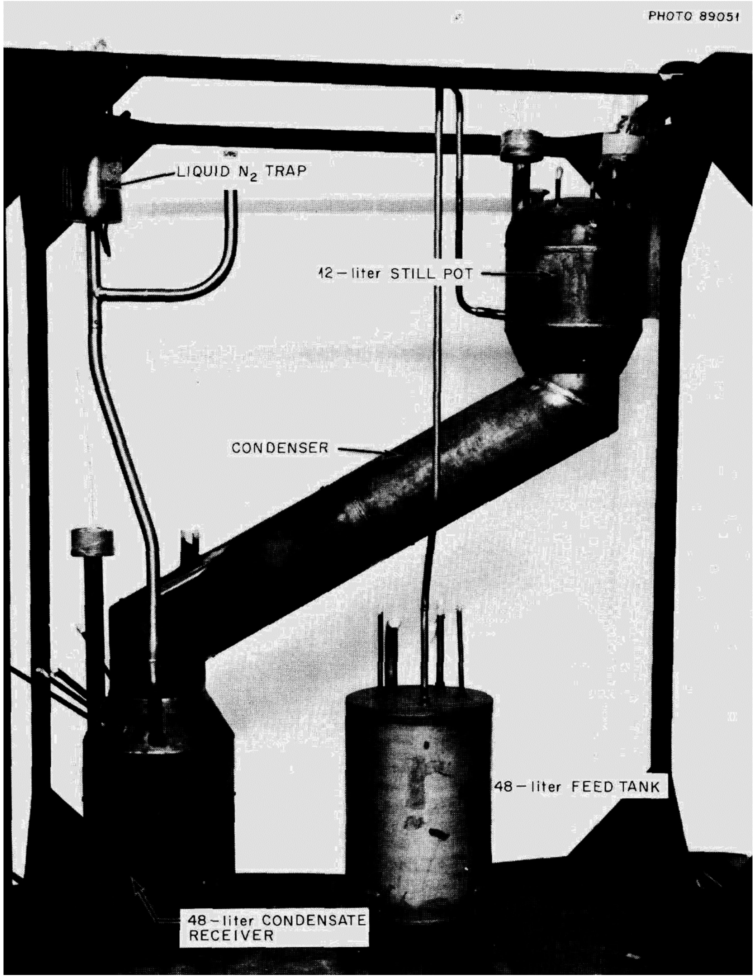

Figure 5: MSRE Distillation Experiment Prior to Installation.

Essentially the same procedure was used in each run. The still is shown prior to installation in Figure 5. Molten salt was charged to the feed tank at 600°C from a heated storage vessel. After the storage vessel was disconnected, the still pot was heated to 900 to 950°C, and the system pressure was reduced to 5 mm Hg. The feed tank was pressurized to about 0.5 atm to force salt into the still pot, and the condenser pressure was decreased to 0.05 to 0.1 mm Hg to initiate vaporization at an appreciable rate. At this time, the liquid level in the still pot was switched to automatic control, and salt was fed to the still pot in this mode at a rate slightly greater than the vaporization rate. The argon feed valve to the feed tank remained open (forcing more salt into the still pot) until the liquid level in the still pot rose to a given point; the valve was then closed until the salt level dropped to another set point. After about one still pot volume had been processed, the temperature of the still was raised to the desired operating point (approximately 1000°C). When the desired quantity of salt had been distilled, distillation was stopped by increasing the condenser pressure to 5 mm Hg. Then, 8 to 10 liters of the initial salt mixture was used to flush the high-melting salt from the still pot and to produce a salt mixture in the still having a liquidus temperature of less than 700°C.

During each run, distillation rates were determined by measuring the rate of rise of the condensate level in the receiver. The distillation rate is fixed by the conditions that the frictional pressure loss through the passage between the vaporization and condensation surfaces equals the difference between the vapor pressure of the salt in the still pot and the pressure at the lower end of the condenser. Thus, the distillation rate could be increased by either increasing the still pot temperature, which increases the salt vapor pressure, or decreasing the condenser pressure. The salt vapor pressure was assumed to be that of salt of the composition 90-7.5-2.5 mole% LiF-BeF_2-ZrF_4. A mixture of this composition produced vapor having a composition of approximately 65-30-5 mole% LiF-BeF_2-ZrF_4 and hence should approximate the composition of material in the still pot at steady state.

For operation under conditions where the vapor pressure of the still pot material was 1 mm Hg or greater, distillation rates of 1.5 ft^3 of salt/(day-ft^2) or greater could be obtained. Rates of this order were adequate to permit distillation to be used as a process step.

Two difficulties were encountered: (1) condensed ZrF_4 and unidentified molybdenum compounds in the vacuum line completely restricted flow on two occasions, and (2) a deposition of nickel and iron in the salt feed line to the still almost stopped the flow after the first two runs and caused a noticeable restriction in the replacement feed line after the fourth run.

The major metallic constituents of the deposition in the vacuum line were zirconium and molybdenum. The first restriction was removed by cutting into the vacuum line; the second was removed during the last run by heating the vacuum line to about 950 to 1050°C, thereby redistributing the material. Examination of the vacuum line during postoperational inspection showed that the free cross section of the pipe at the point of exit from the receiver was equivalent to about 50% of the original cross section. The material obstructing the vacuum line analyzed 39.4% zirconium and 11.6% molybdenum; F^- and O^{2-} were the major anions.

The cause for the metal deposition in the salt feed line was not completely understood. Two possible sources of the deposited material were: suspended metals and/or dissolved fluorides introduced with the feed salt, and corrosion products. The possibility that system corrosion may have been a factor was suggested by the composition of the deposits, ~0.9 wt% Co and 0.7 to 2 wt% Mo (both of these metals are constituents of Hastelloy N), and of the plug in the vacuum line (high molybdenum content). The extent of corrosion necessary to produce the materials found would have been very small and could not have been detected by the wall thickness measurements. Another possible source of corrosion products was the corrosion coupons in the still pot (although no coupon was severely corroded). A hypothesis for the reduction and deposition of dissolved fluorides was based on the observation that higher-valence fluorides are, in general, more volatile than lower-valence fluorides of the same element. This condition could have caused the still pot salt to be reducing in nature with respect to the feed salt and could have caused reduction and deposition of relatively noble metals at the entrance to the still pot.

Postoperational inspection showed the still to be in satisfactory condition for radioactive operation. Wall thickness measurements over the still pot and at both ends of the condenser showed an average decrease in wall thickness of only 1.6 mils. Length and diameter measurements showed changes of only 0.026 in. between points about 50 in. apart. Visual inspection of the inside of the still pot revealed that the metal was in good condition. The walls were shiny, and there was no evidence of pitting or cracking. Radiography also showed no evidence of physical change.

5 Two-Fluid Molten-Salt Breeder Reactors (1964-1967)

Not long after the successful startup of the MSRE, greater attention was turned to designs for future molten-salt breeder reactors (MSBRs) that would use thorium fuel. Little had been done on future breeder reactor design during the construction of the MSRE, although a 1964 progress report contained a section by Beecher Briggs that described current ORNL thinking on breeder reactors.

The effort to define a molten-salt breeder reactor was driven in large part by the desire to define a follow-on experiment to the MSRE, which ORNL internally called the "Molten-Salt Breeding Experiment," or MSBE. In order to define the technological goals of an MSBE, it would first be necessary to define an MSBR. Therefore the design team began devoting more and more effort to this reactor concept.

The result of their analysis was described in ORNL-4528, *Two-Fluid Molten-Salt Breeder Reactor Design Study*. It was a 1000-MWe plant that had four individual reactor units, two of which are depicted in Figure 6. Each provided approximately 550 thermal megawatts of heating power to a series of steam generators. The steam from each reactor module fed a single large 1000-MWe steam turbine.

The motivation for smaller, modular reactor units was a desire to achieve a high capacity factor. Individual units could be taken offline and repaired or maintained while the plant itself continued to operate at a fractional electrical output.

5.1 Chemical Processing

The chemical processing system for the reactor is shown in Figure 8. In the reactor, nuclear fission reactions take place that heat the salt and release high-energy neutrons. These neutrons are slowed down by collisions with the atoms of the graphite moderator to increase the probability that they will cause other reactions. About half of these neutrons are absorbed by the thorium in the blanket salt of the reactor, which consists of highly-depleted lithium fluoride (HDLiF), beryllium fluoride (BeF_2), and thorium tetrafluoride (ThF_4).

As thorium absorbs neutrons, it rapidly transmutes into ^{233}Pa, which has a 27-day half-life, decaying into ^{233}U. It is very undesirable that ^{233}Pa absorb another neutron before it decays to ^{233}U, since that would cause it to transmute into ^{234}U, which is not a reactor fuel. Therefore, ORNL engineers and chemists felt that it would be important to remove protactinium from the blanket of the reactor along with any uranium that had already formed from the decay of protactinium. They anticipated using a technique called "reductive extraction" to accomplish this removal. It involved introducing a stream of the blanket salt (containing very small amounts of protactinium and uranium) into the bottom of a extraction column. At the top of the same extraction column, labeled "Blanket Extractor" in Figure 8, a stream of liquid metallic bismuth would have been introduced containing 3000-4000 ppm of metallic thorium. Contact between the metallic thorium and the protactinium and uranium tetrafluorides dissolved in the salt led to an exchange of fluoride ions. First uranium and then protactinium would have been reduced from tetrafluorides to metals

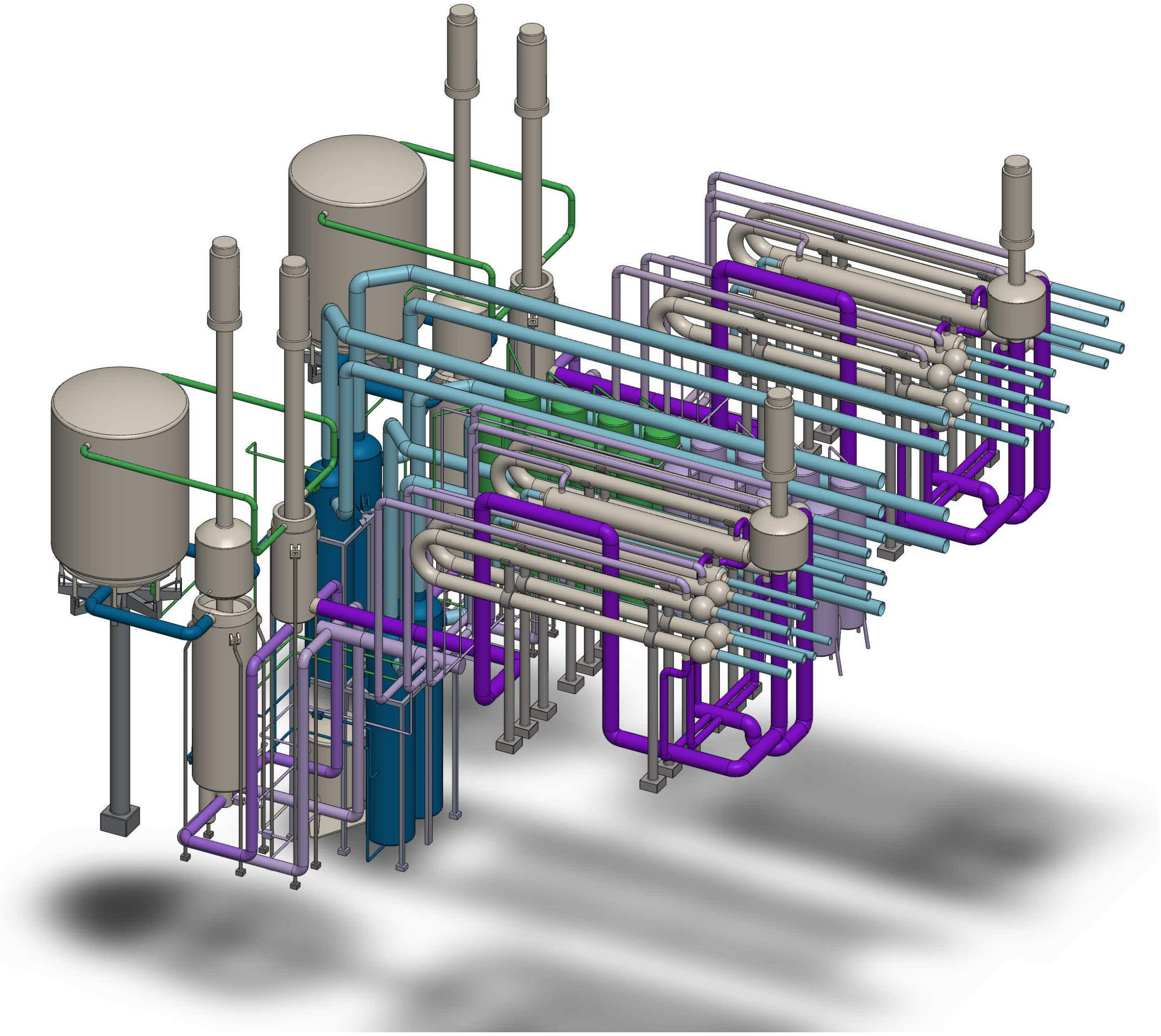

Figure 6: Two modular reactor units with their heat exchangers and steam generators, described in ORNL-4528. The flow channels for the fuel salt are colored in dark blue, the blanket salt in green, hot coolant salt in light purple, and cooler coolant salt in dark purple. The steam channels are shown in light blue.

