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CHEMISTRY—SEPARATION PROCESSES FOR
PLUTONIUM AND URANIUM

Symposium on the Reprocessing of Irradiated Fuels

Held at Brussels, Belgium
May 20-25, 1957

BOOK 2

UNITED STATES ATOMIC ENERGY COMMISSION

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AEC Technical Information Service Extension
Oak Ridge, Tennessee

Symposium
on the Reprocessing of Irradiated Fuels

Held at Brussels, Belgium
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BOOK 2
Session IV

Technical Information Service Extension
Oak Ridge, Tennessee

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Session
IV

Non-aqueous Processing

NON-AQUEOUS PROCESSING—AN INTRODUCTION

S. Lawroski*

May 1, 1957

The preceding portion of this symposium has dealt with those recovery and purification methods which are characterized by their use of aqueous solutions for reprocessing spent nuclear fuels. As already made clear from the earlier discussions on fuel dissolution, it is not always easy to solubilize in aqueous media some of the reactor fuel compositions which have been developed or envisioned by the fuel fabrication technologists. Moreover, when these methods are employed for fuel recovery the overall reactor fuel cycle takes the rather complicated form shown schematically in Figure 1. An examination of this figure reveals that many operations must still be performed after the chemical purification step before the recovered fuel can be re-introduced to the nuclear reactor. From an economic standpoint there are two important consequences resulting from a fuel cycle with this degree of complexity. One of these is the expense of conducting each of the operations noted and the second is the large inventory of fuel which

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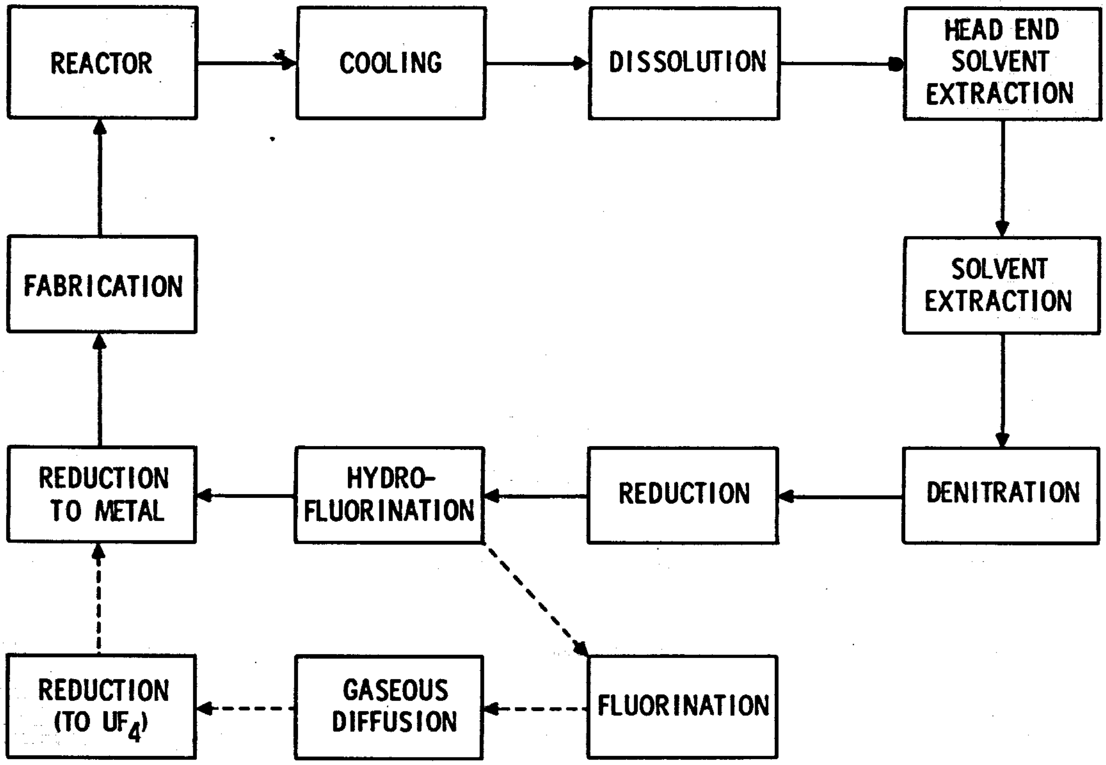

Fig. 1 - Reactor fuel cycle with solvent extraction process.

is accumulated in the various steps of the fuel cycle. Because of these disadvantages and others such as long cooling time (for decay of shorter half-life fission products) and difficult waste problems with aqueous processes, determined efforts to simplify this fuel cycle have led to serious considerations of non-aqueous processing methods.

For some time now, non-aqueous processes have been under intensive study to establish their chemical and engineering feasibilities. In the next several presentations the results obtained thus far on fluoride volatility processes and on pyrometallurgical processes will be reported. Although the application of these methods poses some very difficult problems, e.g., operating with molten metals at temperatures of 1200°C. or above, preparation and handling of PuF_6, and containment of corrosive salts at high temperatures, the experience and results to date have been sufficiently encouraging to command tremendous interest and continued development efforts.

A compelling reason for this interest stems from the fact that these methods offer considerable promise of reducing the number of operating steps currently required in the reactor fuel cycle. A schematic flowsheet for a reactor fuel cycle employing the fluoride volatility process for purification of uranium is shown in Figure 2. A comparison of this flowsheet with that shown in Figure 1 (purification by solvent extraction) reveals that a lesser number of operating steps is required for the reactor fuel cycle in which a fluoride volatility separations process is employed. This reduction in number of steps occurs whether or not an isotopic re-enriching operation is performed between the recovery step and the re-introduction of fuel to the reactor. A still further simplification of the fuel cycle may be obtained with a pyrometallurgical type of process. This is illustrated in Figure 3 which depicts a fuel cycle envisioned with the use of pyrometallurgical processing for a power reactor of the fast breeder type. It will be noted that remote fuel fabrication is required because only partial decontamination is obtained with this type of process.

Another important feature of non-aqueous reprocessing methods is that they are much less susceptible to deleterious radiation effects than are certain

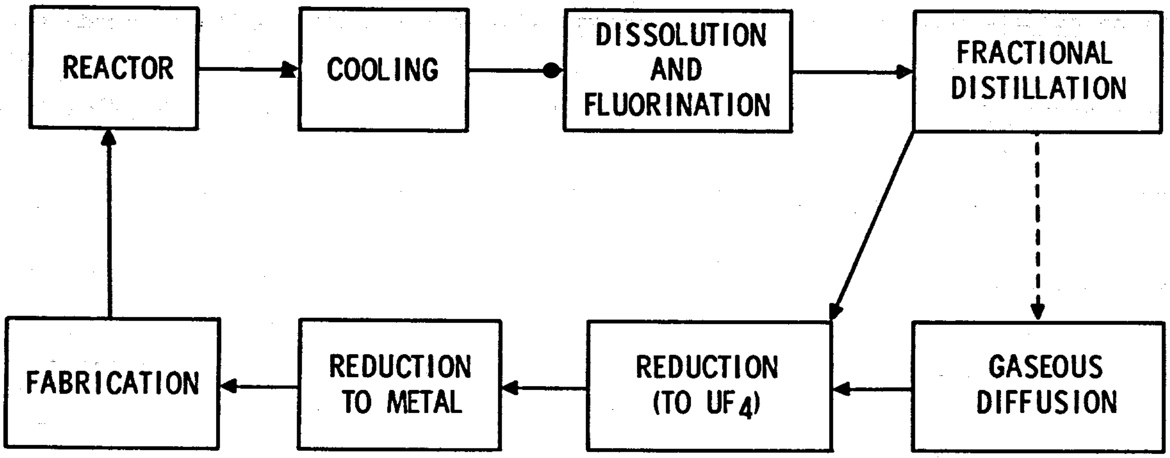

Fig. 2 - Reactor fuel cycle with fluoride volatility process.

important aqueous methods, such as solvent extraction types using organic solvents. This means that shorter cooling periods and higher concentrations of irradiated materials can be readily accommodated. As a result, there can be less inventory of fissionable material. In addition, there is a great potential advantage offered

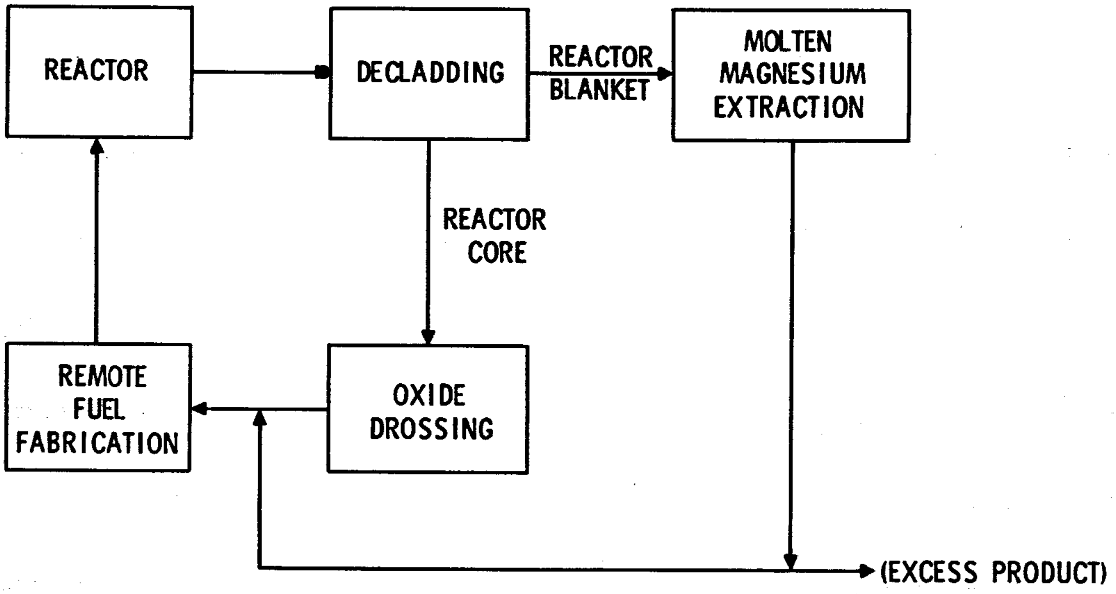

Fig. 3 - Reactor fuel cycle with pyrometallurgical process.

by non-aqueous methods for obtaining the fission products in highly concentrated form. This can enable more economic utilization or storage of these by-products. The compactness of these processes is particularly outstanding in the case of pyrometallurgical methods since, in this case, the purification of irradiated reactor material is generally achieved while retaining the metallic state throughout. Since neutron moderating materials are absent, the critical mass problems are less severe than with aqueous methods. Mention should also be made here that some of the pyrometallurgical methods can adequately purify the fuel for re-use without losing certain expensive alloying metals (e.g., zirconium, niobium, ruthenium, and molybdenum) which are added in fuel fabrication to improve the fuel. With present processes these materials are difficult to recover economically and so the recovery is not attempted.

The first non-aqueous method for reprocessing spent nuclear fuels which will be presented in this portion of the symposium is the fluoride volatility process. Various aspects of this process will be presented by Drs. Cathers, Rodger and Vogel. Although various volatility processes might be envisioned, the inherent favorable characteristics of the fluoride system have resulted in its selection for detailed investigations.

A basis of purification and recovery by the fluoride volatility processes is suggested by the information given in Figure 4. This information shows that

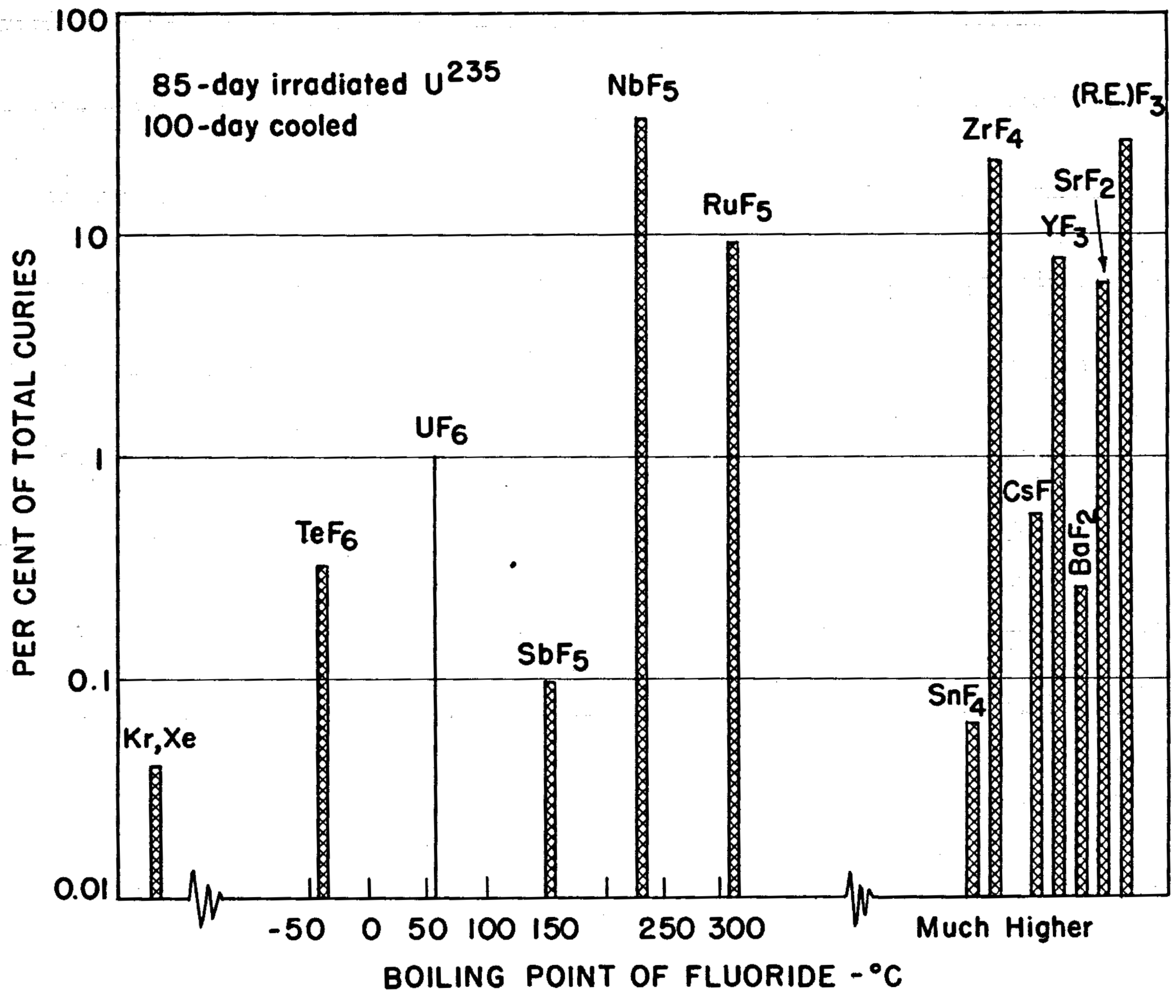

Fig. 4 - Per cent of total curies for individual fission product fluorides as a function of the boiling points.

the differences in volatilities of the important fluorides encountered in irradiated material are more than adequate for practicable use of fractional distillation. Except for tellurium (and molybdenum, but this is a short half-life fission product) which yields a fluoride much more volatile than UF_6, the fission products form fluorides which are much less volatile than UF_6. Therefore, the fission products can be readily separated from uranium by fractional distillation of the fluorides. The same situation exists for plutonium hexafluoride as for uranium hexafluoride since both of these have very nearly the same volatilities. However, as will be mentioned later, it is much more difficult to fluorinate plutonium than uranium to the hexafluoride. Ordinarily, the plutonium is fluorinated to lower fluorides which are not volatile. This difference in ease of hexafluoride formation may be advantageously used to obtain uranium-plutonium separations. As will be discussed by Dr. Cathers, the separation of uranium hexafluoride from the fission products can also be done by an absorption-desorption method using sodium fluoride.

In the present status of development the fluoride volatility processes appear to be especially favorable for applications in which enriched uranium is to be recovered. For these applications, the non-volatility of the lower fluorides of plutonium affords a means of decontaminating the uranium from plutonium as well as from fission products. From laboratory and pilot plant studies it has already been established that excellent decontamination and recovery of uranium from fission products can be achieved by the use of fractional distillation techniques with the fluoride volatility process. In Figure 5 are illustrative results obtained in pilot plant tests of this process. As a matter of fact, it appears that it is more simple to achieve decontamination factors of the order of 10^7 to 10^8 by a fluoride volatility process than by solvent extraction methods. The reason for this is that the chemistry of the fluoride volatility process is simpler than the chemistry encountered in solvent extraction methods. For a similar reason the effects of high radiation levels during processing is believed to be less of a problem for the fluoride volatility processes than for solvent extraction methods.

	DECONTAMINATION* FACTOR	% ACTIVITY OF NATURAL U
TELLURIUM	1.4×10^6	
IODINE	2.3×10^5	
ALL FISSION PRODUCTS	1.3×10^8	
PLUTONIUM	10^4	
TOTAL BETA		2
TOTAL GAMMA		1

$$* \frac{\text{ACTIVITY / GRAM } UF_6 \text{ IN CHARGE}}{\text{ACTIVITY / GRAM } UF_6 \text{ IN PRODUCT}}$$

Fig. 5 - Uranium hexafluoride separation from fission products and plutonium.

In addition to the use of fractional distillation with fluoride volatility processes, absorption-desorption cycles with NaF have been successfully used to purify uranium hexafluoride. The results of work related to processing of high alloy enriched fuels will be presented in more detail by Dr. Cathers.

At the moment, the major problem with the use of a fluoride volatility process for enriched fuels is concerned with the techniques and materials of construction for the feed dissolution step. This problem arises from the fact that stringent dissolution conditions are needed to dissolve the high alloy compositions ordinarily associated with the use of highly-enriched fuels. At present such dissolution is performed by the dispersion of hydrogen fluoride gas in fused salt media held at elevated temperatures. However, answers to this problem already appear imminent through the use of graphite-lined dissolution equipment. There is currently considerable interest in volatility processes for high alloy enriched fuels because of the waste handling and storage problems which are encountered when aqueous recovery methods are used. The volatility processes give much less volume of waste which may be more economically dealt with than wastes obtained from aqueous processes.

The application of a fluoride volatility process to natural uranium fuels or to low alloy fuels generally has also been studied extensively. In this case, interhalogen agents such as BrF_3 and ClF_3 dissolve the fuel satisfactorily and no serious problems of materials selection exist for the dissolution step. This step is followed by fractional distillation. The results have been very encouraging in both laboratory and pilot plant tests. This work will be reported by Dr. Vogel. As he will undoubtedly mention, there is, however, a problem when plutonium recovery is also desired. The reason for this, as noted earlier, is that the formation of plutonium hexafluoride is not nearly as easily accomplished as that of uranium hexafluoride. In addition, the chemical reactivity of plutonium hexafluoride makes it a difficult material to handle in ordinary equipment without decomposition to non-volatile plutonium fluorides. Recent studies on the preparation of plutonium hexafluoride and its transport behavior in metal equipment have been much more encouraging than would have been expected from the earlier studies along these lines. Therefore, there has been renewed hope for the prospect of producing plutonium hexafluoride and handling this process material in purification operations with irradiated fuel. If this hope is borne out by continued work, it is believed that the fluoride volatility process method will prove appreciably superior to solvent extraction methods. Until the recent encouraging results it appeared that plutonium from irradiated natural uranium would have to be recovered by solvent extraction techniques from the residues obtained after the recovery of uranium by volatility methods.

Preliminary cost estimates have indicated that the combination of uranium recovery by a volatility process and of plutonium recovery by solvent extraction would be only slightly more economic than the use of solvent extraction for recovery of both products. Similar preliminary estimates have shown that a process capable of recovering both uranium and plutonium by a volatility process would be very advantageous. This fact, together with the likely future use of plutonium fuels, has stimulated interest in working out the preparation and handling problems of plutonium hexafluoride.

The next non-aqueous method which will be discussed is the pyrometallurgical or pyrochemical type. There are several varieties of pyrometallurgical methods. All of them are characterized by the inherent compactness resulting from avoiding bulk chemical conversions of the material during purification. That is, the material is processed while largely maintained in the metallic state. In addition, features common to these methods are the high temperature of operation and the low decontamination of product from fission products. However, the partial decontamination is believed to be adequate for reuse of fuel in power reactors but will necessitate remote handling of fuel during fabrication. The versions of pyrometallurgical processing which have received the most study are oxide drossing (sometimes also referred to as oxide slagging or melt refining) and solvent extraction of molten irradiated fuel with either immiscible metals or fused salts. In addition, some investigations have been made of zone refining and fractional distillation but these did not appear to be immediately promising or practicable. One other type which has received only limited study but which nevertheless appears still quite promising is non-aqueous electrolytic refining.

