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CONCEPTUAL ENGINEERING DESIGN AND
ECONOMIC EVALUATION OF THE BURN-
ACID-LEACH AQUEOUS PROCESS AND OF
THE BURN-FLUORIDE-VOLATILITY PROCESS
FOR RECOVERING SPENT ROVER FUEL AT
THE IDAHO CHEMICAL PROCESSING PLANT

(Title Unclassified)

E. L. Nicholson

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CHEMICAL TECHNOLOGY DIVISION

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E. L. Nicholson

June 8, 1965

Exempt from CCRP Re-review Requirements
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by authority of Dr. H.F. McDuffie, ORNL, letter Sept. 24, 1973

by GG TSC, date 10/29/73

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CONCEPTUAL ENGINEERING DESIGN AND ECONOMIC EVALUATION OF
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E. L. Nicholson

ABSTRACT

Two detailed, conceptual process, equipment, and plant designs were prepared for facilities for recovering spent Rover fuel (highly enriched uranium-graphite) at the Idaho Chemical Processing Plant. The results of the study indicate that the fluoride-volatility process is preferred on both economic and technical grounds.

Both processes employ a common fuel shipping, storage, and charging system and use continuous, fluidized-bed oxidation of the fuel as the first step of the head-end operation. Subsequent operations in the aqueous process include batch leaching the ash with 5 *M* HF—10 *M* HNO₃ in two parallel lines of Teflon-lined leaching and feed-preparation equipment, followed by solvent extraction to decontaminate and recover the uranium as uranyl nitrate. Post-burning operations in the fluoride-volatility process include the continuous fluidized-bed and moving-bed fluorination of the ash followed by partial condensation to remove niobium pentafluoride and passage of the UF₆ through heated sodium fluoride pellets to completely decontaminate the uranium. The uranium is recovered as uranium hexafluoride.

The cost studies for both processes were made for a daily capacity of 30 kg of ²³⁵U and an estimated total load of 10,500 kg of ²³⁵U.

The estimated daily operating cost, including amortization of only the new equipment, is \$15,010 for the fluoride-volatility process and \$14,430, \$16,410, and \$20,833 for the aqueous process, depending on whether interim storage in existing tanks, interim storage in new tanks, or interim storage plus subsequent waste calcination, respectively, is adopted for the aqueous waste. No capital costs were included for the use of the existing solvent extraction plant. The corresponding unit costs are 50 cents per gram of ²³⁵U for the fluoride-volatility process and 48.1 cents, 54.7 cents, and 69.4 cents per gram of ²³⁵U for the aqueous process with the waste-storage options given above.

The fluoride-volatility-process wastes are in a form immediately suitable for ultimate disposal. Therefore, the comparison is \$15,010 per day for fluoride-volatility process and \$20,833 per day for the aqueous process. The burn-nitric-acid-leach process was shown to be more expensive, since the value of the uranium that would be lost by this simplified process would exceed any savings in equipment and waste-disposal costs. Also, a brief study of operational problems indicated that the fluoride-volatility process would probably be simpler to operate than the aqueous process.

An independent processor that did not already have shielded solvent extraction and radioactive liquid waste disposal facilities would probably select fluoride volatility as the preferred process.

1. INTRODUCTION

The purpose of the Rover program is to develop nuclear-rocket-propulsion systems for space missions. The ground-test subprogram has progressed through the initial test of the Kiwi series of reactors and is now preparing to test higher performance engines with the objective of developing the 5000-Mw Phoebus reactor. This test program will require the recovery of thousands of kilograms of slightly irradiated, fully enriched uranium from the graphite-base fuel elements.

The Division of Reactor Development, U.S. Atomic Energy Commission, requested that the study reported here be prepared with the specific objective of fitting the process into the Idaho Chemical Processing Plant. Consequently, the aqueous process uses their existing solvent extraction and waste disposal system, while the fluoride-volatility process requires a completely new system for the decontamination and recovery of the uranium.

Chemical and engineering development studies have been done at Oak Ridge National Laboratory and at Brookhaven National Laboratory to develop aqueous and fluoride-volatility processes for recovering the uranium from this fuel. Both processes require combustion of the graphite as the first step. Complete recovery of the uranium requires that the niobium oxide, resulting from the combustion of the niobium carbide (protective liner for the coolant passages) be completely dissolved or fluorinated. Otherwise the uranium that has diffused into the liner during exposure to high temperatures during fuel fabrication and reactor operation will be lost.

Development studies, although incomplete with respect to demonstrating all the equipment for each process, have shown that the processes are chemically feasible, that they will have a uranium recovery of better than 99% with ample

decontamination from fission products, and that only a small amount of additional equipment development work would be required to prepare a detailed engineering design for the recovery plant.

The purposes of this report are: to review the applicable development data, to select the best aqueous and the best fluoride-volatility process, to prepare conceptual designs for a recovery plant for each process, and to estimate the processing cost.

The results indicate that the fluoride-volatility process is preferable.

2. FUEL ELEMENT DATA

2.1 Current Fuel

The present Rover fuel element (starting after Kiwi-B-202) is a hexagonal graphite rod pierced with 19 longitudinal coolant holes. The fully enriched uranium fuel is present as a dispersion of pyrolytic carbon-coated uranium dicarbide microspheres in the graphite matrix. The coolant channels and the hot end are coated with niobium carbide by a vapor-deposition process to minimize erosion and corrosion by the hot hydrogen. Some uranium diffuses into the niobium carbide liner as a result of exposure to high temperatures during fabrication and reactor operation.

The uranium loading in the fuel rods varies across the core to improve reactor performance. For example, about 18 different uranium loadings were used in the Kiwi-B-4D-202 fuel rods¹ to promote even fission distribution in the core. This unusually large number of different uranium loadings was partially due to the 202 core's being a mixture of oxide and beaded fuel; however, it is indicative of the variation to be expected in uranium content of individual fuel rods from any core. Partial elements, consisting of longitudinal slices of standard elements and having 16 coolant holes, are used at the core perimeter to fill voids between the hexagonal fuel-element arrays and the perimeter filler slats. Reactor operation has resulted in some breakage of fuel rods and loss of material by erosion and corrosion, and many rods have been cut up or broken as part of the postoperation evaluation program. Also of interest to the fuel processor is the proposed practice of gluing unloaded sections to the hot end of the fuel element¹ and the possibility of thermocouples or melted thermocouple material² being attached to the spent fuel.

The fuel in earlier cores, except for the 212 beaded fuel rods in Kiwi-B-4D-202, consisted of homogeneously dispersed, uranium-carbide-loaded elements having many different lengths and several cross-sectional shapes and was not as extensively coated with niobium carbide. However, a considerable amount of uranium is in this niobium carbide. The first core used 1/4-in.-thick flat plates and had no niobium carbide. Some deterioration of the early cores has occurred due to hydrolysis of the uranium dicarbide by atmospheric moisture.

2.2 Fuel Element for This Study

The objective of the Rover program is to develop a 5000-Mw Phoebus reactor to use in NERVA (Nuclear Engine for Rocket Vehicle Application),¹ and it is probable that Phoebus will use a uranium-graphite fuel³ similar to the current Rover fuel. Although the uranium content of the core is not fixed yet, it has been estimated⁴ to be 352 kg of ²³⁵U.

It has been assumed for this study that the spent fuel comes from a Phoebus reactor, containing 400 kg of enriched uranium, that has operated at a power level³ of 5000 Mw for 30 min,⁴ and has been cooled for one year before processing. Since Phoebus core and fuel element design have not been specified yet, weighted average fuel-rod composition⁵ and dimensions,⁶ approximating those of the Kiwi-B-4A fuel element, were assumed. This information is given in Fig. 1. The average composition of the fuel is 15.7% fully enriched uranium, 10.5% niobium, and 73.8% carbon. The uranium is present as carbon-coated particles; the coating may be the newer combination coat of precipitated carbon⁷ covered with pyrolytic carbon. It is assumed that insignificant amounts of other elements will be present. For example, less than 100 ppm of iron is present in this fuel,³ compared with about 0.5% iron⁸ in the Kiwi-A fuel.

2.3 Fuel Irradiation, Product Specifications, and Theoretical Fission-Product Decontamination Factors

The fuel is calculated to have a burnup of about 0.035% of the uranium originally present. This may be compared with 0.0011% burnup for the Kiwi-B-4D-202, estimated² from the total power integral of 1.14×10^{11} watt-seconds. About ten times this former burnup was achieved in the Kiwi-B-4D-301 test, while much lower burnups were achieved in earlier tests. Rover fuel is quite "cool" compared to the usual Idaho Chemical Processing Plant fuel, which has a burnup of about 30%; however, it still presents a significant radiation hazard. IBM 7090 calculations were made with the Phoebe computer code⁹ to determine fission-product activity in the spent core as a function of cooling time. The results are summarized in Table 1. The fission-product heat generation, however, is insignificant, and shipping cask cooling will not be a problem.

There are no specifications for the permissible fission-product radioactivity level in highly enriched ²³⁵U returned to the AEC. The only specifications are for natural uranium, which must not exceed the background radioactivity level of natural uranium. This is unrealistic for ²³⁵U because of its higher specific activity. Uranium recovered from Rover fuel would probably go into a fuel-refabrication cycle and should not have to meet cascade-feed specifications, which appear to be the basis for the present standard for uranium returned to the AEC. Therefore, in this study it is assumed that the fission-product activity of the recovered ²³⁵U product should not exceed ten times the beta and gamma radioactivity of enriched ²³⁵U in equilibrium with its

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Fig. 1. Kiwi-B-4A Fuel Element.

Table 1. Radioactivity of the Assumed Phoebe Core as a Function of Cooling Time

Core: 400 kg 93.4% ^{235}U

Irradiation: 5000 Mw (thermal) for 30 min (117.9 g fission products, 0.035% burnup)

Cooling Time (months)	Total Beta Activity			Total Gamma Activity			Total Heat Generation (w)
	Watts	Curies	β Curies per g U	Watts	Curies	γ Curies per g U	
3	271	1.55×10^5	0.386	340	8.62×10^4	0.215	611
6	128	6.55×10^4	0.164	125	3.19×10^4	0.0797	253
12	54	2.48×10^4	0.062	29	7.57×10^3	0.019	83

daughters (232 β counts/min/mg U; 11 γ counts/min/mg U).⁹ For 1-year-cooled fuel, the required theoretical gross decontamination factors are 6×10^3 for beta radioactivity and 2.3×10^4 for gamma. These theoretical decontamination factors are based on the rather hard beta and gamma energy radiation usually present in the product from a solvent extraction system and the total fission-product energy spectrum in the spent fuel, which includes some very soft, inefficiently counted components. Therefore, if the above decontamination factors are realized, it is probable that the product will be considerably less radioactive, insofar as handling difficulties are concerned, than the assumed maximum permissible level of ten times more radioactivity than equilibrium ^{235}U .

Certain fission products such as Tc, Kr, Br, and Se will be volatilized during fuel combustion,¹⁰ thus significantly reducing the theoretical fission-product decontamination factors required of the succeeding aqueous or volatility processes.

The aqueous solvent extraction process should produce specification-grade product in one or at most two cycles of solvent extraction. Laboratory tests of the batch volatility process¹¹ and comparisons of this data with niobium decontamination factors obtained in cold pilot-plant tests at Brookhaven National Laboratory (BNL) indicate that the continuous fluorination process should also produce specification-grade product. This is discussed in Sect. 6.3.3 in detail.

3. REPROCESSING PLANT DESIGN CAPACITY AND LOCATION

A design capacity of 30 kg of ^{235}U per day for the reprocessing plant was selected on the advice of Idaho Chemical Processing Plant (ICPP) personnel.¹² This value was based on the present capacity of the aqueous reprocessing systems at the ICPP and estimates of future commitments of the plant schedule to other fuels. The capacity of the fluoride-volatility process was also set at 30 kg of ^{235}U per day, although the volatility process is completely independent of equipment in the existing plant. The design capacity may have to be revised when the backlog of Rover fuel and the NERVA schedule is definitely known and the reprocessing-plant startup date is fixed. It was assumed that the fuel would be processed in 30-day campaigns. This figure is significant only in its effect on the number of fuel shipping casks and the size of certain chemical supply tanks, such as the liquid-fluorine trailer.

The Hot Pilot Plant Building, CPP-640, at the ICPP is unused and was assumed to be available for Rover fuel recovery. The building has two shielded cells designed and partially equipped for remote manipulation and crane operations such as cask unloading, dry fuel storage, and fuel charging. It also has three adjoining, conventional, shielded reprocessing cells. Only minor modifications are required for installation of the proposed processes. It is assumed that the containment methods in current use at the ICPP would also be used for the Rover installation.

All volatility-process operations would be exclusively in CPP-640. Aqueous-process solvent extraction feeds would be prepared in CPP-640 but would be sent to existing facilities in the main plant to complete the recovery of the enriched uranium. This report does not consider the design or the cost of any modifications that might be required to process Rover fuel in the main-plant solvent extraction or waste storage facilities.

4. SELECTION OF THE PROCESSES FOR THIS DESIGN STUDY

Early work on Kiwi-A fuel showed that uranium recovery by combustion and nitric acid dissolution of the ash, or by grinding the graphite and acid leaching, or by the fuming nitric acid disintegration—leaching method was possible, although no comparative engineering evaluation was made of the proposed processes at that time. The addition of a niobium carbide protective layer on the fuel element surfaces, and the later change from a uranium oxide dispersion fuel to beaded fuel, caused drastic changes in the reprocessing development program. Uranium diffusion into the niobium carbide liner occurred as a result of high temperatures during fabrication and reactor operation and required that the liner be dissolved or fluorinated to effect complete uranium recovery.

The chemical resistance of the intact, coated, fuel beads ruled out direct disintegration—leaching methods such as electrolytic disintegration in acids or disintegration with fuming nitric acid. Fine grinding to less than 200 mesh was ruled out because of the abrasiveness of the niobium carbide—uranium carbide, the difficult leaching and filtration problems encountered with the resulting graphite flour, and the feed-adjustment operation required to destroy organic acids formed in the leach solution.

Some hope has been expressed that the proposed newer "skinned" and pyrolytic carbon-coated fuel beads would contain the uranium so efficiently that no uranium would diffuse into the niobium carbide liner. This has been extensively discussed before, and the quotation⁷ given in Appendix 1 summarizes current opinion on this subject. Los Alamos has also recommended that it would be unwise to assume that the niobium carbide liner of the beaded fuel would be free of uranium.* They pointed out³ that the oxide fuel used in Kiwi-A' through Kiwi-B-4D-202 contained about 5% of the uranium in the liner. This uranium would be lost if the recovery plant provided only a burn—nitric acid leach system. Unfortunately, the aqueous process for dissolution of the niobium carbide liner or niobium oxide from oxidation of the liner requires a mixture of hydrofluoric acid and nitric acid and is highly corrosive.

* Very recent data from experiments with beaded rods from the Kiwi-B-4D-202 test confirm the rupture of the bead coating and increasing migration of uranium into the NbC liner with the temperature gradient from the cold to the hot end of the rod.^{37,83}

Thus, the only three processes considered suitable for recovery of spent fuel were digest-burn-dissolve (DBD), burn—mixed acid leach, and burn-fluorinate.

The conceptual DBD process¹³ was studied to estimate the equipment and operational requirements for a capacity of 30 kg of ²³⁵U per day. It was concluded that further consideration of DBD was unwarranted in view of the excellent niobium oxide dissolution and uranium recovery obtained by BNL^{14,15} with mixed nitric acid—hydrofluoric acid leaching of fluidized-bed combustion ash using the nonoptimized F/Nb ratio of about 12.

The only aqueous process that was considered suitable for complete recovery of spent Rover fuel is burn—mixed acid leach followed by solvent extraction.

The burn-fluorination process was originally conceived as a complete recovery process for fuel containing niobium. The only variations of it are found in different approaches to combustion and fluorination reactors and in trapping systems. The best of these have been selected for this study.

The last major point in selection of the best process is the choice between either a fixed-bed reactor or a fluidized-bed reactor for graphite combustion and for fluorination. The fixed-bed reactor is somewhat simpler in that only one reaction vessel is required and an inert fluidizing medium such as high-purity alumina is not required. However, it has been clearly demonstrated by the development programs at ORNL and at BNL that the fixed-bed reactor (either in the graphite oxidation or the ash fluorination application) is very inferior to a fluidized bed for a high-capacity production system. The unresolved problems of fixed-bed reactors are temperature control to prevent hot spots and premature vessel failure, slagging, remote removal of residues, nonuniform gas distribution, and inefficient overall utilization of oxygen and fluorine because of the long tailing-out periods for each fixed-bed reaction. Corrosion is more severe with the fixed-bed reactor because the vessel must resist both high-temperature oxidations and fluorinations or high-temperature oxidation and aqueous solutions of acid. The fixed-bed reactor is also not as easily adapted to a fully continuous system as is a fluidized-bed reactor. The continuous fluidized-bed oxidation and both a batch and a continuous fluidized-bed fluorination process have been successfully demonstrated by BNL. Therefore, for both the burn—mixed acid leaching and burn-fluorination processes, the fluidized-bed approach has been used wherever possible.

5. FUEL HANDLING

The following fuel-shipping system has been assumed for this design study and should be compatible with the Nuclear Rocket Development Site (NRDS) facilities and with the Idaho Hot Pilot Plant.

5.1 Storing and Handling of Fuel at the NRDS

Spent cores Kiwi-A through Kiwi-B-1A are presently stored in lead-shielded casks, ranging in weight from 3 to 20 tons, at the NRDS.¹⁶ These casks may not be suitable for cross-country fuel shipments under present regulations. Some of the oxide fuel has deteriorated due to atmospheric moisture hydrolyzing the uranium carbide. Broken elements and other nonstandard materials are also in storage. Starting with Kiwi-B-1B, the fuel has been stored in unshielded, poisoned, aluminum boxes. These boxes are stacked on a flatcar, the pile is covered with a weatherproof metal security cover, and the flatcar is stored on a remote siding. Three cores may be stored on each flatcar. The Mechanical Assembly-Disassembly (MAD) building is provided with the necessary railroad tracks, hot cells, and remote cranes and manipulators to dismantle the spent cores, inspect the fuel, and package it for storage.¹⁷ It is assumed that arrangements could be made to use this facility to repackage the fuel for shipment to the reprocessing plant.

5.2 Preparation of the Fuel for Reprocessing and Shipment

The early reprocessing development work at ORNL and BNL envisioned charging full-length fuel rods to the burners. As the development work proceeded, it became apparent that charging the burner with small, broken pieces of fuel would simplify the burner-charging problem,¹⁸ improve burner efficiency, and eliminate handling the fuel as individual rods at the reprocessing plant. It has been assumed that the fuel would be broken, chopped, or crushed at NRDS into short lengths and packaged in geometrically safe, disposable cans for shipment to the ICPP. The Kiwi-A flat plates and the rods from subsequent reactors, these rods ranging in length from 8 in. to 52 in. and in cross section from circular to hexagonal, could all be packaged in one standard container for shipment. Broken rods, scrap from physical tests, and partially hydrolyzed material can be handled by this system.

One of the objectives of the fuel-chopping or rather fuel-breaking experiments^{19,20,21} was to minimize the production of fines to avoid a filtration problem due to carbon fines in the digest-burn-dissolve process. This limitation does not exist for the fluidized-bed burner, as this burner can accept fine material for feed, although a high proportion of coarse material is preferred to ensure formation of the packed fluidized-bed above the support grid where most of the burning occurs. The fuel breaking is characteristic of breaking a brittle material, and very little shearing occurs before the rod is broken. Maximum blade penetration before rod rupture is about 10 mils. Less than 1% of the fuel is reduced to pieces smaller than the desired cut. High temperatures in the reactor slightly decrease the mechanical strength of the fuel.² Otherwise, the effect of fuel irradiation on breaking characteristics is negligible.