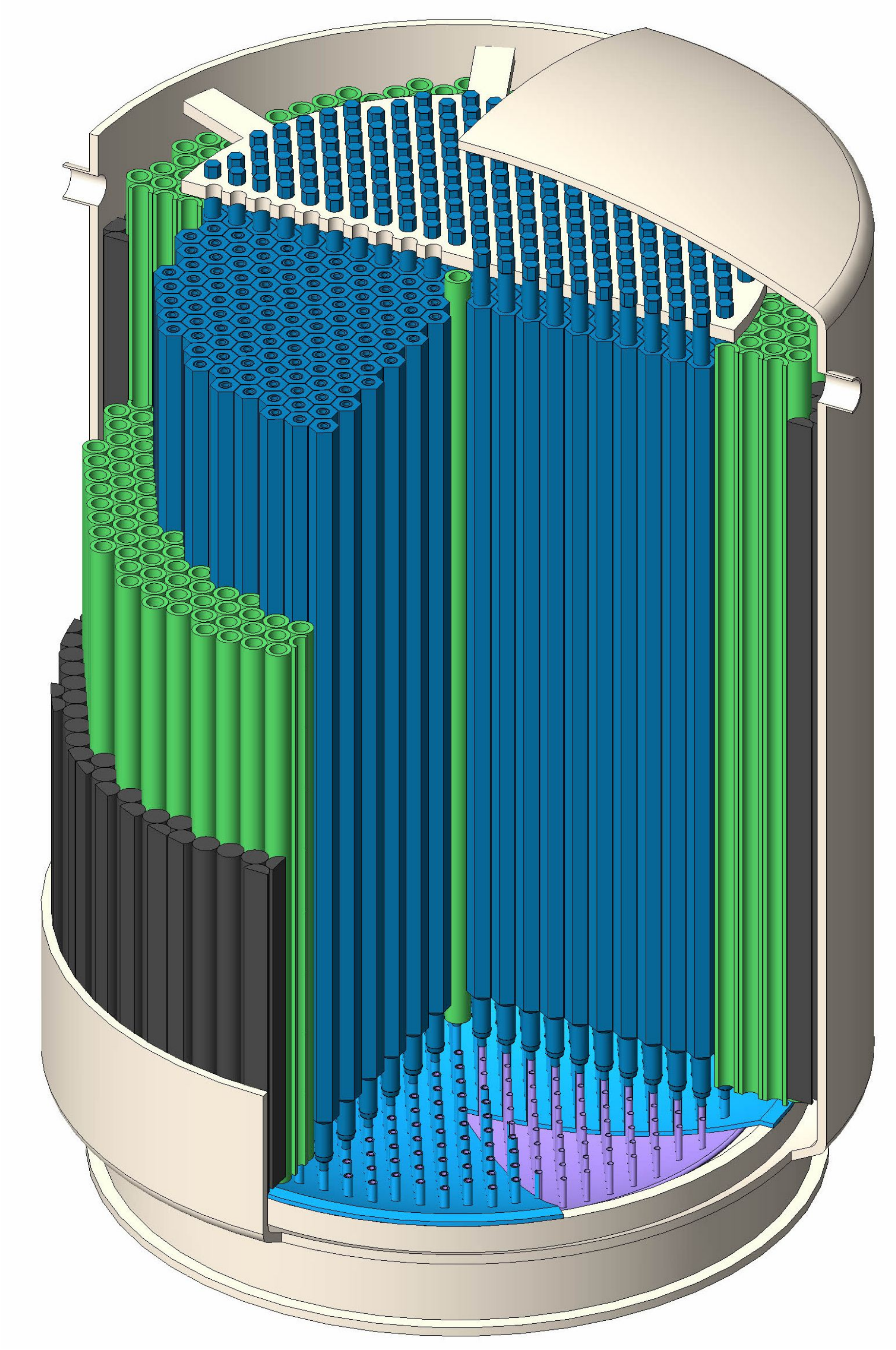

Figure 7: Cutaway view of the interior of one of the modular reactor units described in ORNL-4528. The reactor has three regions: the core region, shown in blue, consists of hexagonal graphite prisms with internal recursive channels for the flow of fuel salt. The blanket region, shown in green, consists of simple graphite cylindrical channels open at each end, filled with blanket salt. The reflector region, shown in dark grey, consists of cylindrical extrusions of graphite. The entire structure is contained in a vessel made of Hastelloy-N. The core region is attached to a plenum structure at the base of the reactor which collects salt as it enters the reactor and as it leaves.

while the thorium in the bismuth was oxidized to a tetrafluoride. The oxidized thorium entered the blanket salt while the reduced uranium and protactinium entered the bismuth stream. Thorium was an ideal reductant because the removed protactinium was replaced by an equivalent amount of the fertile material. ORNL researchers estimated that 96% of the protactinium and uranium present in the blanket would be removed by this technique, and that which was not removed was not lost; it simply stayed in the blanket fluid and was removed on another chemical processing pass.

The bismuth stream, containing small amounts of dissolved metallic protactinium, uranium, and unused thorium reductant, was directed towards a hydrofluorination column, where the metallic Th, Pa, and U were oxidized to tetrafluorides in the presence of a "decay salt" mixture, likely a very similar combination to that used in the blanket salt. The decay salt was routed back to the decay tank, where ^{233}Pa is given time to decay to ^{233}U outside of the neutron flux of the reactor. The bismuth stream emerging from the hydrofluorinator was loaded with new metallic lithium and thorium to serve as reductants.

To remove decayed uranium from the decay salt, fluorination with molecular fluorine (F_2) was proposed. Fluorination would promote UF_4 to UF_6, but would leave protactinium behind. Thus it represented a simple technique to separate the desirable uranium product from protactinium which still needed time to decay. The UF_6 generated in the column marked "Decay Fluorinator" in Figure 8 was then directed to a reduction column, where the UF_6 was directly reduced to UF_4 in the presence of LiF-BeF_2 salt that had been purified in a distillation column.

Fuel salt processing involved fewer chemical processing steps. Fuel salt, consisting of lithium fluoride, beryllium fluoride, and uranium tetrafluoride, and containing a certain concentration of fission product fluorides, was first directed to a fluorination column, marked "Fuel Fluorinator" in Figure 8. The fluorination process had to be very efficient to prevent excessive losses of uranium to the next process. UF_6 generated through fluorination was directed to the same reduction column as UF_6 that had been generated from the fluorination of decay salt.

The fuel salt, essentially stripped of uranium, passed into a distillation vessel where it was heated to temperatures of 1000°C at very low pressures. In these conditions, LiF and BeF_2 boiled out of the salt and were condensed on the top interior surface of the still, then directed to a collection region and pumped to the reduction column. Fission product fluorides, which did not boil off in this process, collected at the base of the distillation unit and were periodically tapped off for transfer to another area where they were prepared for disposal.

The purified LiF-BeF_2 and the UF_6 generated through fluorination were recombined into a fuel salt by passing hydrogen gas through the reduction column. Hydrogen reduced UF_6 to UF_4, generating HF in the process, which was then used in the hydrofluorinator as the reactant.

Using these processing techniques, it was anticipated that thorium could be introduced to the system, first as a reductant in bismuth. Since the amount of reductant far exceeded the minimum amount needed to reduce protactinium and uranium, a great deal more thorium would be used than was actually consumed in the reactor's blanket. An alternative process would have utilized an electrolytic cell to electrolyze ThF_4 in the presence of bismuth, creating metallic thorium dissolved in bismuth and bismuth trifluoride (BiF_3). But BiF_3 was a very corrosive agent to the structural materials that might be employed in the system. This alternative approach was depicted in Figure 9.

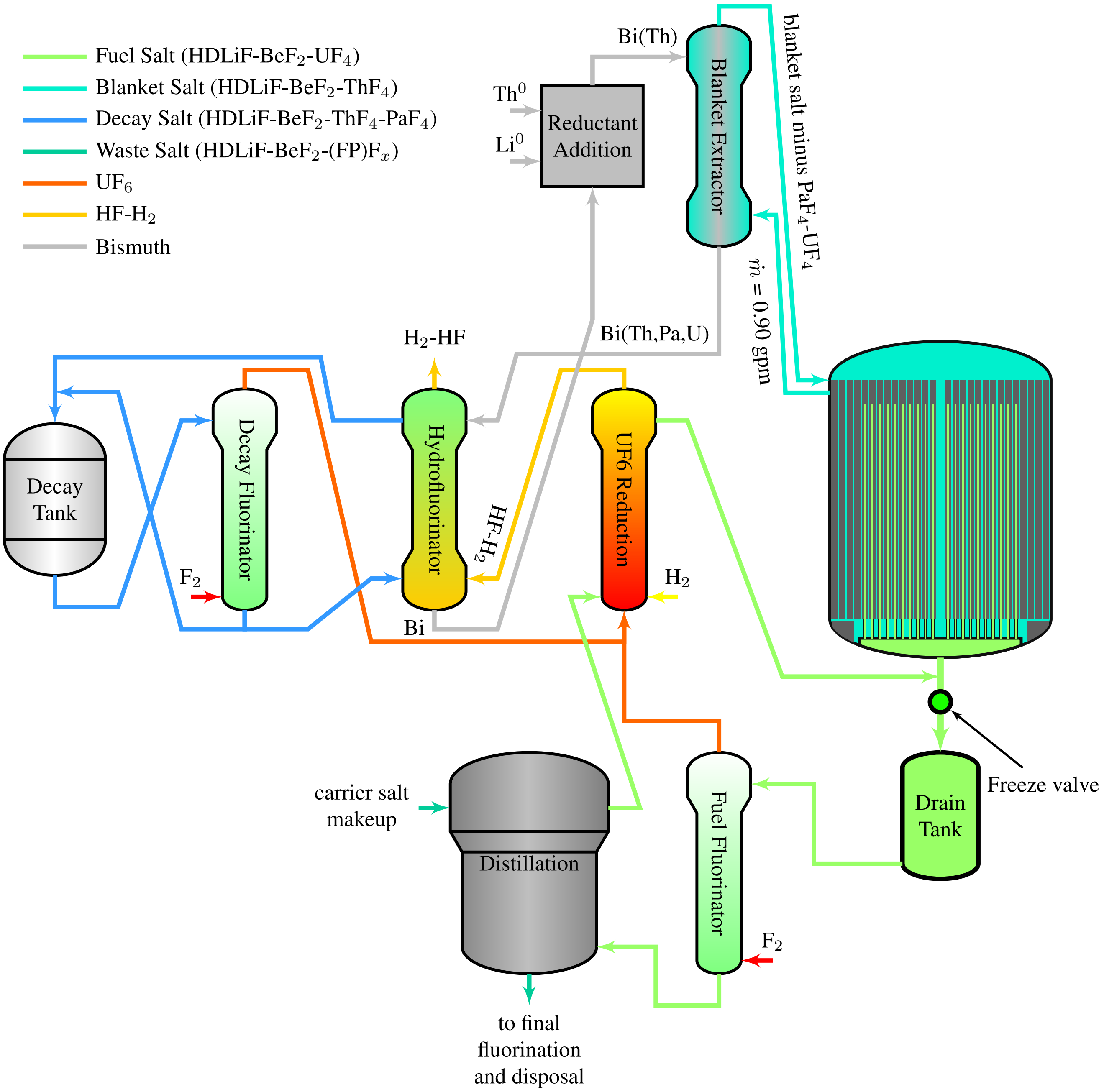

Figure 8: Chemical processing flow diagram for modular 250-MWe two-fluid reactor described in ORNL-4528.

With thorium metal supplied by an electrolytic cell rather that directly supplied, an individual thorium atom would likely undergo multiple passes through the extraction column (oxidized to salt in the hydrofluorinator and reduced back to metal in the electrolytic cell) before it first entered the blanket salt by being oxidized to salt while it reduced a protactinium or uranium ion to metal. In the blanket, thorium would eventually absorb a neutron, forming protactinium which would be removed in the extraction column by reduction to metal in bismuth. That metallic protactinium would be oxidized to protactinium tetrafluoride in the hydrofluorinator and pass into the decay tank. After undergoing radioactive decay to ^{233}U, the newly-formed uranium tetrafluoride would be removed from the decay tank by fluorination to UF_6. The UF_6 would pass to the reduction column, where it would be reduced to the tetrafluoride through contact with hydrogen, but this time it would be a part of the fuel salt and pass back into the reactor.