A review of the basic principles and the experimental results of studies of pyrometallurgical methods will be presented by Dr. Feder and Mr. Burris. As mentioned above, oxide drossing and non-aqueous solvent extraction have received the most attention. Studies on these have consisted of laboratory as well as semiworks development work.

The extension of these studies through the pilot plant stage is now planned in conjunction with three prototype power reactor projects. The Argonne EBR-II (Experimental Breeder Reactor - II) project will have a reprocessing pilot plant utilizing oxide drossing for purification of the enriched uranium or plutonium core and, on a demonstration basis, a molten magnesium extraction process for reprocessing the blanket material of depleted or natural uranium. The Brookhaven LMFRE (Liquid Metal Fuel Reactor Experiment) contemplates the incorporation of a pilot plant with a fused salt extraction process on the liquid bismuth-uranium fuel employed in this reactor. The Atomics International SRE Project (Sodium Reactor Experiment) contemplates the use of oxidative drossing for purification of the uranium fuel used in this reactor.

The basis for the oxidative drossing process is the relative differences in stability of the various metal oxides as summarized in Table 1. Thus it is evident that many of the fission products and, particularly, the rare earths, cerium, and strontium can be preferentially oxidized and removed as oxide dross. In addition, some of the fission products such as cesium and the rare gases are volatilized under the operating conditions employed during drossing. From the combined effects of volatilization and oxide drossing the type of removal shown in Table 2 is expected. It will be noted that the fission products which remain with the purified metal are for the most part metals which metallurgists have found to give beneficial effects to fuel under irradiation. Some of the metals also improve the physical properties from a fabrication standpoint. Thus, the incomplete removal of fission products obtained with these methods may prove advantageous and compensate for some of the disadvantages of remote fuel

Table 1—(GIBBS) FREE ENERGY OF FORMATION OF OXIDES AT 1500°K

Oxide	$-\Delta F°$(kcal/gm-atom oxygen)
$\frac{1}{3}$ La_2O_3	109.7
$\frac{1}{3}$ Ce_2O_3	107.0
$\frac{1}{3}$ Nd_2O_3	105.7
SrO	102.0
$\frac{1}{3}$ Pu_2O_3	99.0
$\frac{1}{2}$ UO_2	98.9
$\frac{1}{3}$ ZrO_2	97.0
BaO	95.0
NbO	66
$\frac{1}{2}$ MoO_2	38
$\frac{1}{2}$ TeO_2	4.7
Cs_2O	3.6
$\frac{1}{2}$ RuO_2	−2.7

Table 2—FISSION-PRODUCT SPECTRUM AND FISSION-PRODUCT REMOVAL BY PYROMETALLURGICAL PROCESSING

(175-day irradiation, 15-day cooling, plutonium fast fission)

	Total fission products, wt. %	Method of removal
Rare gases (Kr and Xe)	13	Volatilization
Alkali metals (Rb and Cr)	11	Volatilization
Iodine	1	Volatilization*
Alkaline-earth metals (Sr and Ba)	5	Oxide drossing
Yttrium and rare earths	28	Oxide drossing
Zirconium	7	Carbide drossing
Light transition metals (Nb, Mo, and Tc)	11	†
Platinum group metals (Ru, Rd, and Pd)	20	†
Heavy transition metals (Ag, Cd, In, Sn, Sb, and Te)	4	
	100	

*Recent experiments do not show appreciable volatilization of iodine.

†Levels of these fission products may be controlled by periodically processing with molten zinc using selective precipitation.

fabrication required in this instance. Periodically, an auxiliary process will be needed to control the level of those fission products which are not removed by oxide drossing and volatilization. For this purpose, another pyrometallurgical process involving selective precipitation from molten zinc is being studied. This process is expected to be useful also for recovery of valuable products in the oxide dross.

The study of solvent extraction employing molten metals immiscible with molten uranium has been largely done with magnesium and silver. While core purification may be possible with the use of silver, the work on magnesium has been primarily directed to the processing of uranium blanket material for concentration and recovery of plutonium. Laboratory and semi-works results have shown magnesium to possess more than adequate extractability and selectivity for solvent extraction of plutonium from molten uranium. Demonstration tests with synthetic blanket material have already been made on a kilogram scale using uranium-plutonium charges containing up to 1 per cent plutonium. After the separation of the magnesium phase from the uranium phase, the magnesium has been distilled to concentrate the plutonium. This step, too, has been satisfactorily tested on a kilogram scale. From all the work done to date it appears that magnesium extraction will be feasible for concentrating the plutonium in blanket material to concentrations sufficiently rich for replenishing the core with fissionable material.

The use of solvent extraction processes employing fused salts has been extensively studied at Brookhaven in connection with the purification of their liquid bismuth-uranium fueled reactor. The Brookhaven investigators have used fused mixed chlorides to extract many of the fission products which have high capture cross sections with neutrons of thermal energies. Most of their work has already been reported in the open literature. It will also be summarized by Mr. Burris in his presentation on economics and proposed engineering applications of pyrometallurgical processes.

As mentioned earlier, the pyrometallurgical methods give only partial decontamination, i.e., less than ten-fold reduction in overall fission product removal. Therefore, the use of these methods is very much dependent on an economic remote fuel fabrication operation. Such an operation is now envisioned for the EBR-II project and the Metallurgy Division at Argonne has been studying this problem. The results on synthetic fuels with composition simulating that obtained from pyrometallurgical processing by oxide drossing and volatilization during melting have been very encouraging. The metallurgists using equipment shown sketched in Figure 6 have succeeded in fabricating up to 20-inch lengths of 1/8-inch diameter fuel which requires only being cut to length. Tolerances of ±0.001 inch in diameter have been produced in approximately 96 per cent of the castings. The method by which they accomplish this is to use Vycor tubing coated with washes of colloidal graphite and sized to produce fuel with the desired dimensions of diameter and length. In operation of this method, the fuel charge and a bundle of Vycor tubes (closed at one end) are placed in a furnace and the furnace evacuated. The furnace is connected to an argon pressure vessel. When the furnace is evacuated the molten fuel charge is brought up so that the ends of the Vycor tubes are covered. At the same time the valve connecting the argon pressure to the furnace is opened and the connection to vacuum equipment is closed. This causes the fuel to be drawn up into the Vycor tubes. By proper heat balance and temperature control the fuel is immediately solidified in the Vycor tubes. Later the Vycor tubing is broken away. A remarkable degree of dimensional uniformity has been obtained in experiments which have simultaneously produced up

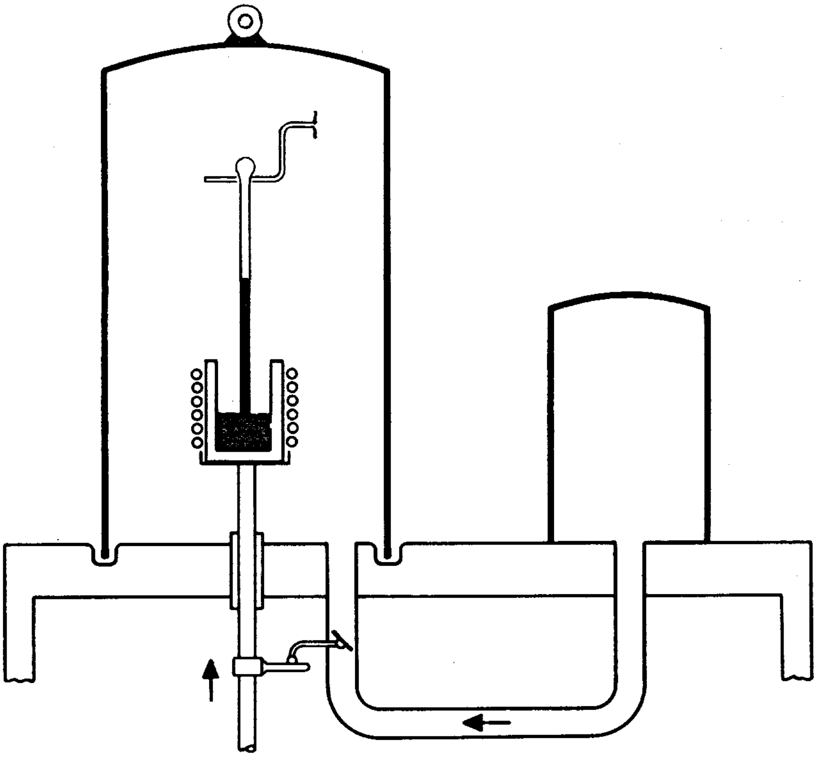

Fig. 6 - Injection casting furnace.

to 30 pieces of fuel in this manner. Because of the simplicity of this operation and of subsequent fuel fabrication steps, it is believed that remote fabrication of fuel such as will be used in the EBR-II will prove practicable. The success of this is obviously very important to the intended use of the pyrometallurgical pilot plant for the EBR-II project. The development of remote fuel fabrication techniques may also prove to be valuable in conjunction with even processes which thoroughly remove fission products. This is because recycle of some fuels, at least, will lead to radioactivity problems from heavy isotopes, if not from fission products.

Mock-ups of various parts of the pyrometallurgical processing plant for the EBR-II project are being designed and some already are constructed. In the experimental work conducted to date on oxide drossing and solvent extraction with molten magnesium, the problems of contaminating environments have been of minor nature. This fact has been very encouraging and also very important in expediting experimental results in both the laboratory and in the semiworks. It will also be an important factor in the design and operation of the contemplated pilot plant.

At the present time, the non-aqueous methods of processing lack the completeness of development and extensive operating experience which the aqueous solvent extraction processes have undergone. This is of itself a major disadvantage but it may be well to recall that a similar situation once existed for solvent extraction processes relative to the earlier developed and used precipitation processes. While it is, perhaps, too early to predict the success or failure of non-aqueous processes, the earlier mentioned potential advantages of these processes has stirred a tremendous interest in them. Studies of their engineering problems and economic capability for specific applications have been well started. Some of the results of these studies will be presented in more detail by Dr. Rodger and Mr. Burris for fluoride volatility and pyrometallurgical processes, respectively.

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FLUORIDE VOLATILITY PROCESSES FOR LOW ALLOY FUELS

R. C. Vogel and R. K. Steunenberg*

May 1, 1957

I. Introduction

In a fluoride volatility separations process the species in the irradiated fuel are all converted to the fluorides. The uranium hexafluoride can then be separated by distillation from the fission product fluorides. It is believed that the conversion of the fission products and uranium to the fluorides leads to a relatively easy separations problem in decontaminating the uranium. The problems involved in the separation of uranium hexafluoride from the fission product fluorides are depicted graphically in Figures 1 and 2. The activities are plotted as the percentages of total curies and the percentages of total beta and gamma watts against the boiling points of the fluorides. It is of course appreciated that the boiling points are only approximate indications of the separations problems. However, it is clear that there is a wide difference in volatility between uranium hexafluoride and the important fission product fluorides. Fluoride volatility processes are also particularly attractive because of the unique role which uranium hexafluoride can play in the field of nuclear energy.

The subject of this paper is the application of fluoride volatility processes to that important group of irradiated fuel elements consisting of natural or slightly enriched uranium containing fission products and plutonium of recoverable amounts. Blanket materials in the future may be

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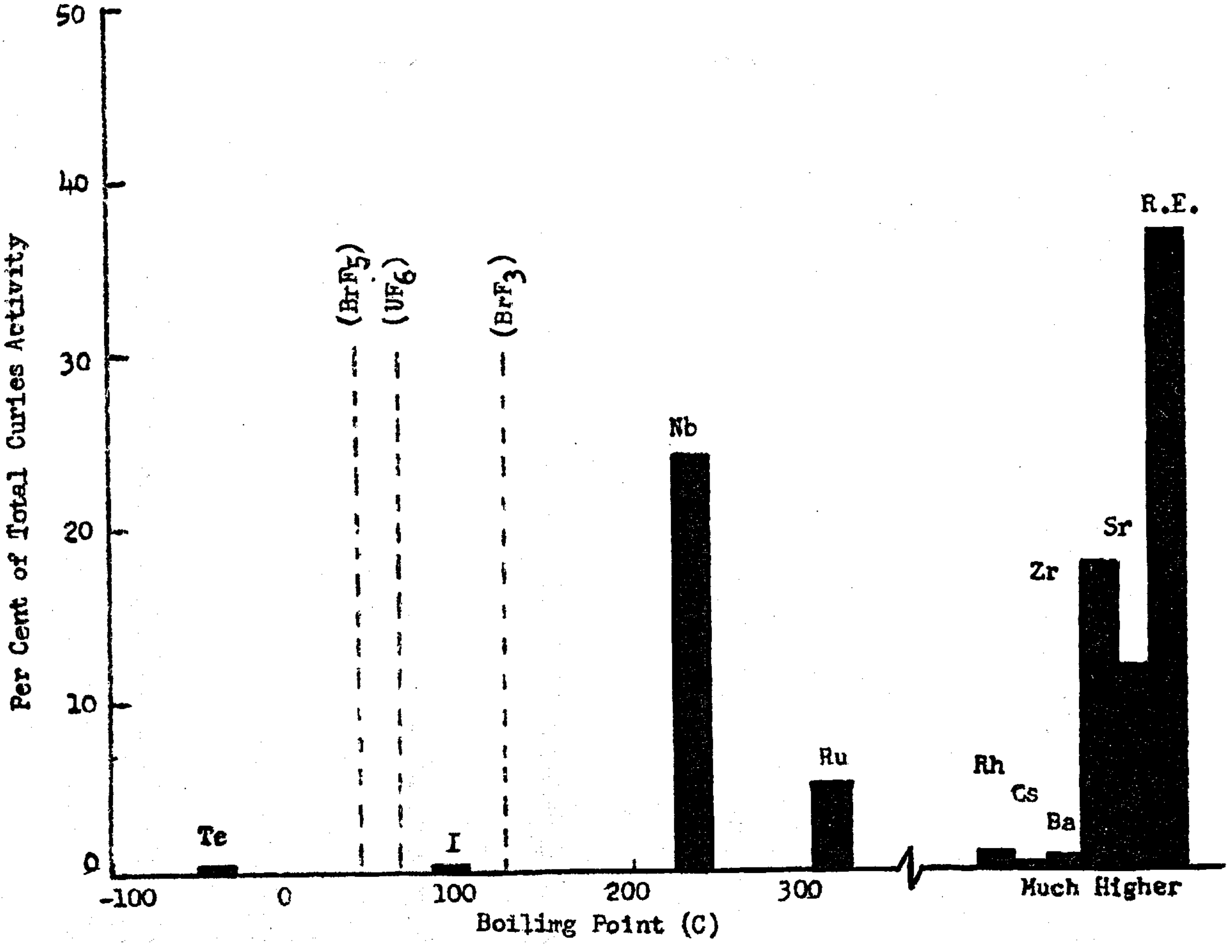

Fig. 1 - Fraction of total curies activity as a function of boiling points of the fission product fluorides.

of a similar nature. The uranium may be canned in aluminum, zirconium or a zirconium alloy. Depending on the irradiation conditions the plutonium concentration in uranium can vary from parts per million to several per cent. Similarly the fission product concentration may vary between wide limits. Work has been carried out at Argonne, Brookhaven, and Oak Ridge National Laboratories on the development of fluoride volatility processes for materials of this type. Oak Ridge National Laboratory has done laboratory and pilot plant work using the chlorine trifluoride dissolution of the fuel elements. The effort using the bromine trifluoride dissolution of uranium has been carried into the pilot plant stage at Argonne[1] and Brookhaven[2] National Laboratories. A Brookhaven dissolver now under construction is of the continuous type while the Argonne dissolver is of the batch type.

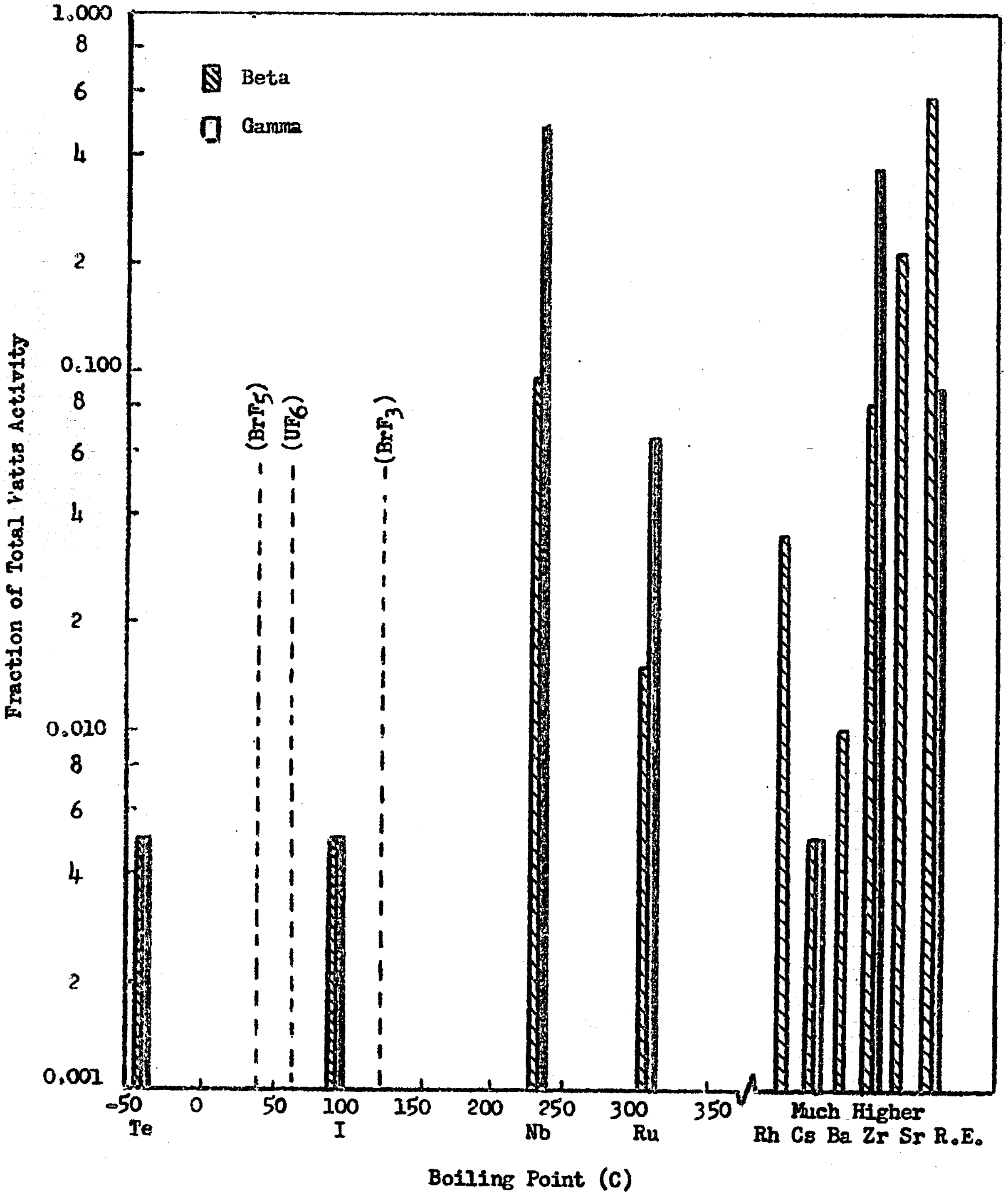

Fig. 2 - Beta-gamma energies of the fission product fluorides as a function of their volatility.

