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FLUORIDE VOLATILITY PROCESSING OF REACTOR FUELS

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FLUORIDE VOLATILITY PROCESSING OF REACTOR FUELS

Fluoride volatility processing of spent power reactor fuels has been under development at other sites for a number of years. It has been proposed that the process could be utilized as a close-coupled processing plant, or as a general purpose separations plant. The advantages of the process are purported to be:

> "(1) Fewer, and sometimes simpler, processing steps;
>
> (2) The use of reagents with low susceptibilities to deleterious radiation effects;
>
> (3) Reduced criticality problems, owing to the absence of neutron moderating chemicals in the process;
>
> (4) Radioactive waste products in solid form and small volume.
>
> "On the other hand, the volatility processes have the disadvantage that they generally require operation at elevated temperatures, where corrosion problems must be carefully considered. The problem of safe containment of volatile plutonium hexafluoride also requires careful consideration, although recent experimental evidence indicates that the problem may be no more serious than that for dusty forms of plutonium."[1]

Hanford separations have been primarily solvent extraction oriented and no fluoride volatility has been done. In the interest of maintaining a leadership position in the nuclear chemical processing field, it is expedient that volatility processing know-how be obtained at Richland. This report presents the published basic volatility process flowsheets and is intended primarily as an elementary introduction to the process.

The fluorides and chlorides of some elements have relatively low boiling points. Uranium hexafluoride is a solid that sublimes at atmospheric pressure at 55.2°C. Since its triple point is 64°C. and 22 lb/in^2 abs., it can easily be handled as a gas, liquid or solid. Uranium hexafluoride is stable in an inert atmosphere and in many dry gases that are not strong reducing agents. Plutonium hexafluoride is a volatile substance with physical properties similar to those of uranium hexafluoride. However, PuF_6 is much less stable and is also subject to decomposition by its own alpha radiation. Most fission product fluorides are non-volatile and the decontamination from those fission products that are volatile is easily done by selective sorbtion or by distillation.

The principal volatile fluorides of interest in fluoride volatility processing are as follows:

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[1] "Reprocessing of Nuclear Reactor Fuels by Processes Based on Volatilization, Fractional Distillation and Selective Adsorption", AA Jonke, ATOMIC ENERGY REVIEW, Vol. 3, No. 1, International Atomic Energy Agency, Vienna, 1965.

Component	Boiling Point, °C.
TeF_6	- 39
IF_7	4.5
MoF_6	35
UF_6	55.2
NpF_6	56.4
TcF_6	55.3
PuF_6	62.2
IF_5	98
SbF_5	150
NbF_5	234
RuF_5	227

The volatile fluorides can be sorbed and desorbed on beds of solid fluoride in a manner analogous to collection of ions on ion exchange resins. Sodium fluoride is the sorbent commonly used for the decontamination of UF_6. Other solid fluorides, such as MgF_2, have been used for sorbing specific materials such as NpF_6 and TcF_6 from the UF_6 vapor. LiF shows promise for collection of PuF_6.

A typical purification of UF_6 is accomplished by passing the UF_6-fluorination gas mixture over a NaF bed at 100°C. Essentially all of the UF_6 is collected on the NaF since the vapor pressure of UF_6 over the NaF complex at 100°C. is about 2×10^{-3} mm. Desorption consists of heating the UF_6-NaF complex bed to 400°C., while passing the fluorination gas through the bed. The gas stream containing the desorbed UF_6, is passed through a second NaF bed at 400°C. and finally cold-trapped at about -60°C.

In laboratory tests with highly irradiated fuel, the behavior of fission products in the NaF beds were established as follows:

- Not sorbed on NaF at 100°C:	IF_7, TeF_6
- Completely sorbed at 100°C:	UF_6, NpF_6, PuF_6, NbF_5
- Partially sorbed at 100°C., but desorbed more easily than UF_6:	MoF_6; possibly TcF_6
- Completely desorbed at 400°C:	UF_6, NpF_6, remaining TcF_6, MoF_6
- Irreversibly filtered and/or sorbed at 400°C:	ZrF_4, NbF_5, CeF_4, CrF_5, PuF_6; possibly RuF_5 and fluorides of Cs, Sr and rare earths.