A motorized fuel-rod breaker²² was designed, built, and successfully tested. It has a maximum capacity of about four 52-in. rods per minute and can handle

either circular or hexagonal cross-section rods while breaking them into pieces no longer than $3/4$ in. The design can be readily adapted to hot-cell operation. No experiments have been conducted on Kiwi-A flat-plate breaking, since this can be done with a simple pneumatic cylinder-driven plunger and anvil assembly. Alternatively, a special feeder tube could be incorporated in the rod breaker.

The concept of crushing the fuel rods with a simple laboratory-sized jaw crusher should be investigated before final design of the fuel crushing and packaging facility is commenced. The jaw crusher is a very cheap, simple, reliable, and rugged piece of machinery and should be even simpler and more versatile than the rod breaker. Coarsely crushed fuel (say, $1/2$ -in. lumps) should give fewer problems in burner feeding than the $1/2$ - to $3/4$ -in.-long pieces of the $3/4$ -in.-diam fuel rods that would be produced by the rod breaker.

5.3 Fuel-Shipping Can and Can-Filling System

Rather than recommend expensive fuel-shipping cans that would have to be decontaminated and reused, cheap, screw-top, $5\frac{1}{2}$ -in.-diam by 57-in.-tall, heavy-gage cans have been selected for shipping the chopped fuel. The details of the cans are shown by drawing 10827-N-114-E (see list of drawings in Appendix 2). The cans will be discarded when they are contaminated on the outside or damaged. They are geometrically safe, and the can height is fixed by the cask, which must pass through the Idaho Hot Pilot Plant mechanical-cell doorway. The fuel can is estimated to hold 23.7 chopped or crushed "design rods" when filled loosely to the working depth of 54 in. Vibration of the cans during filling would permit more fuel to be put in each can and is recommended. The cans are normally handled by the cross bar on the recessed, screw-cap lid.

The remotely operated can-loading system at the NRDS requires (1) a rod chopper or crusher; (2) vibrated, sintered-metal air-cleaning filters so airborne dust from chopping can be contained, filtered, and the dust of the filters dislodged by vibration and returned to the fuel can; (3) a can positioner to hold the can during loading and capping operations (it should be capable of vibrating the can during filling to utilize the can volume efficiently); and (4) a "capper" if it is not feasible to attach the lid with manipulators. A cursory investigation²³ of the concept indicated that the complete loading system could be contained in an equipment package $2\frac{1}{2}$ ft wide, 4 ft long, and 12 ft in overall height. An alternative concept requiring vertical transport of the crushed fuel could be contained in an equipment package $2\frac{1}{2}$ ft wide, 6 ft long, and 7 ft tall.

5.4 Fuel-Shipping Cask

Shielding calculations were made for a fuel carrier capable of holding 19 cans of chopped fuel, which is equivalent to 13.45% of a full core (the final carrier design holds slightly less, i.e., 12.74% of a full core).

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The results of the calculations for the carrier holding 13.45% of a full core are:

Cooling Time (months)	Lead-Shielding Thickness (in.)	
	10 mr/hr at 100 cm	200 mr/hr at Surface
3	5.91	4.56
6	5.02	3.69
12	4.07	2.86

Four inches of lead plus 1-1/4 in. of steel shielding are provided by the carrier, thus permitting shipment anytime after 8 months of cooling. Heat generation in the cask is only 11 watts at the design cooling time of one year. The cask weighs about 15 tons empty and about 15.4 tons loaded. It is 4 ft 4-1/2 in. in diameter and 6 ft 1-3/4 in. high. The conceptual design of the fuel-shipping cask is detailed by drawing D-57649 (Appendix 2). Borosilicate foam-glass filler between can sleeves in the cask acts as a fixed poison and also prevents water from filling the space between fuel cans in case of an accident. The foam glass has been used²⁴ in a similar application in shipping the unirradiated fuel. Criticality calculations²⁵ show that the proposed cask is safe. A much earlier shipping study²⁶ assumed shipment of whole rods in larger casks, requiring rail transport to Oak Ridge. A smaller cask is required for this study to permit it to be unloaded in the existing building at Idaho. We assumed that the casks would be shipped by a commercial truck line from the NRDS to Idaho. A heavily reinforced steel cage will be provided on the trailer to hold and protect the cask in transit, and two casks might be shipped per trailer. Fuel-canning, fuel-cask, and shipping costs are not estimated in this study.

5.5 Fuel Receipt and Storage at the Idaho Chemical Processing Plant

The conceptual design of the fuel-receipt, storage, and charging system at the Idaho Hot Pilot Plant building, CPP-640, is shown schematically in Fig. 2 and is given in detail by drawings 10827-N-113E and 10827-N-114-E (Appendix 2).

The cask is unloaded from the trailer at CPP-640 and moved into cell 1 on the charging dolly. The lid is removed by the remote bridge crane or by the building crane through a porthole in the cell ceiling, and the cans are placed in the storage rack with the heavy-duty manipulator, as illustrated, or by a simplified, single-purpose telescoping arm mounted on the remote bridge crane. Since the latter device is much cheaper than the manipulator, it was actually the system chosen for the process cost estimate. Viewing is by closed-circuit television, since windows are not provided in this cell.

The cans are stored in steel pipe sleeves on 8-in. centers in the 209-can-capacity storage rack. Closer spacing was not investigated but may be practical.

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Fig. 2. Fuel Storage and Fuel Charging Cells, CPP-640.

Neutron poisons are not required²⁵ between can holders in the dry storage rack provided the H:U ratio is ≤ 10 . To guarantee this, precautions should be taken so that the storage rack cannot be flooded. Fuel cans that are accidentally water-logged by a cask accident during shipment should be drained and dried before being placed in the storage rack. Storage space is provided for 209 fuel cans, but 260 may be stored if the concrete cover slabs and supporting ledges shown on drawing 10827-N-113-E are eliminated from the storage cell. This is recommended because there now seems to be very little advantage in temporarily covering the top of the storage array with concrete slabs. A 2-ft-thick concrete shield wall is provided at the front of the storage rack to minimize radiation streaming outside the cell when the cell-1 shield door is open. Space is available on the top of the shadow shield to install a scale for verifying the can weight, if this operation is desired.

5.6 Fuel Charging System

The fuel cans are loaded into small portable racks holding six cans each and are transferred as needed to cell 2 by the charging dolly; 11.2 cans of chopped fuel are required per day. In cell 2, the manipulator picks up the fuel can and places it on the transfer cart of the fuel-can dumping and handling mechanism. The transfer cart moves the can to the decapper station, where the lid is removed by an air motor operating in a dust-collector housing. The opened can is then delivered by the transfer cart to the can-loader mechanism on the rotary dumper. The can loader seals the open top of the can to the ball valve on the chopped-fuel inlet of the rotary dumper. The rotary dumper swings the can in a 150° vertical arc, and the fuel is dumped into the 3.8-ft³ working-volume (equivalent to an 11-hr supply of fuel) chopped-fuel hopper. A microphone on the hopper and the hopper capacitance probe for determining the height of the fuel pile monitor the dumping operation and the feeding of chopped fuel to the fluidized-bed burner. The can loader is vibrated, and compressed air from jets is blown into the inverted can to remove any dust clinging to the inside of the can. The rotary dumper then returns the can to the vertical position, where it is picked up by the transfer cart. After visual inspection of the interior of the can, the lid is replaced, and the can is either discarded or returned to the storage rack in cell 1 for reuse. The cost estimate assumes that the fuel cans are flattened to half their original volume and are discarded. The can-dumping operation is observed through the cell-viewing window. Since the radiation level of the fuel is low (see Sects. 2.3 and 8.2), electrical and pneumatic components can be of conventional design. The electro-pneumatic control system for the can-dumping operation can be completely automated, if desired. The cost estimate assumes that the dumping operation is completely automated.

This highly mechanized dumping system was chosen in preference to a much simpler system that would require extensive use of the manipulator to perform all the can-handling operations. The choice was made because the mechanized system requires a minimum of intricate operations with the manipulator, it permits much better containment of dust, and it minimizes the possibility of spilling the fuel on the cell

floor. It is probable that the system can be simplified by eliminating the transfer cart. For example, the manipulator would put the fuel can directly on the can-loader arm of the rotary dumper for decapping and dumping. Time was not available to exploit this concept.

The chopped fuel is fed continuously to the fluidized-bed burner located in cell 3 by a horizontal variable-speed screw conveyor at the bottom of the fuel hopper. The design of the hopper bottom, conveyor feeder, and screw conveyor should be investigated in detail to ensure operability. Crushing the fuel into pieces even smaller than the nominal 3/4-in. lump would be better for the hopper and screw-feeder system.

5.7 Problems in Uranium Accountability

The extreme heterogeneity of the spent fuel (noted in Sects. 2.1 and 5.1) will make the precise determination of the uranium content of any shipping can or even any fuel cask very difficult. Even with careful bookkeeping on each fuel piece and with no loss of fuel due to reactor operation or subsequent inspection, there will undoubtedly be the problem of rod identification and the inevitable discrepancy between the actual uranium content of any given fuel element and the estimated content assigned by the manufacturer. Fine grinding or crushing and coal-pile sampling might be the only direct way to solve this problem, but it would be very expensive and could be challenged because of the difficulty of sampling solids.

Similar problems of solids sampling will exist at the chemical plant, but the uncertainty may be of a lower degree, since the solids to be discharged from the process will be in small-volume waste streams, which normally should be of low uranium content. Perhaps the best overall approach to accountability would be to use the best estimate of the total uranium content of the core and the output (product plus waste) analysis at the chemical plant. The aqueous process may have a slight advantage in this respect, since it generates a relatively small amount of solid waste and can provide a solvent extraction feed sample before further processing. Accountability simply will not be as easy as it has been for metallic fuels.

6. PROCESS DESCRIPTION AND MATERIAL-BALANCE FLOWSHEETS

The process material-balance flowsheets are illustrated schematically by Figs. 3 through 9 and are given in detail by drawing E-57683 (Appendix 2) for the aqueous process and drawing E-57705 (Appendix 2) for the fluorination process. Each process uses the same fuel-handling and fluidized-burner system; this burner system will be described only once and will be followed by descriptions of the aqueous and fluorination "tail ends." The process feed rate is 11.1 chopped fuel rods per hour, or 1.25 kg U, 0.83 kg Nb, and 5.86 kg C per hour.

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Fig. 3. Fuel Charging and Fluid Bed Oxidation.

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Fig. 4. Ash Dissolution.

Fig. 5. Alumina Recycle.

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Fig. 6. Feed Adjustment.

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Fig. 7. Fluid Bed Fluorination and Alumina Disposal.

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Fig. 8. UF_6 Cleanup and Waste Salt Disposal.

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Fig. 9. UF_6 Recovery and Fluorine Disposal.

6.1 Fluidized-Bed Oxidation of Rover Fuel^{14,15,18,27,28,29,30,31}

6.1.1 General Description

The fluidized-bed oxidation of the fuel converts the graphite to carbon dioxide and carbon monoxide and the uranium and niobium carbides to their oxides. The fluidized bed of alumina acts as an efficient heat transfer agent, thereby preventing hot spots and clinker formation. The alumina also suspends the smaller fuel lumps, thereby facilitating rapid oxidation, and dilutes the finely powdered uranium and niobium oxides to yield a free-flowing burner product (Fig. 3).

The fluidized-bed burner is fed continuously with chopped fuel, alumina, and preheated 100% oxygen, which also fluidizes the alumina. Ninety-five percent of the oxygen is consumed¹⁴ by the various oxidation reactions to yield an off-gas containing 5% O₂, 4.7% CO, and 90.3% CO₂. The CO content of the off-gas is below the flammability limit but does not appear to be predictable by a previously published correlation,³² probably because of excess oxygen and the catalytic effect of metal oxides on converting CO to CO₂ to give the high utilization of oxygen.

The oxidation reaction in the fluidized bed is extremely smooth and easily controlled, and the principal oxidation reactions are:

The reaction proceeds at a fluidized-bed temperature of 700 to 750°C and at a superficial gas velocity of about 0.76 ft/sec at the bed midpoint pressure of 14.6 psia and average temperature of 725°C. Since the bed can operate successfully at gas rates up to about 1 ft/sec, a capacity oversize factor of about 30% is indicated. Continuous oxidation rates of 1.8 to 2.1 kg C per hour per ft³ of bed were obtained in the pilot plant.^{14,31} The combustion waste gases are cooled in the top of the reactor, filtered to remove entrained carbon dust and metal oxides, and exhausted to an off-gas system operating at 20 in. of water vacuum below the Idaho standard atmospheric pressure of 12.25 psia. The reactor is electrically heated to start the reaction and is air-cooled. The average heat flux, based on the inside area of the reactor, is about 9000 Btu hr⁻¹ ft⁻², or less than 2800 Btu hr⁻¹ ft⁻² of outside surface area on the finned outer wall. The experimental heat transfer coefficient from bed to wall is estimated¹⁴ to be about 85 Btu hr⁻¹ ft⁻² °F, which indicates an operating temperature of about 640°C for the wall.

Equal parts of 60- and 90-mesh Norton Blue Label R.R. alumina are fed to the reactor to maintain good fluidization as the alumina is loaded to 30 wt % U_3O_8 plus Nb_2O_5 . The carbon content of the discharged bed is less than 0.1%. If the starting alumina contains an appreciable amount of fines (for example, equal parts 60-, 90-, and 120-mesh alumina), fluidization will deteriorate as additional fines are produced by the oxidation reaction. This will eventually result in loss of fluidization, channeling, and hot-spot formation. It has been demonstrated that such a condition can be corrected by adding coarse alumina to restore the correct balance between fine and coarse material.³¹ Thus, a mixture of 60- and 90-mesh alumina is specified as the starting material to permit loading to the design value of 30 wt % U_3O_8 plus Nb_2O_5 . The coarse alumina carrier is also desirable because it produces beds that are highly permeable to fluorinating or leaching reagents.

The design study assumed that all of the used alumina from the fluorination process would be discarded and that the alumina in the aqueous process would be classified to reject 15% as fines and that 85% would be reused with a makeup stream of fresh alumina. When fresh alumina is contacted with fluorine, a small fraction is converted to AlF_3 . This AlF_3 , if recycled to the burner, becomes an aggressive corrosion agent³¹ (fluorinator) at around 700°C and may volatilize some uranium and niobium as oxyfluorides.^{19,33} Although it is possible to remove most of the AlF_3 by classifying and discarding the fines, it was decided to discard all the alumina and eliminate any possibility of corrosion of the burner by AlF_3 (Ref. 31). In the aqueous process, the prevention of fluoride recycle will depend on washing to remove traces of the leaching reagents from the used alumina. It was assumed that this can be done and that fluoride corrosion of the burner will not present a problem. This assumption is very questionable and requires experimental verification. Burner corrosion during oxidation indicates a rate less than 4 mils/year for the nickel-201 pilot plant burner^{15,31} and can be expected to be less than this if type 310 stainless steel or Inconel is used for the plant burner, since either of these is better suited for high-temperature use.

The fluidized-bed product is continuously withdrawn, cooled in a natural-convection cooler, and continuously transported pneumatically to a holdup reservoir for feeding to the aqueous or to the fluorination recovery system described in later sections.

6.1.2 Fission Product Behavior During Fuel Oxidation

Fission product volatility has been studied in several batch, laboratory-scale oxidation experiments^{11,34,35} that have been conducted in conjunction with aqueous- and fluorination-process studies. Within limits imposed by extrapolation of small-scale batch burning of single pieces of fuel to a full-scale, continuous, fluidized-bed burner, the fission product behavior is estimated for the plant to be as follows: A minor amount of cesium and possibly as much as 20% of the ruthenium will volatilize from the top of the bed and will be carried by the waste CO , CO_2 , and O_2 .

These gases are immediately cooled to less than 200°C and contain a large amount of dust. The dust and condensed ruthenium and cesium will be trapped by the sintered-metal filters and then dropped back into the bed. Practically no escape of ruthenium and cesium is anticipated in the combustion off-gases, since sintered-metal filters are extremely efficient in this service.^{3,34} There is strong evidence from other work³⁶ that the combination of the high bed temperature (700°C) and reducing conditions (CO and finely divided carbon) in the upper part of the fluidized bed may be quite effective in repressing ruthenium volatilization.

In the lower portion of the bed, near the bed take-off, very little carbon is present, and the gas is almost 100% O₂ at 700°C. This may strip some ruthenium and cesium from the reactor product, thus refluxing ruthenium and cesium in the reactor. The magnitude of this reflux, until steady state is reached with the reactor discharge, is unknown, but the steady-state buildup is probably minor for both ruthenium and cesium. No other evidence of fission product volatility was observed in the laboratory-scale combustion experiments.

Consideration of the half-life and chemical properties of other radioactive fission products¹⁰ indicates that krypton and long-half-life iodine will be discharged with the combustion gases. Selenium and technetium oxides are appreciably volatile at 200°C and probably will escape through the sintered-metal filters and possibly through the absolute filters to the combustion off-gas. If the off-gas filtration temperatures are low, these two elements might be retained in the top of the burner or in the absolute filters. Tellurium oxide has a slight vapor pressure and may reflux in the reactor to an even more limited extent than cesium, as noted above.

To summarize, radioactive krypton, iodine, and probably selenium and technetium will be in the combustion off-gases. A slight buildup of ruthenium and cesium and possibly tellurium will occur in the reactor, and then all will follow the bed product stream. Other fission products will proceed directly to the bed product. Supplemental treatment of the burner off-gas by passage through silica-gel beds³⁶ is probably not needed for this low-burnup fuel. The yields of ¹²⁹I, ⁷⁹Se, and ⁹⁹Tc are low and should not present a hazard even if discharged from the plant stack. At this time, there seems to be no need for further cleanup of the off-gas, such as by an aqueous scrubbing system.

6.2 Mixed-Acid Leach and Solvent Extraction

The flowsheet for the leaching process is shown schematically by Figs. 4, 5, and 6 and is given in detail by drawing E-57683 (Appendix 2).