II. Laboratory Data - Bromine Trifluoride Process

The pertinent points of the chemistry of the bromine trifluoride process for the recovery and decontamination of uranium and plutonium are discussed in this section. The chemistry of the chlorine trifluoride process is very similar. Since bromine trifluoride does not dissolve the common materials used for canning uranium, the slugs must be decanned mechanically or by the common aqueous methods. The reaction of uranium with bromine trifluoride is

$$U(s) + 2\,BrF_3(\ell) \longrightarrow UF_6(\ell) + Br_2(\ell) \quad .$$

A rapid and reversible reaction between bromine and bromine trifluoride also takes place in the gas phase according to the equation

$$Br_2 + BrF_3 \rightleftharpoons 3\,BrF \quad .$$

The plutonium is fluorinated to the tetrafluoride and is insoluble. The bromine trifluoride can be completely regenerated with fluorine by the reaction

$$3\,F_2 + 3\,Br_2 \longrightarrow 2\,BrF_3 \quad .$$

The volatile components are removed from the dissolver by volatilization and separated by distillation. The plutonium can be recovered through solvent extraction techniques by dissolving the residue in aqueous aluminum nitrate. It is hoped that advances in the techniques of handling plutonium hexafluoride may eventually lead to a process in which both the uranium and the plutonium are volatilized from the dissolver as the hexafluorides. The important fission product fluorides in approximately 100 day cooled fuels are relatively non-volatile. The only exceptions to this in 100 day cooled material are tellurium hexafluoride (B.P. -39°C) and iodine pentafluoride (B.P. 100°C). This latter fission product is not in high enough yield to appear in Figures 1 and 2. The tellurium hexafluoride distills overhead as a forecut while the iodine pentafluoride remains in the bromine trifluoride and can be recycled back to the dissolver. A possible flowsheet demonstrating these operations which is being developed at Argonne National Laboratory is shown in Figure 3.

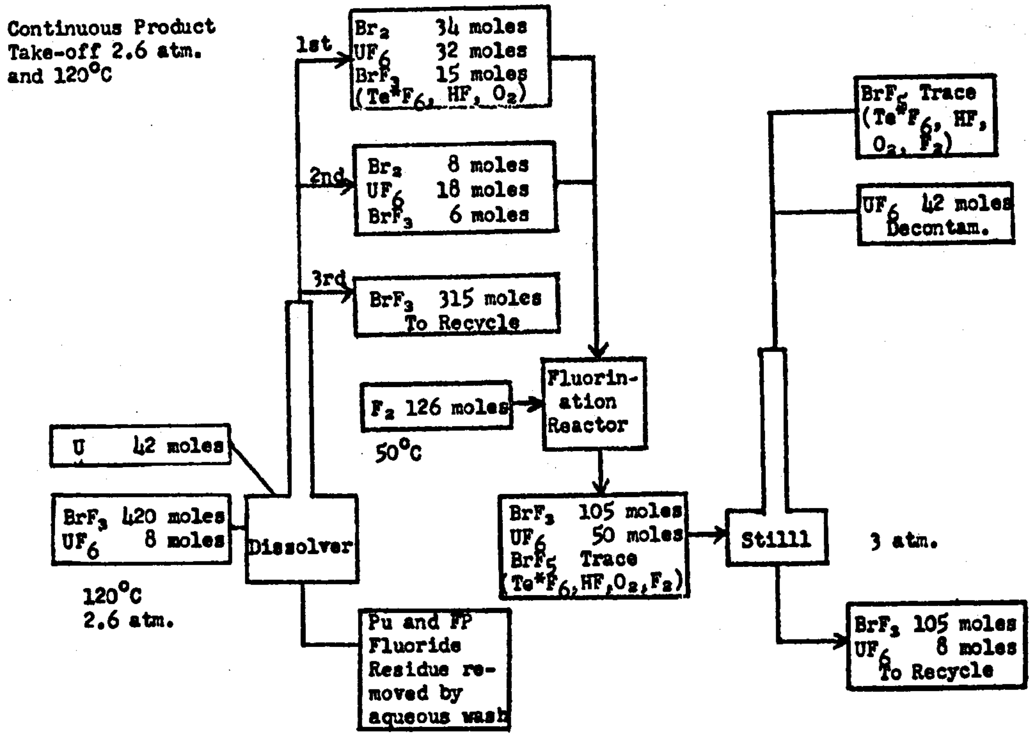

Fig. 3 - Continuous product **removal flow sheet for processing natural uranium.**

A possible flowsheet involving continuous dissolution is shown in Figure 4.[3] This type of flowsheet is being developed by Brookhaven National Laboratory. In this scheme of processing the chemistry is essentially the same except that bromine pentafluoride rather than fluorine is used to fluorinate the bromine formed during the dissolution.

A. Uranium Dissolution:

1. The Need for a Liquid Phase

When uranium metal is converted directly to the hexafluoride in an atmosphere of fluorine the heat released is about 2200 kcal/kg of uranium. Even with modest amounts of uranium it has not proven practical to remove this amount of heat when generated in a solid-gas reaction. A study

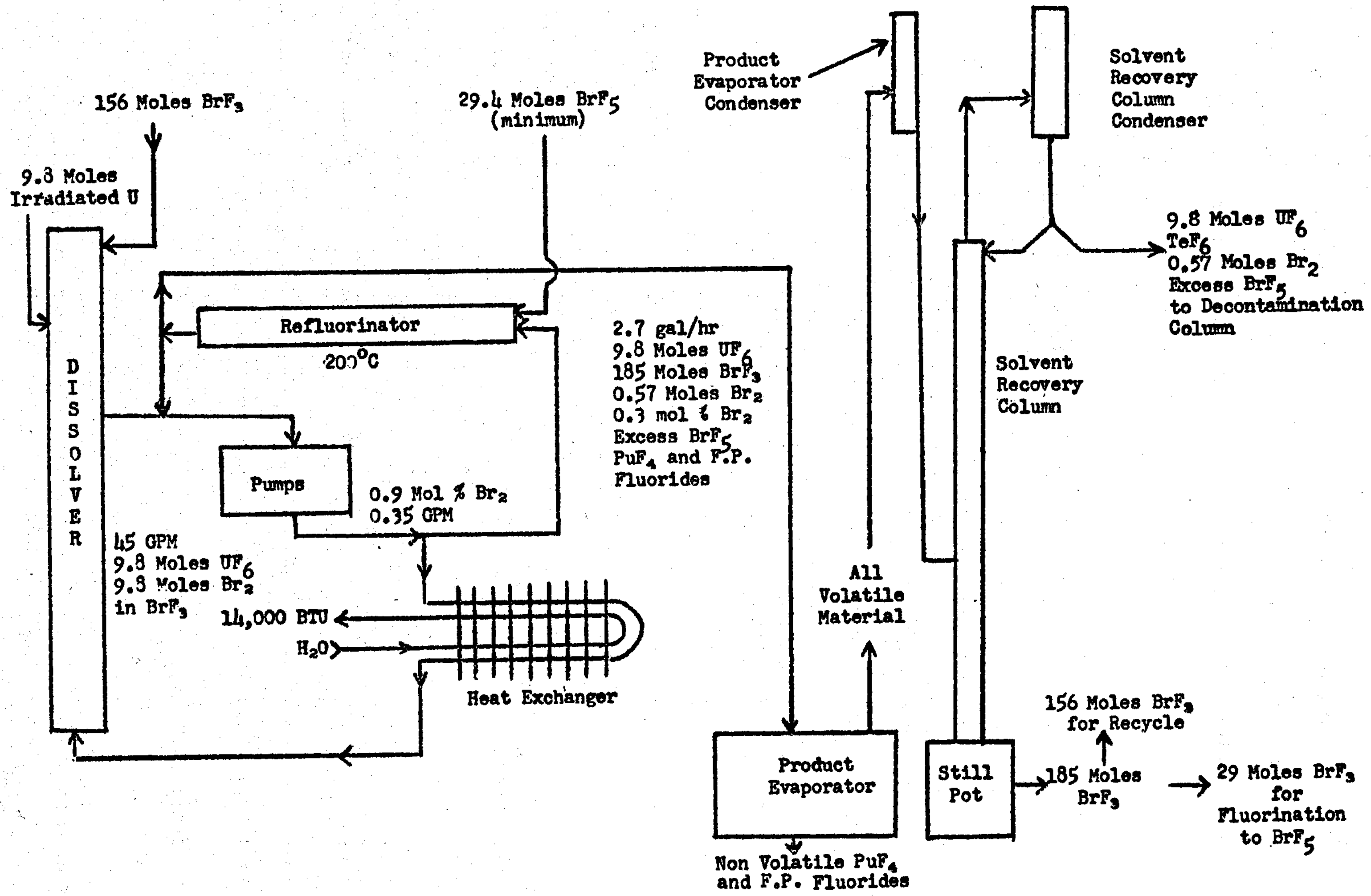

Fig. 4 - Continuous dissolution flow sheet for processing natural uranium. Submitted by personnel of Brookhaven National Laboratory. Quantities expressed in gram moles on hourly basis unless stated.

has been made of the ignition of uranium and other metals in liquid and gas phase fluorinating agents. It was shown when a liquid phase is maintained, even at temperatures considerably above the boiling point, that ignition of bulk uranium does not occur. The data in Table 1 show that the reaction is a smooth one. In Tables 2 and 3 are presented data for the ignition of uranium in various vapor phase fluorinating agents. Data are also available for the reactions of various other materials which might be involved in a fluoride volatility processes.[4]

Table 1

EXPOSURE OF URANIUM METAL TO LIQUID FLUORINATING REAGENTS

Reprinted from "Behavior of Uranium and Other Selected Materials in Fluorinating Reagents", Stein, L. and Vogel, R. C., Ind. and Eng. Chem. 48, 418 (1956).

(Approximately 3 grams of alpha-rolled uranium used in each experiment.)

Run No.	Reagent	U Temp, °C Initial	U Temp, °C Final	Contact Time, min	Results
12	BrF_3	170	180	44	Smooth reaction
13	BrF_3	205	205	26	Smooth reaction
19	BrF_3	210	210	16	Smooth reaction
31	BrF_3	25[a]	160	17	Smooth reaction
27	$BrF_3 + UF_6$[b]	195	220	22	Smooth reaction
33	BrF_5	130	170	25	Smooth reaction
35	BrF_5	25[a]	160	23	Smooth reaction
41	ClF_3	25[a]	70	7	Smooth reaction

[a] Uranium and halogen fluoride heated together from room temperature.

[b] Initial solution, 10.3 mole % UF_6.

Table 2

IGNITION OF URANIUM METAL IN VAPOR-PHASE FLUORINATION

Reprinted from "Behavior of Uranium and Other Selected Materials In Fluorinating Reagents", Stein, L. and Vogel, R. C., Ind. and Eng. Chem. 48, 418 (1956).

Approximately 3 grams of alpha-rolled uranium used in each experiment. Pressure: BrF_3 at vapor pressure of liquid reagent - i.e., at 145°, 165°, and 201°C, vapor pressures are 1364, 2384, and 5840 mm, respectively.

Run No.	Reagent (Vapor)	Initial Uranium Temp, °C	Ignition Temp, °C	Vapor Contact Time, min
	A. Uranium Exposed to Vapor after Immersion in Liquid.			
13	BrF_3	205	205	2
14	BrF_3	205	205	2
15	BrF_3	155	185	8
16	BrF_3	135	150	20
17	BrF_3	145	205[a]	48
18	BrF_3	150	150	2
19	BrF_3	210	210	1
20	BrF_3	185	185	1
21	BrF_3	190	190	2
22	BrF_3	185	185	2
23	BrF_3	210	210	2
24	BrF_3	175	175	2
25	BrF_3	205	205	1
26	BrF_3	260	260	1
30	BrF_3	170	170	1
31	BrF_3	160	160	2
28	$BrF_3 + UF_6$[b]	160	170	17
32	$BrF_3 + UF_6$[b]	145	175	18
49	$BrF_3 + Br_2$[c]	135	170	11
50	$BrF_3 + Br_2$[d]	150	160	13
51	$BrF_3 + Br_2$[e]	135	160	14
52	$BrF_2 + Br_2$[f]	145	160	7
	B. Uranium Exposed to Vapor without Prior Liquid Immersion.			
105	BrF_3	25	190	68
106	BrF_3	25	190	70

---

[a] BrF_3 inadvertently distilled into cold trap; ignition produced by addition of more BrF_3 vapor at 205 C.

[b] Initial solution, 10.3 mole % UF_6.

[c] Initial solution, 9.9 mole % Br_2.

[d] Initial solution, 4.5 mole % Br_2.

[e] Initial solution, 17 mole % Br_2.

[f] Initial solution, 16 mole % Br_2.

Table 3

IGNITION OF URANIUM METAL IN VAPOR-PHASE FLUORINATION

Reprinted from "Behavior of Uranium and Other Selected Materials in Fluorinating Reagents", Stein, L. and Vogel, R. C., Ind. and Eng. Chem., 48, 418 (1956).

Run No.	Reagent	Approx. Pressure at Ignition, mm	Initial U Temp, °C	Ignition Temp, °C	Vapor Contact Time, min
34	BrF_5	5300	170	225	7
33	BrF_5	5500	170	240	20
35	BrF_5	>6000	160	225	21
38	ClF_3	750	25	No ignition[a,b]	33
43	ClF_3	750	25	275[a]	25
36	ClF_3	1250	25	No ignition[c]	50
39	ClF_3	2000	25	225	29
37	ClF_3	2550	25	270	45
40	ClF_3	2800	25	205	24
42	ClF_3	3600	25	270	28
41	ClF_3	5750	70	235	31
44	F_2	900	25	No ignition[d]	52
45	F_2	4600	25	260	24
46	F_2	4800	25	355	33
47	F_2	4900	180	375	36

---

[a] Gas from cylinder allowed to flow over heated uranium at atmospheric pressure.

[b] Run terminated at 205°C.

[c] Temperature surged from 330° to 410°C, upon reducing pressure at end of run.

[d] Run terminated at 340°C.

2. The Rate of the Uranium Bromine Trifluoride Reaction

Like all heterogeneous reactions the rate of dissolution is a function of the geometry of the solid, the purity and local crystal orientation in the metallic structure as well as the surface area and degree of agitation. In addition to the data cited below there are rate data available on pilot plant scale dissolutions which will be covered in a later section.

a. Whirling Cylinder Experiments: The kinetics of uranium dissolution in bromine trifluoride have been investigated by whirling cylinders of uranium in the dissolving reagent. Only a modest amount of uranium was allowed to dissolve before the experiment was stopped. This led to constant surface area and solution composition throughout the experiment. Typical data are given in Table 4. These data are for high purity beta quenched uranium. At 85°C, using pure bromine trifluoride and conditions similar to those indicated in Table 4, it was found that alpha rolled commercial grade

Table 4

SELECTED EXPERIMENTS ON THE DISSOLUTION OF PURIFIED URANIUM IN BROMINE TRIFLUORIDE SOLUTION

Dissolution rate is measured by weight loss of pure uranium cylinder rotating at a peripherial speed of 3000 cm/min over a 15 minute interval.

Dissolving Medium[a]	Temp, °C	Penetration Rate,[b] mm/hr
BrF_3	65	0.010 ± .001
	85	0.015 ± .001
	105	0.036 ± .001
BrF_3 - Br_2 (5 mole %)	85	0.05 ± .006
(10 mole %)	85	0.08 ± .006
BrF_3 - UF_6 (5 mole %)	85	1.6

---

[a] No appreciable change in concentration took place during the experiment.

[b] The indicated error is the average deviation from the mean of several runs.

uranium dissolved about three times as rapidly as beta quenched pure uranium. In pure bromine trifluoride, variations in stirring speed have no discernible influence on the rate, and the temperature dependence corresponds to an activation energy of 6 to 7 kcal/mole. There is, however, a considerable rate increase when uranium hexafluoride is added to the solution.

b. Batch Dissolution Without Area Control: Batch dissolutions were carried out on approximately 10-gram uranium samples. In these experiments area control was sacrificed but temperature and solution composition were maintained constant. The data are given in Table 5. From these data the most important conclusion is that uranium hexafluoride at 75°C accelerates the reaction more than an equivalent concentration of bromine (Run 4 vs Run 3) in agreement with the whirling cylinder experiments.

c. Selection of Conditions for Uranium Dissolution: From the data indicated above it is clear that a wide range of uranium dissolution rates is available. The rate of the reaction can best be controlled by the selection of a temperature and a pressure for dissolution. The pressure can be maintained constant by bleeding off the products of the reaction at the appropriate rate. This determines the uranium hexafluoride concentration in the dissolver solution.

B. Plutonium Behavior in a Fluoride Volatility Process

Earlier investigations with bromine trifluoride dissolutions of irradiated uranium containing small amounts of plutonium (ca. 10 ppm) gave uranium hexafluoride fractions with detectable plutonium concentrations. It was feared that a similar fraction of plutonium would be volatilized when uranium containing a higher concentration of plutonium was employed. Later experiments in which more concentrated plutonium alloys were dissolved have shown that there was no appreciable volatile plutonium carried over with the uranium hexafluoride fraction even when the dissolutions were carried out with bromine trifluoride solutions containing bromine or uranium hexafluoride.

Table 5

RATE OF REACTION OF COMMERCIAL GRADE ALPHA-ROLLED URANIUM WITH BROMINE TRIFLUORIDE SYSTEMS

Conditions: Each experiment started with new cylinder; area not controlled; one hour at 75°C unless otherwise indicated; volume BrF_3 200 ml; volume vapor space 50 ml; approximate initial sample area 5.6 cm^2; system shaken during dissolution; uranium sample tied to end of thermocouple well; data corrected by subtracting amount dissolved in heating and cooling cycle.

Run Number	2[a]	1[a,b]	3	4	5	6	7[c]
Mol % BrF_3	~100	100	97.1	97.2	96.7	94.5	94.5
Mol % UF_6		0.04		2.8		2.9	2.9
Mol % Br_2			2.9				
Mol % BrF_5					3.3	2.7	2.7
Blank, wt loss[d]	0.1095	0.0437	0.1868	0.4493	0.0894	0.4280	2.5626
Original wt	11.0738	11.2916	9.8892	10.6130	11.1600	9.8377	11.3063
Total wt loss in run	0.1825	0.7259	0.3802	2.2383	0.2682	3.3879	~10
Net wt loss	0.0730	0.6772	0.1934	1.7910	0.1788	2.9599	~ 7
Wt loss, %	0.65	6	2.0	16.9	1.6	31.5	~70
Very approx. penetration rate, mm/hr	0.007	0.06	0.02	0.17	0.017	0.23	~ 0.74

---

[a] Pure BrF_3 attack giving small honeycomb type holes at the end, while Br_2 and UF_6 solutions give pits of greater diameter.

[b] A possibility existed that this solution was initially contaminated with UF_6; it was analyzed and found to be 0.04 mol % UF_6.

[c] Experiment run at 120°C; due to an incident the run time was 25 minutes instead of 60 minutes. Results only approximate.

[d] On separate cylinder, taken through heating and cooling cycle only.

The data are presented in Table 6. These observations are also in agreement with the data of Malm and Weinstock[5] which indicate that plutonium hexafluoride is reduced to a non-volatile form by bromine trifluoride.

If all volatile material is removed from the dissolver via the vapor phase, the residual non-volatile plutonium and fission product fluorides may be washed from the dissolver periodically with an aqueous aluminum nitrate solution capable of solubilizing these fluorides. Such a solution might be processed for the plutonium by familiar solvent extraction methods.

Table 6

PLUTONIUM VOLATILITY EXPERIMENTS

Experiments carried out on unirradiated 400 ppm plutonium in uranium alloy.

Series A: Attempts to prepare PuF_6 from BrF_3 dissolver solutions.

Run No.	Weight of Uranium-Plutonium Alloy (grams)	Reagent	Approximate Dissolution Time (hours)	Average Temp °C	Total Volatile Plutonium (per cent)	Uranium Material Balance (per cent)
1	0.5758	BrF_3	4.1	100	(0.115)[b]	95.5
2	0.6243	BrF_3	9.3	105	0.043	94.7
3	0.8421	BrF_3	6.4	115	0.006	95.5
4	0.8203	12.4 mole % Br_2 in BrF_3	9.5	100	0.009	96.4
5	0.6967	12.8 mole % Br_2 in BrF_3	(8)[a]	105	0.017	83.4
6	0.7215	11.3 mole % UF_6 in BrF_3	(2)[a]	95	(0.175)[b]	92.2

Series B: Residue from BrF_3 dissolution subjected to various treatments.

Run No.	Weight of Uranium-Plutonium Alloy (grams)	Reagent Used to Treat Plutonium Fluoride Residue	Contact Time (hrs)	Average Temp °C	Total Volatile Plutonium (per cent)
7	1.4362	BrF_5	2.0	50	0.077
8	0.7246	BrF_5	1.0	40	0.069
9	1.3286	$BrF_5 + F_2$	4.8	25	0.034
10	1.3286	$BrF_5 + F_2$	4.2	25	0.026
11	1.3286	F_2	1.6	120	0.002
12	1.3286	ClF_3	1.1	120	0.006

---

[a] The experiment was interrupted overnight.

[b] The low-level plutonium analyses were done by the LaF_3 method; the results are probably high due to uranium background.

This procedure is satisfactory from a chemical point of view. It does offer engineering difficulties in view of the incompatibility of bromine trifluoride solutions and aqueous solutions and the potential hazards involved in employing such solutions in the same equipment.