Exposed to neutrons, ultimately the ^{233}U would fission into two fission products, each of which would rapidly form fluorides from the four fluoride ions released in the fission of uranium tetrafluoride. Depending on the chemical nature of the two fission products, one or the other might pass out of the fuel salt as a noble gas or be collected on an interior surface as a noble metal. But if the fission product was an alkali metal, like rubidium or cesium, or an alkaline earth metal, like strontium or barium, or a lanthanide like cerium, lanthanum, neodymium, or samarium, it would be removed from the reactor when a stream of fuel passed into the distillation column and the LiF-BeF_2 solvent was boiled away from the fission products.

Hence, a thorium atom enters the bismuth extraction column and ultimately two fission products are removed from the reactor as a noble gas, a noble metal, or as the distillate at the base of the distillation column.

5.2 Fluorination Experimental Development

Fluorination converts the uranium tetrafluoride in the salt to volatile hexafluoride according to the reaction:

$$\mathrm{UF_4 + F_2 \rightarrow UF_6}$$

Since some fission and corrosion products (Mo, Ru, Nb, Cr, Te, and Tc) also form volatile fluorides, the gases were to be passed through traps of MgF_2 and NaF pellets at 400°C. These sorbers would retain the contaminants while passing UF_6, which would have been subsequently collected in a cold trap at -70°C for recycle to the reactor fuel stream.

Previous experience with batch fluorination of UF_4 in molten salt showed that nearly complete volatilization of UF_6 could be obtained at reasonable rates by sparging the salt with fluorine. The major problem associated with making this step continuous was corrosion, for which a frozen layer of salt on the vessel wall appeared to be the best strategy for mitigation.

Tests on a batch frozen-wall fluorinator were conducted in support of the molten-salt fluoride volatility process. Internal heat generation was provided by resistance heating, using nickel electrodes and 60-cycle AC power. This system was operable with gas flowing through an unheated

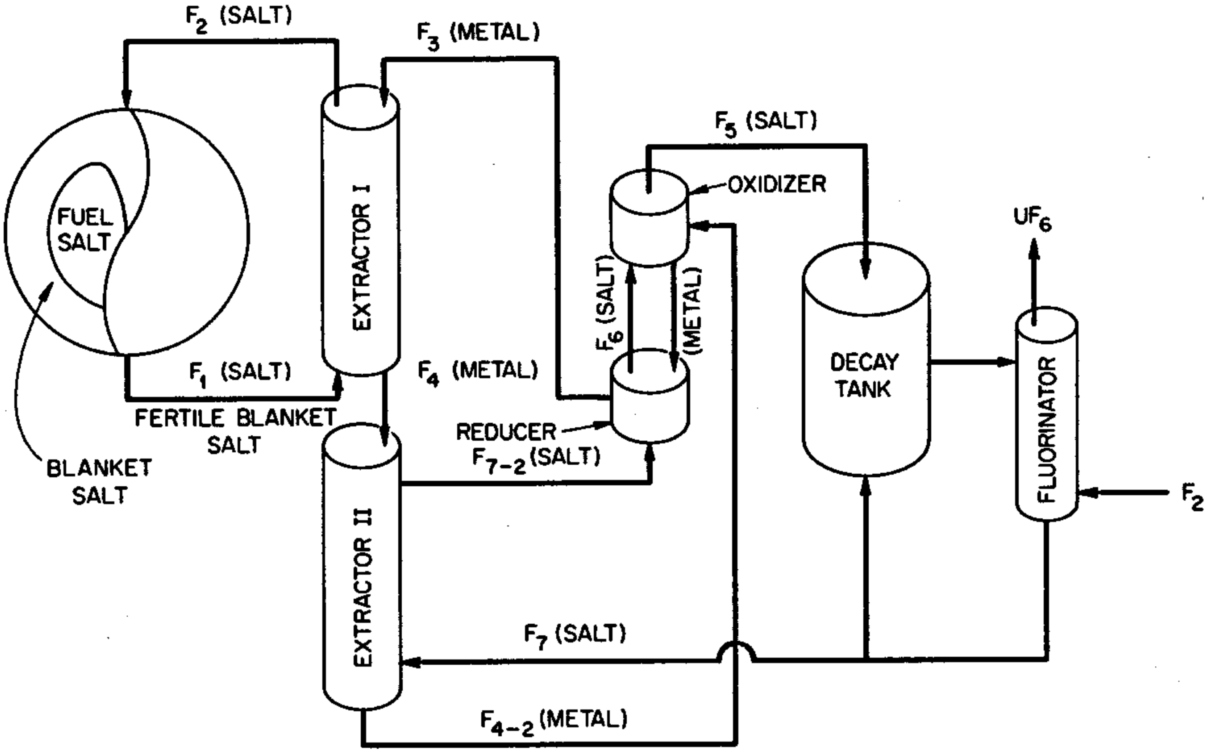

Figure 9: Use of an Electrolytic Cell to Generate Metallic Reductants for a Two-Fluid MSBR. (from ORNL-4254, figure 27.1)

line that entered the fluorinator at a point below the surface of the molten salt. Electrodes would not be necessary for a fluorinator operating on the fuel stream from an MSBR since adequate internal heat generation will be provided by decay of fission products in the salt.

For the reference 1000-MWe reactor it was necessary to cool the fuel stream for 1.5 days to reduce the specific heat generation rate to 3×10^4 BTU/(hr-ft^3) to facilitate temperature control.

Further studies of continuous fluorination were undertaken in 1966 using a 1-in.-diam nickel column having a salt depth of 48 in. No provision was made for corrosion protection by a frozen layer of salt and corrosion rates were, as expected, quite severe. Fluorination tests in which molten salt (NaF-LiF-ZrF_4) containing 0.5 wt % UF_6 was contacted countercurrently with fluorine at 600°C demonstrated removal of uranium from the salt with 96 to 99.4% efficiency in a 1-hr period of continuous operation. The flow rates (cc/min) for the molten salt and the fluorine were 15 and 70 (STP) respectively. Material balances were complicated by the inevitable corrosion of the nickel vessel. Complete removal of uranium from the salt with no corrosion would yield, for the above conditions, a UF_6 concentration of 17.6 mole% in the off-gas. Observed concentrations ranged as high as 35 mole% UF_6.

In 1967, experimental studies of continuous fluorination of molten salt were made in a system consisting of a 1-in.-diam, 72-in.-long nickel fluorinator and auxiliary equipment (Figure 10), which allowed the countercurrent contact of molten salt with fluorine. The fluorinator off-gas passed through a 400°C NaF bed for removal of chromium fluorides, a 100°C NaF bed for removal of UF_6, and a soda lime bed for F_2 disposal. A gas chromatograph was used to analyze the off-gas for F_2, UF_6, and N_2 just prior to its passage through the 100°C NaF bed. The uranium concentration in the salt after fluorination was determined from salt samples.

Fluorination tests were made in which molten salt (41.2-23.7-35.1 mole% NaF-LiF-ZrF_4) containing UF_4 was contacted countercurrently with a quantity of fluorine in excess of that required for conversion of UF_4 to UF_6. During a given experiment, salt and fluorine feed rates, operating temperature, and UF_4 concentration in the feed salt were maintained constant. However, these parameters were varied from one experiment to the next, as follows: operating temperature, from 525 to 600°C; salt feed rate, from 5 to 30 cm^3/min; fluorine feed rate, from 75 to 410 cm^3/min; and UF_4 concentration in the feed salt, from 0.12 to 0.35 mole% UF_4.

The effects of salt throughput, operating temperature, and initial UF_4 concentration on uranium removal during steady-state operation are shown in Figure 11. The data were based on the average uranium concentration in the fluorinated salt, which was determined at 15-min intervals during 1- to 2-hr periods of steady-state operation. A salt depth of 48 in. was used in the fluorinator in all tests, and the fluorine feed rate was varied from 215 to 410 cm^3/min (STP). Removal of the uranium fed to the fluorinator ranged from 97.4 to 99.9%, with removal in most of the runs being greater than 99%. Uranium removal was observed to decrease as the salt throughput was increased, as the operating temperature was lowered, and as the UF_4 concentration in the feed salt was decreased. As long as the quantity of fluorine used was stoichiometrically adequate, no significant effect of fluorine feed rate was noted.

In 1968, the feasibility of forming and maintaining a layer of frozen salt (which will protect the walls of a continuous fluorinator) was established by laboratory experiments using a countercurrent flow of molten salt and an inert gas. The experimental equipment consisted of a 5-in.-diam by 8-ft-

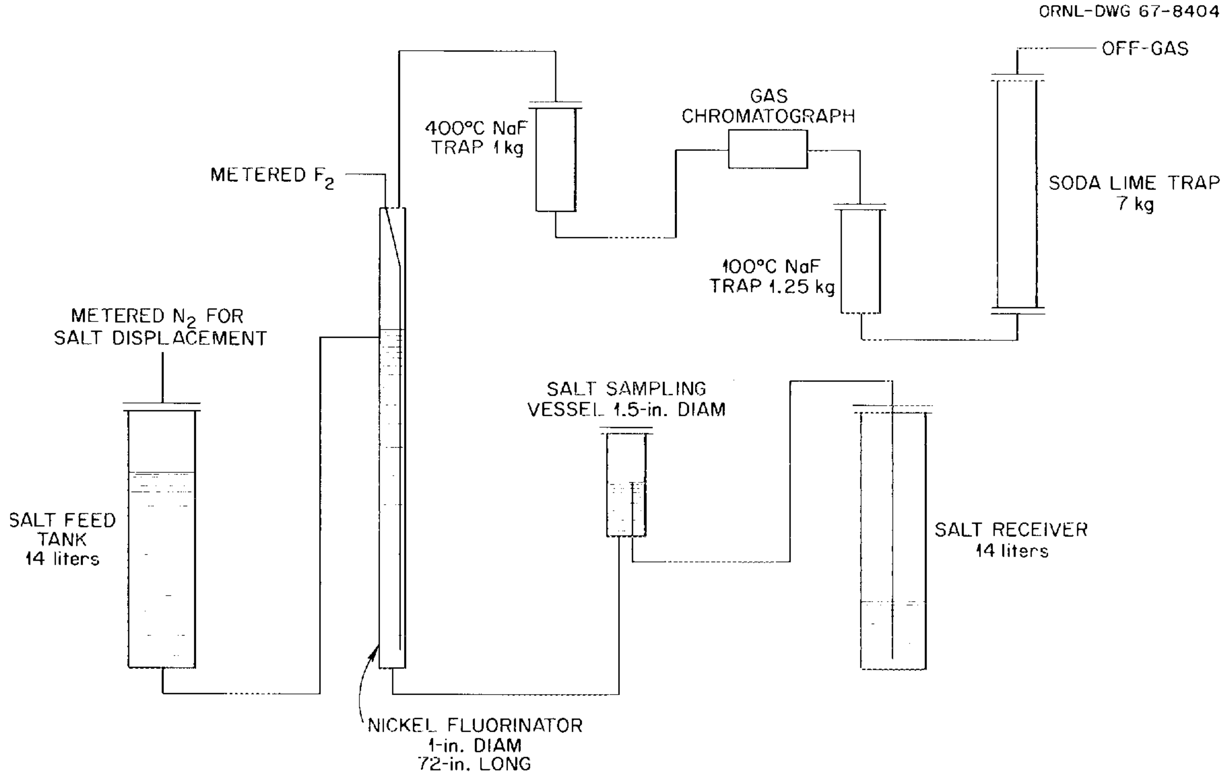

Figure 10: Equipment for Removal of Uranium from Molten Salt by Continuous Fluorination.