6.2.1 General Description of the Leaching Process

The product of the fluidized-bed burner is stored in the ash bin, and four batches of ash per day, each weighing 53.3 kg and containing 7.5 kg U and 4.98 kg Nb,

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are charged as needed to the two parallel leaching lines (Fig. 4). The leaching equipment is geometrically safe and is made of Teflon and Teflon-lined pipe to resist the highly corrosive, hot nitric-hydrofluoric acid. The calculated exposure time for the Teflon lining of the leacher to accumulate a dose of 10^8 r was 15.9 years. Therefore, radiation damage of the Teflon should not be significant during the lifetime of the plant. A two-step leach is used, based on BNL recommendations and ORNL tests,^{14,15,19,22,30,37,38,48} although a one-step leach may be practical.^{11,38} If the one-step leach is practical, processing time can be saved. However, the information on feed-adjustment procedures was too limited when the flowsheets were prepared to permit the assumption that a single-step leach would permit an overall volume reduction in the solvent extraction feed from that shown on the flowsheet, since the adjustment procedure specified dilution to 1.0 M total fluoride.* Recent experiments in small-scale prototype leaching equipment indicates the two-step leach is preferable for the plant.³⁷

The first leach is a downflow, vacuum-assisted, single-pass leach with two bed volumes of hot 6 M HNO_3 to dissolve most of the uranium. The leachant contains cadmium³⁹ as a nuclear poison for safety in case the leach liquor escapes from the equipment. It also permits safe, routine handling of the uranium solutions in the large-diameter feed-adjustment and other vessels. Boron is not used as the nuclear poison since it forms fluoride complexes and thus competes with niobium for the available fluoride. Ninety percent or more of the uranium is dissolved by the nitric acid, depending on the amount of uranium combined with the niobium oxide and the efficiency of contact of the acid with the bed. The solution is filtered by vacuum through the Teflon filter-disk bed support to obtain a reasonable leaching flowrate and rapid wetting down through the 4.6-ft-deep bed. The downflow leach requires 1 to 2 hr with a vacuum of 20 in. of mercury. Boiling 10 M HNO_3 —5 M HF at an F:Nb ratio of 10 is then introduced and circulated upflow^{37,40} through the bed for 6 hr to dissolve the remaining uranium and niobium. The excess leaching reagent, plus any entrained fines, overflows to the recirculation reservoir, from which it is returned by a Teflon-lined pump to the leacher. The leachant is returned to a point just above the filter disk at a rate (about 0.8 ft/min upward velocity in the leacher, about 7 ft expanded depth of bed) that gently fluidizes the bed and ensures good leaching but which does not result in appreciable carryover of the coarse alumina to the leacher reservoir.⁴⁰ Some carryover of the fine Nb_2O_5 will occur; but the reservoirs are also kept at the boiling point, and the circulation pump can handle slurries. A slow flow of air is also maintained upward through the filter disk for agitation to prevent formation of any pockets of unleached material between the top of the disk and the leach liquor return from the recirculation reservoir. After 6 hr of leaching, the

* Feed-solution stability was investigated in detail^{37,38} after preparation of the flowsheets for this report. The results indicate that slightly less aluminum nitrate (0.2 M) can be tolerated in the feed at 1.0 M total fluoride concentration than shown by the flowsheet (0.3 M Al). This does not affect the design, although corrosion might be increased and solvent extraction might be adversely affected.

leacher product is filtered to the vacuum receivers, and the alumina is washed free of uranium and leaching acids. The leaching is assumed to dissolve $\leq 2\%$ of the alumina, and recovery of 99.9% of the uranium and niobium is assumed, based on laboratory- and small-scale pilot plant leaching experiments.

The leaching reactions are:

Very little heat is evolved by either reaction. The Nb_2O_5 is quite refractory; therefore, the dissolving must be done at the boiling point to get an adequate rate, and the leaching reagents should not be more dilute than the specified 10 M HNO_3 —5 M HF . Some reduction in the F/Nb ratio may be possible in the plant; however, at present there are no data to justify a ratio of less than 10.

The washed alumina is slurried with water and transferred to an alumina recovery system where the water is removed by filtration and the alumina is dried (Fig. 5). The dry alumina is fluidized, classified by a cyclone to reject fines, and thus control the particle size of the alumina. It is then returned to the burner with makeup alumina.

6.2.2 Feed Adjustment and Solvent Extraction

The combined leacher product and washes (about 257 liters) in the geometrically safe vacuum receiver is sparged to ensure thorough mixing with the nuclear poison, sampled, and transferred to the 200-gal, Teflon-lined feed-preparation tank, as illustrated in Fig. 6. Adjustment solution, containing aluminum nitrate and nitric acid, is added slowly, with mixing, to give a solvent extraction feed containing 14.0 g/liter of ^{235}U , 9.3 g/liter of Nb, 0.3 M Al^{3+} , 1.0 M F^- , 3.0 M H^+ , and 2.5 g/liter of Cd^{2+} . The aluminum-to-free-fluoride ratio (defined as total fluoride concentration minus five times the niobium concentration) of the prepared feed is 0.6. This ratio, based on a limited number of feed-adjustment experiments with simulated digest-burn-dissolve solutions,⁷ gave a stable solution that has a much lower corrosion rate on stainless steels¹³ (type 304L, 2.1 mils/month; type 347, 0.3 mil/month at room temperature) than did unadjusted solution. It was assumed that the chemical adjustment conditions developed for the lower-fluoride-content DBD solutions will work satisfactorily with the higher-fluoride-content solutions from burn—mixed acid leach (see footnote on page 26). Laboratory-scale solvent extraction experiments^{13,41,42} indicated that a satisfactory solvent extraction flowsheet could be developed for the Idaho extraction system designed for feed solutions containing zirconium or stainless steel. It is assumed for waste-estimation purposes that the solvent extraction column would be a simple extraction column and that scrubbing would be done in a separate scrub column to minimize the volume of high-fluoride solvent extraction waste.⁴³ The following flow ratios and compositions were used for waste estimation purposes:

Extraction column: feed (as above) to solvent (20% TBP) ratio, 3:1.

Scrub column: scrub [0.5 M $\text{Al}(\text{NO}_3)_3$, acid-deficient] to scrub extractant (20% TBP) to organic from extraction column, 0.2:0.04:1.

The uranium loss during solvent extraction with this flowsheet will probably be less than 0.5%, but an adequate decontamination from fission products may require an additional solvent extraction cycle.

Corrosion rates for the long-term storage of the Rover waste in the partially complexed condition (feed solution) are probably excessive, since the corrosion tests to date indicate an acceleration of the corrosion rate with increasing exposure time.

The niobium in the extraction-column waste will precipitate if the fluoride is completely complexed, as for example by combining the Rover waste with large excesses of ICPP aluminum nitrate waste. The precipitate is initially finely divided and easily suspended. It may not be too objectionable if the complexing could be done with low-activity-level aluminum nitrate wastes so heat generation in the layer of precipitate in the bottom of the waste storage tank would be minor.

A sample of simulated waste was evaporated in Teflon.⁴⁴ At a volume reduction factor of 2, a precipitate formed. The evaporation was continued until the volume was one-tenth the original waste volume, and the concentrate was neutralized with an equal volume of caustic. The precipitate of Nb_2O_5 was easily suspended and removed from the container with water. Waste evaporation was not considered for this study because (1) the slurry-handling problems are unattractive and should be avoided if possible, (2) additional Teflon-lined vessels and a complex system of fractionators would be required to recover the mixed acids, (3) a slightly contaminated acid fluoride waste stream would have to be discarded to a waste stream, and (4) special heat exchange equipment such as a platinum-iridium alloy heat exchanger or an induction-heated Teflon exchanger would be required since direct heat transfer through Teflon linings is very poor because of the excellent insulating properties of Teflon.

6.2.3 Leaching and Feed-Preparation Time Cycle

Four batches per day are processed through the two lines of leaching and feed-preparation equipment, thus allowing 12 hr to complete each leaching cycle. It is estimated that 2 hr would be required for leacher charging and the nitric acid leach and that 9 hr would be required for the mixed-acid leach, filtration, washing, and transfer of the alumina. The alumina drying and recycle for each batch of used alumina must be completed in 6 hr, since one drying line serves both leaching lines. If this time cycle proves to be too difficult, additional equipment lines must be

installed or larger leacher batches must be used. The latter is most attractive if a soluble nuclear poison were permitted as the only safeguard against criticality during the leaching operation. This would permit using large-diameter leaching equipment and would reduce the number of leaches to one or two batches per day. However, for this large-vessel approach to be acceptable, it must be demonstrated that the uranium never separates from the alumina. If it does, local uranium concentrations in excess of 1000 g/liter could be attained, and neither soluble nor heterogeneous poisons would be considered adequate.²⁵ For example, uranium concentrations of this magnitude might be achieved by accidentally water-fluidizing a charge of burner ash, then allowing it to settle so that the coarse alumina would separate from the very finely divided uranium oxide, which would then be concentrated in the supernatant liquid. This seemed to be a credible accident in a batch leaching system with a large-diameter leacher. Therefore, it was decided to do the leaching batchwise in geometrically safe equipment and to confirm by analysis that the leacher product was adequately poisoned before transfer to the large feed adjustment vessel. It did not appear possible to invent a simple, geometrically safe, continuous leaching system that could be made of Teflon.

6.3 Fluoride Volatility Process

The material-balance flowsheet for the fluorination process is given in detail by drawing E-57705 (Appendix 2) and is schematically illustrated by Figs. 7, 8, and 9.

A continuous fluorination system was chosen for the design study rather than the batch fluorination system used in most of the development work because of the much higher fluorine utilization, smaller equipment, and simplified operation of the continuous system. Recent experimental work^{29,30,31} with batch fluidized-bed fluorinations indicates that fluorine utilization remained more than 90% independent of fluorine input concentration over the range of 25 to 50% fluorine until the uranium content of the bed was estimated to be below 1%. At this point, the fluorine utilization decreased sharply to a low value for the balance of the batch fluorination run. The reaction mechanism apparently changes to a much slower fluorination and desorption from the surface of the alumina and is responsible for the protracted fluorinations required to reduce the uranium in the alumina to an acceptable discard level. Consequently, overall fluorine utilization in batch fluorinations is reduced to about 25 to 40% because of the inefficient utilization during this prolonged tailing-out period. Others have proposed to improve fluorine utilization by installing fluorine recycle systems to cope with the tailing-out problem in batch fluidized-bed fluorinations.^{45,46} However, these recycle systems must be designed for remote radioactive service with fluorine, are mechanically complex, may require the addition of extra trapping equipment, and are expensive. Other problems of batch fluorination are: (1) the equipment must be considerably larger, compared to the continuous system; (2) the batch fluorination system will be more difficult to operate, since gas concentrations, heat release, etc., are varied throughout the run; (3) the inert gas required to dilute the

fluorine during startup of the batch fluorinator and the large excess of gas used during the tailout period tends to sweep NbF_5 through the separation system, thus adversely affecting the UF_6 - NbF_5 separation and fission product decontamination, and also increasing the consumption of NaF in the hot traps; (4) incompletely fluorinated and finely divided material remaining in the top of the fluorinator and on the filters may drop into the waste alumina as it is being discharged from the reactor and lead to a loss with each fluorination batch; and (5) moist air is more likely to be accidentally introduced into a batch fluorination system than into a continuous system.

This design study proposes to improve the fluorine utilization by volatilizing 99% of the uranium (the easily volatilized fraction) by fluidized-bed fluorination and then recover the remaining uranium by countercurrent fluorination with a small volume of fluorine in a moving bed. Continuous fluidized-bed operations have been extensively used industrially and for various feed materials operations. Perhaps the strongest criticism of the continuous system is that it requires continuous solids-handling devices, good countercurrent contacting in the fluidized bed and moving bed, and gas sealing between some equipment components. Operation of a full-scale glass-and-steel-pipe mockup of the fluorinator with the associated pneumatic solids feeding and transport systems proposed by this study demonstrated that the mechanical concepts required for a continuous fluorinator were workable; however, sufficient manpower and time were not available at ORNL for a detailed study that would have fully developed the feeding and gas-seal systems. In any case, the low irradiation level of the fuel would permit use of very simple mechanical devices and gas seals if the proposed all-pneumatic devices were not sufficiently reliable. Instrumentation for continuously monitoring the UF_6 and F_2 concentrations in gas streams is available and can be readily used for continuous process control. Therefore, the continuous fluorination system described in the following sections was used for this study.

6.3.1 Fluorination

The fluorination is done in the following way (Fig. 7): The ash from the burner is fed continuously to the top of the 3-in.-diam by 5-ft-high fluidized-bed fluorinator, where the U_3O_8 and Nb_2O_5 are continuously fluorinated at 450 to 475°C with 100% F_2 to form volatile UF_6 and NbF_5 . This recovers 99% of the uranium. The remaining uranium is recovered by a 5-hr contact with 100% F_2 (about 10% of the total flow to the system) at 475 to 525°C in a countercurrent moving bed located immediately below the fluidized bed. The uranium loss is $\leq 0.13\%$.

The major reactions are:

Minor amounts of alumina are fluorinated to AlF_3 , and the traces of carbon are apparently converted¹⁰ to CF_4 , since neither carbon residues nor C_2F_2 polymers have been found in the process equipment after batch fluorinations.⁴⁷

A fluorine utilization of 75% is assumed for the system, although it is probable that the overall fluorine utilization will be better than 90%.

The fluorination system operates at a pressure of 5 psi (about 17.3 psia for ICPP conditions) in the top of the fluidized-bed fluorinator. The feed bin is always pressurized slightly above this pressure to prevent backflow of fluorine into the ash feeder and bin.

The midpoint superficial gas velocity in the fluidized bed at 19.25 psia and 450°C is 0.52 ft/sec. The superficial gas velocity in the moving bed at estimated midpoint conditions of 21.75 psia and 525°C is 0.018 ft/sec. These velocities for the fluidized and moving beds appear to be in an operable range. All gas rates throughout the whole fluorination system include allowances for the increasing dilution due to instrument purges, seal-gas leakage, filter blowback, etc.

Undiluted fluorine is used in both the moving bed and the fluidized bed to decrease the size of the fluorination and product-recovery system and to give the best possible conditions for UF_6 - NbF_5 separation by eliminating inert gas where possible. There may be concern about the intensity of reaction at the top of the fluidized bed with the undiluted fluorine feed to the system. The flowsheet assumption of 75% fluorine utilization results in an effective fluorine concentration of about 27.5% at the top of the bed where the feed enters. However, this is approximately equivalent to the startup of a batch fluidized-bed fluorination with 25% fluorine where there were no temperature control problems. But, if there is a temperature control problem in the top of the bed, the excess fluorine can be reduced to an amount only slightly above the stoichiometric requirement and inert gas (very dry air is satisfactory) added to the fluidized-bed gas feed to maintain the correct fluidization velocity. The free fluorine concentration in the disengaging space and feed inlet zone is thereby reduced to a few percent and would be equivalent to the conditions in the upper part of the fluorinator during batch fluorination experiments.²⁹

The operation of the fluidized-bed fluorinator has been described in BNL reports and has generally been satisfactory. The design of the fluidized-bed fluorinator for this study incorporates perforated baffles in the fluidized-bed section to minimize vertical mixing of the solids and to obtain better countercurrent contacting, thus ensuring discharge of alumina containing only a small amount of uranium to the moving bed.

As to the moving bed, experimental work at ANL and BNL indicates that uranium can be almost completely removed from static beds of alumina by prolonged fluorination. The same thing should be possible in a countercurrent moving bed, provided that satisfactory gas distribution and solids movement can be obtained with

the 60- and 90-mesh alumina mixture in the 5-in.-diam by 4.25-ft-tall moving bed. Gas distribution and solids flow do not seem likely to present serious problems, since the principles of gas and solid distribution in moving beds are well known and are extensively used in industry.⁴⁸

The alumina from the moving bed is expected to contain less than 250 ppm U, equivalent to a uranium loss of less than 0.13%. The BNL tests showed an average loss of 0.54% of the uranium via the alumina for their last two runs (RF 14 and RF 15)²⁹ in which the alumina was initially loaded with about 15 wt % U_3O_8 plus Nb_2O_5 . However, part of this loss may have been associated with the U_3O_8 - Nb_2O_5 - Al_2O_3 fines collected on the filter; these fines may have dropped into the bed when the bed was dumped.³¹ If this accidental mixing of fines from the filters had not occurred, the uranium loss might have been considerably lower. Also, fluorination of ash loaded to the design value of 30 wt %, instead of 15 wt %, and fluorination of the bed to the same final uranium content achieved in the RF 14 and RF 15 waste alumina would reduce the 0.54% loss to 0.27%. Hence, it is reasonable to assume that the elimination of the filter fines from the waste would result in an overall loss of only 0.13% for the design conditions. To support this argument, we observe that fluorinating alumina to less than the 250-ppm-U level, which is equivalent to the 0.13% U loss that has been assumed for the flowsheet, has been done repeatedly in both fixed and fluidized beds at BNL and ANL.

Heat generation has been calculated for the conditions assumed for the moving bed; it is 102 Btu/hr. This is equivalent to an adiabatic temperature rise of 20°C for the alumina in the moving bed. Since the fluorination of the residual uranium is slow, even this minor amount of heat generation will be well distributed in the moving bed and should not cause local overheating. A final reason for using the moving bed is that it allows true countercurrent contacting of the alumina with fluorine and thus can counteract any shortcircuiting tendencies of the fluidized bed. Therefore, the moving bed is good insurance against losses via the alumina waste.

Waste alumina from the bottom of the moving bed is discharged continuously, cooled in a natural-convection cooler, and pneumatically transported to a waste alumina holdup bin. The waste alumina is loaded into steel drums for disposal.

The UF_6 , NbF_5 , and unused fluorine from the moving bed flow upward into the bottom of the fluidized bed, where they mix with the primary fluorine feed to the fluidized bed. The UF_6 , NbF_5 , unreacted fluorine, inert gas, and oxygen from the fluidized bed are cooled to 200°C, filtered through sintered-metal filters in the top of the fluorinator, and sent to the UF_6 - NbF_5 separation system described in the following section.

6.3.2 UF_6 - NbF_5 Separation and Fission-Product Decontamination System

The separation of the UF_6 from NbF_5 and the fission products is done by partial condensation of most of the NbF_5 and fission products and sorption of the remaining

traces of NbF_5 and fission products on hot sodium fluoride (Fig. 8). Total condensation of both UF_6 and NbF_5 and subsequent distillation could be used for the separation but would be more difficult to operate than the proposed system. Alternatively, all the NbF_5 and fission products could be removed by trapping on hot sodium fluoride. However, large amounts of sodium fluoride waste would be generated, and uranium losses might be prohibitive.^{33,49} The proposed system, based on experimental work at ORNL, ORGDP,⁵⁰ and BNL^{29,31} is believed to represent the best separation system.

The partial-condensation separation of the NbF_5 and UF_6 is based on the large difference in vapor pressure between the two compounds as given by the following list of physical properties:⁵⁰

NbF_5 :

Melting point 78.9°C , boiling point 233°C

Vapor pressure: $\log_{10} p = -\frac{A}{T} + B$

p = vapor pressure, mm Hg

T = temperature, $^\circ\text{K}$

For liquid, $A = 2779.3$ and $B = 8.3716$

For solid, $A = 3655$ and $B = 10.859$

UF_6 :

Triple point: temperature 64°C , pressure 1.5 atm

Vapor pressure:

Solid UF_6 : $\log_{10} p = 6.38363 + 0.0075377t - \frac{942.76}{(t + 183.416)}$

Liquid UF_6 : $\log_{10} p = 6.93718 - 1091.537/(t + 217.22)$

p = vapor pressure, mm Hg

t = temperature, $^\circ\text{C}$

The flowsheet for the separation of the two components was calculated according to the above relationships; however, better separation has been achieved experimentally than is indicated by the preceding vapor pressure equations.

The first step in the separation is a continuous partial condensation of the NbF_5 at about 90°C . This is calculated to remove 97% of the NbF_5 as a liquid, thus reducing the size of the warm traps that complete the partial condensation. The warm traps collect the NbF_5 as a solid, and less than 0.015% of the NbF_5 throughput is calculated to leave in the UF_6 product gas from the warm traps. When a warm trap is loaded (approximately every three days), it is heated to 90°C to melt the NbF_5 , and the NbF_5 is drained to the waste surge tank while the other trap carries the load. The NbF_5 condensate in the waste surge tank is calculated to contain less than 8% of the uranium throughput but will actually be almost free of uranium, as noted below. The NbF_5 is drained to the sample tank, where a simple batch distillation assumed to be done at three-day intervals to remove traces of UF_6 . A 21% overhead cut is calculated to reduce the uranium loss in the remaining NbF_5 to less than 0.17% of the system input.