To reduce the problem of incompatibility, the plutonium might be removed from the dissolver as a slurry in liquid bromine trifluoride and concentrated in a small auxiliary vessel where subsequent operations should present a substantially reduced hazard. This procedure might involve the addition of a finely divided insoluble fluoride, e. g., aluminum fluoride, to the bromine trifluoride. Alternatively, a high temperature fluorination of the residual plutonium might be employed for this step.

C. Fission Product Behavior in a Fluoride Volatility Process

The best decontamination data are those obtained on the pilot plant scale. Therefore discussion will be deferred on this subject to that section.

As the flowsheet in Figure 3 shows, bromine trifluoride is recirculated to the dissolver. The bromine trifluoride appears to be readily separable by simple distillation from all the fission products except the iodine. Since this reagent would be re-used in the dissolver, no real decontamination is required. The bulk of the fission product waste will be concentrated with the plutonium and will ultimately appear as wastes from the plutonium processing.

D. Stability of Bromine Trifluoride to Irradiation

Serious problems are not expected with bromine trifluoride processes due to irradiation decomposition. This arises since it is proposed that the bromine be fluorinated after the dissolution step. Therefore any species formed as a result of irradiation decomposition could be expected to be converted back to bromine trifluoride.

At Brookhaven National Laboratory bromine trifluoride was exposed to an accumulated gamma ray dosage of 1.7×10^7 r. It was estimated that

0.1 weight per cent of bromine was formed. It was concluded that the amount of bromine produced would be negligible compared to that produced by the dissolution reaction.

At North American Aviation (Atomics International) the chemical effects of 1 Mev electrons in bromine trifluoride were considered.[6] Pressure measurements taken during the irradiation suggested the presence of bromine and bromine pentafluoride. The radiation effect seemed to reach saturation when approximately 10 per cent of the bromine trifluoride was destroyed. A qualitative comparison of irradiation dosage with that expected from highly irradiated spent fuels revealed that little decomposition of bromine trifluoride is to be expected.

E. Corrosion of Possible Equipment Materials in a Fluoride Volatility Process

Corrosion studies have been conducted on several materials of construction commonly used for interhalogen systems. Most of these studies have been static tests.

1. Corrosion of Materials in Interhalogen Systems

Data are given in Table 7 on the corrosion at 125°C of various metals in pure bromine trifluoride and bromine trifluoride containing bromine pentafluoride, bromine or uranium hexafluoride.

The data for nickel, Monel and K Monel show that these metals have excellent corrosion resistance. Inconel and Duranickel also are probably satisfactory. Stainless steel, mild steel, magnesium and aluminum are suitable for less critical applications. Nicloy-9 is unsatisfactory. At Brookhaven National Laboratory stainless steels 302 and 347 were immersed in boiling bromine trifluoride, bromine pentafluoride for 3 months. The penetration rate was around 5 mils/year. Alternate exposure to aqueous systems and bromine trifluoride indicated that these materials were definitely unsuitable for this type of application.

Table 7

CORROSION IN INTERHALOGEN SYSTEMS AT 125 C

(Reprinted from Corrosion Studies Pertinent to Bromine Trifluoride Processes, Schnizlein, J. G., Steunenberg, R. K. and Vogel, R. C., ANL-5557, April 1956.)

Coupons: 1 3/8 in. x 1 3/8 in. x 1/16 in. initially polished with fine steel wool and scouring cleanser paste, washed, degreased and dried at 110 C.

Supports: Insulating Teflon spacers.

Fluoride Film Removal: 1 M $Al(NO_3)_3$, 0.05 M sulfamic acid, pH 0.5

		Penetration in Mils per year[a]											
	Time of Exposure	Pure BrF_3[b]			10% BrF_6 - 90% BrF_3			10% Br_2 - 90% BrF_3			10% UF_6[c] - 90% BrF_3		
Metal	(weeks)	Vapor	Interface	Liquid	Vapor	Interface	Liquid	Vapor	Interface	Liquid	Vapor	Interface	Liquid
Nickel	11	+[d]	+	+	+	0.006	0.012	+	0.002	0.004	0.008	0.018	0.008
Welded Nickel	11	+	0.0004	+	0	0.012	0.005	+	0.001	0.006	0.007	+	0.0008
Monel	11	+	+	0.005	+	0.025	0.029	+	0.020	0.024	0.004	0.003	0
Welded Monel	11	+	+	0.005	0.004	0.029	0.018	+	0.015	0.033	0.005	0.002	0
K Monel	11	0.0002	0.003	0.007	0.009	0.031	0.036	0.008	0.025	0.034	0.005	0.004	0.004
Inconel	11	0.005	0.010	0.027	0.0008	0.045	0.046	+	0.029	0.041	0.020	0.011	0.015
Duranickel	4	0.12	0.28	0.30	0.23	0.30	0.26	0.30	0.37	0.37	0.05	0.02	0.009
Incoloy	4	1.3	3.2	3.6	1.4	1.5	1.7	0.74	1.0	0.9	0.7	1.2	2.5
Aluminum[e]	4	0	0.71	0.70	0.19	0.10	+[f]	0	0.17	+[d]	+	+	+
Magnesium[g]	4	-[h]	-	+	-	-	+	-	-	+	-	-	-
Stainless steel (Type 304)	1	2.8	3.6	3.4	5.3	6	6.9	1.3	2.0	2.0	2.5	2.9	4.1
Stainless steel (Type 347)	1										2.4	3.3	5.9
Mild Steel	1	4.9	7.7	7.8	11	16	19	2.7	4.9	4.1	6.8	5.2	9.0
Nicloy-9	1	-	74	-	-	160	-	-	27	-	-	-	-

---

[a] In cases when the corrosion rate is of the order of less than 0.1-mil penetration per year, the actual numbers carry little significance.

[b] The exposure time for pure BrF_3 nickel through Inconel was 20 weeks instead of 11.

[c] Initial UF_6 concentration in liquid. Removing and replacing samples necessitated some loss of UF_6 so the final UF_6 concentration was 5.1 mole %.

[d] + indicates a weight gain less than 1 mg.

[e] Concentrated HNO_3 wash used to remove fluoride film from aluminum.

[f] Weight gain 7.8 mg total.

[g] No method devised for film removal without attack of coupon. Weight changes are of the same order of magnitude as Duranickel, so penetrations should be of the same order of magnitude.

[h] Minus indicates no measurement made.

In the corrosion tests presented above the corrosion products were allowed to accumulate in the refluxed interhalogen in which the coupons were immersed. Although very low rates of attack were observed, it was necessary to know to what extent the corrosion products in solution might influence the rate. By incorporating a condensate receiver into a loop designed to test valve operations, coupons could be maintained in the bromine trifluoride condensate. The condensate was reheated to 70°C and it overflowed from the coupon container through the test valve back into the still pot. The data in Table 8 show attack at from 4 to 20 times those in static long term tests. However, the rates are still satisfactorily low for any use.

Table 8

CORROSION IN BROMINE TRIFLUORIDE CONDENSATE AT 70°C FOR 650 HOURS

(Reprinted from Corrosion Studies Pertinent to Bromine Trifluoride Processes, Schnizlein, J. G., Steunenberg, R. K. and Vogel, R. C., ANL-5557, April, 1956.)

1 3/8 in. x 1 3/8 in. x 1/16 in. coupons initially polished with fine steel wool and scouring cleanser paste, washed, degreased, and dried at 110°C. Supported in interhalogen condensate between Teflon spacers. Fluoride films were removed with 0.1 M $Al(NO_3)_3$, 0.05 M sulfamic acid, pH 0.5 solution before weighing.

	mil/yr
Nickel	0.036
Welded Nickel	0.024
Monel	0.10
Welded Monel	0.11
K Monel	0.19

Dynamic corrosion tests have been carried out at Brookhaven National Laboratory on Monel plate specimens 1/8 in. thick. The operation of the loop was such that the bromine trifluoride was static for 132 hours at room temperature and flowing for 7.7 ft/sec for 100 hours at 63°C. The plane of the plates was parallel to the line of flow. The corrosion rate was between 3 and 4 mils/year. These samples were examined for stress corrosion cracking and no evidence of it was found in either welded or non-welded areas.

2. Corrosion of Materials by Aqueous Systems

Since the present scheme of processing plutonium-uranium alloys by a fluoride volatility method suggests the removal of plutonium and fission product fluorides from the Monel or nickel vessel by washing it with an aluminum nitrate solution, it was appropriate to investigate the corrosion under these circumstances.

The corrosion of Monel by aqueous aluminum nitrate is acceptable only in a narrow pH range and might become serious because of mal-operation of equipment or operational mistakes. It was found that sulfamic acid is an effective corrosion inhibitor.[7] The conditions of the experiments and typical data are presented in Figure 5 to illustrate the effects of time and sulfamic acid concentration. It is important to emphasize that in this type of operation the total penetration is a function of the ratio of metal area to solution volume, and that the variable of solution pH is controllable only at the beginning of the experiment.

3. Corrosion of Materials in Cyclic Exposure to Aqueous and Interhalogen Systems

Since it is proposed in the processing of plutonium-uranium alloys to expose alternately the dissolving vessel to interhalogen and to aqueous systems it was necessary to examine the corrosion resulting from this type of cyclic operation.[7] A cyclic operation was set up to duplicate that which might be expected in a typical separations plant using the flowsheet previously shown. Coupons of nickel, welded nickel, Monel, welded Monel, K-Monel and Inconel were weighed at the completion of the first, second, third, tenth, twelfth and fourteenth cycles. The attack was uniform throughout the test and weight losses corresponding to about 0.0005 mil per cycle were found for all coupons. From these preliminary corrosion data it appears possible to cycle between interhalogen and aqueous systems under conditions similar to those set forth in the experiment.

III. Laboratory Data - Chlorine Trifluoride Process

Both laboratory and pilot plant work have been carried out at the Oak Ridge National Laboratory on the chlorine trifluoride method of processing reactor fuels. The important process chemistry of the chlorine trifluoride process will be discussed in this section. The chemistry is similar in most respects to that of the bromine trifluoride process.

Since chlorine trifluoride, like bromine trifluoride, does not dissolve the common materials used for canning uranium in slugs they must be mechanically decanned or decanned by the common aqueous methods. The reaction with uranium is

$$U(s) + 3\ ClF_3(\ell) \longrightarrow UF_6(\ell) + 3\ ClF(g) \quad .$$

The uranium hexafluoride is recovered and decontaminated by distillation. The chlorine trifluoride consumed is regenerated by reaction of chlorine monofluoride with fluorine at about 300°C according to the equation

$$ClF + F_2 \xrightarrow{300^\circ C} ClF_3 \quad .$$

In the chlorine trifluoride process as with the bromine trifluoride process the basic reaction consumes only fluorine. The plutonium is fluorinated to an insoluble fluoride. It is recoverable by dissolving the residue in aqueous aluminum nitrate and decontaminating by solvent extraction. The fission product behaviors are essentially the same as in the bromine trifluoride process.

A possible flowsheet demonstrating these operation is shown in Figure 6.

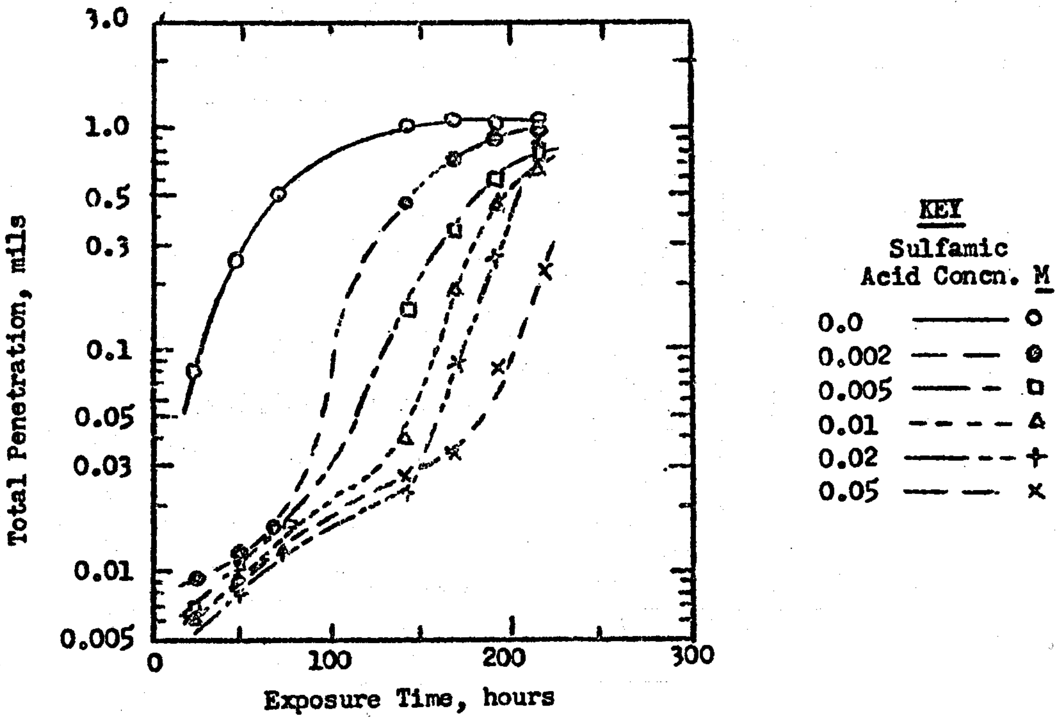

Fig. 5 - Inhibiting nitrate corrosion of Monel with sulfamic acid.

A. Uranium Dissolution

Data on the ignition of uranium by chlorine trifluoride vapor are given in Table 3.

As with the bromine trifluoride uranium reaction the kinetics of the chlorine trifluoride uranium reaction are quite complicated.

1. Rate in Pure Chlorine Trifluoride

Rates of solution of uranium in pure chlorine trifluoride have been estimated. About 1500 hours are required for the dissolution of a 1.43 in. diameter slug at 30°C and 900 hours at 80°C. The uncatalyzed reaction is obviously too slow for the development of a commercially feasible process.

2. Effect of Hydrogen Fluoride Addition

The addition of anhydrous hydrogen fluoride was found to accelerate the reaction between uranium and chlorine trifluoride. The effect of different hydrogen fluoride concentrations on the initial reaction

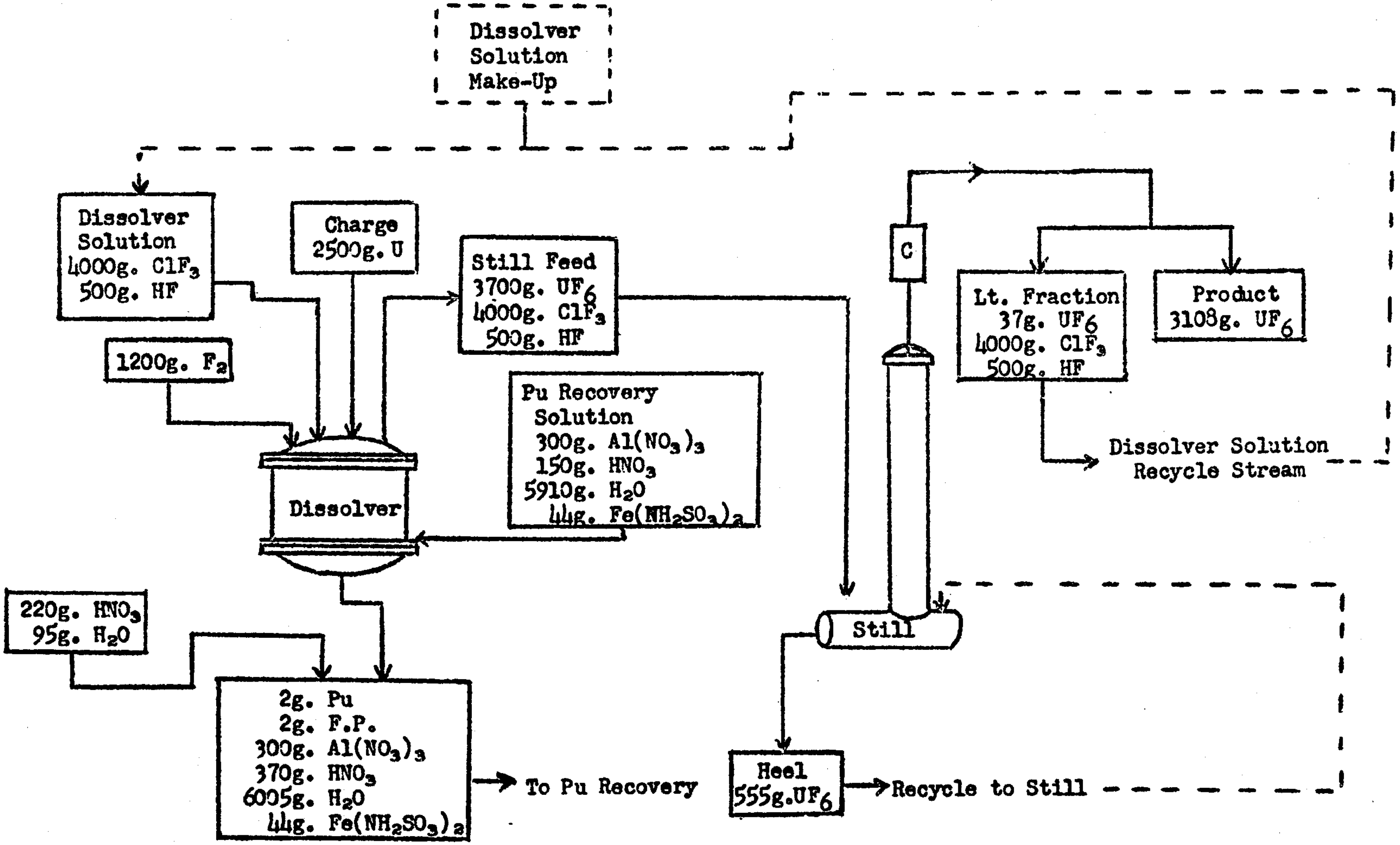

Fig. 6 – Chemical flow sheet. CTF batch type pilot plant, uranium cycle.

rate at 30°C in the absence of uranium hexafluoride in the fluorinating mixture is illustrated in Figure 7. The maximum rate of reaction was obtained at approximately 60 mole per cent chlorine trifluoride (molar ratio of chlorine trifluoride to hydrogen fluoride of 1.5). This rate is more than an order of magnitude faster than the rate obtained using pure chlorine trifluoride.

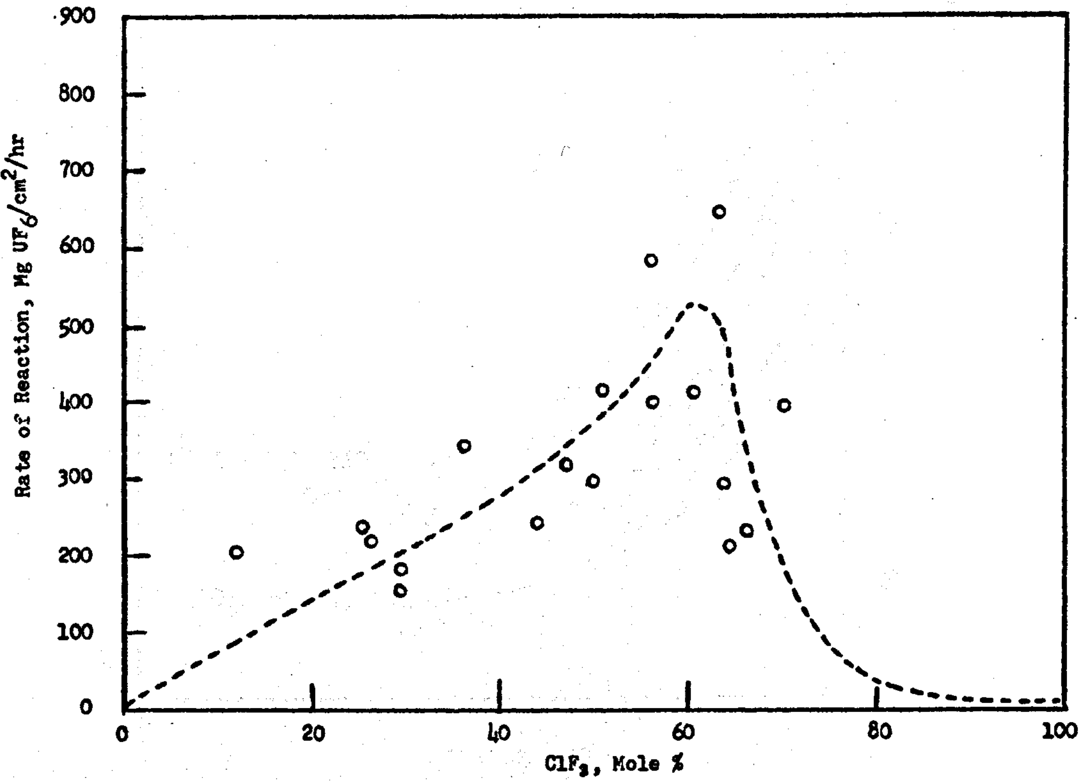

Fig. 7 - Average rate of reaction as a function of hydrogen fluoride concentration at 30°C.