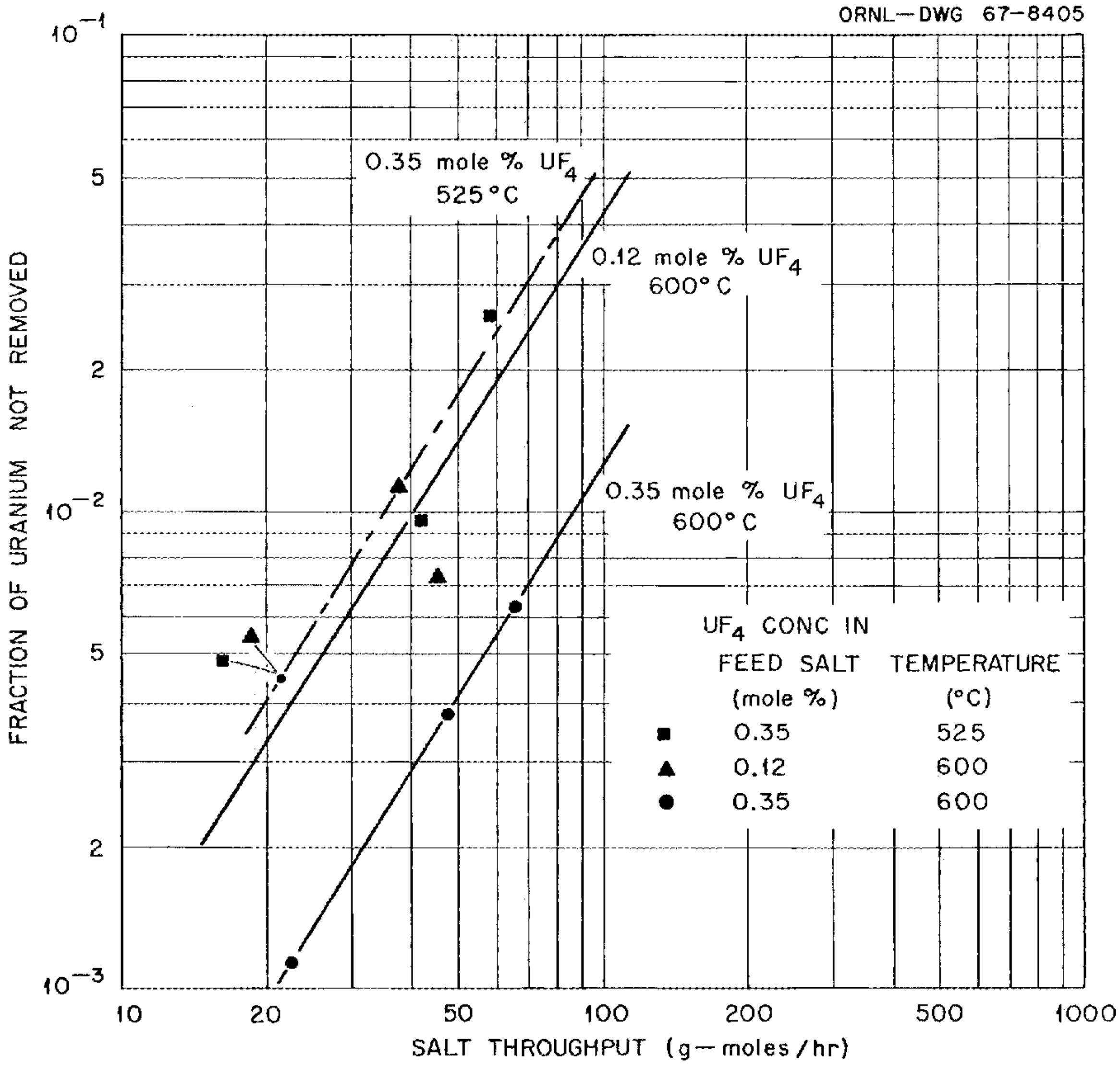

Figure 11: Variation of Uranium Removal with Salt Throughput, Operating Temperature, and UF_4 Concentration in Feed Salt.

high column, fabricated from sched 40 nickel pipe (Figure 12). An internal heat source consisting of three Calrod heaters contained in a 3/4-in.-diam sched 40 Inconel pipe was used to simulate the volume heat source that would be provided by fission product decay in the molten salt. Two sets of internal thermocouples, located near the center of each of two test sections, measured the radial temperature gradient. The location of the interface between the molten and the frozen salt could then be established from these measurements. Each test section was independently cooled by air flowing through spirally wound 3/8-in.-diam nickel tubing. Additional Calrod heaters were wound on the external surface of the fluorinator to provide auxiliary heat during heatup and to provide temperature control at the ends of the column. A 66-34 mole% LiF-ZrF_4 mixture, which has a liquidus temperature of 595°C and a phase diagram similar to the LiF-BeF_2 system, was metered from the feed tank for periods as long as 5 hr. This allowed data to be collected for a 1- to 2-hr period of steady-state operation.

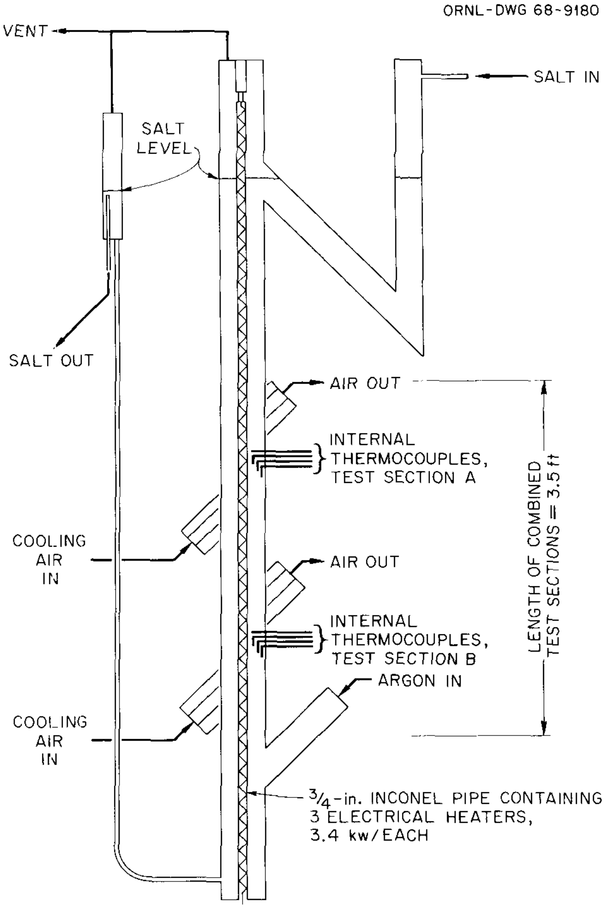

Figure 12: Experimental Equipment for Studying the Formation of a Frozen Salt Layer for Corrosion Protection. All external surfaces were provided with electrical heaters and were heavily insulated.

The principal objective of the experiments (i.e., the demonstration that a layer of frozen salt can be formed and maintained under approximate operating conditions) was achieved. In Table 1, experimental conditions are compared with reference conditions for processing the fuel stream of a 1000-MWe MSBR; the fluorinator has a salt throughput of 15 ft^3/day and an inlet uranium concentration of 0.8 kg per cubic foot of salt, with a 50% fluorine utilization.

Table 1: Comparison of Experimental and Reference Conditions for the Fluorination of 15 ft^3 of Molten Salt per Day

	Experimental	Reference
Salt flow rate, liters/hr	~3.3	17.7
Gas flow rate, std liters/min	0.5-2.0[a]	2.0[b]
Heat flux, W/ft of column height	600-1600	~2000

[a] Argon.
[b] Fluorine.

In general, the thicknesses of the frozen wall and the temperature profiles in the frozen salt were in good agreement with the values that were obtained by assuming radial heat transfer from a volume heat source. The thickness of the frozen wall ranged from 0.3 to 0.8 in., depending on operating conditions. The effect of heat generation in the layer of frozen salt was not simulated in these experiments.

The thermal conductivity of the frozen salt was calculated for each run from the experimentally determined temperature gradient and the measured heat flux; the relative agreement of calculated values was assumed to be indicative of the consistency of the experimental data. Thermal conductivity values calculated from the upper test section data were closely grouped around 0.75 BTU/(hr-ft-°F); however, values from the lower section were more widely scattered and were generally about 100% higher.

The heating-cooling system used on the column produced some variation in the temperature of the external wall (and hence the thickness of the frozen wall); in a typical run, the difference between the temperature of the salt liquidus and that of the wall ranged from 85 to 140°C.

Protection of the fluorine inlet nozzle from corrosion was an anticipated problem that was associated with operation of a frozen-wall fluorinator. A possible solution to this problem consisted of introducing the fluorine through a short section of 3-in.-diam pipe that intersects the fluorinator at a 45° angle. The inlet section would be protected from corrosion by a layer of frozen salt as in the fluorinator. Results of tests indicated satisfactory operation when the surfaces of the inlet section were covered by a layer of frozen salt that was produced by maintaining wall temperatures below the temperature of the salt liquidus. Heat was being supplied to the inlet section by means of turbulence (caused by bubbles) in the molten salt; in an actual instance, heat would be generated in the salt as a result of fission product decay. This method of introducing gas appeared to be feasible, although it will not produce small-diameter gas bubbles.

5.3 Distillation Experimental Development

In order to support the proposed distillation of the LiF-BeF$_2$ carrier salt from fission products, it was necessary to determine the relative volatilities of the lanthanide fission products relative to lithium fluoride. Ideally, the lower the relative volatility of the fission products relative to LiF, the more effective would be their separation through distillation. This work was reported on in ORNL-3830 in May 1965.

The experimental apparatus used to determine relative volatility included a cold finger to condense the vapor phase in a small vessel containing salt brought to the desired temperature and pressure, as shown in Figure 13.

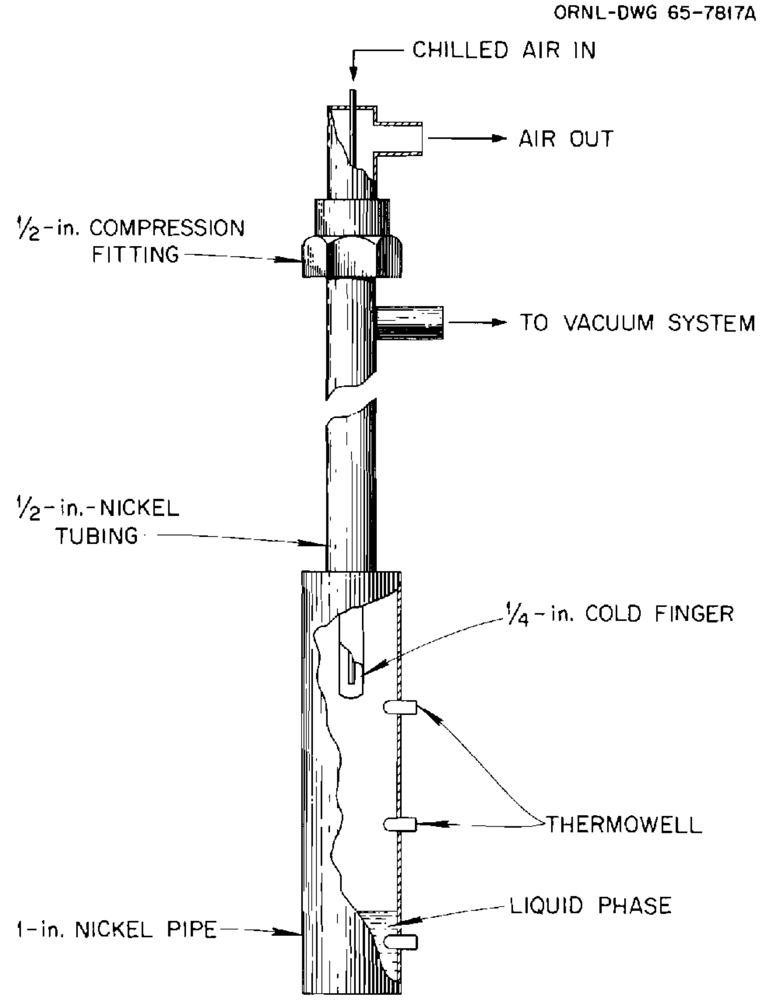

Figure 13: Equilibrium Still with Cold Finger.

The significant fission product lanthanides were analyzed with the exception of promethium. The results of the analysis are given in Table 2. They show that the average relative volatilities of the trivalent rare earths in LiF varied from 0.01 to 0.05. There appears to be a trend toward decreasing relative volatility with increasing temperature. Cerium tetrafluoride showed a relative volatility of about 0.15. Scouting tests with CsF showed it to have a relative volatility somewhere between 6 and 16.

Table 2: Relative Volatilities of Rare-Earth Fluorides in Lithium Fluoride

Test No.	Rare-Earth Fluoride	Liquid Mole Fraction	Average Relative Volatility			
			900°C	950°C	1000°C	1050°C
1	CeF_4	0.0067	0.133	0.167		0.208
2	SmF_3	0.01	0.033			0.009
3	NdF_3	0.01	0.025			0.016
4	PrF_3	0.001		0.038	0.020	0.014
5	EuF_3	0.001	0.041	0.037	0.028	0.012
6	CeF_3	0.01	0.043	0.033		0.018
7	LaF_3	0.001	0.035	0.024		
8	LaF_3	0.01	0.051	0.027	0.011	0.008

The following year another experimental apparatus was used to measure relative volatilities, and this work was reported on in ORNL-3945 in May 1966.

The volatility data was measured with a recirculating vapor-liquid equilibrium still shown in Figure 14. It was not as simple to operate as the cold-finger apparatus, but it was not subject to the same experimental biases. Vapor was continuously generated in the 2-in. still pot, condensed in the 1-in. condenser, and returned as liquid to the still pot. When concentrations reached a steady state, the concentration of the liquid in the still pot and that of the liquid in the condenser were equilibrium values from which relative volatilities could be determined, provided the liquid volumes in the condenser and boiler sections are well mixed. Measurements were made by freezing the salt and cutting the still in pieces to take samples.