Experimental separations tests^{11,29,31,50} indicate that a much better separation of UF_6 from NbF_5 is obtained than can be predicted by the vapor pressure relationships. For example, the uranium in NbF_5 losses of 0.19% at ORGDP, of 0.54% at BNL, and of 0.008 and 0.13% at ORNL in hot tests (Table 2, Sect. 6.3.3) were obtained by partial desublimation of the NbF_5 , without any special step to remove UF_6 from the NbF_5 . It should also be noted that the high uranium losses in the NbF_5 waste stream observed in the ORNL pilot-plant batch-fluorination tests has been traced to incomplete equipment conditioning and moisture in the fluorination-products collection system.⁵¹ Careful attention to these details reduced the uranium loss in the NbF_5 to 0.5% before vacuum distilling the NbF_5 ; this was further reduced to 0.16% by vacuum distillation. The nonvolatile uranium was associated with oxygen that may have been introduced as moisture in the system via the fluorinator vessel walls, which were not conditioned, or via the ash charge to the vessel. The losses reported by BNL may be due in large part to similar moisture problems in their batch fluorination system. These observations on the NbF_5 - UF_6 separation highlight the need for thoroughly conditioning all parts of the fluorination system and for excluding moisture.

A current experimental program⁴² indicates that UF_6 in the UF_6 - NbF_5 mixture shows a positive deviation from Raoult's Law, which probably accounts for the fortuitous improvement in separation. Therefore, it is probable that the batch distillation of UF_6 from the sampling tank, as indicated by the flowsheet, will not be necessary as a routine operation.

Final cleanup of the UF_6 product gas from NbF_5 and fission products is done in the 400°C sodium fluoride traps. The important variables to minimize uranium losses in this operation are the temperature and the fluorine concentration. The temperature must be kept high enough so the UF_6 is not co-sorbed on the NaF pellets with the NbF_5 , leading to high losses.^{33,49} Free fluorine must also be present in the gas feed to the traps to prevent the decomposition of UF_6 at the 400°C operating temperature.⁵² Secondary problems of pellet quality, gas-retention time, and pellet loading with NbF_5 vs NbF_5 breakthrough are important for NbF_5 and fission product

removal but have not been well defined. The flowsheet assumes a sodium-fluoride-trap decontamination factor of 600 for NbF_5 . This is based on 12 runs with constant gas rate at ORGDP.⁵⁰ Recent BNL data³¹ with the same trap installed in the batch fluidized-bed fluorinator system indicates an NbF_5 decontamination factor of about 3000 for the first five fluorination runs. The flowsheet assumption of 600 for the NbF_5 decontamination factor by hot NaF is believed to be conservative because: (1) less NbF_5 will enter the traps, since the continuous fluorination does not have the long tailing-out periods when inert gas sweeps NbF_5 from the NbF_5 warm trap into the sodium fluoride trap (this effect was particularly noticeable in the batch fission-product decontamination tests¹¹ described in Sect. 6.3.3); and (2) the superficial gas velocity through the trap is about 35% of the gas velocity for the BNL tests and about 50% of the gas velocity for the ORGDP tests; also, the pellet bed is 36% longer. This longer contact time with the hot NaF should result in a much better separation from NbF_5 and fission products.

It is assumed that the traps will be replaced weekly. This implies loading the sodium fluoride to an average of 0.1 wt % NbF_5 (580 ppm Nb) before disposal. This may be compared with an average loading of 6400 and 1750 ppm Nb obtained in the two ORGDP tests, 17,000 ppm at BNL, and 40,000 ppm in the fission-product decontamination tests. The very conservative design and replacement schedule for the traps allows for operational upsets in the preceding condenser-warm-trap system and is germane to good NbF_5 and fission-product decontamination factors with the continuous processing system. The calculated Nb decontamination factor is 1.3×10^6 and the uranium product is estimated to contain 0.2 ppm Nb. This may be compared with Nb decontamination factors of $\sim 10^5$ for BNL tests and $\sim 4 \times 10^4$ for ORNL fission-products tests. The uranium products contained 2 to <15 ppm and 23 to 83 ppm, respectively, of Nb. Although the experimental data indicate relatively poor Nb removal, the more efficient equipment called for in this design study should result in attaining the calculated values.

The NaF pellet quality is important in avoiding excessive pellet breakup, dusting, and caking during NbF_5 sorption. A hard, relatively nonporous pellet, obtained by high-temperature decomposition and heat treatment of sodium bifluoride pellets, is desirable at the inlet of the bed to avoid caking. The hard pellets at the inlet could "taper" to a softer, more adsorptive pellet at the exit end to give an optimum balance between freedom from caking and good NbF_5 adsorptive capacity.

The estimated uranium loss (0.024%) to the high-temperature sodium fluoride is based on ORGDP data⁵⁰ averaged for 16 runs and for two batches of sodium fluoride. The ORGDP tests included heating the trap to a high temperature and purging with fluorine to remove UF_6 prior to discard of the NaF. Preliminary BNL results showed uranium losses that were a factor of 10 higher than the ORGDP tests for five runs and one batch of sodium fluoride,⁵³ but the BNL trap was not given a high-temperature desorption treatment to remove uranium prior to sampling. This probably accounts for the higher uranium retention observed in the BNL and ORNL tests (Table 2, Sect. 6.3.3).

Prior to discard, the trap is heated to 450 to 550°C, and a fluorine purge desorbs as much uranium as possible.⁵⁴ A new trap is conditioned in place with fluorine at 400°C before being put on stream. The conditioning and purge flows are very small and are not included in the flowsheet. The fluorine requirement for this and other conditioning and purging operations is easily accommodated by the assumption of only 75% F₂ utilization by the process; it is thought that the fluorine utilization should exceed 75%, thus freeing more than enough fluorine for the small, miscellaneous operations.

The purified UF₆ stream leaves the cell, is filtered to remove any entrained NaF dust, and goes to the UF₆ recovery system, located in an unshielded area.

6.3.3 Fission Product Decontamination

Decontamination from fission products volatilized with the UF₆ and NbF₅ is accomplished with the same system used for NbF₅ removal. A series of laboratory-scale, batch, oxidation-fluorination experiments were conducted with irradiated Kiwi-B-4A fuel samples.^{11,35} The results for oxidation-fluorination runs 1, 2, 3, and 5, which most closely approximate the fluidized-bed temperature conditions, are given in Table 2. The radioactivity level of the fuel was quite low, and some difficulty was encountered in accurately measuring some of the radioactive materials in the product. Nevertheless, the results indicate that the uranium will be adequately decontaminated (see Sect. 2.3) and that collection of the UF₆ on sodium fluoride and subsequent desorption will not be needed to meet the required fission product decontamination factors. Elimination of this step simplifies the process.

The experimental equipment did not incorporate gas filters other than the clean, sintered-metal supports used for the NaF beds. Any aerosols containing nonvolatile fission products would tend to be entrained throughout the system, even though gas velocities were very low in the reactor. A large excess of fluorine was used, thereby increasing the transfer of both volatile and nonvolatile fission products. It is probable that transfer of nonvolatile fission products will be a smaller problem in the plant because the dust-coated filters in the fluorinator will be highly efficient for aerosol removal³ and because gas volumes are minimized.

The six- to sevenfold excess of fluorine used in the experiments also caused a considerable transfer of NbF₅ from the partial condenser to the NaF trap and ultimately into the product. At the condenser temperature of 80°C, 30% of the NbF₅ was found in the NaF trap, resulting in 40,000 ppm Nb in the NaF, and the uranium product was contaminated with 23 to 83 ppm of Nb. The NbF₅ transfer throughout the system and the accompanying fission product breakthrough should be compared with NbF₅ decontaminations of 4.4×10^4 to 2×10^5 for BNL tests and with the much lower NbF₅ transfer, gas velocities, and NaF loadings with NbF₅ postulated for the plant. For example, the residence time for process gas in the NaF traps is about eleven times that used in the tests with spent fuel.

Table 2. Decontamination Factors and Uranium Recovery for Batch Oxidation and Fluorination of Kiwi-B-4A Fuel

Oxidation at 800°C; fluorination, 3 hr at 420°C, 1 hr at 530°C

Material	Reactor	Partial Condenser	400°C NaF Cleanup Trap	Overall Decontamination Factor
Elements Volatilized During Fluorination				
Inactive niobium	1.02	2.4, 5.5 ^a	1870, 470 ^a	4.6×10^3 , 2.6×10^3 (a)
⁹⁵ Nb γ	1.03 ^b	2.4, 7.3 ^a	2820, ^b 3400 ^a	7×10^3 , 2.8×10^4 (a)
¹⁰⁶ Ru β	1.9	2.1	1700	5.5×10^3
Elements That Should Remain in the Fluorination Ash				
⁹⁵ Zr γ	24	9.2	45 ^b	$>5.1 \times 10^3$ (c)
¹⁴⁴ Ce β	47	8.6	29 ^b	6.3×10^3
⁹⁰ Sr β	36	6.2	47 ^b	$>5.3 \times 10^3$ (c)
¹³⁷ Cs γ	135	13	2 ^b	$>1.6 \times 10^3$ (c)
Total rare earths	41	7.6	4 ^b	>700 (c)
Distribution of Uranium in the System				
Uranium losses, %	0.17 ^d	0.008, 0.13 ^a	0.108, 0.16 ^a	99.62% overall recovery

^a First value is for runs 1, 2, and 3 with 100°C condenser temperature; second figure is for run 5 with condenser at 80°C.

^b Estimated value because of missing data in one or more experiments.

^c Average lower limit value because of missing data. Real decontamination factor is probably greater than this value.

^d One-half to two-thirds of this loss was found in a cool area in the top of the reactor. The remainder of the loss was associated with corrosion products in the bottom of the reactor.

It is believed that the net result of the factors of (1) lower gas flow per unit of NbF_5 and UF_6 , (2) better filtration of the fluorinator product gas, (3) a more efficient partial condensation of NbF_5 , and (4) a longer residence time and lower NbF_5 loading on the 400°C NaF trap will result in a better decontamination from NbF_5 and fission products than obtained in the BNL or ORNL experiments.

The following assumptions were made in an attempt to estimate the fission-product decontamination performance for the plant: (1) the theoretical decontamination factor for inactive niobium calculated for the plant has a direct relationship to the decontamination for inactive and fission product Nb observed in the laboratory hot tests and (2) the decontamination factor for other fission products will exhibit a similar improvement. Table 3 presents the predictions for fission product decontamination based on the above assumptions. The actual decontamination factors probably lie between the prediction extrapolated from BNL cold tests and the estimate for the plant flowsheet. In any case, it appears that the plant will easily exceed the estimated decontamination requirement of 2.3×10^4 for gross gamma and 6.3×10^3 for gross beta activity, as given in Sect. 2.3.

6.3.4 UF_6 Product Collection

The purified UF_6 is trapped in 8-in.-diam, low-temperature, copper cold traps that operate at -40°C (Fig. 9). The vapor-pressure relationship for UF_6 cold-trapping is given in Sect. 6.3.2. The stripped gas leaves the traps at -34°C and carries about 0.4% of the UF_6 . This UF_6 is completely recovered by trapping on sodium fluoride. The uranium content of the exit gases from the cold traps could be reduced considerably by using -60°C refrigeration units for the cold traps at a small additional expense. After loading a cold trap with UF_6 , it is isolated from the system, heated to 70°C , and the liquid UF_6 is drained into standard product cylinders for enriched UF_6 . Recovery is calculated to be 99.7% of the uranium in the fuel.

The stripped gas from the cold traps goes to a large NaF trap that operates at 30°C and quantitatively traps the remaining uranium. This NaF trap can also be used as an emergency trap to retain all the uranium in case of a malfunction of the preceding cold-trap system. In actual practice, such malfunctions are very rare.^{50,54}

The absorption reaction⁵² for collection of UF_6 on NaF is:

The equilibrium relationship for trapping UF_6 on sodium fluoride is:⁵²

$$\log_{10} p = 10.88 - 5090/T,$$

where

Table 3. Predicted Fission Product Decontamination Factors for the Plant

Contaminant	Results of ORNL Batch Hot Test	Extrapolation of Fission Product Decontamination Factors Obtained by Batch Hot Tests	
		According to BNL Pilot Plant Cold Tests	According to Predicted Inactive Nb Decontam- ination for the Plant
Inactive niobium	$\sim 4 \times 10^3$	$\sim 10^5$ (observed)	1.3×10^6 (calculated for process flowsheet)
$^{95}\text{Nb } \gamma$	2.8×10^4	7×10^5	9×10^6
$^{106}\text{Ru } \beta$	5.5×10^3	1.4×10^5	1.8×10^6
$^{95}\text{Zr } \gamma$	$> 5.1 \times 10^3$	$> 1.3 \times 10^5$	$> 1.7 \times 10^6$
$^{144}\text{Ce } \beta$	6.3×10^3	1.6×10^5	2×10^6
$^{90}\text{Sr } \beta$	$> 5.3 \times 10^3$	$> 1.3 \times 10^5$	$> 1.7 \times 10^6$
$^{137}\text{Cs } \gamma$	$> 1.6 \times 10^3$	$> 4 \times 10^4$	$> 5.2 \times 10^5$
Total rare earths	> 700	$> 1.8 \times 10^4$	$> 2.3 \times 10^4$

p , partial pressure of UF_6 over NaF, mm Hg,

T = absolute temperature, °K.

This is a very efficient trapping method for UF_6 . Only $3.2 \times 10^{-4}\%$ of the UF_6 fed to the trap is estimated to leave the trap in the waste gases. With the very dilute UF_6 in the normal feed to the trap, the best trapping efficiency is obtained by operating the trap at room temperature rather than at $100^\circ C$. With high UF_6 -content feed gas, such as might occur in an emergency, the trap should be operated at about $100^\circ C$ to decrease the UF_6 absorption rate so the pellets at the trap inlet will not fuse and sinter due to local absorption of a large amount of UF_6 and consequent heat evolution at the trap inlet. This is not a problem with the normal low UF_6 content in the gas fed to the trap. The uranium absorbed by the trap is recovered by heating to $400^\circ C$ and purging the trap with a small amount of diluted fluorine to sweep the desorbed UF_6 from the trap and to counteract the small amount of decomposition that occurs at elevated temperatures as shown by the following reaction:⁵²

The NaF trap holds 160 kg of NaF and has a uranium holding capacity in excess of 30 kg even after repeated regeneration.⁵⁴ Therefore, regeneration of the trap is required only at long intervals and the NaF consumption of this trap is negligible. The fluorine requirement for the regeneration is small and is not included in the flowsheet. A typical regeneration would require about 1-1/4 hr at $400^\circ C$ and a gas flow not greater than 40 scfh. The gas consists of 20% F_2 and 80% inert gas.⁵⁴ The regeneration would be done during a plant shutdown, and the desorbed UF_6 would be collected in one of the regular cold traps. The waste gases from the NaF trap go to the fluorine disposal system, which is discussed in the next section.

6.3.5 Fluorine Disposal System

The waste gases are almost free of any radioactivity and could be scrubbed with caustic in the usual way for removing the fluorine. However, this method generates a considerable amount of aqueous waste and requires chemical makeup and some operating supervision. The fluorine disposal method used routinely at Goodyear Atomic Corporation, Portsmouth, Ohio,⁵⁵ is recommended here because it is simpler, does not generate any solid or aqueous waste, and prevents any possibility of aqueous solutions accidentally entering the equipment.

The fluorine reacts with SO_2 according to the following reaction:

The temperature of the reactants must be $\geq 205^\circ C$ to ensure prompt ignition and smooth reaction over all fluorine concentration ranges. With 10 mole % fluorine

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or greater in the feed gas, no heating is required to sustain the reaction after initiation. The reaction readily goes to completion even when only the theoretical amount of SO_2 is used. The sulfuryl fluoride has a boiling point of -55°C at atmospheric pressure, is practically insoluble in water, does not irritate the eyes or skin, and is quantitatively less toxic than sulfur dioxide, even when inhaled.⁵⁶ The threshold limit value for an 8-hr daily exposure to SO_2F_2 is four times the limit permitted for fluorine gas (threshold limit value for continuous exposure is 0.1 ppm fluorine in air).

The waste gases and SO_2 are heated to $\geq 205^\circ\text{C}$ and are contacted in a burner with a 25% excess of SO_2 to form SO_2F_2 . The excess of SO_2 allows for possible error in fluorine concentration in the waste gas and serves as a tracer since SO_2F_2 is odorless. The SO_2F_2 , SO_2 , and inert gases then go to a safety trap packed with 4-mesh activated alumina. The safety trap provides an emergency short-term fluorine disposal capability in case of a malfunction of the fluorine disposal burner and will also react with any escaping UF_6 (ref. 54). Any reaction in the trap will be readily detected by an abrupt temperature increase. The gases from the safety trap are then filtered and discharged to the vessel off-gas system and the plant stack.

7. PROCESS EQUIPMENT AND EQUIPMENT FLOWSHEETS

The general features of the process have been described in the preceding sections. Special features of the equipment and process operations are described in this section and are referenced to the appropriate schematic figure previously given in the report and to the detailed engineering drawings not included in this report to minimize printing problems. See Appendix 2 for list of drawing numbers.

7.1 Fuel-Charging and Fluidized-Bed Oxidation Flowsheet (Drawing E-57712 and Figs. 2 and 3)

The fuel charging system is illustrated in detail by drawings 10827-N-113-E and 10827-N-114-E and has been described in Sect. 5.6. The level of the crushed fuel in the feed bin is detected by a Teflon-sheathed capacitance probe. The air pressure in the bin is about 20 in. of water below the cell pressure; the pressure in the top of the fluidized-bed burner is slightly lower so that there is a slight air flow from the fuel bin into the top of the burner.

The 101 Fluidized-Bed Burner is made of type 310 stainless steel, which is a high-temperature, oxidation-resistant, tough alloy. The burner is 10-in.-diam by 7-1/2-ft-high, with a 20-in.-diam by ~4-ft-high disengaging, gas cooling, and gas filtration section on top. The reactor is electrically heated and air-cooled. The heating and cooling system is divided into two zones because very little heat generation occurs below the fuel support grid and heating may usually be required there. Heating is required to start a run. It is also required during the tailing-out period at the end of a run to ensure complete oxidation of the graphite. The cooling

system is designed to provide intensive cooling of the reactor immediately above the grid, where most of the burning occurs. Oxygen is supplied by a Linde converter which stores liquid oxygen and supplies gaseous oxygen on demand. The oxygen, after being preheated by passing through small pipes in direct contact with the hot wall of the burner, enters the bottom of the fluidized bed through a ball-check gas distributor in the lower cone. These ball-checks have been used extensively in similar applications in feed materials fluidized beds and have given good service.⁵⁰ The fuel-support grid is located 2 ft above the lower cone as in the BNL 4-in.-diam fluidized burner. Three perforated-plate distributors are installed below the grid to promote uniform fluidization and gas distribution and to minimize short-circuiting of carbon particles into the discharge pipe. Thus, the last traces of carbon particles will be burned in the lower section before they can be discharged with the bed product. Combination thermocouple-well and pressure-probe taps into the bed are provided for control. Further consideration of the design indicates that these wells and probes might be introduced through the top of the vessel, instead of through the side wall, to simplify vessel design. The level of the bed is determined by pressure drop through the bed or by an air-cooled thermocouple probe. The probe utilizes the difference in heat transfer between air inside the probe and the hot fluidized bed on the outside to determine the approximate level of the hot bed. A capacitance probe cannot be used because of the high temperature and the electrically conductive graphite. The burner off-gases are cooled by the finned cooler assembly in the disengaging section. The fins are cut and twisted to promote heat transfer, to intercept slugs of material ejected by bubbles from the bed, and to protect the filters from direct thermal radiation. The sintered-metal filters, preferably reinforced for longer life, are provided with jet assemblies for automatic blowback to remove dust deposits if necessary. The flanged top of the burner permits filter replacement and access to the interior of the vessel and is sealed with a stainless-steel-and-Teflon spiral-wound gasket. Decontamination spray nozzles are provided for the off-gas plenum and the interior of the vessel. The burner is controlled by regulating the fuel feed rate, the alumina feed rate, the bed-product withdrawal rate, oxygen feed rate, and temperature. Carbon inventory in the bed, off-gas composition and flow, and pressure drop through the bed are also useful operating guides.