3. Effects of Uranium Hexafluoride and Hydrogen Fluoride Additions

The presence of uranium hexafluoride in the reaction mixture was found to influence the rate of the reaction in a complicated way. This is demonstrated in Figure 8. The addition of uranium hexafluoride to those chlorine trifluoride-hydrogen fluoride solutions which gave the maximum rates in the absence of uranium hexafluoride depressed the rate of reaction. The rate was found to be essentially independent of uranium hexa-

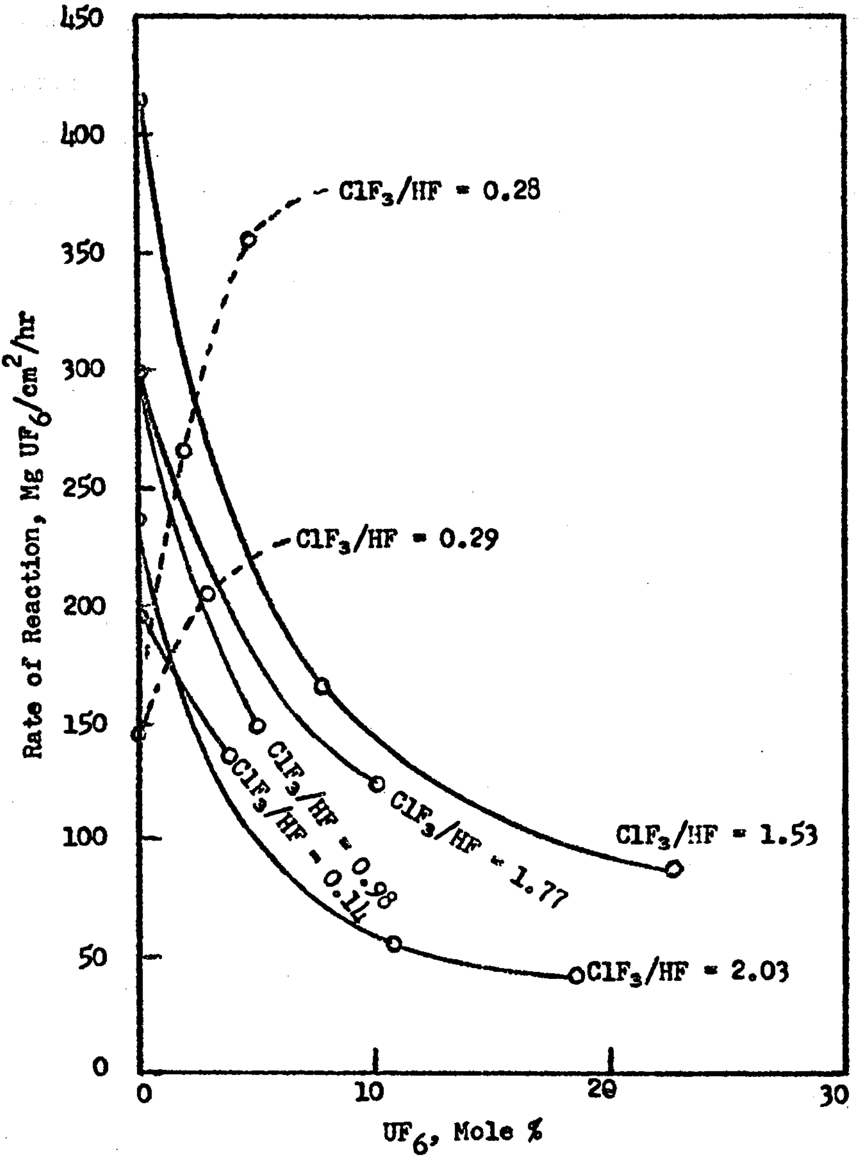

Fig. 8 - Influence of uranium hexafluoride upon rate of reaction at various mole ratios of chlorine trifluoride to hydrogen fluoride.

fluoride concentration at a mole ratio of chlorine trifluoride to hydrogen fluoride of 0.3.

4. Effect of Temperature

Using the composition of the dissolver solution of a molar ratio of chlorine trifluoride to hydrogen fluoride of 0.3 the temperature dependence of the reaction was investigated between 10 and 90°C. The reaction proceeded smoothly under all conditions studied and gave no indications of becoming uncontrollable at elevated temperatures. The reaction rates expressed in terms of the time required to dissolve a 1.43 in. diameter slug and in terms of the rate of removal of uranium metal are given in Table 9. A plot of log K vs. 1/T gives a break at about 48°C. The equations for the rate constant below and above 48°C are, respectively

$$\log K = 4.5041 - \frac{759.8}{T}$$

and

$$\log K = 5.6783 - \frac{4017.7}{T} .$$

K is expressed in moles of uranium per square centimeter per second. It should be emphasized that rather high pressures are associated with the higher temperatures.

Table 9

RATE OF REACTION BETWEEN URANIUM AND HYDROGEN FLUORIDE-CHLORINE TRIFLUORIDE SOLUTION AS A FUNCTION OF TEMPERATURE

Mole Ratio of ClF_3 to HF of 0.3

Temp, C	Time to Dissolve 1.43 inch diameter Slug, hr	$K \times 10^8$ moles U/cm^2/sec
80	18.5	206
75	28.8	132
70	42.0	90.8
60	88.8	41.2
60	89.6	44.4
45	300	13.2
30	345	11,2
20	449	8.4
10	590	6.5

B. Plutonium Behavior in the Chlorine Trifluoride Volatility Process

There has been no indication of plutonium volatility, i.e., formation of plutonium hexafluoride, during the dissolution of irradiated natural uranium in chlorine trifluoride. The plutonium remains behind as a residue with the fission products after the volatile material has been distilled from the dissolver. It can be dissolved in 5 per cent aluminum nitrate at a pH of 0.5.[8] At 100°C the dissolution rate is quite rapid and can probably be dissolved in about 3 hours. The plutonium can be recovered by solvent extraction.

There are corrosion data on Monel at room temperature obtained by Benton and Gustison[8] that appear to be at variance with the data obtained by Schnizlein, Steunenberg and Vogel.[7] For example for 5 per cent aluminum nitrate a pH of 0.5 the former investigators found a corrosion rate of about 150 mils per year while the latter found a rate of about 20 mils per year. Of course, the addition of sulfamate further inhibits this corrosion.

C. Considerations in the Distillation of Uranium Hexafluoride from the Dissolver Solution

There exist uranium hexafluoride-hydrogen fluoride and uranium hexafluoride-hydrogen fluoride-chlorine trifluoride azeotropes. The existence of these azeotropes presents difficulties in isolating pure uranium hexafluoride. One solution to the problem would be to add sufficient chlorine trifluoride to the system to remove hydrogen fluoride as the ternary azeotrope, which contains only a small quantity of uranium hexafluoride. Application of this technique would require an additional unit operation for breaking the chlorine trifluoride-hydrogen fluoride azeotrope. The best solution, however, seems to be to avoid breaking the uranium hexafluoride-hydrogen fluoride azeotrope remaining after the distillation of the ternary azeotrope but to maintain in the dissolver solution a quantity of uranium hexafluoride sufficient to satisfy azeotropic requirements. Then the uranium hexafluoride obtained from the reaction of the solution with uranium can be recovered by distillation.

The fission product considerations are similar to those mentioned in the bromine trifluoride process. The best fission product behavior data are those obtained on a pilot plant scale and will be given in a later section.

IV. Pilot Plant Programs

A. Bromine Trifluoride Process - Argonne National Laboratory

A pilot plant constructed of Nickel and Monel is at present in operation at Argonne National Laboratory.[9] The basic pieces of equipment are a dissolver, three distillation columns and two scrub towers. The methods chosen for handling the bromine fluorides were (1) measurement by weigh tank, (2) sampling and transfer by the vapor pressure of the materials themselves, (3) heating the contents of tanks by heaters metallized to their surfaces, (4) heating the surfaces of tanks with an external blanket heater and maintaining adiabaticily by adjusting to zero the temperature drop across a layer of insulation and (5) heating lines by tracing with electric heating wire and insulating. The latest run carried out at high activity levels have demonstrated a total fission product decontamination factor of over 10^8.

1. Equipment

The pilot plant was designed to demonstrate the flowsheet shown in Figure 3. It is, however, rather flexible and has been also used to demonstrate other processes. About 10 kg of irradiated slugs can be handled. An schematic equipment diagram is presented in Figure 9. A Monel dissolver of 90 liters capacity is provided with external cooling coils bonded to the vessel wall with copper spray metal. Water is used as the coolant. A special hazard is presented by the fact that water and organic liquid coolants react explosively when brought into direct contact with bromine trifluoride or fluorine. If an ordinary coolant jacket were used

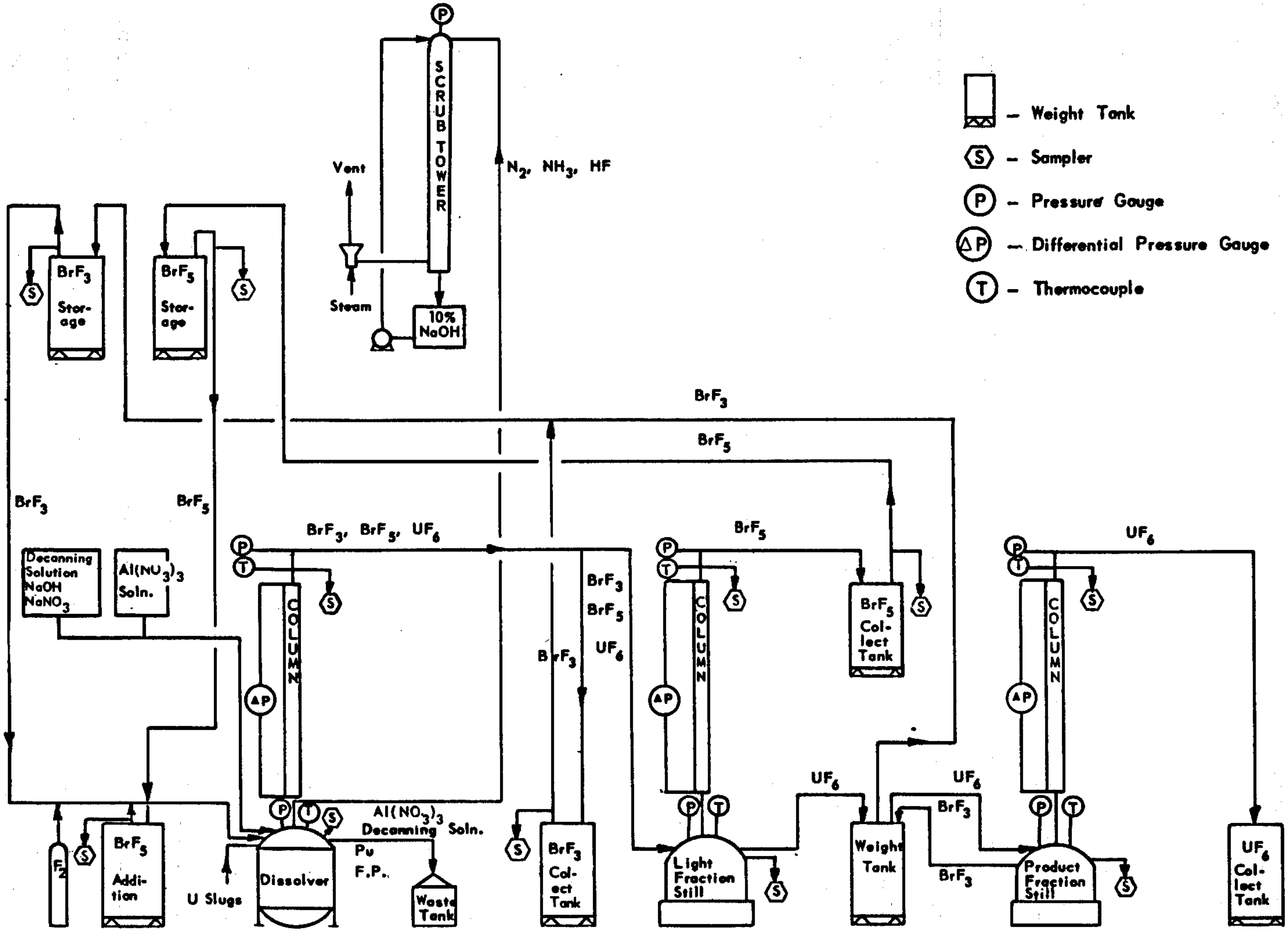

Fig. 9 - Equipment schematic for fluoride volatilization process studies.

for a process vessel, a wall leak might then be catastrophic. Consequently, vessel cooling is provided by separate cooling coils wound around the outside of the vessel and bonded to the vessel wall, with a metallizing technique. A leak in the process vessel wall will not immediately contact the cooling water coil and an alternate path for process fluid is offered. The method of construction as shown in Figures 10 and 11 was used for all vessels and condensers. Steam is used in the dissolver coils for heating, but all other process heating is electrical.

On top of the dissolver a connection is made, through valves, to a 1.75 inch I.D. distillation column with a nine-foot section packed with nickel (0.24 in. by 0.24 in.) Cannon protruded packing. The dissolver is thus used as a still pot. At the top of the column is a reflux condenser and a connection to an overhead vessel to receive the distillation product.

A second purification column unit consists of a 53 liter still pot with electric resistance heaters bonded to the wall with copper spray metal in the same manner as cooling coils. The packed section of this tower is 1.75 inches I.D. and 16 feet long, the packing being Helipak (3019).

Material charged to and discharged from the various process components is determined by weight. Each of the column overhead product receivers is a weigh tank using a remote head scale. This method of measurement was selected because optical liquid level devices are not easily used and because other types tend to be mechanically complicated or require thin metal parts.

Fluorine addition is followed by observing pressure drop in either of two 17.6 cubic feet steel storage tanks. A manifold system permits either of these two tanks to be filled from 6 lb, 400 psi shipping cylinders.

Lines are welded except for connections to vessels themselves and to process valves, which use gasketed joints and standard 150 lb flanges. Most of the liquid lines are 3/8-inch O.D. nickel tubing although some 1/2-inch and 1-inch pipe is also used. The smaller lines use 1/2-inch

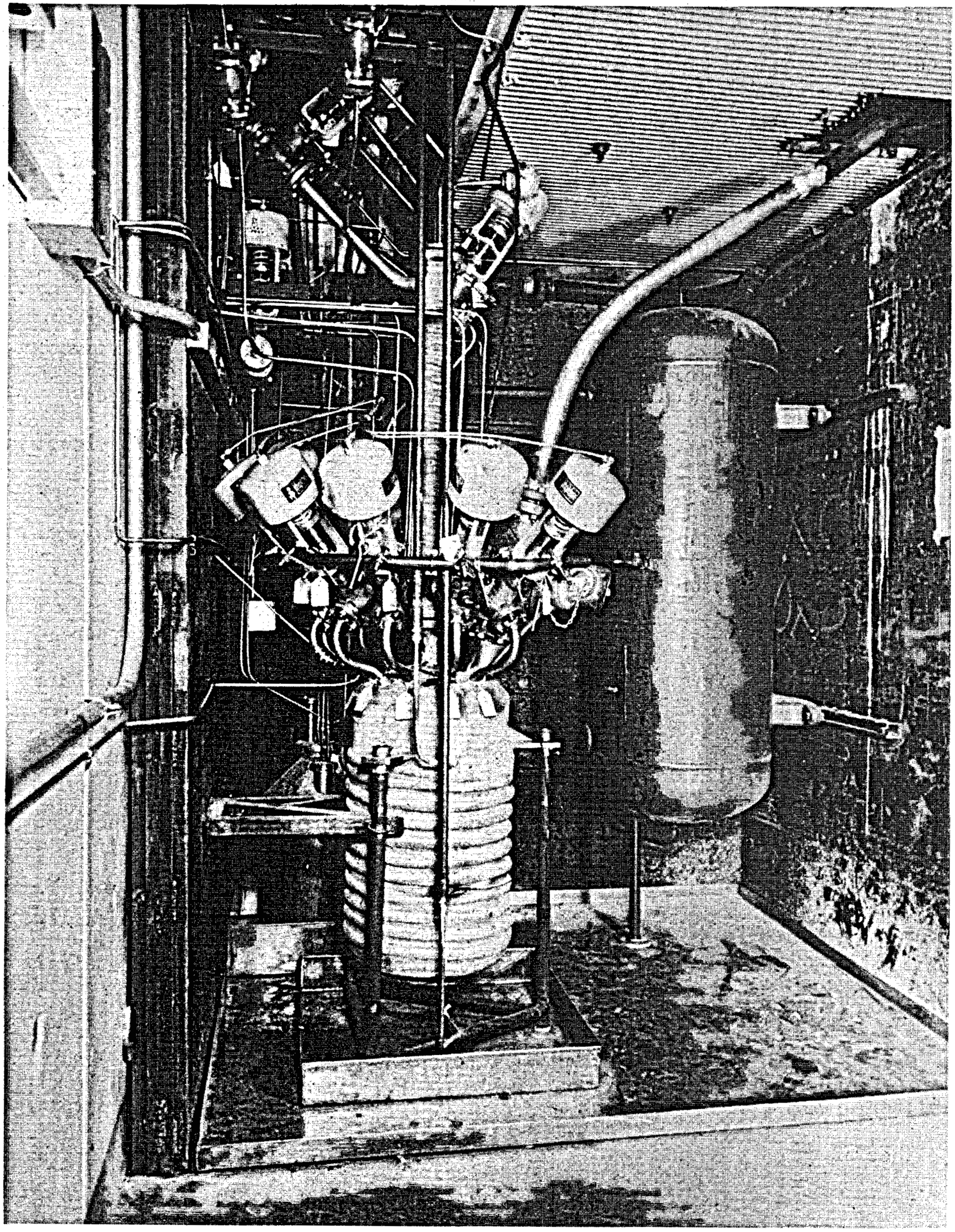

Fig. 10 - Dissolver installed (before insulation).

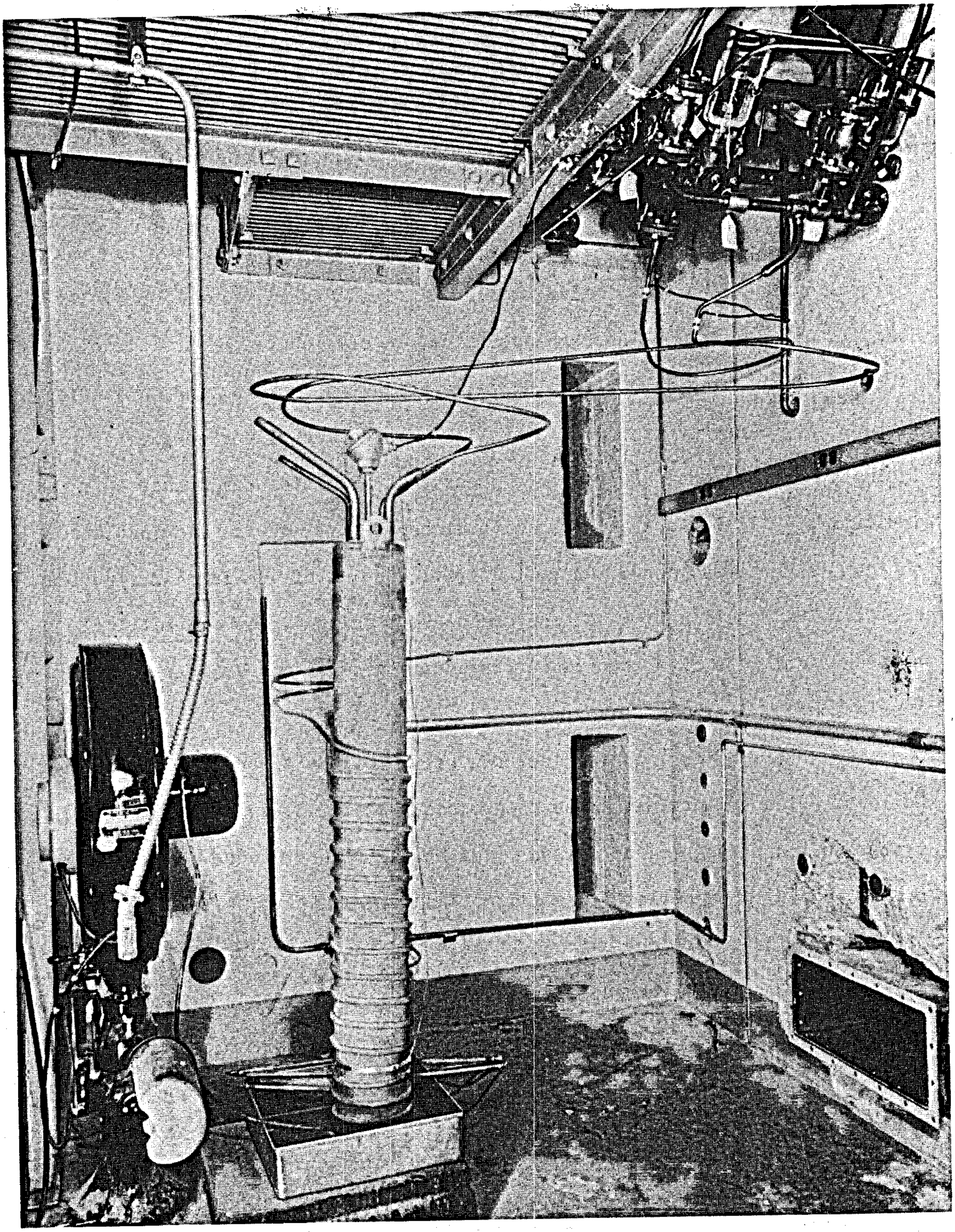

Fig. 11 - Weigh tank installed (before insulation).

valves and flanges, and the later used 1-inch valves and flanges. Gaskets are a spiral wound Flexitallic type, seating on a smooth faced flange surface.