A weight ratio of NaF to total uranium being processed of 2/1 to 3/1 is needed in each of the two NaF beds.

Neptunium and technetium are sorbed on MgF_2, and MgF_2 can be used to decontaminate these materials from the UF_6 vapor and to collect them for recovery. Recent laboratory work is showing potential for LiF for collecting PuF_6 by sorbtion-desorption.

Separation of plutonium and uranium is being accomplished by fluorinating with BrF_3 or BF_5. These compounds convert the uranium to the volatile UF_6 and the plutonium to the non-volatile PuF_4. Completing the fluorination with F_2 converts the PuF_4 to volatile PuF_6 for subsequent purification.

Typical over-all decontamination factors for high burn-up fuel (cooled for six months and processed by the sorption-desorption technique) are as follows:

Fission Product	Decontamination Factor
Sr^{90}	$>10^9$
Cs^{137}	$>5 \times 10^9$
Ru^{106}	$>5 \times 10^8$
Sb^{125}	$>10^8$
Te^{127m}, Te^{125m}, Te^{132m}	$>10^9$
Zr^{95}, Nb^{95}	$>10^{10}$

Decontamination of UF_6 by fractional distillation has also been studied. Although currently proposed flowsheets are somewhat different than those in effect at the time pilot plant studies were being made, a batch distillation run that might be typical of today's flowsheet performance, resulted in the following decontamination factors:

Element	Decontamination Factor
Tellurium	1.4×10^6
Iodine	2.3×10^5
Total fission products	1.3×10^8
Plutonium	$>10^4$

The distillation temperatures ranged from 75-90°C. and the pressure was 45 lbs/in^2 abs.

The compounds TcF_6 and NpF_6 cannot be separated by distillation, since they have volatilities very close to those of UF_6 and PuF_6. These materials can be removed by sorption methods, using solid MgF_2.

The purification of UF_6 by sorption-desorption on NaF is most useful in processing high enrichment fuels where the bulk of the fuel element is aluminum or zirconium and the total amount of uranium processed is relatively small. Thus, the NaF sorption beds are of reasonable size. Currently, for low-enrichment fuels where the quantity of uranium processed is large, the distillation purification method is proposed. The development of practical high capacity continuous sorption-desorption equipment, however, might alter this preference.

The head-end process is important in preparing the fuel for fluorination. Current processes are based on conducting the gas-solid reactions in a bed of fluidized Al_2O_3. The sintered alumina is inert to reactions with HCl, F_2, BrF_3, BF_5 or HF-O_2 mixtures, and provides excellent heat transfer as well as good surface contact with the fuel elements. The fluorination fluid beds are designed such that the entire fuel element can be inserted without preliminary chopping. Where the cladding or alloying ingredient is aluminum or zirconium, the initial treatment is with hydrogen chloride. This volatilizes the Al or Zr as the chloride and converts the uranium to UCl_3. Volatile fission products are also evolved during this step. It has been observed that cerium, cesium, strontium and ruthenium were essentially non-volatile under experimental conditions. Slight volatility (<10%) was exhibited by antimony, tellurium and technetium. The predominantly volatile species (>50%) were zirconium, niobium, krypton and iodine. Of the cladding or alloying materials, $AlCl_3$ and $ZrCl_4$ sublime at 180°C. and 331°C., respectively. The volatilized chlorides are converted to oxides by pyrohydrolysis with steam in a fluidized bed at elevated temperatures. In the case of stainless steel clad fuel elements, the element is destroyed with a mixture of HF and O_2. After the initial pretreatment, the uranium and plutonium (in the case of low assay fuels) are volatilized from the Al_2O_3 bed with the interhalogens, or with fluorine.

Typical flowsheets for high assay fuels by sorption-desorption, and low assay fuels by distillation, are appended.

Frequently the thought of handling fluorine, interhalogen compounds and volatile fluorides at temperatures ranging from -60°C. to 400-500°C., initiates severe mental reservations. However, these materials, with the exception of PuF_6, are not new to industry. Fluorine and UF_6 have been produced in multi-ton quantities at gaseous diffusion plants for many years. More recently, the Allied Chemical Corporation operated a 5,000 ton per year plant to purify uranium from non-radioactive contaminants, by fractional distillation of UF_6. This was accomplished in two continuously operated columns. The first (low boiler) column is 18 inches in diameter and 96 feet high, with 100 bubble-cap trays. The second (high boiler) column has the same diameter and plate spacing, but has only 45 trays. Excellent purification was obtained.