Several runs lasting from 2 to 30 hr were made with this still at 1000°C and 0.5 mm Hg. Relative volatilities for systems of LiF containing from 1 to 2% selected rare-earth fluorides were measured. The relative volatility of cerium apparently lay between 0.0014 and 0.003; the relative volatility of neodymium lay between 0.00055 and 0.00089; and lanthanum had a relative volatility of about 0.00067. These results were reproducible after initial difficulties with still operation were resolved. The principal problems appeared to be: (1) avoiding excessive contamination of the condensate collector when charging the salt to the system, and (2) salt clinging to the walls where it could not be mixed with the bulk of the salt.

The relative volatility of CeF_3 determined by the equilibrium still was about one-tenth of that reported previously from cold-finger measurements, and the relative volatilities of NdF_3 and LaF_3 were one-fiftieth of those previously reported. These more accurate values were low enough to permit comfortable operation of a batch distillation system in the fuel-salt flowsheet.

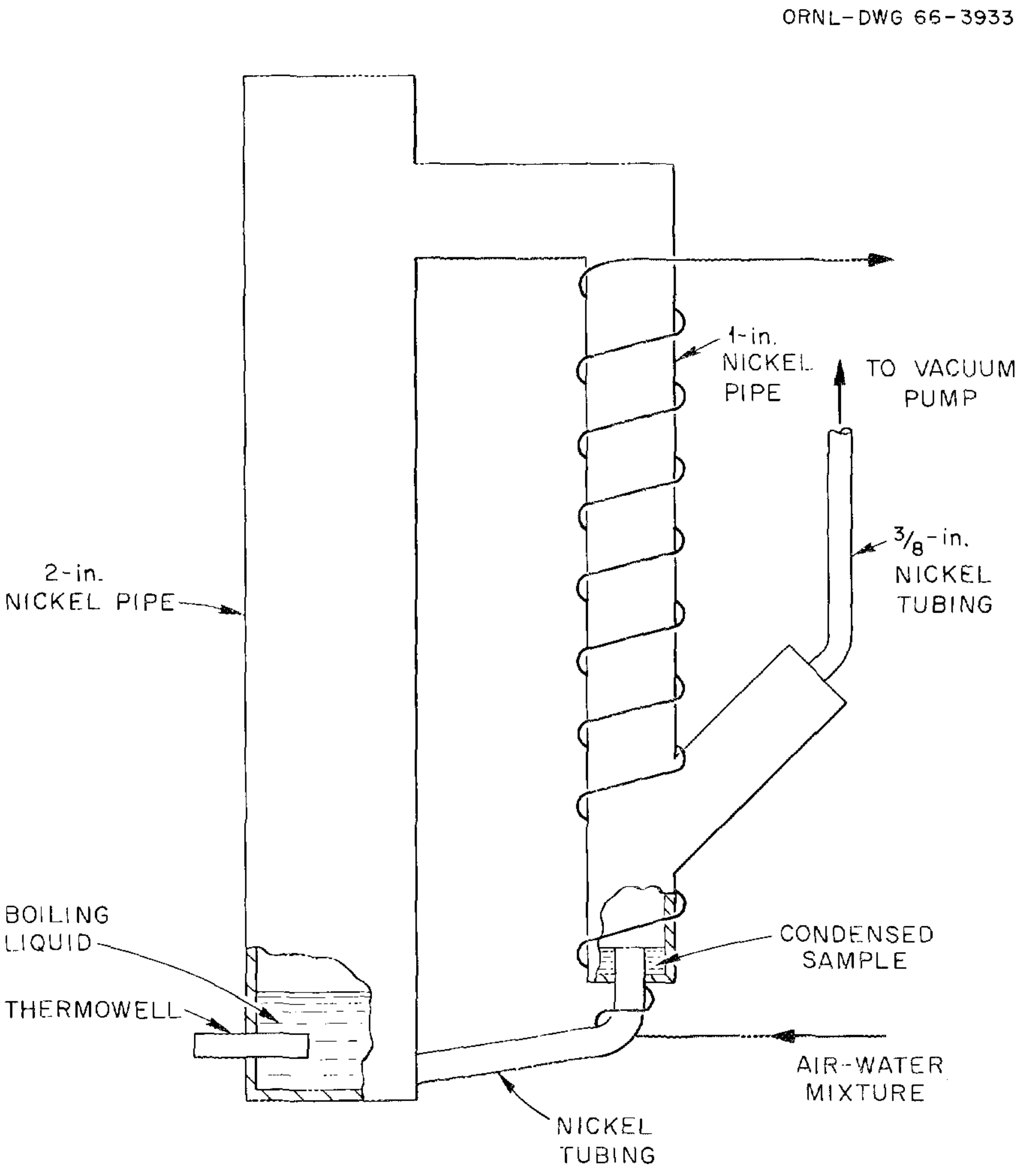

Figure 14: Schematic Diagram of Molten-Salt Equilibrium Still.

6 One-Fluid Molten-Salt Breeder Reactors (1968-1975)

Research into reductive extraction for bismuth and rare-earths (lanthanides) made ORNL chemical engineers particularly optimistic about the application of these processes to molten-salt breeder reactors. At the same time data was coming back to reactor designers on the dimensional stability of graphite at various temperatures in fast neutrons. The data on dimensional stability was not good, and was calling into question the way that graphite was intended to be used in two-fluid reactor designs.

These pieces of information were being compounded by the pressure to develop a concept for a follow-on breeding experiment to the MSRE, and this required that the eventual MSBR have at least a conceptual design into which the MSBE could trace.

This led ORNL MSRP leadership to undertake a serious shift in the design of the MSBR that we think may have been a mistake. They decided to abandon the two-fluid design, where thorium fertile material and uranium fuel material were kept separate, and to pursue a one-fluid design where thorium and uranium were combined in a single salt. At first blush, one might think that this could lead to a profound simplification of the chemical processing system, since there would no longer be a need to chemically remove U or Pa from the blanket, allow it to decay, and chemically add it to the fuel salt. But the reality of ^{233}Pa's decay time and its propensity to absorb neutrons, coupled with ORNL's desire to compete with the LMFBR as a breeder with a short doubling time, led to a more complex chemical processing system than the two-fluid design.

6.1 Chemical Processing

The chemical processing that was proposed for the one-fluid reactor is depicted in Figure 15 and in greater detail in Figure 16. There are several key differences from the chemical processing flowsheet for the two-fluid reactor, and a number of similarities.

In the one-fluid reactor, thorium, uranium, protactinium, and fission products are all mixed together in a single salt. Separation of thorium from lanthanide fission products is rather challenging because of their chemical similarities.[5] In each case, protactinium is extracted from the salt so that it can decay outside of the reactor. But in the case of the one-fluid reactor the need to extract protactinium is more pronounced. This is because of the strong desire to reduce the overall reactor inventory of fissile ^{233}U (and shorten the doubling time) the fuel salt (now containing protactinium) is exposed to a greater time-averaged fluence than is the case in the two-fluid design. In the two-fluid design a simple way to reduce the time-averaged fluence is to increase the blanket inventory, but this is not a realistic option in the one-fluid design because of the aforementioned desire to reduce the fissile inventory and doubling time.

---

[5] This is the same reason why thorium is generally found in rare-earth deposits.

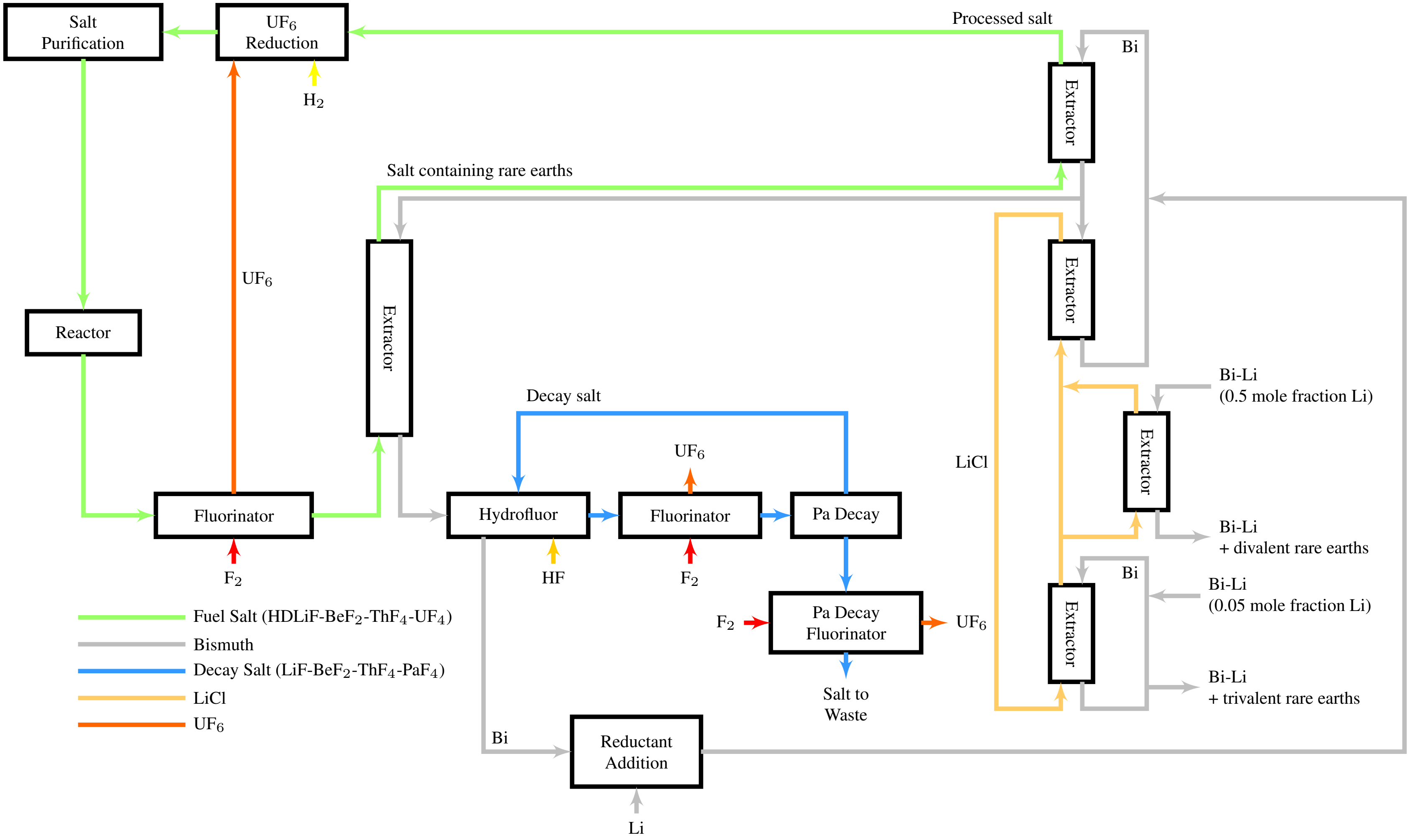

Figure 15: Block Diagram of ORNL MSBR one-fluid chemical processing system

The proposed processing scheme was detailed in the report ORNL-TM-3579, *Design and Cost Study of a Fluorination-Reductive-Extraction-Metal Transfer Processing Plant for the MSBR*, released in May 1972. Fuel salt was first held up for cooling and decay of the shortest lived fission products, then routed to the primary fluorinator, where most of the uranium was removed by fluorination to UF_6 using gaseous molecular fluorine (F_2) as the fluorination agent. The salt, now stripped of most of its uranium, was routed to an extraction column where metallic bismuth containing lithium and thorium as reductants were contacted with the salt. The remaining uranium, protactinium, and zirconium in the salt were reductively extracted to the bismuth, leaving a salt now that only contained fission products (beyond its base composition of LiF-BeF_2-ThF_4). This salt entered another reductive extraction column where bismuth containing lithium contacted the salt to remove lanthanide fission products and some thorium. The salt then passed to a reduction column where UF_6 was reduced to UF_4 in the salt, refueling it and preparing it for return to the reactor. Makeup BeF_2 and ThF_4 were also added and any residual bismuth was removed from the salt. After a final cleanup step and valence adjustment the purified salt was returned to the reactor.

The bismuth containing some uranium, protactinium, and zirconium was directed to a hydrofluorination column where the metallic solutes in the bismuth were oxidized into their fluoride forms in the presence of a decay salt. The decay salt, containing UF_4, PaF_4, ThF_4, and ZrF_4 passed into a decay tank where ^{233}Pa was allowed to decay to ^{233}U. This uranium generated by protactinium decay was removed through fluorination to UF_6 and routed to the reduction column to refuel the purified fuel salt.