The pilot plant has about 30 process valves. These are Monel packless type (Model No. 3064, Fulton Sylphon Division, Robertshaw-Fulton Controls Co.) using a bellows seal with a pneumatically operated stem. The valve is a simple shut off type with Teflon seat gasket and a machined seat integral with the body. Similar smaller 1/4 inch manual valves (Model 1197, Hoke, Inc.) are used on the sampler system. A slug chute for the dissolver is closed with a two-inch lift plug valve activated by an extension handle.

Each vessel is equipped with a thermowell for temperature indication and a Monel bourdon tube pressure transmitter for pressure indication. All lines are traced with nichrome heating wire and insulated to keep temperatures above the solidification point of uranium hexafluoride (64°C). The fractionating columns can be kept adiabatic by controlling heating mantles to give zero temperature differential across a layer of insulation.

Safety features include, (1) a leak detector on each valve bellows, (2) a rupture disc on each process vessel, (3) an emergency cooling system on the dissolver, activated by either a temperature or pressure set point, and (4) an interlook on still pot heaters shutting them off in case of water failure. The operation of the leak detector is as follows. Any leak in the seal bellow escapes first into the leak detector cavity in the valve. The leak detector consists of a Monel wire spring prevented from making electrical contact with the valve body by being tied by a nylon fishing line. Halogen vapors immediately decompose the line allowing the spring to contact the metal valve body and this flashes a light on the panel board.

Two spray towers are employed. One process scrubber is used to dispose of interhalogen vapors by hydrolysis and neutralization in 10 per cent potassium hydroxide. A similar but much larger unit is used to scrub all ventilation air from the equipment area to remove halogens resulting from equipment leakage. This scrub tower has been described elsewhere.[10]

The process equipment is mounted in previously installed concrete shielded cells. All process equipment, including shielding walls and floor personnel access areas for sampling (except the ventilation exhaust air scrubber) is contained in a volume 10 by 36 by 40 feet high. Instruments and controls are centralized on panel boards mounted on the top of the cell structure.

2. Rate of Dissolution on Pilot Plant Scale

The rates of complete slug dissolution on the pilot plant scale are given in Table 10. In the first experiment, D-1, there was no uranium hexafluoride present at the beginning of the dissolution. The rate therefore is much slower. In run D-5 the slugs were lightly irradiated material. In run D-6 the charge was a highly irradiated slug. It appears that the rate of the reaction is reasonable for process application.

3. High Level Run

At the time of writing a single run on high level materials has been carried out to test the flowsheet presented in Figure 3. The data on this run will be discussed in some detail. No attempt was made to recover and decontaminate the plutonium by solvent extraction since it was felt that these procedures are well established. The charge to the dissolver was 13.9 kg of irradiated natural uranium metal that had been cooled 80 days at the beginning of fractionations. The sequence of operations is given in Table 11. The cladding had been removed prior to charging. The dissolution medium consisted of 186 lb bromine trifluoride and 23 lb uranium hexafluoride. After dissolution, the material collected overhead was returned to the dissolver, and the combined solution was slowly sparged with elemental fluorine to regenerate bromine trifluoride from bromine produced during dissolution.

Table 10

SUMMARY OF DISSOLUTIONS

	Dissolver Charge						
Run No.	Uranium (lb)	Solution (BrF_3, BrF_5, UF_6) (lb)	Mols % UF_6 in Soln Initial	Mols % UF_6 in Soln Final[d]	Dissolution Time (hours)	Temp (C)	Pressure (psia)
D-1	7.7[a]	182	0.0	2.5	31	125 132	20 45
D-2	7.6[a]	167	2.9	5.0	8	110 122	38
D-3	22.8[a]	168	2.4	3.0	9	120	30
D-4	8.4[a]	233	3.7	5.1	9	120	40
D-5	5.2[b]	200	2.3	3.7	8	120 140	25 50
D-6	30.6[c]	209	4.6	3.7	14	120	38

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[a] Slugs 1.35 inches diameter.

[b] Slugs 1.10 inches diameter.

[c] Slugs 1.43 inches diameter.

[d] Concentration at end of dissolution before product bleedoff is returned.

The decontamination operations consisted of batch fractionations of the re-fluorinated dissolver solution. Boilup rates were 20 to 62 lb/hr in all distillations. Conditions under which these operations were carried out are summarized in Table 11 (Steps 3 through 5 for the dissolver column, and Steps 6 through 11 for the purification column).

Data on process fractions are summarized in Table 12. After a total reflux start-up period, a small volatile waste forecut (fraction 4, Table 12) was collected and then vented to the process scrubber. A uranium hexafluoride rough product cut, (fraction 5) which included the bulk of the uranium hexafluoride (and more volatile components), was then taken overhead and subsequently transferred to serve as the still pot charge to the purification column.

After a total reflux start-up period in the purification column, two forecuts (fractions 7, 8, Table 12) were taken overhead, serving to remove most of the bromine pentafluoride and tellurium. After another total reflux startup period, the uranium hexafluoride product cut (fraction 10) was taken overhead. Finally, the entire column residue was collected overhead in two portions (fraction 11).

In spite of the rather high activity level and short cooling time of the slugs charged, a very small amount of fission product activity (other than tellurium) followed the uranium hexafluoride overhead from the dissolver solution. Gamma scans of liquid samples of product distillate immediately after collection showed no peaks other than uranium-237, except for very slight tellurium peaks.

To confirm the absence of fission products when the strong uranium-237 peaks were not present, another gamma scan of a product fraction was made later at a total of 140 days cooling. This scan showed no peaks other than those present in natural uranium. The scan range was 30 to 2000 KEV. From the above scans, it was considered that fission products having gammas in the energy region greater than 0.3 MEV were

Table 11

SEQUENCE OF PROCESS OPERATION IN RUN D-6

Step	Description of Operation	Approximate Conditions Temp, C	Press, psia	Reflux Ratio, L/D
	Operations in Dissolver and Column			
1	Dissolution of Slugs	120	40	-
2	Re-fluorination with F_2	50-70	55	-
3	Column start-up	75	45	
4	Volatile waste forecut	75	45	high[a]
5	UF_6 rough product cut[b]	85	45	10
	Operations in Purification Column			
6	Column start-up	85	45	
7	Volatile forecut 1	90	45	20
8	Volatile forecut 2[c]	-	-	-
9	Column start-up	90	45	
10	UF_6 product cut	90	45	20
11	Column residue collection	-	-	-

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[a] Intermittent take-off.

[b] This fraction was used as charge to the purification column

[c] Consisted of hold-up in column collected as separate fraction.

contributing less than one per cent of the gamma activity of aged unirradiated natural uranium. For fission products with energies below 0.3 MEV, there was possible coincidence with the several uranium peaks, but their contribution could not have been greater than 10 per cent of the uranium activity.

The individual fission product decontamination factors were based on chemical separations. The total fission product decontamination

Table 12

COMPOSITION OF PROCESS FRACTIONS - RUN D-6

Step[a]	Description	Amount (lb)	UF_6 Weight %
1	Metal Charge	31.7	-
2	Dissolver Solution after Refluorination	225	27
4	Volatile Forecut	2	4
5	UF_6 Rough Product Cut	66	78
7-8	Purification Column Forecut[b]	23.6	60
10	Product UF_6	21.1	100
11	Column and Still Residue[c]	10.2	100

[a] See Table 11.

[b] Composite of two cuts.

[c] Composite of column holdup and still pot residue.

factor given in Table 13 was calculated as the total activity charged to the dissolver (per gram of total uranium present in the dissolver before distillation) divided by the sum of the activities (per gram of uranium in sample) determined in specific fission product analyses. Justification for this procedure was based on the evidence cited above of the absence of gamma-emitting fission products other than tellurium and iodine and was supported by considerations of the fission yield, half-life, and volatility of fluorides of fission products in general, which limits sources of contamination to tellurium, iodine, antimony, niobium and ruthenium.

A good activity balance on iodine was obtained. Substantially all the iodine entering with the slugs was contained in the recovered bromine trifluoride. A separate iodine removal step was considered feasible, but was not carried out in these operations. The activity material balance around the purification step is poor and it is presumed that this problem will be considered in further runs.

Table 13

URANIUM DECONTANINATION FACTORS - RUN D-6

All data corrected to 90-days cooling.

$$\text{Decontamination Factor} = \frac{\text{activity per gram uranium hexafluoride in charge}}{\text{activity per gram uranium hexafluoride in product cut}}$$

Operation	Tellurium Beta	Iodine Beta	Total Fission Product
Dissolver Distillation:			
UF_6 Rough Product Cut	14	2.2×10^3	1.6×10^3
Purification Distillation:			
UF_6 Product Cut	9.6×10^4	1.1×10^2	8×10^4
Over-all:			
UF_6 Product Cut	1.4×10^6	2.3×10^5	1.3×10^8

Preliminary results indicated that plutonium in any overhead fraction was less than 20 parts per billion uranium.

Bromine compound contamination of uranium hexafluoride product is being studied at the time of this writing. In the run here reported the product fraction contained about 0.6 wt per cent expressed as bromine. Some samples showed as little as 0.01 per cent bromine, but fractionation behavior was not consistent at low bromine levels.
Further work needs to be done to demonstrate that the bromine compound contamination can be substantially reduced.

B. Bromine Trifluoride Process - Brookhaven National Laboratory

There have been two pilot plant units built at Brookhaven National Laboratory. The first one, was called the light ends separations unit. It has now been dismantled. The second unit has been built to study the continuous dissolution of uranium and at the time of writing has just started on cold runs.

1. Light Ends Separation Unit - Equipment

From the early data on the fluoride volatility process it was thought that tellurium and possibly iodine might be limiting fission product activities in the decontamination of uranium hexafluoride. A unit was therefore built at Brookhaven to study the separation of the hexafluoride from the more volatile contaminants. Since it was believed that the eventual process would be continuous it was decided to study the light end distillation separation with tracer amounts of activity as a continuous process with recycling of the column overhead and bottom streams.

The flow sheet for the light end separation unit is shown in Figure 12. The unit consisted of two distillation columns connected with storage tanks, pumps and other auxilaries. These were connected in such a manner that a synthetic mixture of uranium hexafluoride, bromine trifluoride (with or without bromine pentafluoride) and light end fission product activity could be pumped to the first column where the hexafluoride would be stripped of the more volatile components. The column bottoms, consisting of the hexafluoride, bromine trifluoride and such other fission product components not removed as overhead were pumped as feed to the second column where the hexafluoride product was taken off as overhead and the bromine trifluoride removed as bottoms for recirculation.

A detailed description of the various system components can be found in a summary report written by W. R. Page et al.[2] The columns were nine feet high and packed with 5/32-inch ID aluminum single turn helices made from 24 B+S gauge 2S alloy wire. The pumps were 3-gph Lapp pulsa-feeder units with double diaphragm hydraulic pulse transmitting systems. The primary diaphragms were located outside the temperature-controlled box which houses the pilot plant and the pulses were transmitted by means of Kel-F oil to the secondary diaphragms inside the box. These diaphragms actuate check valve systems in the process streams. All pump parts in contact with process fluids were either Monel or Teflon. The flows were metered by means of rotometers.

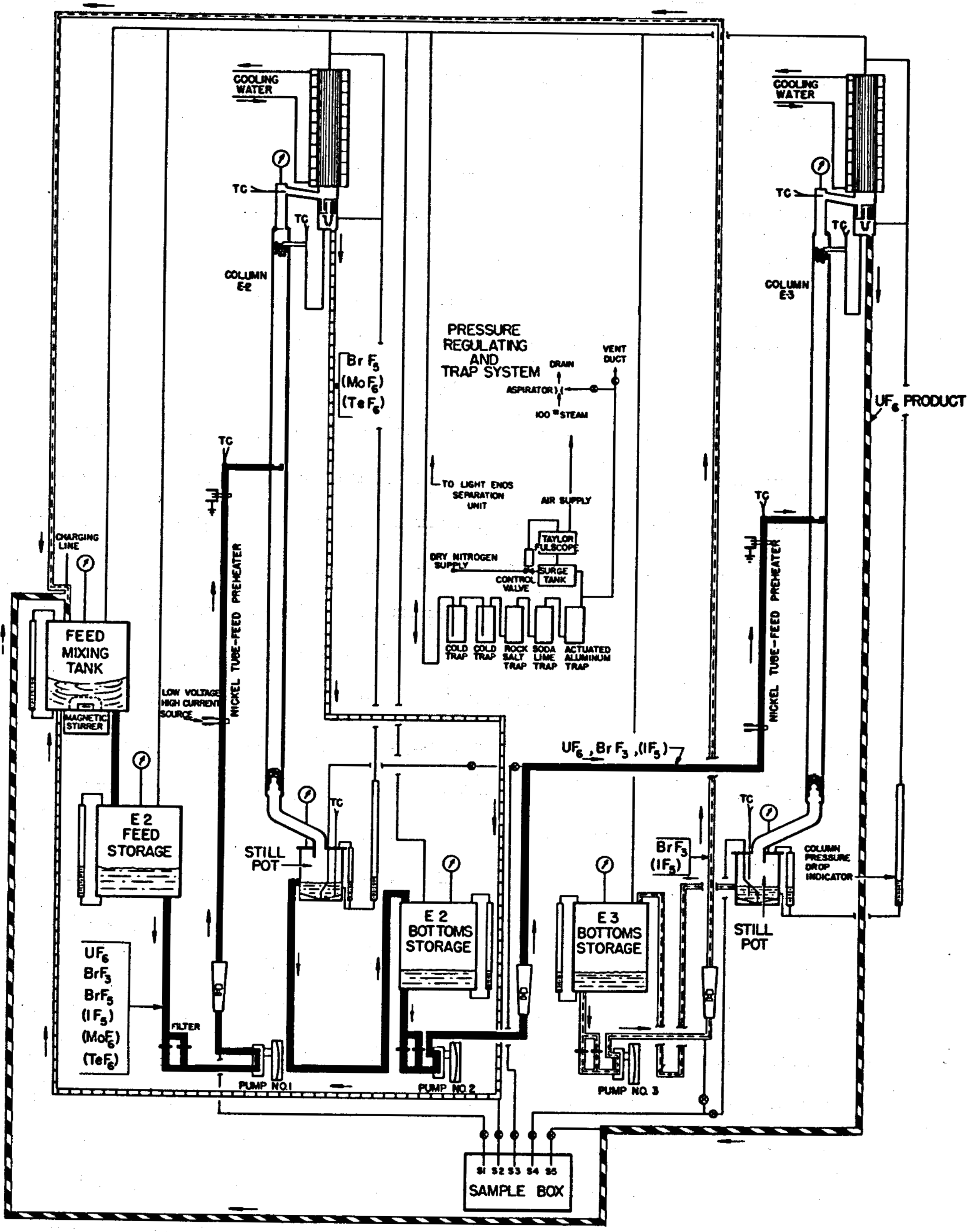

Fig. 12 - Flow sheet of Brookhaven light ends separation unit.

The liquid levels in the storage tanks and still pots were measured with fluorothene sight glasses. The condensers were water cooled and were equipped with liquid dividing heads which were specially constructed so that the gas flowed up from the column by a separate path and the condensed liquid flowed down through a gas seal to a solenoid-actuated nickel bucket which distributes the condensate between distillate and reflux streams. The pressure on the separations unit was regulated by means of an air-actuated diaphragm valve and Taylor fulscope combination as shown in Figure 12.

The feed preheaters for the columns consist of 6-ft lengths of 1/4-in. nickel tubing one end of which was grounded, the other end of which was insulated from the system with a teflon flare union in the line and was connected to a low voltage, high current transformer to permit heating of the nickel tube wall directly. Pressures at various parts of the system were measured with standard Bourdon tube gages. Iron constantan thermocouples in appropriate well structures were used throughout with the leads connected to recorders on the outside of the box.

Aluminum alloys (2S and 3S) were used for construction of most of the equipment. All liquid and gas lines were 2S and 3S 1/4-inch aluminum tubing with the exception of the "A" nickel feed preheaters and the 1/4-inch copper gas transfer lines to the trap system. Parker 17ST, 24ST and 14ST aluminum flare fittings were used in connecting the tubing to the various components of the system.

2. Light Ends Separation Unit - Data and Results

In order to test the system with fission product light end activity, a synthetic feed was made up which consisted of about 3 mol per cent uranium hexafluoride and 97 mol per cent bromine trifluoride to which were added the volatile fluorides from 45 grams of irradiated uranium tetrafluoride. The uranium tetrafluoride had received an irradiation of about 4×10^{18} neutrons/sq cm (3.5 weeks in the Brookhaven reactor) and had cooled for 30 days at the time of processing. The uranium tetrafluoride was fluorinated with a mixture of 100 ml of bromine trifluoride and 20 ml of bromine pentafluoride.

This feed was pumped to the first column at a rate of 1.74 gph. The column head was operated at total reflux and the heat to the feed and still pot was such that the feed was close to its boiling point and the still pot boilup rate was 90.3 gM/hr based on bromine trifluoride. Under these conditions 3.5 per cent of the tellurium activity entering with the feed left with the mixture of uranium hexafluoride and bromine trifluoride overflowing from the still pot. This bottom mixture was then fed at a rate of 1.39 gph to the second column where the uranium hexafluoride was separated from the bromine trifluoride. The second column was operated with a reflux ratio of 30 to 1, with the feed as liquid at the vaporization temperature and with a still pot boilup rate of 57.7 gM/hr of bromine trifluoride. Analysis for tellurium activity per gram of uranium hexafluoride in the uranium hexafluoride product, the feed and the still pot from samples taken during the run showed that the product uranium hexafluoride contained one-sixtieth of the activity of the feed to the second column. The tellurium activity per gram of still pot solution was only slightly less than that found per gram of feed, indicating, a closer association of the tellurium with the bromine trifluoride than would have been expected.

The over-all decontamination factor for tellurium for the two columns was thus about 1700. Since neither iodine nor molybdenum activity was found in the product uranium hexafluoride, the gross gamma decontamination factor for the runs was estimated to be about 10^6 and the gross beta decontamination factor about 2×10^5 based on the activity of the original 45 grams of uranium tetrafluoride. Analysis for bromine in the uranium hexafluoride product showed no detectable halide; analysis would have detected about 1 part bromine in 1000 parts uranium hexafluoride.

The still pot solution contained 0.0005 M fraction uranium hexafluoride in bromine trifluoride.

On the basis of these analyses, the number of plates in the second column was calculated to be a minimum of 18, based on the Raoult's law assumption and the respective vapor pressures. The HETP for the 9 ft of 2-in. column packed with 5/32-in. helics was thus estimated to be less than 6.3 in. Calculations of a similar nature on other runs yielded HETP values of between 4.5 and 6.0 in., roughly twice the values obtained when the column was originally tested with n-heptane and methylcyclohexane.