The new problems in fluoride volatility processing are the radioactive environment and the PuF_6. Both problems are worthy of recognition and of respect, but are not insurmountable. Combination volatility-aqueous processes, to avoid the problems with volatility purification of PuF_6, may be attractive. Work with this process will be the best means of acquiring the know-how required to objectively appraise its potential in relation to solvent extraction processing.

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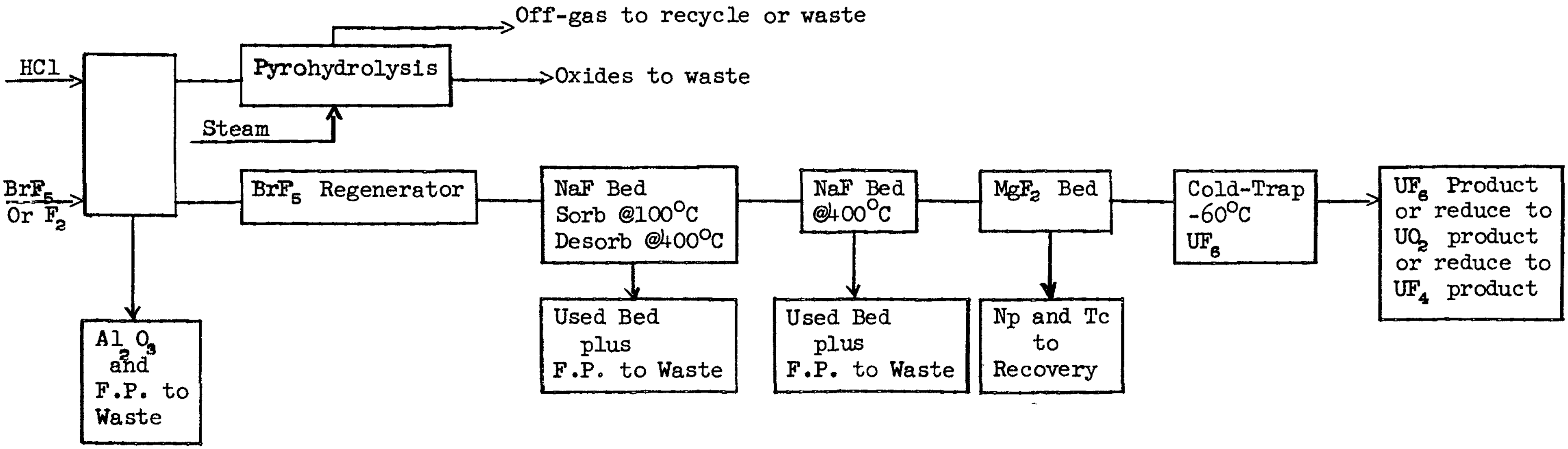
December 14, 1966

REFERENCES

(1) "Reprocessing of Nuclear Reactor Fuels by Processes Based on Volatilization, Fractional Distillation and Selective Adsorption", AA Jonke - ATOMIC ENERGY REVIEW, Vol. 3, No. 1, International Atomic Energy Agency, Vienna, 1965.

(2) Reports and personal communications at:

Argonne National Laboratory
Oak Ridge National Laboratory
Oak Ridge Gaseous Diffusion Plant