The bismuth that had been used to carry the proactinium, having been scrubbed of its chemical passengers in the hydrofluorination stage, was routed to the "metal transfer" stage of the processing system where it was combined with bismuth containing lanthanide fission products that had been extracted from the fuel salt. These bismuth streams contacted a salt stream of lithium chloride. Lanthanides transfer to the LiCl but thorium is left behind, accomplishing a decontamination between these two steps. The LiCl is then was successively contacted with streams of bismuth containing metallic lithium reductant which removed the divalent and trivalent lanthanides in separate columns. The bismuth stream containing trivalent lanthanides was hydrofluorinated in the presence of a salt stream that had been designated for waste. The bismuth stream containing divalent lanthanides was combined with the one emerging from the protactinium extraction column and hydrofluorinated into the decay salt. Hence, both the decay salt and the waste salt were contaminated with fission products. Decay salt was the precursor for the waste salt as it was periodically discarded every 220 days. A final fluorination step captured any decayed uranium before discard.

The fluorinators would use F_2 as the reagent; the hydrofluorinators would use HF, and the reduction column would use H_2. Based on the production and consumption rates, a recycling system for these reagents was proposed. An electrolytic cell would split HF into F_2 and H_2, which would then be used in the fluorinators and reduction column, respectively. HF emerging from the reduction column would be used in the hydrofluorinators or routed to the electrolytic fluorine cell for production of F_2 and H_2. Mixed streams of HF and H_2 would be separated in an HF distillation system. HF would be sent to the electrolytic cell while H_2 would be cleaned up in a caustic scrubber using potassium hydroxide (KOH) in order to capture any residual fluorides. The H_2 stream would be recycled to the system but a small amount (5%) would be directed to an alumina absorber, where any fission products like selenium hexafluoride or tellurium hexafluoride would be trapped. The hydrogen stream would also pass through a charcoal absorber to capture noble gases like krypton and xenon before being released up the stack.

Overall, the chemical processing system required for the one-fluid reactor was substantially more challenging than that required for the two-fluid reactor. The fundamental reason for this challenge is the chemical similarity between thorium and the lanthanide fission products, but it was also compounded by the need to extract protactinium rapidly and its connection to fissile inventory.

It should be noted that all of these challenges applied to the goal of a short-doubling-time molten-salt breeder reactor, which was the challenge ORNL faced in the 1960s as these design concepts were being evaluated. If the reactor wasn't attempting to achieve a high breeding gain, or if it was perhaps not even a breeder at all, but an enriched-uranium-fueled reactor, then many of these challenges might not apply and there would be the potential for tremendous simplification of the chemical processing system. It is important to view these chemical processing systems in the context of the design objectives they were attempting to achieve, which were ambitious then and remain ambitious now.

The capital costs for the chemical processing system of the one-fluid MSBR were given in Table 10 of ORNL-TM-3579 as \$35.6M in 1970 dollars. This was based on a 1000-MWe reactor, a reactor fuel volume of 1683 ft^3, and a processing cycle time of 10 days. This cost correlates to a cost of \$214M in 2013 dollars, or \$0.214/watt installed.

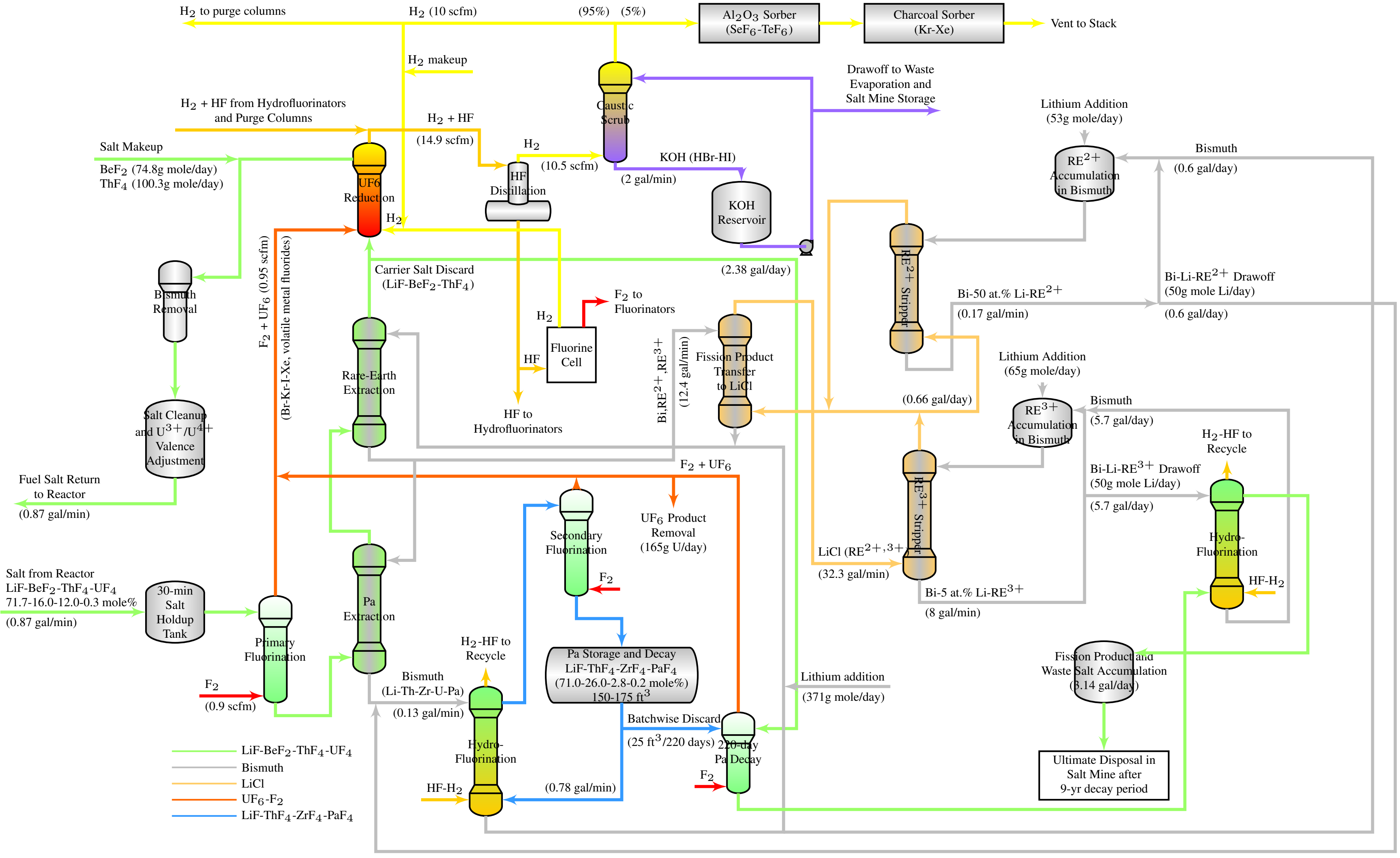

Figure 16: Flow Diagram of the Fluorination-Reductive Extraction-Metal Transfer Process. Values apply to processing a 1000-MWe MSBR on a 10-day cycle.

6.2 Continuous Fluorination Experimental Development

During the time that the one-fluid breeder reactor was the reference design, progress continued to be made in the development of continuous fluorinators, which retained an important position in fuel salt processing. Experimental studies of fluorination of molten salt were carried out in a 1-in.-diam., 72-in.-long nickel fluorinator that allowed countercurrent contact of molten salt with fluorine. In these tests, molten salt (41-24-35 mole% NaF-LiF-ZrF_4) containing UF_4, was countercurrently contacted with a quantity of fluorine in excess of that required for the conversion of UF_4 to UF_6. Experiments were carried out with temperatures ranging from 525 to 600°C, UF_4 concentrations in the feed salt ranging from 0.12 to 0.35 mole%, and a range of salt and fluorine feed rates. The fraction of the uranium removed from the salt ranged from 97.5% to 99.9%.

Axial dispersion in the salt phase was anticipated to be important in the design of continuous fluorinators, and gas holdup and axial dispersion were measured in columns having diameters ranging from 1 to 6 in. using air and aqueous solutions. Data were obtained for wide ranges of viscosity, surface tension, and superficial gas velocity. Correlations for gas holdup and axial dispersion were developed which were believed to be applicable to countercurrent contact of molten salt and fluorine in a continuous fluorinator. These correlations and the data on uranium removal in the 1-in.-diam continuous fluorinator were used for estimating the performance of larger diameter continuous fluorinators.

The combination of molten salt and fluorine results in a highly corrosive environment, and a future continuous fluorinator will need to protect against corrosion by maintaining a layer of frozen salt on surfaces that would otherwise contact both molten salt and fluorine, preventing molten salt from reaching the surface will allow passivation of the nickel to occur.

The feasibility of maintaining frozen salt layers in gas-salt contactors was demonstrated in tests in a 5-in.-diam, 8-ft-high simulated fluorinator in which molten salt (66-34 mole% LiF-ZrF_4) and argon were countercurrently contacted. An internal heat source in the molten region was provided by Calrod heaters contained in a 3/4-in.-diam pipe along the center line of the vessel. A frozen salt layer was maintained in the system with equivalent volumetric heat generation rates of 10 to 55 kW/ft^3. For comparison, the heat generation rates in fuel salt immediately after removal from the reactor and after passing through vessels having holdup times of 5 and 30 min are 57, 27, and 12 kW/ft^3, respectively.

Operation of a continuous fluorinator with nonradioactive salt required a means for generating heat in the molten salt that was not subject to corrosion. Radio-frequency induction heating in fluorinator simulations was studied using nitric acid as was autoresistance heating using 60-Hz power with molten salt (65-35 mole% LiF-BeF_2) in a 6-in.diam fluorinator simulator. Successful operation with auto-resistance heating rates as high as 14.5 kW/ft^3 was carried out; the expected power density in processing plant fluorinators is 12 kW/ft^3. Autoresistance heating was the preferred method, since it could be used over a wider range of operating conditions and since the electrical power supply is much simpler than that required for induction heating.

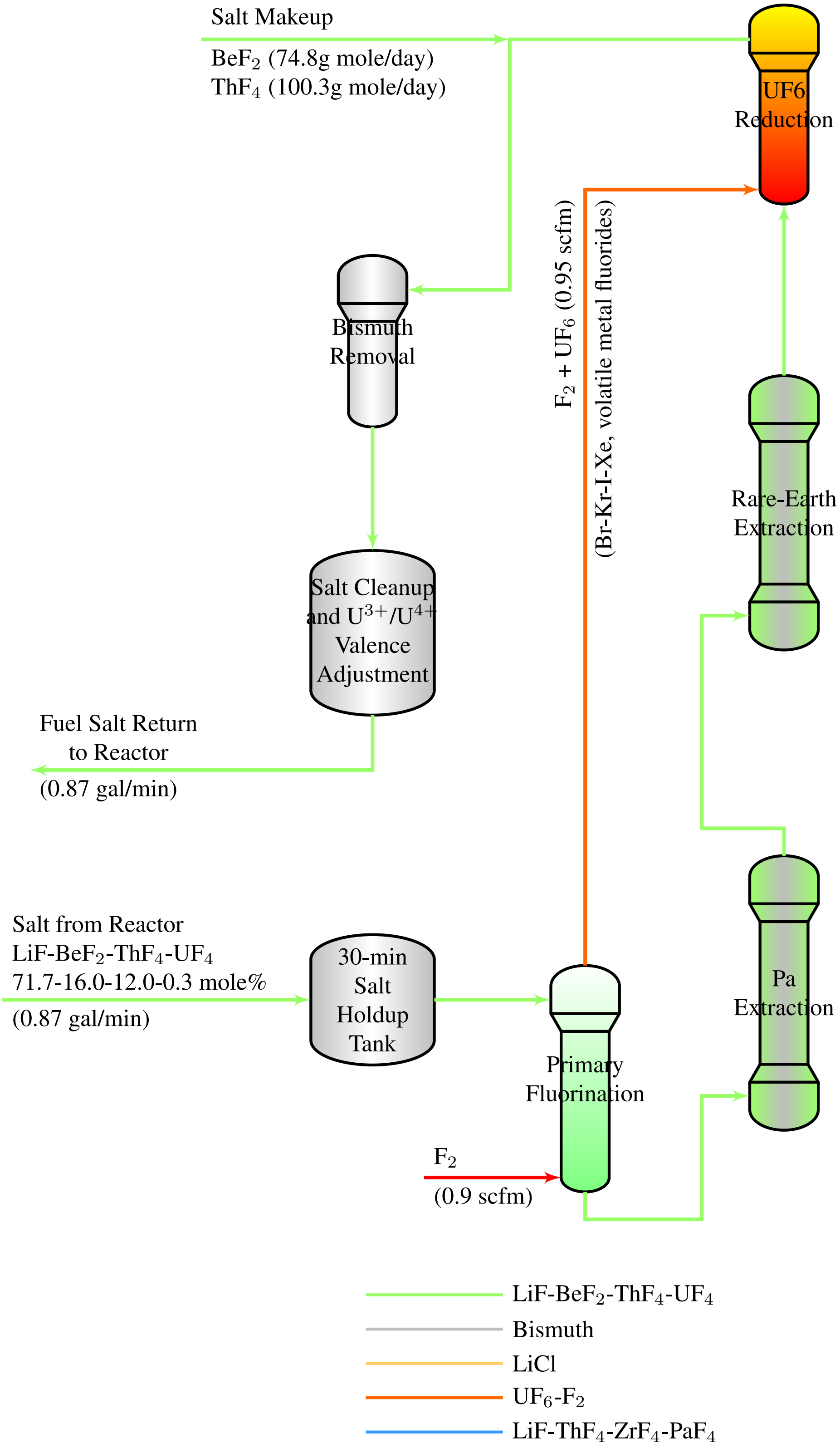

Figure 17: Chemical processing steps applied to the fuel salt of the one-fluid reactor design described in ORNL-4541 and ORNL-TM-3579.