The bed product is withdrawn through the natural-convection-cooled 301 Ash Cooler by the 203 Pneumatic Transport Feeder, which regulates the rate of solid flow.⁴⁸ Either continuous or intermittent withdrawal may be used. The solids accelerating section of the feeder is lined with boron carbide and the transfer line is schedule 160 pipe to resist abrasion by the alumina. An all-steel model of the feeder was built and given a very limited test⁵⁷ in a full-size piping mockup. The feeder performed satisfactorily, although the horizontal section of the solids inlet should be lengthened to permit tight shutoff. Very dry air should be used for flow control and transport to avoid introducing moisture into the fluorination system via the ash. The average off-gas flow from the fuel charging, combustion, and ash transport system, exclusive of the cooling air which is routed directly to the cell ventilation after being monitored for radioactivity, is estimated to be 20 cfm.

Samples of the burner product may be taken with the 602 Solids Sampling Blister, which is modeled after similar sampling devices for radioactive solids.³⁶

The ash is collected in the 403 Ash Bin for feeding to either the fluorination or the aqueous leaching process. The ash bin is provided with off-gas filters and a decontamination spray system similar to the fluid bed burner. A hard-surfaced impact plate deflects the incoming ash stream away from the vessel walls and filters onto the ash pile. The ash level is determined with a capacitance probe. The probe mounting nozzle is air-purged to keep the probe insulator free of dust. The purge connection also serves as a pressure measurement connection. The bin holds a maximum of about 170 kg of ash which is equivalent to 24 kg of U at the design loading of the alumina with 30 wt % fuel oxides.

Withdrawal of solids from the bottom of the ash bin to feed either the fluorination or aqueous process is controlled by a special valve that uses fluidization as the operating principle.⁴⁸ This valve is backed up by a Teflon-sealed, piston-operated, full-bore ball valve for gas-tight shutoff. The ball valve could also serve as the solids-flow control valve, but this double-valve scheme may prolong the useful life of the ball valve by never requiring it to be operated in contact with the column of solids. Purge connections into the ball-valve flanges are provided to blow dust from the ball valve before closing and to clear any line plugging. The double-valve arrangement is used wherever there are critical solids-flow control services that also require gas-tightness. Where absolutely gas-tight shutoff is not mandatory or where infrequent operation is indicated, only the ball valve is used. These valve arrangements are typical throughout both processes.

Criticality safety is maintained in the large-diameter fluidized-bed burner and ash bin by excluding water from the system during normal operation. Before aqueous decontamination, the equipment is flushed with clean alumina and vigorously fluidized to sweep out carbon and uranium dust. The aqueous decontamination reagents are poisoned until analysis of the washes indicate that no criticality hazard exists in the equipment.

7.2 Mixed-Acid Leach Flowsheets

Two equipment lines are necessary for the required throughput. One equipment line is illustrated on the flowsheets; the parallel line is indicated by listing only the item number on the appropriate flowsheets. The leaching and feed-preparation equipment and piping is either solid Teflon or Teflon-lined to resist the mixed nitric-hydrofluoric acid. The Teflon-lined equipment can be built up from standard lined pipe and fittings, so drawings were not prepared for these items. Similar treatment was used for reagent makeup tanks and stainless steel vessels of conventional design. Stainless steel, rather than carbon steel, was specified as backing material for the Teflon-lined equipment and piping in the cell so as to be comparable, equipment decontamination and cleanup-wise, to the volatility process equipment for which

stainless steel sheathing was specified for all thermally insulated and heated vessels and lines. The description of the leaching process in Sect. 6.2 provides most of the process and equipment details.

7.2.1 Burn-Leach Engineering Flowsheet, Sheet 1 (Drawing E-57710 and Fig. 4)

The A404 Leacher Feed Hopper serves as a leacher charge-metering bin for the ash from the 403 Ash Bin and also isolates the geometrically safe aqueous leaching equipment from the ash bin. Two charges of ash, each containing 7.5 kg of ^{235}U are charged by gravity from A404 to each leaching line daily. The A102 Leacher is a steam-jacketed, Teflon-lined, 10-ft-tall, 6-in.-pipe vessel, with a Teflon filter and bed-support disk in the bottom of the vessel.

The A304 Reflux Condenser for the leacher is made of Karbate to resist the acid vapor and condensate. Heat transfer through the Teflon linings of vessels is extremely poor, so reagents are preheated before introduction into the leacher; likewise, the A305 Heater is provided for reheating the leacher overflow liquor contained in the A405A and A405B Recirculation Reservoirs before pumping it back into the leacher. The A302 and A305 Heaters have platinum-iridium heat exchange surfaces to resist the concentrated 10 M HNO_3 —5 M HF . If this metal proves unsatisfactory, an induction-heated Teflon tube could be used to preheat the acids. Pumps (A204A and A204B), rather than air lifts, were chosen to get more precise flow control, to easily empty the recirculation reservoirs at the end of the leaching cycle, and to avoid a deep pit in the cell floor for the submergence of the air lift. The pumps are constructed of Teflon and are duplicated and installed in shielded blisters for convenient maintenance. Makeup tanks and pumps of stainless steel and Teflon-lined steel construction are provided for makeup and addition of the leaching acids and the water washes. A nuclear-poison monitor detects the cadmium poison in the 6 M HNO_3 leachant fed to the process and prevents the addition of any liquids to the leacher if the cadmium poison has been omitted from the leach acid. This eliminates any criticality hazard that might exist if the unpoisoned leacher product solution were accidentally transferred into the feed-adjustment vessel or leaked onto the cell floor. Leach liquors and washes are transferred by vacuum filtration to the A407A through A407E Filtrate Receivers (Fig. 6). The washed alumina remaining in the leacher is fluidized with water and transferred as a slurry to the alumina drying and recovery system.

7.2.2 Burn-Leach Engineering Flowsheet, Sheet 2 (Drawing E-57945 and Fig. 5)

This flowsheet illustrates the alumina drying and reclamation system that serves both lines of leaching equipment. The washed alumina slurry in the leacher is transferred to the stainless steel A103 Alumina Dryer by evacuating the dryer and opening the transfer-line valve. Water is removed by vacuum filtration through the sintered-metal filter disk and then by evaporation. Heat is provided by a steam coil on the outside of the vessel, by an internal steam coil in the bed, and by blowing heated

air through the filter disk and the bed. Off-gas filters in the top of the vessel retain the alumina fines in the vessel as the bed is dried and air-fluidized. Water vapor is condensed and collected with the filtrate water in the transfer-water collection tank. The water is sampled and either reused in feed preparation, sent to waste, or routed to the rework system in the main plant. The dry alumina is pneumatically transported via the A205 Pneumatic Transport Feeder and the A603 Solids Sampling Blister to the A501 Cyclone. The cyclone body is lined with boron carbide and Stellite to resist abrasion. The cyclone underflow, consisting of the coarser fraction of the alumina, is collected in the A409 Alumina Recycle Bin and recycled to the fluidized-bed burner by gravity flow using the fluidized-cup valve⁴⁸ on the bottom of the bin to regulate the alumina flow. The alumina is assumed to be free of fluoride, so a corrosion problem may not occur in the burner. Fines are collected in the A410 Alumina Fines Bin, which is provided with off-gas filters. The fines are transferred by gravity flow to the 806 Waste Alumina Loadout Station, where they are remotely loaded into drums for disposal. One drum is discarded approximately every 12 days. This station is necessary for the fluoride-volatility process also and is described in detail in Sect. 7.3.1.

7.2.3 Burn-Leach Engineering Flowsheet, Sheet 3 (Drawing E-57711 and Fig. 6)

This flowsheet illustrates the final steps of the feed preparation and the off-gas cleanup system. The combined leacher products (6 M HNO₃ leach and 10 M HNO₃—5 M HF leach) and alumina washes in the A407A through A407E Filtrate Receivers is mixed by sparging and sampled to verify the presence of the poison in the solution. The solution is transferred by air pressure to the 200-gal, Teflon-lined A418 Feed Adjustment Tank. Aluminum nitrate adjustment solution is added from stainless steel makeup vessels; the solution is sampled for accountability purposes and then pumped to the main plant for solvent extraction.

Off-gas from the aqueous leaching system is scrubbed with caustic in the A701 Off-Gas Scrubber to remove traces of fluoride. The scrubber is made of stainless steel, and the caustic reservoir is poisoned with boron-bearing stainless steel plates. Scrubbed gases are heated, filtered through absolute filters, and sent to the disposal system.

7.3 Fluidized-Bed Fluorination Flowsheets

The fluorination process is continuous insofar as the fluorination and the flow of UF₆ gas through the system to the collection traps is concerned. The trapping operations to purify and to collect UF₆ are batch operations because it is not practical to design continuous traps for these operations. The batch traps are installed in parallel and are sufficiently oversized so that they are on stream for long times; therefore, essentially continuous operation can be achieved.

The process equipment is made of Monel, nickel-201, Hastelloy-N, or oxygen-free copper, as required for the particular service. Plastic gaskets and ball-valve seals should be calcium-fluoride-impregnated Teflon wherever exposure to fluorine may occur. Process and instrument lines must be heated or purged to prevent plugging by deposits of UF_6 or NbF_5 . Special care must be taken to exclude water from the fluorination system, since water reacts with both UF_6 and NbF_5 to form solid deposits and may result in uranium losses from the system and plugging. The best method to eliminate the water is to introduce only dry feed and very dry gases into the system and to operate the system under a slight positive pressure, as is conventional for feed-materials fluorination systems. The process has been described in Sect. 6.3. Special features of the equipment and process operations are described below.

7.3.1 Fluidized-Bed Fluorination Flowsheet, Sheet 1 (Drawing E-57931 and Fig. 7)

Ash from the 403 Ash Bin is charged to the F404 Fluorinator Feed Bin, which isolates the pressurized fluorinator system from the subatmospheric-pressure burner system. A capacitance probe measures the level of the ash in the bin. Ash is fed to the fluorinator by the F204 Fluorinator Feed Valve, which uses fluidization as the operating principle. A full-sized model of this feed valve was built and tested briefly with alumina, with the following results:⁵⁷

Control Air Flowrate, (liters/min)	Alumina Flowrate, (g/min)
7	117
15.8	835
24.5	1420 (max. capacity)

The required feed rate is about 148 g/min; therefore, this type of feeder could be used for either continuous or pulsed feeding. The ball check gave evidence of nonuniform gas distribution in the shallow cup and required an air blast to free it when the alumina in the downcomer settled. Therefore, additional development work should be done to optimize the design and reduce the air consumption.

The ash from the feeder is introduced into the top of the F102 Fluidized-Bed Fluorinator via a heated and purged feed line. F102 is made of Hastelloy-N and has a 3-in.-diam by 5-ft-tall fluidized-bed section and a 6-in.-diam by 2-ft-5-in.-tall disengaging, gas-cooling, and off-gas filtration section on top. The fluorinator is electrically heated and air-cooled.

Fluorine is supplied from a portable liquid-fluorine tank⁷⁹ that is cooled with liquid nitrogen to prevent evaporation of the fluorine. The fluorine tank is pressurized with helium, and gaseous fluorine is produced on demand by an evaporator unit. The fluorine passes through a NaF trap to remove any traces of HF and is then fed

to the process. The fluorine is preheated by the packed bed (electrically heated) F304 Fluorine Heater and enters the bottom of the fluidized bed through a ball-check gas distributor. A ball check inside the gas-inlet block at the bottom of the fluidized bed prevents bypassing of the main fluorine flow down into the F103 Moving Bed Fluorinator, which is immediately below F102, and thence up the alumina downcomer into the fluidized bed. If this reverse flow occurred, alumina would not flow out of the bottom of F102 into the F103 Moving Bed Fluorinator. It is important to minimize vertical mixing of the alumina in the fluidized bed in order to approach true counter-current contacting of the alumina by the fluorine for maximum efficiency. Therefore, the conceptual design specifies 10 perforated grid plates, spaced vertically at 6-in. intervals in the bed to ensure countercurrent solids-gas contacting and eliminate short-circuiting of feed to the solids outlet to F103. Bed temperatures and the pressure drop are measured, and the bed level is determined with a capacitance probe. The mounting nozzle for the probe is heated and purged to prevent condensation or dust deposition on the pure, sintered-alumina probe insulator. The UF_6 , NbF_5 , O_2 , and unused fluorine from the bed are cooled from $\sim 450^\circ\text{C}$ to $\sim 200^\circ\text{C}$ by the gas cooler fins in the disengaging section and filtered through reinforced sintered nickel filters. The filters are provided with an automatic blowback system, and pebble-bed heaters (F302 and F303 Blowback Gas Heaters) preheat the blowback gas to prevent any condensation in the filters. The filters must be blown back regularly to maintain a low pressure drop and to avoid dropping a large amount of partially fluorinated dust back into the bed each time a filter is cleaned.³¹

Alumina is discharged from the bottom of the fluidized bed and flows as a dense phase directly into the top of the F103 Moving Bed, where the balance of the uranium is removed. The alumina inlet to F103 is designed to introduce the alumina onto the top of the moving bed so that no particle-size segregation occurs; such segregation would result in gas channeling and inefficient fluorination. F103 is made of Hastelloy-N and is 5 in. diam by 4.25 ft high. The vessel is electrically heated and air-cooled so that the alumina can be contacted with fluorine at any desired temperature, within limits imposed by the thermal conductivity of the moving bed, to remove the traces of uranium during the 5-hr residence time in the vessel. Fluorine is introduced into the bottom of the moving bed via a ball check distributor. This distributor may not be operable because of the wedging action of the moving bed, noted in the tests of the F204 Fluorinator Feed Valve. A powder-trap type or an inverted-cup type of distributor may be a better choice for a gas inlet. The final design of both the fluidized-bed and moving-bed vessels should eliminate any stagnant pockets of alumina, since the stationary alumina would eventually be completely fluorinated to AlF_3 .

Alumina is discharged from F103, cooled by convection in the F306 Alumina Cooler and pneumatically transported by the F205 Pneumatic Transport Feeder to the F405 Waste Alumina Bin. Sealing to prevent the escape of fluorine and UF_6 with the discarded alumina is assumed to be done by injection of inert gas at a carefully controlled pressure and flowrate into the F306 Alumina Cooler to act as a buffer. This procedure is used extensively in large-scale fluid-bed operations but may be

impractical on such a small scale. If this proves to be the case, a valve similar to F204 could be used to regulate the alumina discharge from F306 into two parallel blowcases or acid eggs that are always maintained at a slightly higher pressure than the bottom of F103. These blowcases would be used for dense-phase transport⁴⁸ of the alumina to F405, thus eliminating the F205 Pneumatic Transport Feeder and reducing the total transport air requirement. Samples of the waste alumina may be taken by the F603 Waste Alumina Sampling Blister. The F405 Waste Alumina Bin is identical in the 403 Ash Bin except that F405 is taller and has a maximum capacity of 300 kg of alumina, which is equivalent to two days throughput. The alumina is loaded into heavy-duty steel drums at the 806 Waste Alumina Loadout Station, which is located in cell 2 so the power manipulator and crane may be used to handle the drum. The drum incorporates an internal disposable filter so that all dust from filling is retained in the drum. A nozzle is provided for a thief sampler so a sample of the drum contents may be secured before disposal. Ball casters are installed on the cell floor, and the drum sits on a pallet plate for easy maneuverability. A load-cell platform at the filling station is provided to control the drum filling. A drum is filled and taken to the burial ground in a shielded carrier about every 1.8 days. The same drum-loading station must be provided for the aqueous process.

Cooling air from the equipment is monitored to detect fluorine or fluorides before discharge to the cell ventilation system. Such detectors also monitor the cell-ventilation system in each cell.

7.3.2 Fluidized-Bed Fluorination Flowsheet, Sheet 2 (Drawing E-57932 and Fig. 8)

The product gases from F102 Fluid Bed Fluorinator go to the F307 Condenser, which is an integral part of the F407 Waste Surge Tank. Both are made of Hastelloy-N for maximum resistance to NbF_5 . The condenser is 2-1/2-in.-diam by 26-in.-tall and is a finned-tube cold-finger type. The condenser is designed to cool the gases from 200 to 90°C and to condense 97% of the NbF_5 as a liquid, thus drastically reducing the amount of NbF_5 that must be collected by the warm traps. The calculated heat transfer data are:

	Process Gas Cooling	NbF_5 Condensation
Total heat load, Q	167 Btu/hr	485 Btu/hr
Heat transfer film coefficient, h_f	0.94 Btu hr ⁻¹ ft ⁻² °F ⁻¹	1115 Btu hr ⁻¹ ft ⁻² °F ⁻¹
Required surface area, A	2.4 ft ²	0.03 ft ²

F307 has about 4 ft² of heat transfer surface to allow a substantial safety factor for the uncertainties due to the laminar gas flow, the unknown properties of

the condensing NbF_5 liquid film, and the possibility of occasionally distilling some of the contents of F408 back into F407. The condenser is cooled by an 85°C recirculating fluorocarbon liquid, such as C_7F_{16} (hexadecafluoroheptane).⁵⁸ This fluorocarbon has the desirable properties of being inert to fluorine and is hydrogen-free; so no criticality hazard would be created if the coolant leaked into the system. Other more readily available fluoro- or chloro-fluorocarbon compounds could be used but were not investigated.

The F407 Waste Surge Tank is 8-in.-diam by 2-ft-8-in.-high, with a working volume of 5.4 gal at 30% freeboard or about 1-1/3 days throughput of NbF_5 . The bottom outlet from F407 is designed to retain solids, such as the insoluble lower fluorides of uranium, in the vessel. Both F307 and F407 are provided with electrical heaters so they can be heated for fluorine conditioning and can be cleaned of any uranium-bearing residues by fluorination at the end of a campaign.

The partially stripped UF_6 vapor goes from F407 to the F308 and F358 Warm Traps, which operate in parallel at 20°C . They remove the NbF_5 by desublimation, so less than 0.015% of the NbF_5 in the system escapes to sodium fluoride traps. The warm traps are made of Monel, are 4 in. in diameter by approximately 7 ft long, and are the hairpin or bayonet coolant tube-cross baffled type.^{59,60} This type is simpler to fabricate, particularly in Monel, and can be heated and cooled faster than the original "egg-crate baffled" K-25 cold traps.⁶¹ The design was approximated, since not all the necessary physical properties of NbF_5 are available. Also, it has been stated that design by the j-factor method for gas cooling only is satisfactory for UF_6 traps if the entering gas contains less than 4 mole % of the condensable component.^{59,62} The heat transfer coefficient is roughly estimated to be $0.21 \text{ Btu hr}^{-1} \text{ ft}^{-2} \text{ }^\circ\text{F}^{-1}$; the calculated heat transfer surface area is 19 ft^2 ; and 24 ft^2 of heat transfer area is provided. The fins at the trap entrance are widely spaced because the entering gas is saturated and NbF_5 deposition will start at the trap inlet. A fume filter is provided at the trap exit to minimize NbF_5 carryover. The traps are cooled by an 18°C recirculating, inert fluorocarbon liquid system. When a trap is loaded to the maximum allowable pressure drop, it is taken off-stream, heated to $\sim 90^\circ\text{C}$ by the fluorocarbon, and the NbF_5 drains into F407 for disposal. Electrical heaters are provided on the trap so it may be conditioned and any uranium deposits may be recovered by fluorination prior to equipment decontamination.