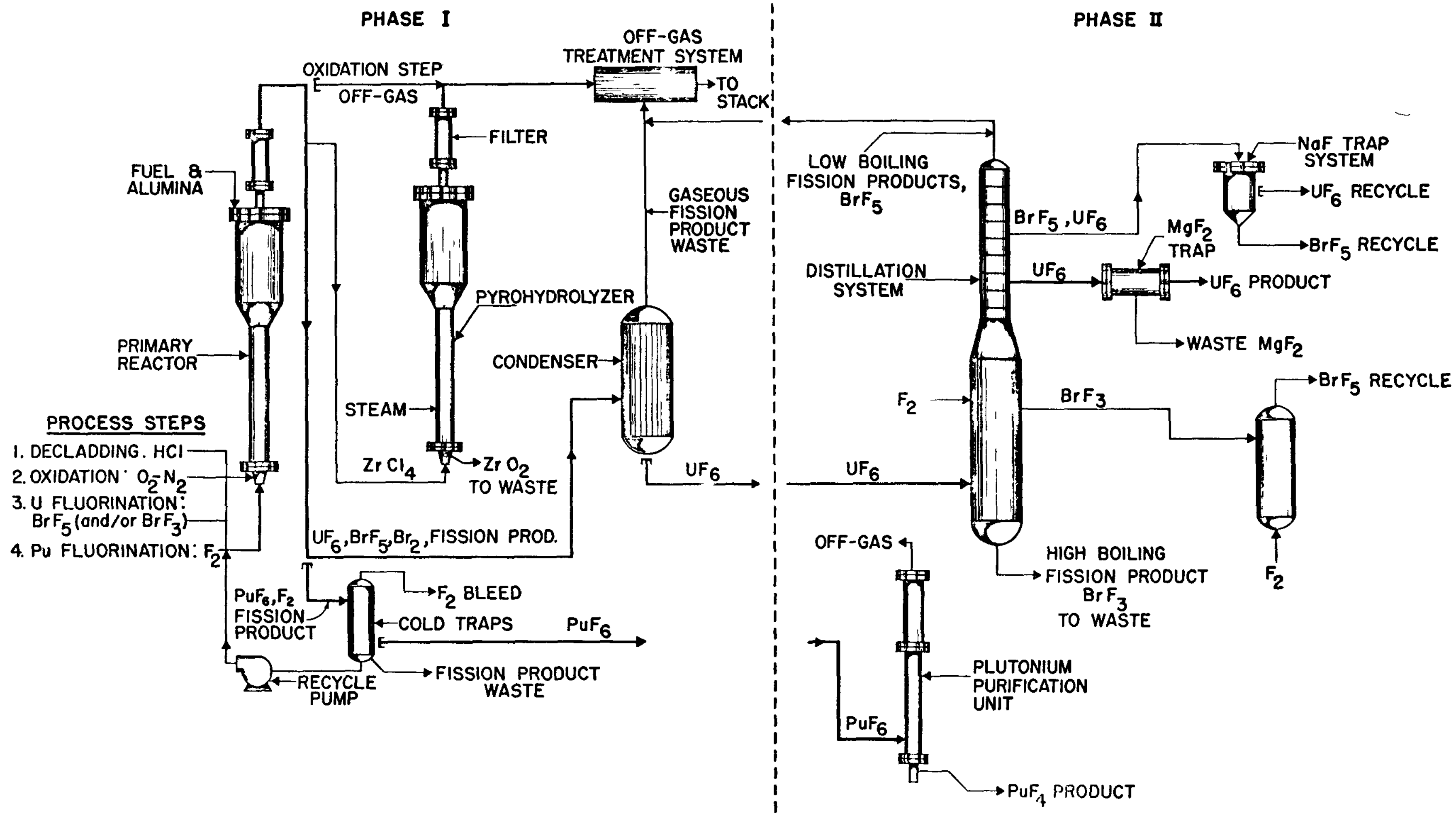


FLUORIDE VOLATILITY FLOWSHEET FOR HIGH ENRICHMENT URANIUM-ZIRCONIUM OR ALUMINUM ALLOY FUELS

FIGURE I

FLUID BED VOLATILITY PROCESS INTERHALOGEN REFERENCE FLOWSHEET

AUGUST 19,1966



NOMINAL PROCESS CONDITIONS

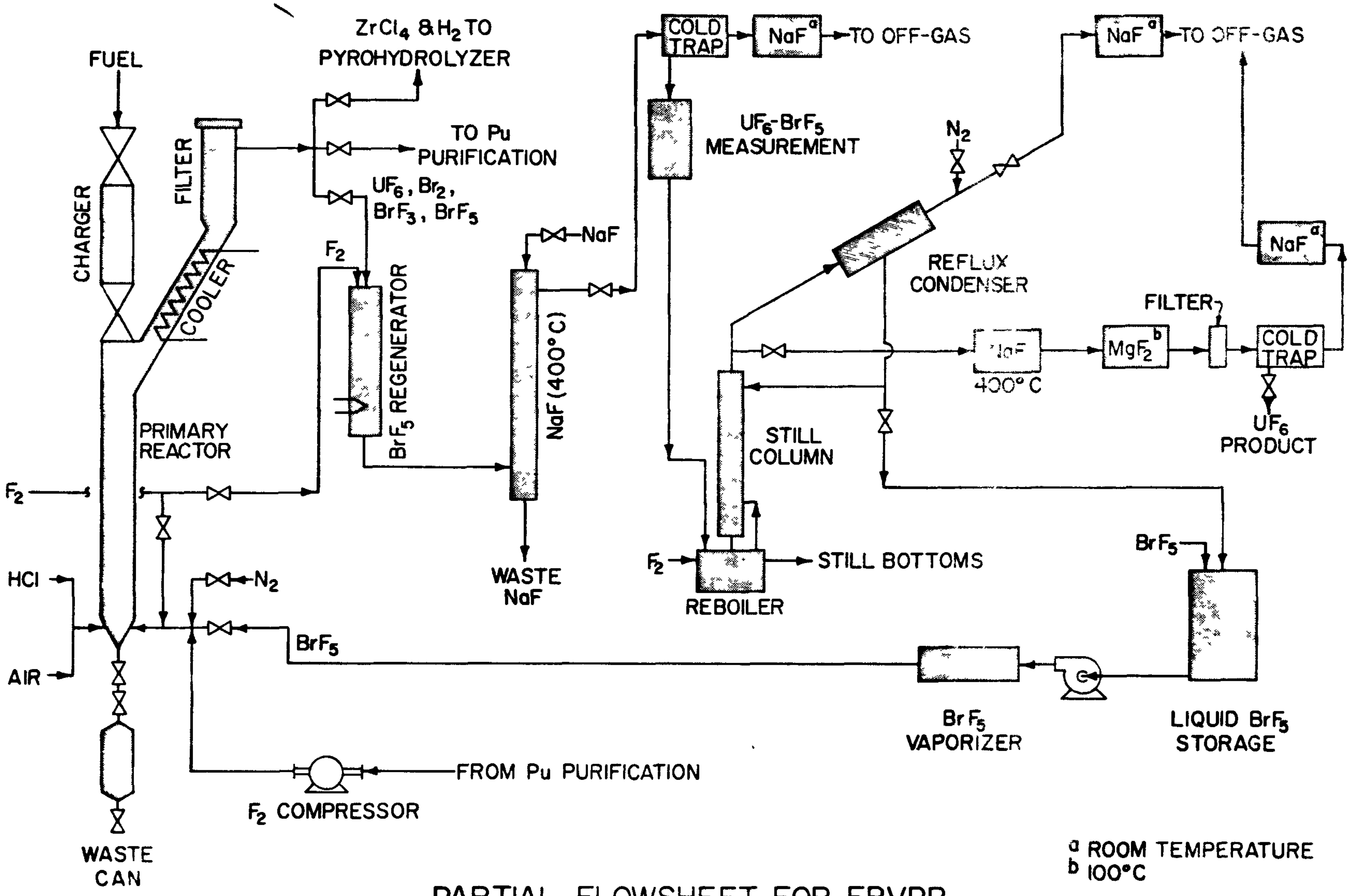
PROCESS STEP	REAGENT	REAGENT CONCENTRATION (V/O)	TEMPERATURE (°C)
DECLADDING	HCl	60-90	400
PYROHYDROLYSIS	STEAM	3X STOICH	350
OXIDATION	O_2	15-25	450
URANIUM RECOVERY	BrF_5	5-15	300
PLUTONIUM RECOVERY	F_2	10 → 90	300 → 550
URANIUM PURIFICATION (DISTILLATION)	---	---	80-90, 40-50 PSIA

ANL FLOWSHEET

FIGURE II

CE - 6032

ORNL DWG 66-8414 R2



PARTIAL FLOWSHEET FOR FBVPP

ORNL FLOWSHEET

FIGURE III

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