6.3 Reductive Extraction Experimental Development

Reductive extraction, which was considered as a protactinium removal technique while the two-fluid reactor was the reference design, assumed a much larger role in the one-fluid design. Consequently, ORNL researchers operated a salt-bismuth reductive extraction facility in which uranium and zirconium were extracted from salt by countercurrent contact with bismuth containing reductant. More than 95% of the uranium was extracted from the salt by a 0.82-in.-diam, 24-in.-long packed column. The inlet uranium concentration in the salt was about 25% of the uranium concentration in their one-fluid reference MSBR. These experiments represented the first demonstration of reductive extraction of uranium in a flowing system. Information on the rate of mass transfer of uranium and zirconium was also been obtained in the system using an isotopic dilution method, and HTU values of about 4.5 ft were obtained.

Correlations were developed for flooding and dispersed-phase holdup in packed columns during countercurrent flow of liquids having high densities and a large difference in density, such as salt and bismuth. These correlations, which were verified by studies with molten salt and bismuth, were developed by study of countercurrent flow of mercury and water or high-density organics and water in 1- and 2-in.-diam. columns packed with solid cylinders and Raschig rings varying in size from 1/8 to 1/2 in. Data was also obtained on axial dispersion in the continuous phase during the countercurrent flow of high-density liquids in packed columns, and a simple relation was developed for predicting the effects of axial dispersion on column performance.

The successful operation of salt-metal extraction columns was dependent upon the availability of a bismuth-salt interface detector. To this end, a successful demonstration was made of an eddy-current-type interface detector that consists of a ceramic form on which bifilar primary and secondary coils are wound. Contact of the coils with molten salt or bismuth was prevented by enclosing the element in a molybdenum tube. Passage of a high-frequency alternating current through the primary coil induced a current in the secondary coil whose magnitude was dependent on the conductivities of the adjacent materials; since the conductivities of bismuth and salt are quite different, the induced current reflected the presence or absence of bismuth. The detector appeared to be a practical and sensitive indicator of either salt-bismuth interface location or bismuth level.

Design and development work was initiated on a reductive extraction process facility that would allow operation of the important steps for the reductive extraction process for protactinium isolation. The facility would have allowed countercurrent contact of salt and bismuth streams in a 2-in.-diam., 6-ft-long packed column at flow rates as high as about 25% of those required for processing a 1000-MWe MSBR.

6.4 Metal Transfer Process Experimental Development

All aspects of the metal transfer process for the removal of rare earths were demonstrated in an engineering experiment. The equipment consisted of a 6-in.-diam compartmented vessel in which were present about 1 liter each of MSBR fuel carrier salt, bismuth saturated with thorium, and LiCl. The fluoride salt initially contained $^{147}NdF_3$ at the tracer level and LaF_3 at a concentration of 0.04 mole fraction. During the experiment, the rare earths were selectively extracted into the LiCl along with a negligible amount of thorium. Provision was made for circulating the LiCl through a chamber containing bismuth having a lithium concentration of 38 at.%, where the rare earths and thorium were removed. The distribution ratios for the rare earths remained constant during the experiment at about the expected values. About 50% of the neodymium and about 70% of the lanthanum were collected in the Li-Bi solution. The final thorium concentration in the Li-Bi solution was below 5 ppm, making the ratio of rare earths to thorium in the Li-Bi greater than 10^5 times the initial concentration ratio in the fuel salt and thus demonstrating the selective removal of rare earths from a fluoride salt containing thorium.

A larger metal transfer experiment was put into operation that used salt and bismuth flow rates that are about 1% of the values required for processing a 1000-MWe MSBR, and the preliminary design was carried out for an experiment that would have used a three-stage salt-metal contactor and flow rates that are 5 to 10% of those required for a 1000-MWe MSBR.

6.5 Fuel Reconstitution Experimental Development

To reconstitute the fuel salt, UF_6 would be directly absorbed in MSBR fuel carrier salt containing UF_4, resulting in the formation of soluble non-volatile UF_5. Gaseous hydrogen reacts with dissolved UF_5 reducing it to UF_4

Since both UF_6 and UF_5 are strong oxidants, experiments were conducted primarily to find a material that was inert to these species. They showed that, at 600°C, nickel, copper, and graphite are not sufficiently inert but that gold is stable both to gaseous UF_6 and to salt containing up to 6 wt % UF_5. Consequently, subsequent studies were conducted in gold apparatus.

Results from several experiments showed that UF_5 dissolved in molten salt slowly disproportionates to UF_6 and UF_4 and that the rate of disproportionation is second order with respect to the concentration of UF_5. The studies also indicate that the solubility of UF_6 in the salt is low.

6.6 Removal of Bismuth from Fuel Salt

In a processing plant, the fuel salt would be contacted with bismuth containing reductant in order to remove protactinium and the rare earths. It would be necessary that entrained or dissolved bismuth be removed from the salt before it is returned to the reactor, since nickel is quite soluble in bismuth (about 10 wt %) at the reactor operating temperature. Efforts to measure the solubility of bismuth in salt have indicated that the solubility is lower than about 1 ppm, and the expected solubility of bismuth in the salt under the highly reducing conditions that will be used is very low. For these reasons, bismuth can only be present at significant concentrations in the salt as entrained metallic bismuth.

In order to characterize the bismuth concentration likely to be present in the salt after it is contacted with bismuth, ORNL periodically sampled the salt in engineering experiments involving contact of salt and bismuth. The results indicated that the bismuth concentration in the salt in most cases ranged from 10 to 100 ppm after countercurrent contact of the salt and bismuth in a packed-column contactor; however, concentrations below 1 ppm were observed in salt leaving a stirred-interface salt-metal contactor in which the salt and metal phases are not dispersed. One of the difficulties was that of preventing contamination of the samples with small quantities of bismuth during cleaning of the samples and the ensuing chemical analyses.

It was expected that contact of the salt with nickel wool would be effective in removing entrained or dissolved bismuth, since a large nickel surface area can be produced in this manner.

A natural circulation loop constructed of Hastelloy N and filled with fuel salt was operated by the Metals and Ceramics Division for about two years; a molybdenum cup containing bismuth was placed near the bottom of the loop. Reported concentrations of bismuth in salt from the loop (<5 ppm) were essentially the same as those reported for salt from a loop containing no bismuth. No degradation of metallurgical properties for corrosion specimens removed from the loop containing bismuth was noted.

7 Denatured Molten-Salt Reactors (1976-1980)

In May 1974, India detonated a nuclear weapon that had been made from plutonium it had extracted from a heavy-water research reactor. Coming several years after the ratification of the Nuclear Non-Proliferation Treaty (which India had not signed) it caused a great deal of political discussion about the role of breeder reactors, plutonium, and chemical reprocessing. During the 1976 election Democratic candidate Jimmy Carter pounded incumbent President Gerald Ford on the topic of nuclear proliferation and chemical processing, leading Ford to announce five days before the election that the United States would suspend plans to chemically process spent nuclear fuel. The presidential election was close, but Jimmy Carter won and continued the newly-announced policy.

In his announcement on October 28, 1976, Ford specifically mentioned that "nuclear power" produced plutonium that could be used to fuel other nuclear reactors or for nuclear weapons.[6] That statement remains highly debatable to this day. Nevertheless, the thorium-fueled breeder reactors that were being designed by ORNL did not produce any appreciable amount of plutonium during their anticipated operations. One might have wondered why this did not lead to their elevation in priority and status in the planning of the ERDA (the successor organization to the AEC). But there is no indication that this happened.

Early in his adminstration, Carter announced that solar energy would be his prime focus and that he would cut back drastically on "the concentration involving the breeder reactor and a plutonium society."[7] He reiterated his concerns about proliferation and asserted that the US had vast inventories of coal that could be burnt for power. He also announced that there would be further investigations into reactors that did not involve "direct access to materials that can be used for nuclear development."[8]

A few weeks later, Carter announced to a joint session of Congress that the central effort in ERDA's fast-breeder reactor program, the Clinch River Breeder Reactor, would be deferred indefinitely.[9] In a fact sheet accompanying his speech, he announced that the US "breeder" program would be redirected toward evaluation of alternate breeders, fuels, and advanced converter reactors with emphasis on nonproliferation and safety concerns.[10]

After the second cancellation of the Molten-Salt Reactor Program in 1976, there was a brief effort during the Carter Administration to evaluate reactors that had enhanced proliferation resistance. This effort was undertaken by a small subset of researchers from the original MSRP, including Dick Engel, Harold Bauman, Warren Grimes, and Herb McCoy. Their results were published in

---

[6] Gerald Ford, "Statement on Nuclear Policy," October 28, 1976, http://www.presidency.ucsb.edu/ws/?pid=6561

[7] Jimmy Carter, "Interview With the President Remarks and a Question-and-Answer Session With a Group of Publishers, Editors, and Broadcasters," March 25, 1977, http://www.presidency.ucsb.edu/ws/?pid=7241

[8] Jimmy Carter, "Nuclear Power Policy Remarks and a Question-and-Answer Session With Reporters on Decisions Following a Review of U.S. Policy," April 7, 1977, http://www.presidency.ucsb.edu/ws/?pid=7315

[9] Jimmy Carter, "NATIONAL ENERGY PLAN - Address Delivered Before a Joint Session of the Congress," April 20, 1977, http://www.presidency.ucsb.edu/ws/?pid=7372

[10] Jimmy Carter, "National Energy Program Fact Sheet on the President's Program," April 20, 1977, http://www.presidency.ucsb.edu/ws/?pid=7373

two ORNL reports in August 1978[11] and March 1979[12].

Their point-of-departure was the ORNL reference design MSBR, using a single fluid and a sophisticated chemical processing system described previously. Among the modifications considered were elimination of the breeding gain, a reduction in the power density (and specific power) so that protactinium isolation could be avoided, and.several conceptual variations in the fuel processing cycle. Denaturing the reactor with depleted uranium was not initially considered because that would lead to substantial plutonium production and would forego one of the basic advantages of the use of thorium fuel. But their conclusion was that the reference MSBR did not meet the new, more-rigorous standards that Carter had announced.

7.1 Chemical Processing Concepts

The chemical processing system for the denatured MSR also used the reference MSBR as the point-of-departure, but it became even more complex, as shown in Figure 18. Denaturing the uranium was the root cause of this additional complexity:

1. In the reference MSBR, the uranium content was predominantly fissile (^{233}U) whereas in the denatured MSR the uranium content was predominantly fertile (^{238}U). The fissile content had much higher levels of ^{253}U than the reference MSBR, and all of the uranium had to be preserved in the chemical processing steps. This meant that much more uranium would need to be fluorinated and carefully returned to the fuel salt at the end of processing than in the MSBR case.
2. The presence of ^{238}U led to the generation of ^{239}Pu and other isotopes of plutonium. The thermal-neutron spectrum of the denatured MSR also meant that a significant fraction of this plutonium would not fission on the first pass, leading to the formation of transuranic nuclides like americium and curium. The plutonium was a valuable fissile resource and also needed to be carefully preserved in the chemical processing steps so that it could be returned to the fuel salt. But plutonium was not chemically separable by fluorination and would come out of the salt in the same bismuth extraction step that removed protactinium from the salt.
3. The goal of a breeding gain in the reference MSBR (~7% surplus fuel generated per annum) was replaced by a less-ambitious goal of "break-even" breeding, where the reactor only supplied enough fissile to compensate for its consumption. This less-ambitious goal was still quite challenging for the denatured MSR because ^{239}Pu was an inferior fissile fuel in the thermal spectrum compared to ^{233}U, generating fewer neutrons per absorption of a thermal neutron.
4. The core power density of the reactor had been decreased considerably, leading a fissile inventory approximately three times greater than the reference MSBR (for the same electrical power generation). This further increased the amount of fluid that needed to be processed.