Final purification of the UF_6 is done in the F702 and F752 NaF Traps, which operate in parallel at 400°C and absorb the last traces of NbF_5 and fission products. Each trap is made of Monel and is 8-in.-diam by 3-ft-tall and packed with 32 kg of NaF pellets. The design of the trap assumes that 1% of the NbF_5 fed to the recovery system, rather than the flowsheet value of 0.015%, is removed by the trap; the trap is loaded to less than 5% Nb and is replaced at weekly intervals. The design assumes a lower loading than was obtained in experimental tests^{11,31,50} and should give adequate NbF_5 and fission-product cleanup. The trap is the annular U-tube type, with the connections at the top for convenient remote replacement. The U-shaped design has the additional marked advantage of collecting any

high-NbF₅-content NaF fines (formed by shattering of the pellets at the trap inlet) at the trap midpoint rather than near the exit where the dust can be swept from the trap and thus contaminate the product. The traps are connected to the piping with remotely operated Marman Conoseal pipe joints with Duranickel flanges and nickel-201 gaskets. Experimental tests indicate that some design modifications on the clamps may be required before these commercial connectors are suitable,⁵⁰ although they maintained gas-tightness through repeated thermal cycling. Cups are inserted in the bed so samples may be taken of the bed at the inlet and exit ends prior to discard of the trap and contents. The traps are installed in cell 2 for remote replacement purposes and are heated with F313 and F363 Clamshell Furnaces. The trap inlet piping and free space above the bed acts as the gas preheater. Conditioning purges from a new trap that is being readied for use bypass the UF₆ cold-trap system so water will not be introduced into the cold-trapping system. Purified UF₆ goes to the collection system.

The NbF₅ collected in F407 drains via a freeze valve to the F408 Waste Sampling Tank. Freeze valves are used on the liquid inlet and outlet lines on F408 for better long-term reliability and tighter shutoff than would be obtained with a metallic-seat, bellows-sealed remote valve. The freeze valves are closed by being cooled with a circulating fluorocarbon and are opened by electrical heating. F408 is a 10-in.-diam by 3-ft-4-in.-tall vessel made of Hastelloy-N and has a working volume equivalent to 2.3 days of NbF₅ waste. The NbF₅ is sampled using the F604 Waste Salt Sampling Blister. Any UF₆ in F408 may be batch-distilled back into the trapping system. Normally, this should not be required (see Sect. 6.3.2). The bottom outlet from F408 is designed so any insoluble uranium compounds will be retained in the tank and can be eventually recovered by fluorination. Waste NbF₅ is removed from the system by isolating F408 from the fluorination system, venting F408 to the off-gas system via a chemical trap, and draining the NbF₅ into a 30-gal steel drum in the F807 Waste Salt Load-Out Station. F807 is located in cell 2 for remote handling of the waste drums. A drum of NbF₅ is discarded to burial every seven days.

7.3.3 Fluidized-Bed Fluorination Flowsheet, Sheet 3 (Drawing E-57933 and Fig. 9)

Purified UF₆ from the F702 and F752 NaF traps leaves the cell and is filtered through F501 and F551 filters to remove traces of NaF dust. The filters are standard sintered nickel or Monel filters and may be lightly shielded if radioactive dust carry-over from the NaF beds is a problem. A continuous UF₆ analyzer monitors the concentration in the product gas stream.

The UF₆ is desublimed and collected in the F314 and F364 cold traps, which operate in parallel at -40°C. Less than 0.4% of the entering UF₆ leaves in the trap vent and is completely recovered by trapping on NaF. The cold traps are made of deoxidized copper for high thermal conductivity, are 8 in. in diameter and 8 ft 8 in. long. They are of the hairpin coolant tube, cross-baffled type.^{59,60} The traps

are designed to have a holding capacity of at least 30 kg of ^{235}U as UF_6 . The gas flow is very low; consequently, the heat transfer coefficient h predicted by the Montillon correlation⁶² is only $0.05 \text{ Btu hr}^{-1} \text{ ft}^{-2} \text{ }^\circ\text{F}^{-1}$. The required heat transfer surface is calculated to be 80 ft^2 , but 106 ft^2 is provided. Plugging curves were not calculated; so the final design may require a slightly different fin spacing than shown by the conceptual design. More baffles could also be used to increase h and reduce the size of the cold trap. The cold trap is chilled by a refrigerated, circulating, heat-transfer liquid. When a trap is loaded to the limit of the allowable pressure drop, it is taken off-stream, purged with inert gas, and the UF_6 is melted and held at about 160°F by heating the heat transfer liquid. The cylinder loading manifold is evacuated, and the product bottles are filled with liquid UF_6 . Lines are heated, and double valving is used on all critical UF_6 or vapor lines. Rupture disks and relief valves are provided on the UF_6 cold traps in accordance with accepted UF_6 handling procedures.^{50,54,63} A hood is provided for the bottle-loading operation, although this is frequently done in the open.⁵⁰ After being drained, a trap is purged of UF_6 vapors into the on-stream trap and then is cooled for the next loading cycle.

Traces of UF_6 in the cold-trap vent gases are recovered by sorbing the UF_6 on NaF in the F703 NaF Backup Trap. The trap is the annular U-tube type, is internally and externally cooled and heated, and is made of Monel. It is 16 in. in diameter and 6 ft tall. Normally, the trap operates at room temperature for maximum removal of the UF_6 from the waste gases. Air cooling is provided in case a high- UF_6 -content gas is ever sent to the trap. The maximum permissible loading rate is estimated to be in excess of 30 kg of ^{235}U per hour. Electrical heaters and thermal insulation are installed on the trap so it can be heated if it is ever used as the primary collector for UF_6 and so it can be desorbed in place when required. The trap is designed for a capacity of 0.2 g of ^{235}U per gram of NaF , which is a typical design capacity value for a trap after 50 loading-unloading cycles.⁵⁴ Initial capacity of the sodium fluoride is approximately three times this value and it decreases with repeated cycling. Normal operations would theoretically load the trap to the 0.2 g of ^{235}U per gram of NaF in 260 operating days; therefore, the useful life-time of the initial charge of NaF will probably exceed the plant life. Uranium is removed by heating and purging with diluted fluorine into one of the cold traps during plant shutdown. Uranium loss to discarded NaF will be much less than 160 g if desorbed at a very high temperature.⁵⁴

The waste gases and a parallel stream of sulfur dioxide are preheated to $\geq 205^\circ\text{C}$ in the F315A and F315 Heaters and reacted in the F104 Fluorine Disposal Reactor to form SO_2F_2 . F104 is made of Inconel, is 4 in. in diameter and 4 ft 8 in. tall, and is steam-cooled, since heat input to the reactor wall may be required at low fluorine feed rates. The burner is designed to dispose of fluorine at twice the normal total feed rate of fluorine to the process. Normal operation of the burner is at about 12.5% of rated capacity. The waste gases go to the F704 Safety Trap, which is made of Monel and is 6 in. in diameter and 6 ft tall. It is packed with 4-mesh activated

alumina. The gases from the safety trap go through small absolute filters and then to the vessel off-gas system and stack. The average process-vessel off-gas flow from the fluorination process is 4.2 scfm.

8. MATERIALS OF CONSTRUCTION

8.1 Graphite Oxidation

The BNL pilot plant fluidized-bed oxidizer was made of nickel-201 because the Rover program originally envisioned oxidation and fluorination in the same vessel. Nickel-201 is a fairly satisfactory, readily available material for this kind of exposure. Nickel analysis of aqueous leach solutions from the early combustion runs indicated combined corrosion and erosion (if any) rates of less than 4 mils/year for oxidation exposure, which is quite satisfactory.³⁴ However, the allowable design stress for nickel-201 is rather low at 650°C, the highest temperature specified by the unfired pressure vessel code for this material. Therefore, type 310 stainless steel was specified for the shell of the fluidized-bed burner, since it is more suitable as a high-temperature alloy. No corrosion tests have been made to confirm this choice, but carburization, scaling, and attack by oxygen appear to be negligible at 700°C.⁶⁴ Tentative decontamination procedures for the burner are given in Appendix 3.

BNL tests showed that recycle of fluorides from the fluorinator to the oxidizer could result in corrosion rates of up to 1 mil/hr at 725°C. Consequently, this is the basis for recommending that alumina should not be recycled to the burner in the fluoride volatility process.³¹ The amount of fluoride recycle to the burner that will occur with the aqueous process is unknown; but, if any significant recycle occurs, Inconel might be more satisfactory than type 310 stainless steel for the burner.

8.2 Aqueous Leaching

The boiling 10 M HNO₃—5 M HF used for the leaching is highly corrosive to all ordinary materials. Teflon or Teflon-lined equipment is the only practical material of construction for the aqueous leaching system. The actual corrosion rate or the probable lifetime of the Teflon or Teflon-lined equipment is not known, although satisfactory performance has been obtained in short-term laboratory and bench-scale leaching tests. The Teflon lining of the leaching vessel is exposed to 718 r/hr and would require 15.9 years of continuous exposure to accumulate an exposure of 10⁸ r. Therefore, radiation damage, by itself, is not expected to affect the Teflon.

Stainless steel backing is specified for the Teflon-lined cell equipment and piping because such an exterior surface will be more suitable for decontamination than the usual carbon steel backing. A drawback of Teflon-lined equipment is that it must be assembled from flanged component pieces. Piping and attachments such

as nozzles, dip lines, etc., require many joints. Consequently, a leak-free system may be difficult to achieve and may not remain tight after prolonged use due to the effects of thermal cycling and the plastic flow properties of Teflon. Decontamination will be very difficult if a lining develops a leak that allows active solution to be trapped behind the liner.

Karbate has been specified for the reflux condensers, where exposure to dilute acids only will be encountered. Platinum-iridium alloy is tentatively specified for the heat exchanger surfaces for the concentrated 10 M HNO₂—5 M HF, since Teflon is a very poor heat conductor.

Corrosion tests indicated that the corrosion rates at room temperature for welded specimens of types 304L, 347, and 309SCb stainless steels were 8.0, 1.5, and 0.4 mils/month,¹³ respectively, in a solution 3 M in HNO₃, 1.0 M in HF, 0.0074 M in U, and 0.125 M in NbOF₃. Increasing corrosion rates with time were observed for the first two alloys. Making the above solution 0.2 M in Al(NO₃)₃ reduced the corrosion rates for 304L and 347 stainless steels, as shown by the following:⁶⁵

Alloy	Specimen Position	Corrosion Rate (mils/month)			
		168 hr	672 hr	840 hr	1008 hr
304L	Vapor	0.4	0.3	0.2	0.2
	Vapor-solution interface	1.4	0.8	0.7	0.6
	Solution	2.1	1.7	1.6	1.2
347	Vapor	0.2	0.2	0.2	0.2
	Vapor-solution interface	0.3	0.2	0.2	0.2
	Solution	0.3	0.2	0.2	0.2

At the end of the tests, the surfaces were free of scale and very slightly roughened.

These experiments indicated that feed solutions and the resulting solvent extraction wastes can be processed in present equipment at the ICPP. However, these solutions are much more corrosive than feed solutions previously considered as rather corrosive for the Idaho Plant.⁴³ Heating and agitation of the solutions may increase the corrosion rate.

8.3 Continuous Fluorination

Corrosion tests have not been conducted at ORNL for either the fluidized- or the moving-bed fluorinator because a considerable amount of data is available from other programs which have approximately comparable environments. A critical review of literature data on corrosion by gaseous fluorine, new studies of protective fluoride

film formation on metals, and conditioning and drying techniques with fluorine and chlorine trifluoride are reported by Barber and Bernhardt.⁶⁶ Specimen preparation, conditioning techniques, fluorine purity, and exposure time have a considerable influence on corrosion rates, since the fluoride film is responsible for the corrosion resistance. These factors were not of major concern to earlier investigators and account for the wide spread in the reported data.

8.3.1 Piping

Steel piping with bellows-sealed Monel valves with metal-to-metal or CaF_2 -impregnated-Teflon-to-metal seals are stated to be satisfactory⁶⁷ for fluorine at pressures up to 75 psig and 400°F. However, this upper temperature limit for steel should be reduced to about 200°F in view of the data of Barber and Bernhardt.⁶⁶ Ring-type gaskets made of Teflon impregnated with 30% CaF_2 are satisfactory for temperatures up to 350°F. Valves are limited to a maximum operating temperature of 600°F, but seat and bellows life could be limited at this high a temperature. Aluminum alloys 99.99, 1100, 3003, and 2024 are satisfactory⁶⁶ at temperatures up to 200°C, and copper is excellent for low-temperature service. Nickel and Monel are, of course, generally satisfactory for all usual applications involving fluorine distribution systems. High-temperature tests up to 1800°F have shown that nickel-200 (A-nickel) is more resistant than Monel^{68,69} and that UF_6 is about one-third as corrosive as fluorine gas.

Monel is specified for all low-temperature fluorine and UF_6 piping, although cheaper materials could be used in many places. Instrument tubing is specified as nickel or Monel inside the cells, and copper tubing outside the cells. Stainless steel is specified for low-temperature and negligible fluorine exposure applications inside the cell. For example, periodic replacement of the waste-alumina transport line may be required due to abrasion; so stainless steel is specified for this line.

8.3.2 Fluorinators

An extensive corrosion-test program was conducted for the ORNL Volatility Pilot Plant fluorinator. The vapor-phase corrosion-test coupons represent the most complete systematic study that can be considered applicable to the Rover fluorination conditions. Molten salt at 500°C was sparged with fluorine while UF_4 in the melt was volatilized as UF_6 . The vapor-phase coupons were splashed with corrosive salt, and appreciable amounts of elements having volatile, corrosive fluorides, such as chromium, were in the melt. Consequently, the corrosion rate^{70,71,72} may be slightly higher than will actually be observed with Rover. Table 4 summarizes the applicable information. Corrosion specimens were also exposed simultaneously in the ORNL Volatility Plant (VPP) fluorinator and generally confirmed⁷³ that nickel is unsatisfactory and that Hastelloy-N and HyMu 80 are superior materials. Slight intergranular attack of HyMu 80 was attributed to either decarburization noted on

Table 4. Vapor-Phase Specimens Exposed to Fluorine in the Fluorinator at 500°C for 148 hr

Material	Corrosion Rate (mils/month)		Type of Attack
	Weight-Loss Basis	Microscopic Examination Basis	
Nickel-201 (L-nickel)	0.1	5.0 - 7.5	Intergranular
Nickel-201, welded ^a	0.16	-	-
Nickel-201, welded ^b	0.13	-	-
INOR-8 ^c	3.0, 1.8	-	Uniform
INOR-8, welded ^d	1.8	-	Uniform
Hastelloy-N ^{c,e}	2.0, 1.6	-	Uniform
Welded Hastelloy-N ^f	4.7	-	Uniform
HyMu 80 ^g	0.1, 0.1, 0.1, 0.0, 0.0	-	Uniform
HyMu 80 ^h	0.5	-	Uniform

^a INCO-41 filler rod.

^b INCO-61 filler rod.

^c Nominal composition 71% Ni, 16% Mo, 5% Fe, 7% Cr.

^d Welded with INOR-8 containing 2% Nb.

^e Alloy from commercial source.

^f Welded with standard INOR-8 rod.

^g Nominal composition: 79% Ni, 4% Mo, 15% Fe, 1.5% Si, 0.5% Mn, 0.05% C, heat-treated before use.

^h Same as g, above, but not heat-treated before use.

the surface of the original specimen or to the use of aluminum nitrate—nitric acid decontamination reagent which was found afterwards to be quite corrosive to HyMu 80. Actual attack rates attributable to fluorination in the VPP are less accurate than the individual BMI tests because the VPP fluorinator was exposed to only molten salt for prolonged periods, and temperatures were not so well controlled.

A marked contrast is observed between the data in Table 4 and recent data⁷⁴ from ANL for specimens of nickel-200 exposed at 475°C to high-purity fluorine diluted to 50 vol % with nitrogen. Corrosion rates for 960 hr of exposure were: 0.9 mil/year for nickel-200 plate, and 0.6 mil/year for welded nickel-200. These results could have been fairly well predicted from previous work⁷⁵ with high-purity nickel and nickel-200 exposed to pure fluorine. The dramatic reduction in corrosion rate, compared with the rates found in the BMI tests, indicates the difference between a clean gas system and an operating system.

Evaluation⁷³ of decontamination-reagent attack has also been made. The decontamination reagents are: hot 0.35 M ammonium oxalate, which is not corrosive and is quite effective⁷⁶ for removing fluoride scales and salts, boiling 0.1 M AlNO_3 —0.01 M HNO_3 , and room-temperature 5% NaOH—2% H_2O_2 —2% sodium tartrate. The second reagent is more corrosive and must be used with care. A 160-hr cyclic exposure with the latter two was used; this, combined with ammonium oxalate washes, was adequate to decontaminate the highly contaminated VPP equipment. The results indicated that INOR-8 was the best material, exhibiting an average corrosion rate of 0.55 mil/month for the cyclic decontamination. HyMu 80 underwent 45 times more penetration (intergranular), and L-nickel underwent 60 times more penetration than INOR-8, and was severely corroded at the welds.

Additional confirmation of the general superiority of Hastelloy-N was observed⁷⁷ in cyclic tests for batch fixed-bed oxidation-fluorination corrosion. The cyclic exposure was at 700°C to 5% CO , 65% CO_2 , and 30% O_2 , followed by exposure at 400°C to fluorine. These tests were much more severe than the proposed continuous fluorination but nevertheless have some validity for materials selection because O_2 will be present in the fluorinator as a reaction product and from instrument purges. INOR-8 was the only material not showing intergranular attack and had a decreasing corrosion rate, which was 9.5 mils/month after 40 cycles. The corrosion film was very adherent, which is significant for fluidized-bed operations where very mild abrasive conditions exist.

From the preceding data it is concluded that Hastelloy-N (INOR-8) is the best structural material for the fluidized- and moving-bed fluorinators and for all fluorine and gas heaters and piping exposed to high-temperature fluorine. HyMu 80 might be a satisfactory, slightly less expensive material if an effective and less corrosive decontamination reagent than 0.1 M $\text{Al}(\text{NO}_3)_3$ —0.01 M HNO_3 were used. This certainly seems possible since ammonium oxalate is quite effective for removing molten salt residues and corrosion products. The corrosion rate at 500°C for Hastelloy-N is estimated to be less than 2.1 mils/month for base metal, and less than 3.3 mils/month

for welded material. Sintered-metal filters in the top of the fluorinator operate at about 200°C; therefore, nickel or Monel should be satisfactory for the filters. Spiral-wound gaskets made from nickel and 30%-CaF₂-impregnated Teflon are specified for the fluorinator top flange and other system flanges operating at moderate temperatures.

8.3.3 NbF₅ Separation System

Corrosion tests⁷⁸ with boiling NbF₅ gave corrosion rates of 0.6, 0.4, and 0.2 mil/month for nickel-201, Monel, Hastelloy-N, respectively. Nickel-201 underwent severe intergranular attack; Monel showed some intergranular attack and copper leaching; and Hastelloy-N underwent only uniform corrosion. Hastelloy-N is specified for F307, F407, and F408 for maximum resistance to NbF₅. Monel is specified for the F308-F358 warm traps, since normal exposure to NbF₅ is limited to a maximum temperature of 100°C. This choice should be re-evaluated from the equipment-decontamination standpoint, since Monel may not resist the decontamination reagents.

The F702-F752 NaF traps operate at 400°C but are discarded regularly. Therefore, Monel is a satisfactory, relatively cheap choice for these traps. Piping used for preheating the trap feed is Hastelloy-N, and all valves are located away from the traps so they are in relatively cool (less than 125°C) locations.

Carbon steel is satisfactory for the NbF₅ disposal drums, since the salt freezes after being dumped into the drum.

8.3.4 UF₆ Product Collection and F₂ Disposal Systems

Copper is specified for the UF₆ cold traps, and Monel is specified for the UF₆ product-handling system piping.