The distillation results indicate that when fission product tellurium in uranium tetrafluoride is fluorinated, part of the tellurium is present in a less volatile form than tellurium hexafluoride since it leaves from the bottom of the first column. However, on being feed to the middle of the second column the activity splits, a small part going overhead and part remaining behind. In later experiments[11] it was confirmed that partial reduction of radioactive tellurium hexafluoride to a non-volatile form by internal conversion reactions does occur. It was demonstrated, however, that bromine trifluoride reoxidizes this non-volatile material to volatile tellurium hexafluoride. It was also found that no non-volatile complex or compound is formed from mixtures of tellurium hexafluoride and uranium hexafluoride. Therefore the tellurium behavior in the pilot plant experiments just cited is different from the data indicated by laboratory work. Also in the high level uranium hexafluoride decontamination experiments carried out at Argonne on overall tellurium decontamination of 10^6 was obtained as compared with the overall factor of 2×10^3 just cited.

On January 20, 1953 a fire and an explosion occurred during a check out of the distillation columns described above. It is believed that the use of aluminum contributed to the difficulties which occurred in in this incident. The direct cause, however, was the breakage of a column feed line spraying interhalogen over combustable insulation. The equipment was badly enough damaged so that it was not rebuilt.

3. Continuous Dissolver

The Brookhaven group felt that the continuous distillation experiments established that continuous operation of this phase of a process for the uranium-plutonium system was possible. They have gone on to construct a continuous dissolver. It is hoped that the over-all data will indicate the feasibility of a completely continuous process of the type suggested by Figure 4.

In the newer Brookhaven unit it is planned to dissolve continuously about 5 pounds of uranium per hour. The dissolver is to be a pipe. The dissolver solution will circulate through the dissolver at about 50 gal/min or eight dissolver volumes per minute. The heat of the reaction is removed by circulating through a heat exchanger. The dissolver solution is to be continuously fed to an evaporator. The condensate from the evaporator is bromine trifluoride, uranium hexafluoride and an amount of bromine pentafluoride depending on the mode of operation of the dissolver; this is fed to a continuous column. The overhead from the column will be uranium hexafluoride with bromine pentafluoride while the bromine trifluoride will be removed from the bottom of the column.

An important contribution of the Brookhaven group to the development of fluoride volatility processes has been the demonstration that a modified Model E chempump may be satisfactory for interhalogen solutions. A detailed description of the equipment is not appropriate at this time since the equipment has not operated for an appreciable length of time. It is very likely that in 18 months such a description, along with run data, will be available in the open literature.

C. Chlorine Trifluoride Process - Oak Ridge National Laboratory

In the chlorine trifluoride pilot plant at Oak Ridge National Laboratory essentially three operations were carried out. The first was dissolution of the uranium, the second was distillation of the uranium hexafluoride from the dissolver solution, plutonium and fission products and the third was the recovery, in an aqueous solution, of the plutonium and fission product fluorides. This procedure followed the flowsheet given in Figure 6. A discussion of the data for three high level runs follows:

1. Dissolution.

In a typical dissolution about 2.5 kg of irradiated uranium, cooled about 90 days, was dissolved in 4.5 kg of dissolver solution at 30°C. The pressure of fluorine maintained on the system was allowed to vary from 30 to 50 psig. About 5 days were required to dissolve, at 30°C, all of a batch of uranium slices varying from 1/8 to 1/2 inch in thickness with a dissolver solution containing about 2 moles of chlorine trifluoride per mole of hydrogen fluoride. Using a dissolver solution having a chlorine trifluoride to hydrogen fluoride mole ratio of 0.3 to 1 at 80°C, the dissolution time for an unsliced slug 1.43 in. in diameter is estimated as 19 hours. When the reaction was complete, as indicated by the cessation of fluorine consumption, the reaction mixture was transferred, as a vapor, to the fractionating column. In the simple distillation from the dissolver a beta decontamination factor of 10^4 to 10^5 for reaction and simple distillation and a gamma decontamination factor of about 10^3 were achieved.

2. Distillation.

The distillation column was constructed of a 4 1/2-ft length of 3/4-in. Monel tubing packed with Podbielniak Heli-Pak. Under total reflux and a throughput of 200 ml/hr, the column had about 28 theoretical plates, giving an HETP (height equivalent to a theoretical plate) of 1.93 in. By suitably adjusting the throughput and reflux ratio the HETP of the column could be varied from 1.93 to 18 in. This distillation results obtained in the three hot runs are given in Table 14. The over-all beta decontamination factor for the process varied from 6×10^6 to 20×10^6, whereas the gamma decontamination factor was about 10^7. During the first

Table 14

SUMMARY OF DISTILLATION DATA AND DECONTAMINATION DATA FOR HIGH LEVEL RUNS

Run Number	1	2	3
Throughput, ml/hr	155	200	200
Reflux Ratio	59	13.7	7.5
HETP, in.	2.7	9.0	18
Theoretical Plates	20	6	3
Uranium Recovery[a]			
Product	58	80	76.5
Forecut	42	3.5	12.1
Heel		16.5	11.4
Decontamination Factors, Product UF_6[b]			
Pr, Y, Nd	3.4×10^6	10^6	3.2×10^6
Zr	9×10^5	$\sim10^7$	$\sim10^7$
Ru	7.5×10^5	$\sim10^7$	$\sim10^7$
Te	$\sim10^6$	7×10^6	$\sim10^7$
Cs	4×10^5	$\sim10^7$	$\sim10^6$
Ce	3×10^6	$\sim10^8$	5×10^6
Sr	$\sim10^7$	$\sim10^7$	10^7
Pu	7.3×10^4	10^5	2.5×10^5

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[a] Per cent of the uranium in the still charge.

[b] Decontamination factor is defined as $\left(\frac{\text{activity in charged Uranium per gram}}{\text{activity in product uranium per gram}}\right)$

run a low product yield of 53 per cent was obtained because a completely adequate distillation technique was developed only after the completion of this run. The last two runs were made with the column head operating at 66 C during the entire distillation. This method of operation ensured that all components in the system were liquid at all times. Since the column was a batch column and the holdup was about 20 to 25 per cent of the total amount of uranium hexafluoride charged, a product fraction containing 75 to 80 per cent of the uranium charged would be the largest fraction obtainable. The data in Table 14 show the decontamination effected by the process for individual fission products.

3. Plutonium Fluoride Dissolution

The plutonium and fission-product fluorides were recovered from the reactor pot with a 5 per cent aluminum nitrate solution at a pH of 0.5. The plutonium recovery solution contained about 1 gram of plutonium per liter. The dissolution was carried out at room temperature and required about two days. With temperatures near 100 C, a dissolution time of 2 or 3 hours is probable. The aqueous aluminum nitrate solution can be processed by modified solvent-extraction techniques.

V. Possible Improvements - Plutonium Hexafluoride

Although it is possible that a fluoride volatility process is somewhat less costly in the processing of uranium-plutonium systems than solvent extraction, the full potential of a volatility process has probably not been realized until plutonium is converted to the hexafluoride and separated from fission products through its volatility. A possible procedure might involve the following steps: (1) dissolve the uranium-plutonium alloy in bromine or chlorine trifluorides; (2) distill the dissolver solution leaving a non-volatile residue of plutonium and most of the fission products; then decontaminate the uranium hexafluoride by distillation; (3) heat the non-volatile residue to perhaps 400 C and fluorinate with fluorine to form plutonium hexafluoride; ruthenium and niobium pentafluorides will probably volatilize at this point; (4) decontaminate the plutonium hexafluoride by distillation; (5) remove the fission products by dissolving them in a fused fluoride and store them in this form.

There are certain areas for intensive development work if a flowsheet of this type is to be put on a firm basis. Early data on the preparation of plutonium hexafluoride indicated that a temperature in the neighborhood of 600 C was necessary to fluorinate plutonium tetrafluoride at a practical rate to the hexafluoride. Also, early data on the stability of the hexafluoride were discouraging as far as process applications. Recently, however, encouraging information has been accumulated on the kinetics of fluorination of plutonium tetrafluoride by fluorine gas, on the kinetics of decomposition and on methods of handling the material without decomposition. Experimental work needs to be started on the fission product removal and storage problems.

A. Kinetics of Fluorination of Plutonium Tetrafluoride

Experiments have been carried out at Argonne National Laboratory to establish the temperature necessary to achieve a practical rate of fluorination of plutonium tetrafluoride. These experiments were done on two different batches of material (designated as A and B) and on the residue obtained by dissolving plutonium uranium alloys in bromine trifluoride. The data consist of weight losses of plutonium tetrafluoride over a specified period. The data have been converted to a rate per square centimeter of exposed top surface area. It was assumed that the samples were uniformly spread over the bottom of the reaction boat. The data are shown in Table 15 and Figures 13 and 14. It can be seen that the rates are considerably greater for fluorination of residues from the bromine trifluoride dissolution of plutonium-uranium alloys than those obtained for fluorination of plutonium tetrafluorides from batches A or B. It can also be seen from a comparison of Figures 13 and 14 that the temperature coefficients of the rate of the reaction are different for the residues from the bromine trifluoride dissolutions. Extrapolation of the data obtained using dissolution residues indicates a rate of fluorination of plutonium tetrafluoride of about 200 grams hr^{-1} ft^{-2} at 300 C. Application

Table 15

FLUORINATION OF PLUTONIUM TETRAFLUORIDE AT ELEVATED TEMPERATURES

Flow system; fluorine at one atmosphere; flow rates 50-200 cc/min, tube 0.625 in ID. Rate calculated from weight loss and the top surface area of the sample. Surface area calculated from the reaction vessel geometry, weight and bulk density of 1.3 g/cc. (Experimental for batch A.)

			Rate (mg hr^{-1} cm^{-2})			
Temp (C)	Sample wt[a] (mg)	Time (min)	PuF_4 Batch A	PuF_4 Batch B	PuF_4 5% Pu-U Alloy Dissolution[b]	PuF_4 10% Pu-U Alloy Dissolution[b]
25	77.4	30	0			
200	54.1	60	2.5			
200	44.3	75		3.0		
200	38.5	30			41	
250	54.1	45	2.9			
250	49.1	45	4.2			
250	52.1	120		9.9		
250	41.2	20			64	
300	52.3	45	15			
300	321.5	20	27[c]			
300	632.4	20	28[c]			
300	54.0	45		27		
300	49.5	6			185	
300	48.2	6			224	
375	57.2	20	74			
375	318.1	20	98[c]			
375	629.7	20	80[c]			
375	52.1	20		91		
375	49.6	10		82		
375	95.8	10			226	
375	53.1	6			293	
375	42.0	5			222	
375	45.7	6			222	
375	87.3	6			314	
375	175.3	6				285
375	48.4	6				175
450	50.0	5		242		
500	57.1	5	281			
500	46.7	5		367		
500	39.1	1			734	
600	47.7	1.5	586			
600	51.8	1.5		826		

---

[a] Initial sample weight. Surfaces areas are calculated on the basis of average sample weight.

[b] Residue from the dissolution of alloy in bromine trifluoride with subsequent removal of bromine fluorides and uranium hexafluoride.

[c] Special reaction vessels. Top surface area accurately controlled at 2.11 cm^2.

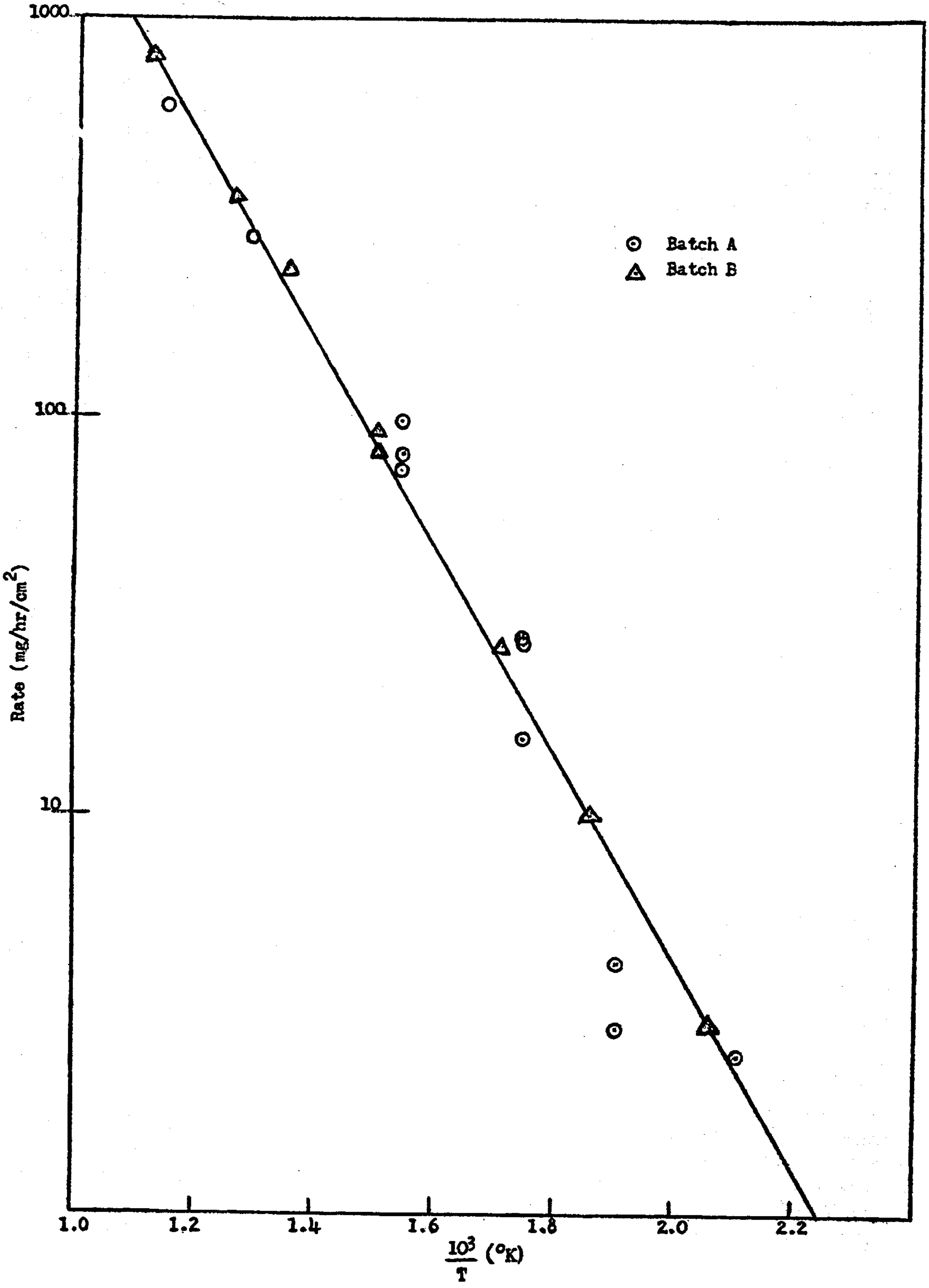

Fig. 13 - Rate of fluorination of plutonium tetrafluoride. Submitted by personnel of Argonne National Laboratory.

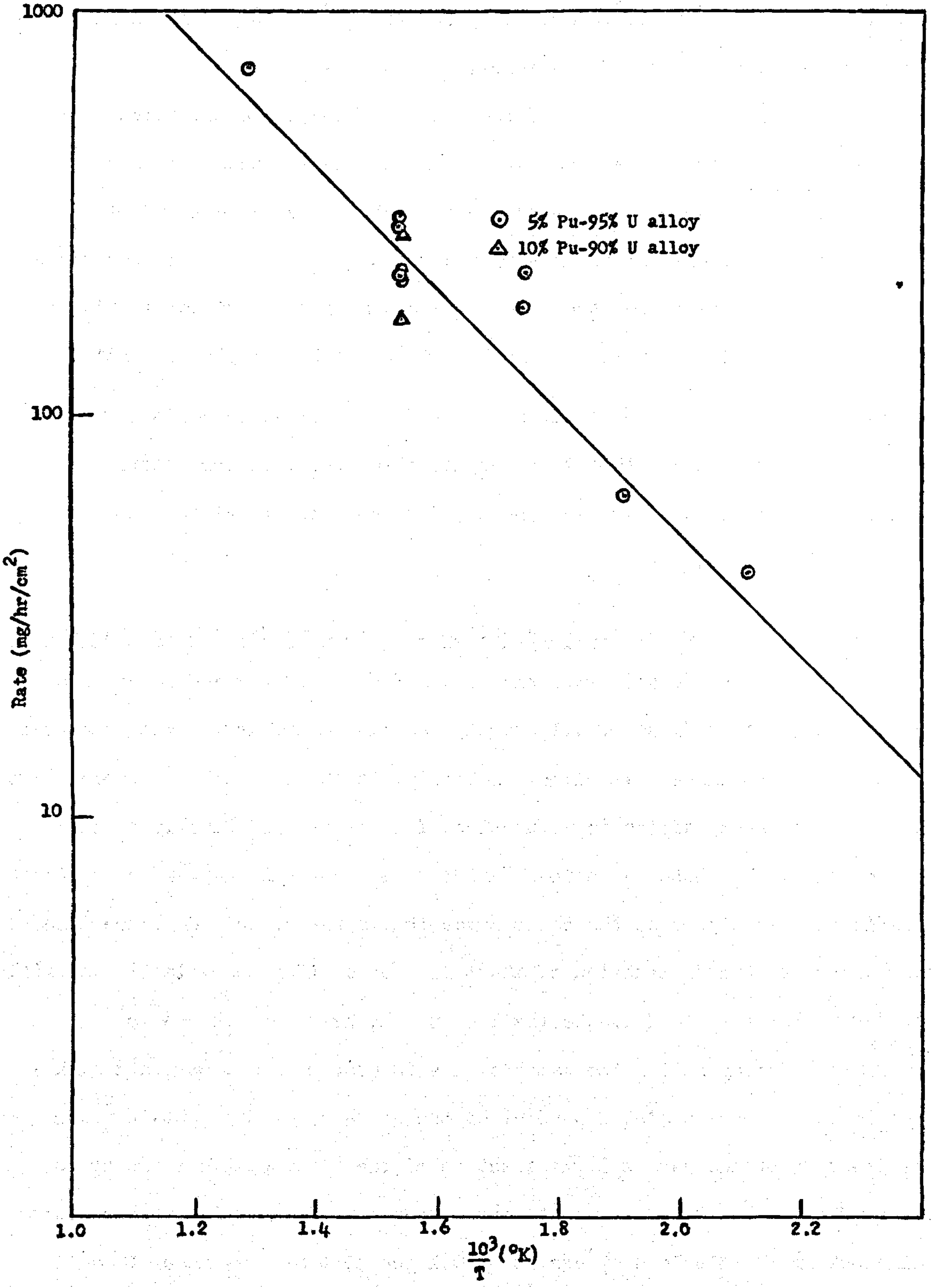

Fig. 14 - Rate of fluorination of plutonium tetrafluoride residues (bromine trifluoride reaction residue). Submitted by personnel of Argonne National Laboratory.

of this value to process scale equipment should recognize the fact that the geometry of the laboratory apparatus restricted the depth of the tetrafluoride to about 1.25 mm for an average (50 mg) sample.

A more detailed study of the rate of fluorination of batch A of plutonium tetrafluoride was undertaken. Samples were exposed repeatedly to fluorine at the same temperature and the weight loss determined at selected times. These experiments were carried out at various temperatures. It was found that even when the fluorination was carried out until only 10 per cent (at 200°C) or 1 per cent (at 500°C) of the original starting material remained the rate of fluorination did not decrease seriously.

It is believed that these experiments show that the reaction of fluorine and plutonium tetrafluoride proceeds at a practical rate at modest temperatures.

B. Stability of Plutonium Hexafluoride and Some Methods for Handling It

Plutonium hexafluoride has acquired at well deserved reputation for instability. It is first of all, highly reactive and thus subject to chemical reaction with container materials. Secondly, it is chemically unstable. The rate of this decomposition is a function of temperature. Finally it is decomposed by the alpha radiation of plutonium. For example when plutonium hexafluoride is stored as the solid phase the amount of this decomposition corresponds to the destruction of about 1.5 per cent of the volatile material per day.[5] In order to decrease the loss of the hexafluoride due to irradiation decomposition the material can be stored as a vapor in a nickel container. In this state, dependent on the geometry of the container and the pressure of the gas, a large fraction of the alpha particle energy is absorbed by the walls of the container and does not result in decomposition. Weinstock and Malm's losses were about 0.1 per cent per day under these conditions. Thus, the thermal instability and radiation decomposition can be minimized by keeping the containers below 100°C and by keeping the plutonium hexafluoride in small amounts, diluted with an inert material, or in the gaseous state where possible.