---

[11] ORNL-TM-6413, "Molten-Salt Reactors for Efficient Nuclear Fuel Utilization without Plutonium Separation."

[12] ORNL-TM-6415, "Development Status and Potential Program for Development of Proliferation-Resistant Molten-Salt Reactors."

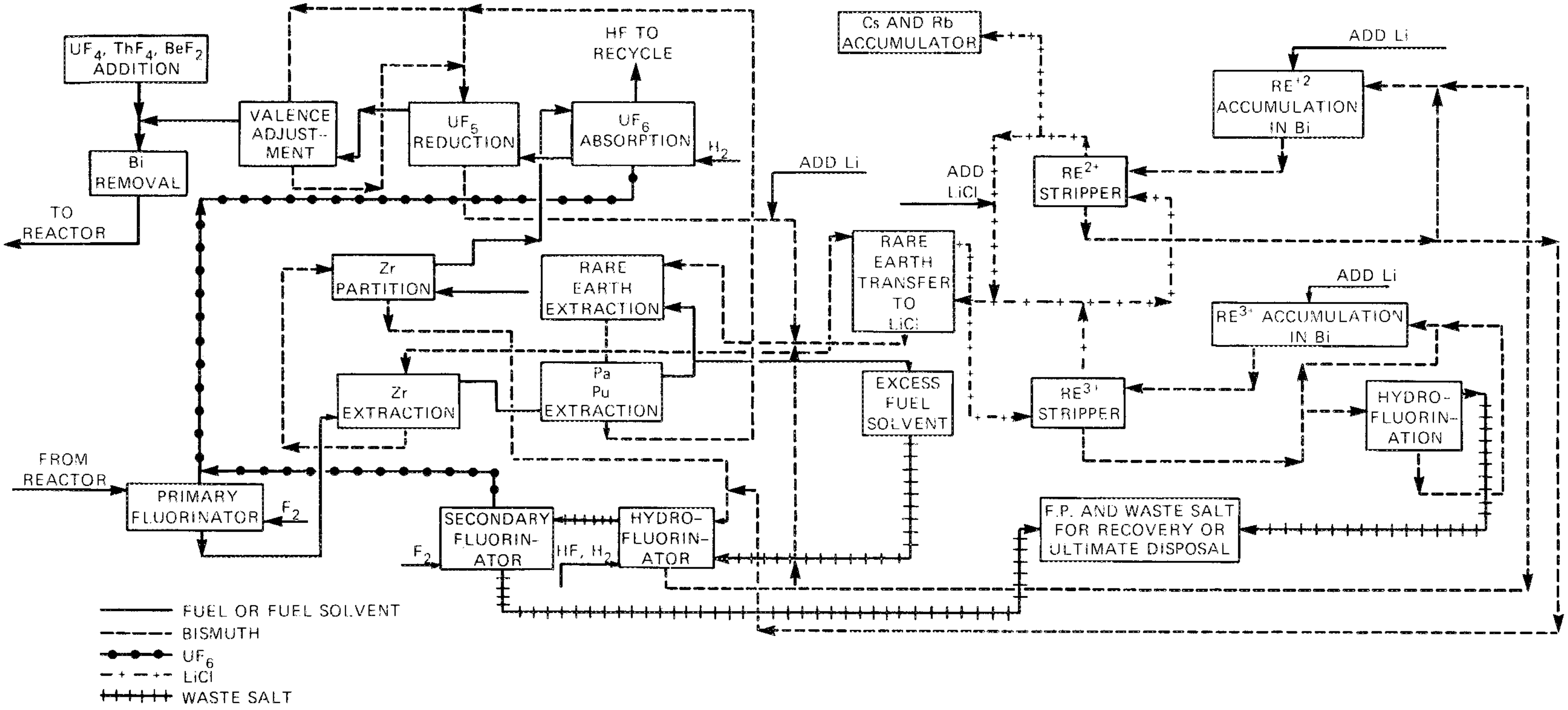

Figure 18: Denatured MSR chemical processing flowsheet (from ORNL-TM-6415, pg 105).

5. The long-term buildup of transplutonic (americium, curium, berkelium, californium) nuclides represented a substantial neutronic loss to the reactor, with approximately two neutrons consumed on transplutonic generation for every neutron released in the fission of a transplutonic nuclide. Substantial uncertainty existed as to whether these transplutonic nuclides should be disposed of at the end of reactor operation or recycled to the next generation of reactor core, where they would continue to exert a neutronic "drag" on the performance of the reactor.

From a chemical processing and neutronic performance standpoint, denaturing the uranium in the molten-salt reactor had no benefits and many disadvantages. Only the political mandate to consider denatured operation pushed research in this direction.

Changes to the processing flowsheet were necessary because of the presence of large quantities of plutonium in the fuel salt. All uranium, protactinium, and plutonium would need to be chemically extracted from the salt before rare-earth fission products could be removed using reductive extraction techniques similar to the reference MSBR. One of the challenges of Pa-Pu removal was that fission-product zirconium would also be removed and later reintroduced to the fuel salt. A careful partial oxidation of the extractive bismuth was proposed to address this concern, followed by hydrofluorination of bismuth containing zirconium and uranium into a waste salt. Improved techniques for zirconium removal were considered highly desirable.

To accommodate the higher inventories in the fuel of uranium, plutonium, and zirconium, more highly-depleted metallic lithium would be used as a reductant, which increased processing costs and also increased the rate at which fuel salt solvent would need to be discarded. An increase in the solvent discard rate also reduced the effective consumption of thorium as an energy resource.

It was also proposed to carry a much higher fraction (~10%) of the uranium in the salt as a trifluoride (UF_3) rather than as a tetrafluoride (UF_4). It was anticipated that this would lead to immediate reduction of fission product selenium and tellurium and their complete retention in the fuel.

Processing techniques for gaseous fission products (xenon and krypton), noble-metals (molybdenum, technetium, etc.) and tritium were relatively unchanged from the reference concept.

7.2 Later Concepts

The final report on the denatured MSR concept was issued in July 1980 (ORNL-TM-7207). In this report, chemical processing techniques that had been proposed in earlier reports (fluorination, reductive extraction) had been eliminated, beyond basic techniques like hydrofluorination to control oxygen contamination. With the abandonment of overt chemical processing came a decrease in the conversion ratio of the reactor, to the point that a break-even conversion ratio was no longer achievable. The DMSR concept now became yet another example of a reactor that burned ^{235}U as its primary fissile fuel, albeit it in a rather exotic way when compared with conventional solid-fueled reactors.

This was summed up as follows in ORNL-TM-7207 as an inevitable consequence of low-enrichment uranium fuel:

> The presence of ^{238}U in a DMSR, combined with the effects of flux flattening, sufficiently reduces the nuclear performance so that a net breeding ratio substantially greater than 1.0 probably could not be achieved, even with full-scale fission-product processing.

With the abandonment of breeding, the motivation to continue to consider the use of thorium diminished as well. Since the 1980 report was the last ORNL paper to describe molten-salt reactor designs and development, it is reasonable to assume that this represented the very last effort at ORNL in this field. Perhaps if further funding had been available, molten-salt reactors that used uranium fuel exclusively might have been the next stage of development. Such burner reactors would have retained the physical advantages of molten-salt reactors (high temperature operation at low pressure) but would have lost the fuel cycle advantages of thorium (highly efficient fuel use and minimal transuranic production). However, if such reactors were ^{235}U burners in either incarnation, it would have been desirable to avoid the additional complications that thorium introduced because of its chemical similarity to the lanthanide fission-products.

7.3 Chemical Processing Experimental Research

Since the effort to investigate denatured molten-salt reactor concepts took place after the Molten-Salt Reactor Program had been cancelled, there were no chemical processing research activities that took place to accompany the conceptual effort.

8 Conclusions

Chemical processing techniques have always influenced the design of molten-salt reactors. In particular, the technique of fluorination has been considered as a process to separate uranium from thorium, an important consideration for the blanket fluid of a thorium breeder reactor.

The earliest ideas for molten-salt reactors were intended for use as aircraft reactors, and had minimal consideration for chemical processing. Later, as molten-salt reactors were intended as central station electrical power generators, then more elaborate schemes were devised to move uranium from blanket to core, and to remove fission products from the fuel salt of such reactors.

Thorium is chemically similar to the lanthanide fission-products that are so important to remove from a molten-salt reactor (after xenon), and so molten-salt reactor types that keep fuel and blanket salts separate (two-fluid designs) feature the simplest and most effective chemical processing systems.

Later interest in one-fluid reactor types that combine fertile and fissile fluids were propelled by advances in chemical processing. It was believed that lanthanide fission products could be removed even in the presence of thorium. Continued investigation of one-fluid processing demonstrated that the initial hopes for simplicity would not be realized, and that one-fluid reactors would have rather complex chemical processing systems, particularly if they hoped to achieve good breeding performance.

After cancellation of the Molten-Salt Reactor Program in 1976 there was a smaller and shorter effort to examine denatured molten-salt reactors that continued until 1980. The denatured MSR amplified the complexity of the one-fluid thorium breeder with the inferior performance and additional chemical species of the uranium-plutonium fuel cycle. An already complex chemical processing system became even more complex before chemical processing to remove lanthanide fission products was abandoned altogether in the final version of the denatured MSR. A uranium-only version of the MSR was never considered in detail, although it probably represented a simpler and equally effective incarnation of the denatured MSR.

The two-fluid thorium-fueled MSR probably represents the simplest approach to a high-performance thermal breeder reactor that efficiently uses nuclear fuel resources, provided that the core design issues can be satisfactorily solved.

9 Recommendations

Although the precise sequence of chemical processing techniques for future liquid-fluoride reactors has not yet been decided, one can safely say that certain techniques will be utilitized in a future system.

The most essential and potentially most challenging is the technique of uranium separation by fluorination. Fluorination is exquisitely useful as a chemical processing technique in a liquid-fluoride reactor running on either the thorium or uranium fuel cycles because the fuel is already in the ideal chemical state for the application of fluorination. In the thorium fuel cycle, fluorination can easily separate uranium from thorium in the blanket salt, or separate uranium from fission products in the fuel salt in a two-fluid reactor. In a one-fluid reactor, fluorination was the bulk separation technique used to remove most uranium before finer processes like reductive extraction were applied. In the uranium fuel cycle, fluorination could be used to remove the fuel from a salt mixture contaminated by fission products.

Fluorination, by its very definition, will involve using a reactive fluorination agent. An ideal fluorination agent would react quickly and completely with the uranium in the salt and leave all structural materials alone. Such an agent may not exist but represents an ideal towards which to strive.

Molecular fluorine (F_2) is most often discussed as the fluorination agent and is very aggressive towards the structural materials of a fluorination system. ORNL did not demonstrate a long-lived fluorination system even though they did demonstrate many subcomponents that would be necessary in such a system, such as the frozen-wall principle. Other fluorination agents may be more promising in a liquid-fluoride reactor than molecular fluorine, with reduced toxicity and less aggressive towards structural materials. The disadvantage of alternative fluorination agents is their technology is still in its infancy, but they should be investigated in greater detail.

Reductive extraction techniques, where liquid metallic bismuth containing reductants contact a fluoride salt, also show great promise and should be investigated further. But bismuth will dissolve the nickel-alloy structural materials (such as Hastelloy-N) that dominate the construction of the reactor vessel and primary loop. It is very important that techniques to screen bismuth out of the returning flows to the reactor be demonstrated and developed to a point where one could comfortably operate them for an extended period of time.

The technique of high-temperature distillation has promise but may be superceded by reductive extraction as a technique for the removal of fission products from the fuel stream of a two-fluid reactor, provided that reductive extraction techniques are developed to maturity. Distillation also has high-temperature materials challenges and the basic challenge of trying to boil away the bulk of the material of the fuel salt in order to isolate a small waste fraction. Reductive extraction may be a better way to remove troublesome fission products from the fuel salt.

Electrolytic cells to regenerate the reactants of a reductive extraction system are another area that deserves closer attention. Most work on electrolytic cells ended with the one-fluid reactor design that became the ORNL baseline, but a future two-fluid reactor, using reductive extraction to remove protactinium and uranium from the blanket, may need an electrolytic cell to prevent excessive consumption of thorium as a reductant.

A basic advantage to all of these chemical processes is that, with the exception of protactinium, they can be developed and demonstrated in a laboratory using stable simulants for fission products and low-activity actinide simulants (thorium and depleted uranium). This ability is a basic developmental advantage over the uranium fuel cycle, which would require expensive and highly-active plutonium to undertake a truly realistic chemical processing demonstration. This fact facilitates an early "non-nuclear" demonstration of chemical processing techniques, and this report recommends that that proceed as soon as financial resources would permit.