Monel is specified for the balance of the equipment and piping except that steel is specified for the SO₂ supply system and Inconel is specified for the F104 fluorine disposal reactor because of its resistance to fluorides and SO₂ at high temperatures.

9. CAPITAL AND OPERATING COST ESTIMATES

9.1 Capital Cost Estimate

The capital cost for the installation of the fluorination process is estimated to be \$1,614,000, and the capital cost for the installation of the aqueous process is estimated to be \$1,624,000. The daily amortization costs are based on a projected Rover program load⁸⁰ of 10,500 kg of ²³⁵U and are \$4610/day and \$4640/day, respectively. The monetary value of existing buildings, services, and process

equipment (solvent extraction, waste disposal, off-gas system, etc.) that may be required was not included in the capital-cost estimate for either process.

The capital-cost estimate for the equipment was prepared by making a detailed estimate of the cost for each item, as shown by the appropriate conceptual-design drawing or flowsheet. Allowances were made for high-quality fabrication and stainless steel vessel supports for cell equipment. The Teflon-lined cell equipment for the aqueous process was assumed to have stainless steel as the liner-backing material to facilitate decontamination of the exterior of the equipment. Volatility equipment and piping in the cell were assumed to be sheathed with stainless steel for the same reason. Piping costs were calculated by estimating the lengths required, with appropriate allowances for sleeves through concrete, bends, special treatments (such as heating and insulating), materials, valves, fittings, etc. Similar detailed treatment was given to each of the categories listed in Table 5. The cost of the head-end is added to the cost of the rest of the process, and the sum is factored for indirect construction costs, architect-engineer costs, and contingency (Table 6).

9.2 Operating Cost Estimate

The major component of the operating cost is the standard fixed charge of \$9000 a day for operating the Idaho Chemical Processing Plant.⁸¹ The variable components of the daily operating cost are itemized in Tables 7 through 10, and the sum of the operating and capital costs is given in Table 11.

The variable components of the operating cost were estimated according to the requirements of the material-balance flowsheet and the assumptions given in the text. No charge is tabulated for the value of the uranium that may be lost because each process should give almost complete recovery of the uranium.

9.2.1 Gases and Chemicals

The cost of the gases and chemicals (Table 7) was estimated from actual quotations or from ORNL stores prices. The price for fluorine was quoted as \$3.50 to \$4.00 a pound, FOB factory; \$4.00 a pound was used since the demand is irregular and the quantity is relatively small. The fluorine consumption is based on a 75% utilization of the fluorine. Hydrofluoric acid for the aqueous process is purchased as anhydrous HF, and an existing facility is used to prepare the concentrated aqueous solution.

9.2.2 Expendable Equipment and Solid-Waste Disposal Costs

Expendable equipment costs are shown in Table 8, and the cost of transport and burial of these items is given in Table 9. Burial of the solid wastes is assumed to

Table 5. Capital-Cost Estimate Breakdown^a

	Installed Cost (dollars)		
	Head-End ^b	Fluorination ^c Process	Aqueous Process
Process equipment ^d	\$ 183,700	\$ 207,100	\$ 235,000
Piping	77,200	77,500	157,300
Instrumentation ^e	36,800	136,200	94,100
Process electrical services	7,000	50,000	13,000
Personnel and building radiation monitoring	50,000	-	-
Building and cell modifications	30,400	30,300	7,000
	<u>\$ 385,100</u>	<u>\$ 501,100</u>	<u>\$ 506,400</u>

^a Does not include construction indirect costs, design, inspection, or contingency.

^b Fuel-cask unloading, fuel storage, feeding, burning, waste-alumina disposal system, waste carrier, additional remote crane, and TV viewing system.

^c Includes fluorine supply system and liquid fluorine trailer.

^d Includes sample, filter and pump blisters, hoods, off-gas filtration equipment, etc.

^e Includes heated and ventilated housings for fluorination system instrument transmitters.

Table 6. Project Capital-Cost Estimate

	Head-End Plus Fluorination Process	Head-End Plus Aqueous Process
Head-end	\$ 385,100	\$ 385,100
Fluorination process	501,100	-
Aqueous process	-	506,400
Subtotal	\$ 886,200	\$ 891,500
Construction indirect costs, 32%	283,600	285,300
Subtotal	\$ 1,169,800	\$ 1,176,800
Engineering design and inspection, 20%	234,000	235,400
Subtotal	\$ 1,403,800	\$ 1,412,200
Contingency, 15%	210,600	211,800
Total project cost	\$ 1,614,400	\$ 1,624,000
Daily amortization charge	\$ 4,610	\$ 4,640

(Based on 10,500 kg ^{235}U = 350 operating days for program)

Table 7. Gases and Chemicals Costs

	Fluorination Process (\$/day)	Aqueous Process ^a (\$/day)
O ₂ at \$0.09/lb ^b	\$ 79.40	\$ 79.40
Alumina at \$0.70/lb	230.40	38.50
Fluorine at \$4.40/lb ^c	451.20	-
NaF pellets at \$1.24/lb ^d	12.50	-
SO ₂ at \$0.14/lb	7.60	-
HNO ₃ at \$0.04/lb	-	39.20
HF at \$0.26/lb	-	24.50
Cd(NO ₃) · 4H ₂ O at \$0.67/lb	-	22.20
Al(NO ₃) ₃ · 9H ₂ O at \$0.256/lb	-	138.00
KOH and miscellaneous chemicals	-	10.00
	<u>\$ 781.00</u>	<u>\$ 352.00</u>

^a Includes first solvent extraction cycle chemicals, except for solvent and kerosene wash.

^b From Linde liquid oxygen converter on the site.

^c Four dollars per pound of liquid fluorine, FOB Metropolis, Illinois, plus \$0.40 per round-trip-mile delivery charge for tank trailer; one trailer load every 30 days.

^d Purchased as NaF-HF pellets and converted to NaF by heating.

Table 8. Expendable-Equipment Daily Cost

	Fluorination Process (\$/day)	Aqueous Process (\$/day)
Fuel shipping cans ^a at \$4.50 each	\$ 50.40	\$ 50.40
F702-F752 traps at \$2800 each ^b	400.00	-
406 Waste alumina drum at \$68 each	37.80	5.70
F409 waste salt drums at \$50 each	7.10	-
Total	\$ 495.00	\$ 56.00

^a Assumes discard of all cans after using once.

^b Assumes discard of a trap every 7 days; however, the useful life of the trap may be much longer.

Table 9. Solid Waste Disposal Daily Costs^a

	Fluorination Process (\$/day)	Aqueous Process (\$/day)
Fuel shipping cans burial ^b	\$ 39.50	\$ 39.50
NaF trap burial	2.50	-
Waste alumina burial	69.40	10.40
Waste salt burial	7.50	-
Total	\$ 119.00	\$ 60.00

^a Costs based on \$125 per round trip of the 13.5-ft³ waste carrier, which weighs about 5-1/2 tons. The cost includes transportation, burial of carrier contents, health physics monitoring, and carrier cleanup. (Cost of carrier is included in process equipment.)

^b Cans flattened to half the original volume and packed in carrier.

represent permanent storage. One shielded solid-waste carrier is required by either process, and the carrier is sized to hold the waste alumina drums. The fuel-shipping cans are flattened and folded to fit into the waste carrier. Reuse of some of the fuel cans, and less frequent discard of the NaF traps, would reduce daily costs considerably. Alumina-disposal costs for the aqueous process would increase if a higher discard rate is necessary to control the particle size or to minimize fluoride recycle to the burner.

9.2.3 Liquid-Waste Storage Costs

Liquid-waste storage costs have been estimated (Table 10) for the assumed process, but on the basis of only one cycle of solvent extraction. The cost of storage for the 1AW has been estimated for three storage schemes, as described below, since this waste is corrosive and requires special handling. The 1AF contains 14 g of ^{235}U per liter, and soluble poisons are required for criticality prevention. If concentration control, rather than homogeneous poisons, is used for criticality prevention in the 1AF, then the volume and disposal cost for 1AW may be increased.

The other wastes, such as those from 1B column, off-gas scrubber, solvent recovery system, waste-evaporator condensates, etc., are assumed to be evaporated and stored in existing tanks at an assumed storage cost of \$0.50/gal or a total of \$32 a day. No aqueous wastes are generated routinely by the fluoride-volatility process.

The three storage schemes considered for the aqueous process waste are as follows:

1. Storage in existing tanks.

Cost: \$0.50/gal of 1AW.

This assumes that operation of the waste calciner has emptied sufficient stainless-steel tankage so storage space is made available for the Rover waste. The waste is mixed with low-level aluminum nitrate waste to complex the fluoride in order to reduce corrosion and is stored. Mixing equipment must be installed. When the Rover waste is mixed with aluminum nitrate wastes, the niobium will precipitate. Therefore, a charge of \$0.50 per gallon of Rover waste is made to cover the extra capital and operating costs for transferring the low-level aluminum nitrate waste, for mixing it with the Rover waste, and for returning the slurry to the storage tank. This waste disposal scheme is considered to be an interim solution to the storage problem, since the long-term corrosion problems for this method are unknown. If the Rover program generates the projected load of 10,500 kg of ^{235}U , then about 300,000 gal of blended wastes will be stored, assuming a volumetric ratio of 2:1 (Rover waste: low-level aluminum nitrate waste).

Table 10. Liquid Waste Storage Costs

	Storage Cost (\$/day)
1. Interim Storage in Existing Tanks	
IAW storage, with \$0.50/gal charge for blending	\$ 289.00
Low-level wastes in existing tanks	<u>32.00</u>
Total	\$ 321.00
2. Interim Storage in a New Stainless Steel Tank	
IAW storage at \$4.00/gal	\$ 2,268.00
Low-level wastes in existing tanks	<u>32.00</u>
Total	\$ 2,300.00
3. Ultimate Disposal	
IAW interim storage, with \$0.50/gal charge for blending	\$ 289.00
Operating cost of calciner	5,320.00
Storage bin for calcined solids	<u>1,084.00</u>
Subtotal	\$ 6,693.00
Low-level wastes in existing tanks	<u>32.00</u>
Total	\$ 6,725.00

2. Storage as acid waste in a new stainless steel tank.

Cost: \$4.00 per gallon of 1AW.

This assumes that precipitates in the waste tanks are undesirable and that a large, uncooled, lightly shielded, stainless steel storage tank is built to store the waste. The tank may be made of a stainless steel alloy that is more resistant to fluoride attack than either types 304L or 347 stainless steels. The tank is assumed to have a capital cost of \$4.00 per gallon of stored Rover 1AW; approximately 200,000 gal of storage space is required. This waste-disposal scheme is considered to be an interim solution to the storage problem, since corrosion will eventually force replacement of the tank. Replacement costs are not considered.

3. Ultimate disposal by calcining and dry storage.

Cost: \$11.80 per gallon of 1AW.

This assumes that the waste would be blended and stored on a temporary basis, as in the first method, and that it would then be calcined with suitable additives to repress fluoride volatilization. The resulting calcine would be permanently stored in bins. The cost for this operation would include the blending cost of \$0.50/gal, plus the additional operating cost for the calciner, and the cost of the dry-solids storage bins. The following assumptions were made to derive the cost of calcining and bin storage:

- a. The calciner feed rate is 60 gph, and the Rover waste has previously been blended with one-half its volume of stored aluminum nitrate waste.
- b. The volume of the calcined solids is one-tenth the volume of the liquid feed.
- c. Fluoride volatilization can be satisfactorily repressed by adding calcium nitrate to the feed.
- d. Calcined-solids storage will be in 24-in.-thick bins, with 12 bins per storage vault. Cooling is provided so other, more radioactive wastes can be stored in the same bins, since small bins for just the Rover waste would be uneconomical.
- e. The standard fixed charge of \$9000 for the ICPP plant applies to the calciner when it is operated; this is necessary because the calciner cannot be operated simultaneously with the Rover head-end and solvent extraction due to the limited number of ICPP operating

personnel. This charge is assumed to also include operating chemicals, supplies, and maintenance. The capital cost of the ICPP calcining facility is assumed to have been already written off by other waste-calcining campaigns.

The cost of the original 24-in.-thick solids storage bins at the ICPP is estimated⁸² to be \$529,000, equivalent to a present-day cost of \$666,000 for the 7000 ft³ of usable solids storage space. The storage bin cost is then \$95.30 per ft³ of bin = \$1.27/gal of calciner feed = \$1.91/gal of Rover 1AW, since the cost of storing the solids from the aluminum nitrate wastes, which was blended with the Rover waste, is charged to Rover.

The Rover 1AW, plus the aluminum nitrate addition, totals 851 gal/day. The calciner can process 1440 gal/day. Therefore, the fixed operating charge for the calciner that must be assessed against Rover is equivalent to $(851 \text{ gal/day} \div 1440 \text{ gal/day}) \times \$9000/\text{day} = \$5320/\text{day}$.

Only the last waste-disposal method can be considered to be permanent and therefore equivalent to the fluoride-volatility waste-disposal method.

9.2.4 Total Daily Operating and Capital Costs

The daily operating and capital costs, as derived in the preceding sections, are shown in Table 11. The cost of the fluorination process is \$15,010/day; the cost for the aqueous process ranges from \$14,430/day to \$20,833/day, depending on whether interim or ultimate storage is selected for the aqueous waste. In my opinion, the best way to compare the two processes is to compare the volatility cost of \$15,010/day with the aqueous-process cost of \$20,833/day, since the wastes are in comparable ultimate-disposal systems. A small additional charge may be advisable to allow for sealing the volatility-process dry wastes in concrete directly in the burial trenches, but the cost for this will not alter the favorable position of the volatility process. The costs do not include the charge for fuel shipping, which will be the same for either process.

There is a question whether the operating crew at Idaho is large enough to conduct all the steps of the aqueous process, including solvent extraction, on a continuous basis, or whether sequential operation, as is usually done for the much simpler aluminum-fuels processing system, would be necessary. The answer to this question is: If sequential operation of the plant is necessary, the number of operating days would be increased and the total reprocessing cost for the aqueous process would be much higher than shown above if normal accounting procedures are used. However, this problem should not be encountered with the fluoride-volatility process since it is simpler and requires considerably less equipment. Moreover, the fluoride-volatility process is conducted in one building.

Table 11. Total Daily Operating and Capital Costs

	Fluorination Process (\$/day)	Aqueous Process (\$/day)
Gases and chemicals (Table 7)	\$ 781.00	\$ 352.00
Expendable equipment (Table 8)	495.00	56.00
Solid-waste disposal (Table 9)	119.00	60.00
Daily operating charge	9,000.00	9,000.00
New-equipment amortization (Table 6)	4,610.00	4,640.00
Liquid-waste storage (Table 10)		
Interim storage in existing tanks	-	321.00
Interim storage in new tanks (symbol *)	-	2,300.00*
Ultimate disposal (symbol **)	-	6,725.00**
Total cost	\$ 15,010.00	\$ 14,430.00
		\$ 16,410.00*
		\$ 20,833.00**
Processing cost, \$/g ^{235}U	\$ 0.50	\$ 0.481
		\$ 0.547*
		\$ 0.694**

9.3 Economics of a Burn—Nitric Acid Leach Process

An alternative to the two principal processes investigated in this report is the Burn—Nitric Acid Leach Process. This process might at first glance be considered attractive because only nitric acid would be used for leaching, thereby seeming to allow for simpler, cheaper equipment and lower waste disposal costs. However, this would result in the loss of the uranium that is in the niobium carbide liner.

A superficial examination indicates that the daily amortization charge for the equipment would be approximately \$3300. Other costs would be about the same except that interim waste storage costs might be reduced to about \$200/day. (This does not put the waste in ultimate storage.) Thus, the daily operating and capital cost for this process would be about \$12,970/day. The difference between the daily cost of the volatility process and this system is \$2040. This difference, at the current price of \$12.68 per gram of ^{235}U , is equivalent to a maximum loss of 0.5% of the ^{235}U that could be tolerated by the "cheaper" aqueous process if it is to be competitive with the more expensive volatility process. However, it is known that the current fuel contains more than 0.5% of the ^{235}U in the niobium carbide;⁴⁰ earlier cores contained much more. Therefore, the economics of the simpler Burn—Nitric Acid Leach Process are unfavorable.

10. SUMMARY OF PRINCIPAL CONCLUSIONS

The principal conclusions of this study are summarized as follows: The cost estimates indicate that the capital cost of the new equipment required for each proposed process is almost the same. However, the operating-cost analysis indicates that the fluoride-volatility process is substantially cheaper than the aqueous process if the aqueous wastes are converted to solids for ultimate disposal. The wastes from the fluoride-volatility process are suitable for ultimate disposal without further treatment.

The conceptual fuel-shipping system for chopped or crushed fuel will result in minimum handling of rods and will permit packaging the various sizes and shapes of fuel elements in standard containers for shipment to the processing plant.

A fuel-cask unloading and fuel-storage facility of ample capacity can be provided in cell 1 of the ICPP Hot Pilot Plant Building. Fuel shipping during the projected 30-day processing campaign will be necessary.

Continuous fluidized-bed oxidation of the fuel is the preferred combustion method, is easily controlled, and has a high oxygen utilization efficiency. Volatilization of fission products during oxidation will be a minor problem.

The aqueous process uses a two-step leach of the ash; the first leach is with nitric acid, and the second is with 5 M HF—10 M HNO_3 to dissolve the Nb_2O_5

to recover the uranium that has diffused into the niobium. Uranium is recovered from the prepared feed solution by conventional solvent extraction.

The fluoride-volatility process uses continuous fluidized-bed fluorination followed by continuous moving-bed fluorination of the alumina to reduce the uranium loss to a very low value, with an overall fluorine utilization of better than 75%. The separation of the UF_6 from volatile NbF_5 and fission products is done by partial condensation of the impurities and sorption of the remaining NbF_5 and fission products on hot sodium fluoride pellets. The purified UF_6 is collected by cold trapping and is shipped as a solid.

Removal of fission products will be adequate, and more than 99% of the uranium should be recovered by either the aqueous or the fluoride-volatility process.

Uranium accountability will not be as simple as it has been for fuels previously processed at ICPP. For example, it may be very difficult to obtain an accurate input analysis. Waste and product analysis may be the only way to account for the uranium; waste analysis will be complicated for either process because of the difficulties in sampling solids. This is a greater problem with the volatility process than with the aqueous process but is not a major obstacle for either one.

Satisfactory materials of construction are available for each system, although corrosion by the feed and waste solutions for the aqueous process is greater than desired for long-term operation or for waste storage.

Radioactive fluoride-volatility systems have been successfully designed, fabricated, and operated at ORNL. However, the Teflon-lined system required for the aqueous process is completely new to radioactive service, and it may be difficult to prevent leakage because of the large number of flanged joints, all-Teflon valves and pumps, and the complex piping system.

Leak-detection methods for the fluorination system are fast and extremely sensitive. In the equipment for the aqueous process, a leak in the Teflon lining may penetrate between the Teflon and the backing material until a large amount of radioactive solution has accumulated in a nearly inaccessible location, making it difficult to detect and decontaminate.

Criticality control for the fluorination system is simple because it is a dry system, and no serious restraints are placed on equipment sizes or operating procedures. Criticality control for the aqueous system is more complicated since geometrically safe equipment must be used for the leaching step. Also, a soluble nuclear poison is the prime safeguard during feed adjustment and in the feed solution. If the feed is diluted to utilize the simpler system of concentration control, this would substantially increase the volume and hence the cost of waste disposal.

The fluoride-volatility process is continuous, and all operations are conducted in one building. The process can probably be run by the existing operating crew at ICPP. On the other hand, the aqueous process requires operation of much more equipment and is a batch operation, thus requiring more labor and supervision. The solvent extraction and waste-disposal facilities are assumed to be operated concurrently in other buildings. It may be difficult for the present crew to operate this much equipment simultaneously. If sequential operations are used, then the processing cost will be increased substantially by the additional in-plant days if normal cost-accounting procedures are used.

The fluorination-process equipment is compact and can be readily fitted into one process cell and unused PM area space. Ample room is available in the cell for installation and maintenance. The aqueous process requires a large number of equipment units and can be crowded into one cell with recirculating and transfer pumps placed in an adjacent cell. Additional cell space may be required for the aqueous process to relieve congestion.

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~~CONFIDENTIAL~~

APPENDIX 1

JUSTIFICATION FOR THE BELIEF THAT A RECOVERABLE AMOUNT
OF URANIUM WILL BE IN THE NIOBIUM CARBIDE LINERS

The following is quoted from ORNL-TM-799, Sect. 3.4.1:

"It would be theoretically possible to design an aqueous process for recovery of uranium from irradiated Rover fuel containing microspheres covered with perfect skins in which only nitric acid would be used. The success of the process would depend upon all portions of the reactor being held at 2400°C or less. A fluidized-bed burner could oxidize the fuel at about 700°C, and the uranium in the ash would be completely soluble in nitric acid. The undissolved niobium oxide would be discharged with the inert bed.

"Unfortunately, there is every reason to believe that portions of every reactor operating at full power in the near future will attain temperatures in excess of 2400°C, then fuel temperatures of between 2400 and 2500°C are required in the smaller-diameter cores to compensate for large amounts of cooler hydrogen bypassing the core structure. There is also a very severe control problem of measuring and controlling temperatures in the region of 2400 to 2500°C. Finally, it has been estimated that the 'hot-spot' temperatures in the reactor may be as much as 300°C above the average in any region, due to irregularities in hydrogen flow.

"It has been concluded by members of the Chemical Technology Division at Oak Ridge National Laboratory that a chemical process for irradiated graphite Rover fuel even of the most advanced type must be capable of recovering uranium which has migrated to the niobium carbide liner. This uranium will be in solid solution with niobium oxide after low-temperature combustion. Data are still not available with which to predict accurately the total percentage of uranium in solid solution, but our best estimates are 3 to 5%. It should be noted that, for advanced Rover fuel, cold scrap processing with pure nitric acid may be quite feasible."

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APPENDIX 2

EQUIPMENT AND DRAWING LIST

A three-digit serial number is the primary identification for each equipment item. The chief function is indicated as follows:

100 series	Chemical Reactors
200 series	Transfer Devices
300 series	Heat Exchangers
400 series	Vessels
500 series	Filters, Separators
600 series	Samplers
700 series	Absorbers, Adsorbers, Scrubbers
800 series	Mechanical Equipment

The prefix "F" indicates assignment to the fluoride volatility portion of the process, and the prefix "A" indicates assignment to the aqueous process. The prefix letter is omitted when the item is required by each process. Parallel equipment lines are indicated by adding 50 to the serial number. Duplicated items within an equipment line are indicated by letter suffix.

The equipment items are cross-indexed to the appropriate equipment flowsheet and to the conceptual equipment design drawing or to the description used for cost-estimating purposes. Supplemental descriptive information is given on the equipment flowsheets in some instances.

Item No.	Item Name	Reference Flowsheet	Equipment Drawing or Description
<u>Fuel Charging and Fluidized-Bed Oxidation:</u>			
101	Fluidized-Bed Burner	E-57712	E-57713, E-57714, E-57715
201A and 201B	Cooling Air Blowers	E-57712	Buffalo Forge Blower
202	Vacuum Pump	E-57712	Laboratory vacuum pump
203	Pneumatic Transport Feeder	E-57712	A-SK-312
301	Solids Cooler	E-57712	A-SK-310
401	Chopped Fuel Hopper	E-57712	10827-N-114-E
402	Al ₂ O ₃ Makeup Bin	E-57712	2-ft-6-in.-diam by 6-ft-tall, stainless steel, cone bottom

Item No.	Item Name	Reference Flowsheet	Equipment Drawing or Description
403	Ash Bin	E-57712	B-SK-313
601	Combustion Gas Sample Filter Blister	E-57712	1-in. lead shielded, two-compartment blister, ~2 ft long, ~12 in. high, ~8 in. deep
602	Solids Sampling Blister	E-57712	2-in. lead shielded blister with ball-socket manipulator, blister is ~2 ft long by ~2 ft high by ~2 ft deep
801	Fuel Can Transport Cart	E-57712	10827-N-114-E
802	Fuel Can Decapper	E-57712	10827-N-114-E
803	Fuel Can Dumper	E-57712	10827-N-114-E
804	Screw Conveyor	E-57712	10827-N-114-E
805	Screw Conveyor	E-57712	2 in. diam by 1 ft long variable speed, sealed, stainless steel screw conveyor
-	Oxygen Supply System	None	Linde "ATX" system: liquid oxygen converter, capacity ~160,000 ft ³ at NPT; delivery rate ~450 ft ³ at (NPT)/hr

Burn-Leach Process:

A102	Leacher	E-57710	6-in. stainless steel pipe, 10 ft tall, Teflon-lined. See C-SK-318 for heating jacket details
A152	Leacher	*	6-in. stainless steel pipe, 10 ft tall, Teflon-lined. See C-SK-318 for heating jacket details
A103	Alumina Dryer	E-57945	C-SK-318
A204 A & B	Leacher Recirculation Pump	E-57710	Teflon-lined, variable speed, Vanton or diaphragm pump

Item No.	Item Name	Reference Flowsheet	Equipment Drawing or Description
A254 A & B	Leacher Recirculation Pump	*	Teflon-lined, variable speed, Vanton or diaphragm pump
A205	Pneumatic Transport Feeder	E-57945	A-SK-312
A206	Vacuum Jet	E-57945	Stainless steel vacuum jet
A207	HNO ₃ Transfer Pump	E-57710	Stainless steel Chem-pump
A208	HNO ₃ -HF Transfer Pump	E-57710	Teflon-lined Vanton pump
A209	HNO ₃ -HF Metering Pump	E-57710	Teflon-lined, variable-speed Vanton pump
A210	HNO ₃ Metering Pump	E-57710	Teflon-lined, variable-speed Vanton pump
A211	Nuclear Poison Transfer Pump	E-57710	Stainless steel Chem-pump
A212	Wash Water Pump	E-57710	Variable-speed, Teflon-lined Vanton pump
A213	Vacuum Jet	E-57711	Teflon vacuum jet
A263	Vacuum Jet	*	Teflon vacuum jet
A214	Adjustment Solution Transfer Pump	E-57711	Stainless steel Chem-pump
A215	Adjustment Solution Metering Pump	E-57711	Stainless steel Chem-pump
A216A	Feed Transfer Pump	E-57711	Stainless steel Chem-pump
A216B	Feed Transfer Pump	E-57711	Stainless steel Chem-pump
A217	Scrubber Solution Transfer Pump	E-57711	Stainless steel Chem-pump
A218, A219, A220	Steam Jet	E-57711	Stainless steel steam jets
A221, A222, A223	Steam Jet	E-57945	Stainless steel steam jets
A224	Steam Jet	E-57710	Teflon steam jets
A274	Steam Jet	*	Teflon steam jets
A302	HNO ₃ -HF Heater	E-57710	Platinum-iridium alloy heat exchanger, ~5 ft ²
A303	HNO ₃ Heater	E-57710	Stainless steel Ross heat exchanger, ~5 ft ²

Item No.	Item Name	Reference Flowsheet	Equipment Drawing or Description
A304	Reflux Condenser	E-57710	Karbate heat exchanger, $\sim 5 \text{ ft}^2$
A354	Reflux Condenser	*	Karbate heat exchanger, $\sim 5 \text{ ft}^2$
A305	Recirculation Heater	E-57710	Platinum-iridium alloy heat exchanger, $\sim 5 \text{ ft}^2$
A355	Recirculation Heater	*	Platinum-iridium alloy heat exchanger, $\sim 5 \text{ ft}^2$
A306	Condenser	E-57945	Stainless steel Ross heat exchanger, $\sim 5 \text{ ft}^2$
A307	Dryer Air Heater	E-57945	A-SK-317
A308	Off-Gas Heater	E-57711	Stainless steel Ross heat exchanger, $\sim 20 \text{ ft}^2$
A404	Leacher Feed Hopper	E-57710	Teflon-lined, 6-in. stainless steel pipe, 4 ft 6 in. high with cone bottom
A405 A & B	Recirculation Reservoirs	E-57710	Teflon-lined, 6-in. stainless steel pipe, 10 ft tall
A455 A & B	Recirculation Reservoirs	*	Teflon-lined, 6-in. stainless steel pipe, 10 ft tall
406	Alumina Waste Drum	E-57931	D-57941
A407 A, B, C, D, E	Filtrate Receivers	E-57711	Teflon-lined, 6-in. stainless steel pipe, 12 ft tall
A457 A, B, C, D, E	Filtrate Receivers	*	Teflon-lined, 6-in. stainless steel pipe, 12 ft tall
A408	Transfer Water Tank	E-57945	Stainless steel 6-in. pipe, 10 ft tall
A409	Al ₂ O ₃ Recirculation Bin	E-57945	A-SK-314
A410	Al ₂ O ₃ Fines Bin	E-57945	B-SK-315
A411	HNO ₃ Makeup Tank	E-57710	Stainless steel 175-gal tank
A412	HNO ₃ -HF Makeup Tank	E-57710	Teflon-lined, 400-gal carbon steel tank

Item No.	Item Name	Reference Flowsheet	Equipment Drawing or Description
A413	HNO ₃ -HF Weigh Tank	E-57710	Teflon-lined, 50-gal carbon steel tank
A414	HNO ₃ Weigh Tank	E-57710	Stainless steel, 25-gal tank
A415	Nuclear Poison Makeup Tank	E-57710	Stainless steel, 25-gal tank
A416	Wash Water Weigh Tank	E-57710	Stainless steel, 50-gal tank
A417	Poison Metering Burette	E-57710	Glass pipe, 4-in.-diam by 3-ft-tall
A418	Feed Adjustment Tank	E-57711	Teflon-lined, 200-gal stainless steel tank
A468	Feed Adjustment Tank	*	Teflon-lined, 200-gal stainless steel tank
A419	Adjustment Solution Makeup Tank	E-57711	1000-gal stainless steel tank
A420	Adjustment Solution Weigh Tank	E-57711	100-gal stainless steel tank
A421	Scrubber Solution Makeup Tank	E-57711	100-gal stainless steel tank
A501	Cyclone	E-57945	C-SK-308
A502	Filter	E-57710	Stainless steel micro-metallic 600-12 filter
A503A, A503B	Absolute Filters	E-57711	100 cfm absolute filters
A603	Solids Sampling Blister	E-57945	1-in. lead shielded blister with ball socket manipulator; blister is ~2 ft long by ~2 ft high by ~2 ft deep
A604	Recirculation Pump Blister	E-57710	2-in. lead shielded, two-compartment blister; blister is ~2 ft high by ~6 ft long by ~2-1/2 ft wide overall

Item No.	Item Name	Reference Flowsheet	Equipment Drawing or Description
A654	Recirculation Pump Blister	*	2-in. lead shielded, two-compartment blister; blister is ~2 ft high by ~6 ft long by ~2-1/2 ft wide overall
A605	Transfer Water Sample Blister	E-57945	Existing sample blister, install block valves on sampler lines
A606	Filtrate Sampler Blisters	E-57711	Existing sampling blister, convert to Teflon jet and piping, install block valves on sampler lines
A656	Filtrate Sampler Blisters	*	Existing sampling blister, convert to Teflon jet and piping, install block valves on sampler lines
A607	Feed Adjustment Tank Sample Blister	E-57711	Existing sample blister, convert to Teflon jet and piping
A657	Feed Adjustment Tank Sample Blister	*	Existing sample blister, convert to Teflon jet and piping
A608	Off-Gas Scrubber Sample Blister	E-57711	Existing sample blister
A609	Feed Transfer Pump Blister	E-57711	2-in. lead shielded, two-compartment blister; blister is ~2 ft high by 6 ft long by ~2 ft wide
A701	Off-Gas Scrubber	E-57711	50-gal stainless steel tank with 6-in.-diam by 8-ft-tall packed column, boron stainless steel poison plates in 50-gal tank

Item No.	Item Name	Reference Flowsheet	Equipment Drawing or Description
806	Waste Alumina Loadout Station	E-57931	D-57941
<u>Fluorination Process:</u>			
F102	Fluid Bed Fluorinator	E-57931	E-57716
F103	Moving Bed Fluorinator	E-57931	E-57716
F104	Fluorine Disposal Reactor	E-57933	E-57938
F204	Fluorinator Feed Valve	E-57931	A-SK-311
F205	Pneumatic Transport Feeder	E-57931	A-SK-312
F206 through F210; F260	Refrigerant Recirculation Pump	E-57932, E-57933	Stainless steel Chem-pump
F211	Vacuum Pump	E-57932, E-57933	Laboratory size vacuum pump
F302 through F305	Gas Heaters	E-57931	A-SK-317
F306	Alumina Cooler	E-57931	A-SK-310
F307	Condenser	E-57932	E-57936
F308, F358	Warm Trap	E-57932	E-57934
F309 through F312	Heat Exchanger	E-57932	Ross 300-8, 2.4 ft ² stainless steel heat exchanger
F313, F363	Furnace	E-57932	D-57943 Special Hevi-Duty, vertical, clam-shell furnace for 8-5/8-in.-OD by 3-ft-tall trap, ~5 kw, 3-zone, top and bottom of furnace also heated
F314, F364	Cold Traps	E-57933	E-57935
F315A, F315B	Gas Heaters	E-57933	A-SK-317
F316, F366	Heat Exchangers	E-57933	Ross 300-8, 2.4 ft ² stainless steel heat exchanger
F404	Fluorinator Feed Bin	E-57931	A-SK-309
F405	Alumina Waste Bin	E-57931	B-SK-319
406	Alumina Waste Drum	E-57931	D-57941
F407	Waste Surge Tank	E-57932	E-57936
F408	Waste Sampling Tank	E-57932	D-57937
F409	Waste Salt Can	E-57932	D-57940
F410 through F413	Expansion Tanks	E-57932	3-in. carbon steel pipe by 2 ft tall with gage glass

Item No.	Item Name	Reference Flowsheet	Equipment Drawing or Description
F414, F464	Expansion Tanks	E-57933	6-in. carbon steel pipe by 2 ft tall with gage glass
F501, F551	Filters	E-57933	Micrometallic Monel filter 800-6 with 5 μ S-1-6 star filter
F502, F552	Absolute Filters	E-57933	Standard 8-in. by 8-in. Fiberglas, fireproof absolute filter
F603	Waste Alumina Sampling Blister	E-57931	See A603 except 2-in. lead shielding
F604	Waste Salt Sampling Blister	E-57932	See A603 except 2-in. lead shielding
F605	Filter Blister	E-57933	1/2-in. lead shielded, two-compartment blister, ~18 in. high by ~3 ft long by ~1 ft deep overall
F701	Chemical Trap	E-57932	3-in. Monel pipe by 2-ft-tall, packed with soda-lime
F702, F752	NaF Trap	E-57932	D-57939
F703	NaF Backup Trap	E-57933	E-57938
F704	Safety Trap	E-57933	6-in. Monel pipe by 6-ft-tall packed with activated alumina
F705, F707	UF ₆ Trap	E-57933	3-in. Monel pipe by 2-ft-tall packed with sodium fluoride
F706, F708	Chemical Traps	E-57933	3-in. Monel pipe by 2-ft-tall packed with soda-lime
806	Waste Alumina Loadout Station	E-57931	D-57941
F807	Waste Salt Loadout Station	E-57932	D-57940
F808, F858	Cold Trap Refrigeration Unit	E-57933	Tenney Engr. Co. "Kolpack" two-stage Freon 22 - Freon 13, -100°F refrigeration unit
-	Fluorine Supply System - Trailer-mounted liquid fluorine tank to hold 3200 lb of liquid fluorine; ~40 ft ³ , ~1/2-in.-thick reinforced Monel inner tank, ~3-ft-6-in.-OD by ~4-ft-8-in. overall.		

Item No.	Item Name	Reference Flowsheet	Equipment Drawing or Description
(Continued)	40 psig operating pressure, encased in ~4-ft-diam by ~5-ft-2-in. overall type 304L stainless steel tank, outer surface polished, liquid nitrogen in annulus. Whole assembly encased in reinforced ~5-ft-OD by ~6-ft-2-in.-long horizontal carbon steel tank, space between carbon steel and stainless steel tanks filled with expanded perlite and evacuated. Liquid to gas converter integral with unit; similar in principal to Linde "ATX" system but designed for fluorine tank pressurization by helium. Trailer equipped with relief valves, chemical traps, double valving on fluorine lines and fail-closed remotely-operated shutoff valves. Tank attachment to trailer designed so tank weight can be determined with load cells.		

Supplementary Drawings:

<u>Drawing No.</u>	<u>Title</u>
E-57683	Fluidized-Bed Oxidation and Mixed Acid Leach: Head-End Material-Balance Flowsheet (classified)
✓ E-57705	Fluidized-Bed Oxidation and Continuous Fluorination Material-Balance Flowsheet (classified)
D-57944	Location of Waste Alumina and Waste Salt Stations and NaF Traps in Cell 2
D-57949	Proposed Rover Fuel Shipping Cask Assembly
E-57942	Cells 3 and 4 Equipment Layout - Aqueous Processing
✓ E-57950	Fluoride Volatility - PM Area and Cell 3 Equipment Layout
10827-N-113-C	Storage and Handling Cells - Isometric and Plan

APPENDIX 3

DECONTAMINATION OF STAINLESS STEEL

The following information is quoted from a letter July 10, 1964, from A. B. Meservey to E. L. Nicholson regarding decontamination of the fluidized-bed burner:

"You have requested my recommendations for descaling and decontaminating type 310 stainless steel which has been in contact with a fluid bed of alumina and irradiated uranium carbide at 700°C in an atmosphere of oxygen. Because of the discontinuance of the decontamination research program, it will not be possible for us to do necessary experimental work in order to choose the best decontamination method. If someone does make this study, however, I would expect that a suitable method can be based on one or more of the following possibilities.

- "1. Treat for 1 to 3 hr in 0.4 M oxalic acid—0.1 M NaF—0.015 M H₂O₂ at 90 to 95°C. The H₂O₂ concentration will have to be maintained by periodic addition of 30% H₂O₂. If the scale dissolves, decontamination should be complete. The corrosion rate is about 0.02 mil/hr (W. D. Manly, Gas-Cooled Reactor Program Semiannual Progress Report for Period Ending March 31, 1963, ORNL-3445, p. 196, July 9, 1963).
- "2. The latest modification of the alkaline permanganate-ammonium citrate method may be used. This normally involves a boil of several hours with NaOH-KMnO₄, followed by water rinsing and then boiling with ammonium citrate. There have been some successes and some failures with this method, depending on the type of scale encountered. Consult Dr. J. A. Ayres, General Electric at Hanford, for details.
- "3. Boil for several hours with full strength inhibited phosphoric acid such as Deoxidine 170 (Amchem) or Turco 4512. After the scale is dissolved, residual ruthenium and niobium can be removed with hot oxalic acid containing 0.1 to 0.5 M H₂O₂. The life of the latter mixture is limited (probably several hours at 60°C).
- "4. Dissolve the scale by treating for 1 to 3 hr with 0.4 M chromous sulfate—0.5 M H₂SO₄ at 80 to 85°C. The chromium is reduced by circulating it through zinc (R. D. Baybarz, U.S. Patent 2,981,643, assigned to USAEC). Rinse with water, and then remove the deposited ruthenium and niobium with oxalic acid—H₂O₂, as in method 3."

INTERNAL DISTRIBUTION

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