Nickel is one of the best container materials and the losses on vessel walls due to chemical reaction can be minimized by proper prefluorination. The effect of prefluorination of nickel equipment with respect to recovery of plutonium hexafluoride is illustrated by the results from several experiments shown in Table 16. In these experiments the equipment was prefluorinated under various conditions. Plutonium hexafluoride was condensed in a nickel trap and then revaporized in a helium stream. The loss in volatile plutonium hexafluoride was a measure of the inadequacy of prefluorination. It also must be remembered that radiation decomposition was occuring simultaneously. Prefluorination for 90 minutes at 560°C is

Table 16

RELATIONSHIP OF PREFLUORINATION CONDITIONS TO VAPORIZATION OF PLUTONIUM HEXAFLUORIDE FROM A NICKEL TRAP

Equipment: The trap consisted of a "U" tube of 3/8 in. O.D. nickel heated by resistance winding. Length about 35 cm, internal surface area approximately 70 cm^2.

Experimental Conditions: PuF_6 vaporized from trap by a helium flow rate of 100 cc/min for 30 min. PuF_6 was kept as a solid in the trap for a period of 20 minutes to one hour. 12 to 21 mg of plutonium used in each experiment.

		Per cent PuF_6 Decomposed (i.e. amount remaining in trap)			
Prefluorination Temp (C)	Time of Prefluorination (min)	15	30	60	90
280		100			
300			71		
330				70	
420			(47)		
450			70		8.7
490			(28)		
560			69		4.4

apparently sufficient to allow recovery of much of the plutonium. The two figures in parentheses seem to be out of line for an unknown reason. These experiments are, of course, with rather small amounts of plutonium. When the amount is increased it is believed that a smaller fraction will be lost. Experiments need to be carried out to tests this assumption.

In addition a study was made of the decomposition of plutonium hexafluoride on nickel wool in which decomposition temperature, prefluorination conditions and the atmosphere (helium or fluorine) were varied. In these experiments nickel wool was inserted in a nickel tube furnace. Plutonium hexafluoride was passed through the nickel wool and caught in a cold trap. The nickel wool was removable from the tube furnace and the plutonium was recovered by leaching. The plutonium found on the nickel wool was thus a measure of the amount of plutonium hexafluoride lost by decomposition. The area of the nickel wool was estimated to be 1500 cm^2 and was held in a tube 0.625 inch ID and 10 inches long. The prefluorination conditions of the nickel wool were varied as well as the decomposition temperature. The hexafluoride was prepared by passing fluorine over plutonium tetrafluoride at 500°C. When the decomposition was studied in the presence of fluorine the gaseous mixture was passed directly into the nickel wool. When the decomposition was studied in the absence of fluorine the hexafluoride was trapped in a liquid nitrogen trap placed between the preparation furnace and the nickel wool decomposition zone. The plutonium hexafluoride was then removed by volatilization in a helium stream purified by passing through a charcoal trap immersed in liquid nitrogen. The data are given in Table 17.

The following conclusions may be drawn:

(1) The decomposition product can be refluorinated at modest temperatures. (See vertical column 2.) Thus, with no prior prefluorination of the nickel wool, less plutonium hexafluoride decomposition product is found as the temperature increases if the transport of the hexafluoride is done in

Table 17

DEPENDENCE OF RATE OF DECOMPOSITION OF PLUTONIUM HEXAFLUORIDE ON TEMPERATURE

Definitions:

$$\text{Residence time} = \frac{\text{volume of packed tube}}{\text{flow rate of carrier gas}}$$

$$\%\ PuF_6\ \text{decomposed/sec.} = \frac{(PuF_6\ \text{decomposed})(100)}{(PuF_6\ \text{used})(\text{residence time})}$$

Experimental Details:

Linear flow rate about 12.5 cm/min.
Residence time varied from 70 to 200 seconds.
Surface area of packing about 1500 cm^2.
Experiments used 1 to 20 mg of plutonium.
Nickel packing was prefluorinated except where indicated otherwise.
Helium used as carrier gas except where noted.

Decomposition Temperature (C)	% PuF_6 Decomposed per Second									
Prefluorination Conditions: Temp (C)	a	210	250	350	350	450	450	450	560	560
Prefluorination Conditions: Time (min)	a	75	30	30	90	30	60	90	30	90
120	1.8^b	0.09^b		0.01^c 0.13 0.13						
180	0.9^b		0.05^b	0.12		0.51 0.30 0.04^c	0.63	0.12 0.07	0.07	0.11
240	0.3^b			0.94 0.01^b	0.82	0.38				

[a] Nickel packing not prefluorinated.

[b] Fluorine used as carrier gas instead of helium.

[c] Doubtful values.

the presence of fluorine. Since it is to be expected that the rate of decomposition will increase with increasing temperature the decomposition product can be assumed to be refluorinated. In experiments not reported here it has been found possible to move the decomposition product through a nickel wool plug by fluorination below 250°.

(2) As prefluorination conditions become more severe, less plutonium hexafluoride decomposes in the absence of fluorine. For example, for a decomposition temperature of 240°C the per cent decomposing decreases from 0.9 to 0.4 as the prefluorination temperature is raised from 350 to 450°. For a decomposition temperature of 180° the percent decomposed per second decreases as the prefluorination conditions become more severe although the trend is not very marked.

(3) The effectiveness of transporting plutonium hexafluoride in a fluorine atmosphere can be appreciated by comparing the experiments done with and without fluorine when the equipment was prefluorinated for 30 minutes at 350° and the decomposition studied at 240°, i.e. 0.9 per cent vs 0.01 per cent.

The results of these experiments indicate that plutonium hexafluoride can be transported in a fluorine atmosphere when (1) the temperature is 250° or higher and (2) an excess of fluorine is present. It is believed that experiments are necessary to clarify further the proper conditions for keeping and transporting plutonium hexafluoride. These experiments should be carried out at higher plutonium levels.

The Knolls Atomic Power Laboratory has also carried out work with plutonium hexafluoride. This program has not had the direct objective of the development of a separations process. The investigators were interested in (a) methods of preparing the hexafluoride by induction heating, (2) some of the chemical reactions of the hexafluoride and (c) the consumption of plutonium hexafluoride on possible materials of construction. The latter program objective is particularly pertinent to separations process development. These investigators have made a study of the stability of the fluoride layer resulting from prefluorination at temperatures from 75 to 175°C. The samples were prefluorinated at the selected temperatures for 1 hour at 25 mm pressure. The prefluorination was followed by an exposure to 10 mm pressure of plutonium hexafluoride for 1 hour at 75°C. The samples were then counted and the data reported in micrograms cm^{-2}. The data are shown in Figure 15. For all the metals except nickel the optimum prefluorination temperature lies within the range studied. The abrupt rise in deposition rate for the other metals suggests a partial destruction of the passivating metal fluoride layer due to enhanced fluorine corrosion as the prefluorination temperature is increased. It is not appropriate to compare these data with the Argonne data just cited since the range of prefluorination conditions is quite different. However it appears that the data do not disagree.

C. Corrosion Studies Pertinent to Plutonium Hexafluoride Preparation

Corrosion studies have been carried out on nickel in a fluorine atmosphere to see if corrosion difficulties would be expected in the plutonium hexafluoride preparation step. The data are given in an abbreviated form in Table 18. These data indicate that even at temperatures of 550°C nickel may be a satisfactory material of construction. Since, it was found that the preparation proceeds at a much more rapid rate than originally anticipated an operating temperature of much less seems reasonable. These corrosion studies were not carried out in the presence of plutonium and such a study should be eventually done. There are indications that the presence of plutonium does not complicate the corrosion problem. A boat used for the preparation of plutonium hexafluoride under a variety of conditions was sectioned and examined metallographically by R. J. Dunworth and L. Kelman of the Metallurgy Division of Argonne National Laboratory. It was found that there was no evidence of intergranular penetration.

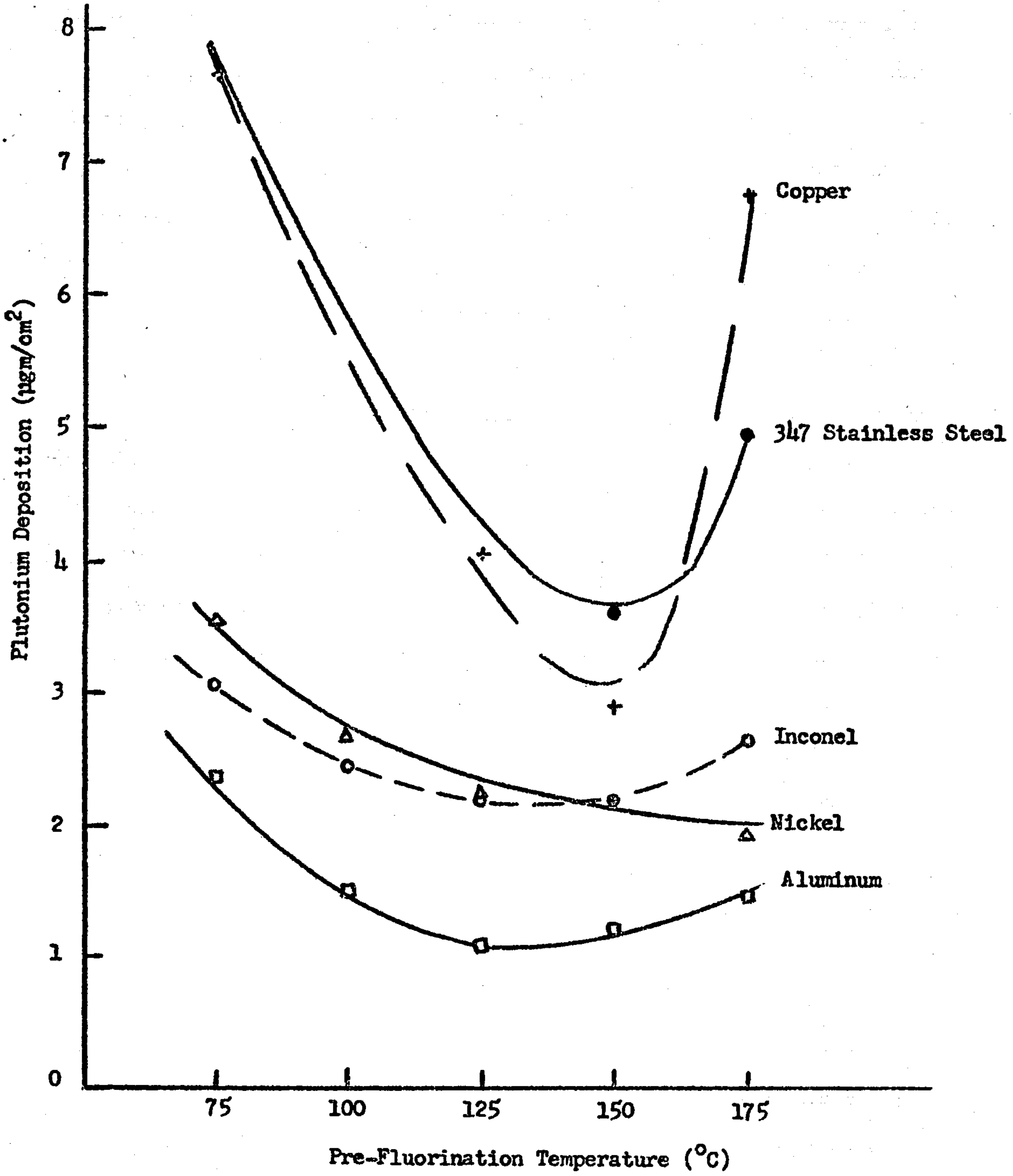

Fig. 15 - Effect of prefluorination temperature on subsequent plutonium deposition.

VI. Comparison of Fluoride Volatility and Conventional Processes

Of prime interest is a comparison among a fluoride volatility process with aqueous plutonium recovery, an all fluoride volatility process and an aqueous solvent extraction process. Some idea may be gained by considering the block diagrams in Figures 16, 17 and 18.

Table 18

CORROSION OF MATERIALS IN GASEOUS FLUORINE AT ATMOSPHERIC PRESSURE

Sample area: 1 to 2 in^2
Time: 2.5 to 6 hours

Corrosion data calculated from weight gains of sample.

	Corrosion Rate mils/year		
Temperature, °C	550	650	750
Material			
Nickel	4	60	350
Monel		40	2900
Inconel	3200	7100	25000
Copper	110	430	750

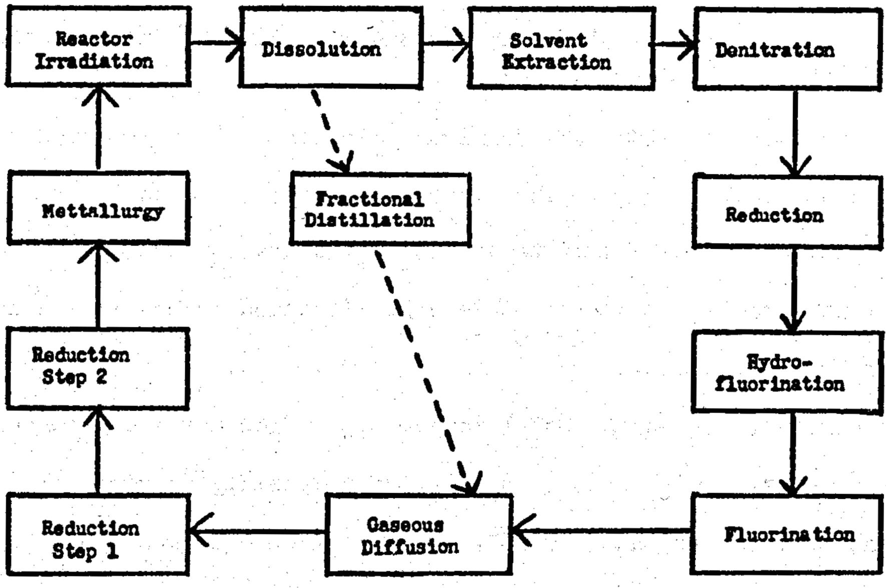

Fig. 16 - Uranium cycle - plutonium production reactor. Simplification introduced by fluoride volatility process.

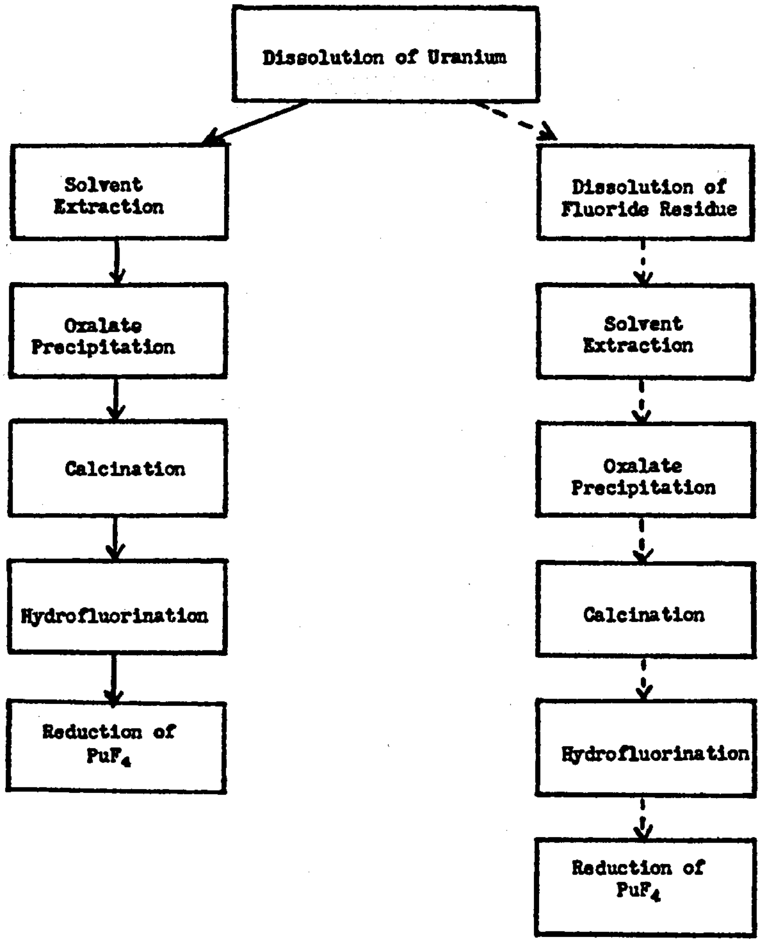

Fig. 17 - A typical plutonium cycle - plutonium production reactor. Fluoride volatility process.

Let us first consider the uranium cycle for a plutonium producing reactor shown in Figure 16. The impressive simplification in the number of steps in obvious. Instead of ten steps in the uranium cycle there are only six. It is also important that this simplification occurs in the handling of the bulk constituent.

In Figure 17 is shown the plutonium block flowsheet for the conventional procedure compared with that of a fluoride volatility process. It is important to remember that the solvent extraction equipment for the fluoride volatility process is scaled to handle only the plutonium, while that for the conventional process handles the bulk constituent. It is clear from this figure, however, that plutonium handling will not be greatly simplified by the fluoride volatility process. Figure 18 shows the simplification involved if an advanced volatility process is achieved.

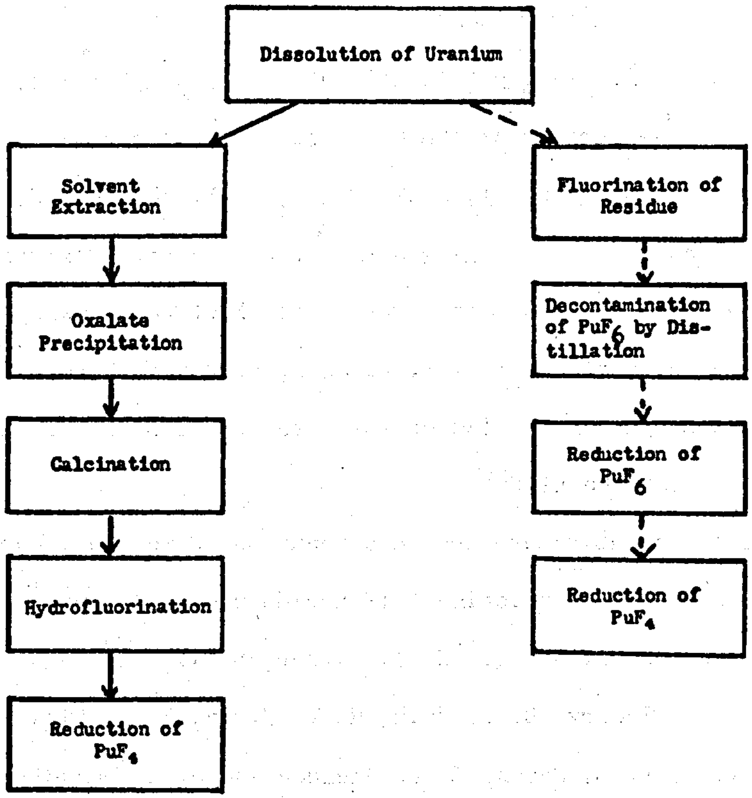

Fig. 18 - A typical plutonium cycle - plutonium production reactor. Advanced fluoride volatility process.

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*Special Scientific Employee on loan from Union Carbide Nuclear Company.
**Special Scientific Employee on loan from Hercules Powder Company.

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FLUORIDE VOLATILITY PROCESS FOR HIGH ALLOY FUELS

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May 1, 1957

Introduction

The processing of high alloy uranium fuels with good corrosion resistance is difficult by aqueous methods. This is the case for fuel elements with a core or cladding of zirconium or stainless steel. An attractive alternative is fused salt dissolution of these materials in conjunction with fluoride volatility processing. The essential steps of a fused salt--fluoride volatility process are shown schematically in Fig. 1. The fused salt dissolution converts the solid fuel alloy into a liquid containing UF_4, which is readily fluorinated to volatile UF_6. The UF_6 product is decontaminated in the last step to the extent required by future use.[1-4]

The fused salt--fluoride volatility process has a number of advantages over aqueous processing. A major advantage is that the product UF_6 is returnable to either the diffusion process or metallurgy without many of the chemical conversion steps necessary in aqueous processing. The fission product waste is also more highly concentrated and in a solid form convenient for disposal. The absence of water reduces the criticality problem and makes the process applicable to highly enriched fuels. The nature of the process indicates a high plant capacity relative to aqueous processing although not as high as that of metallurgical processing.

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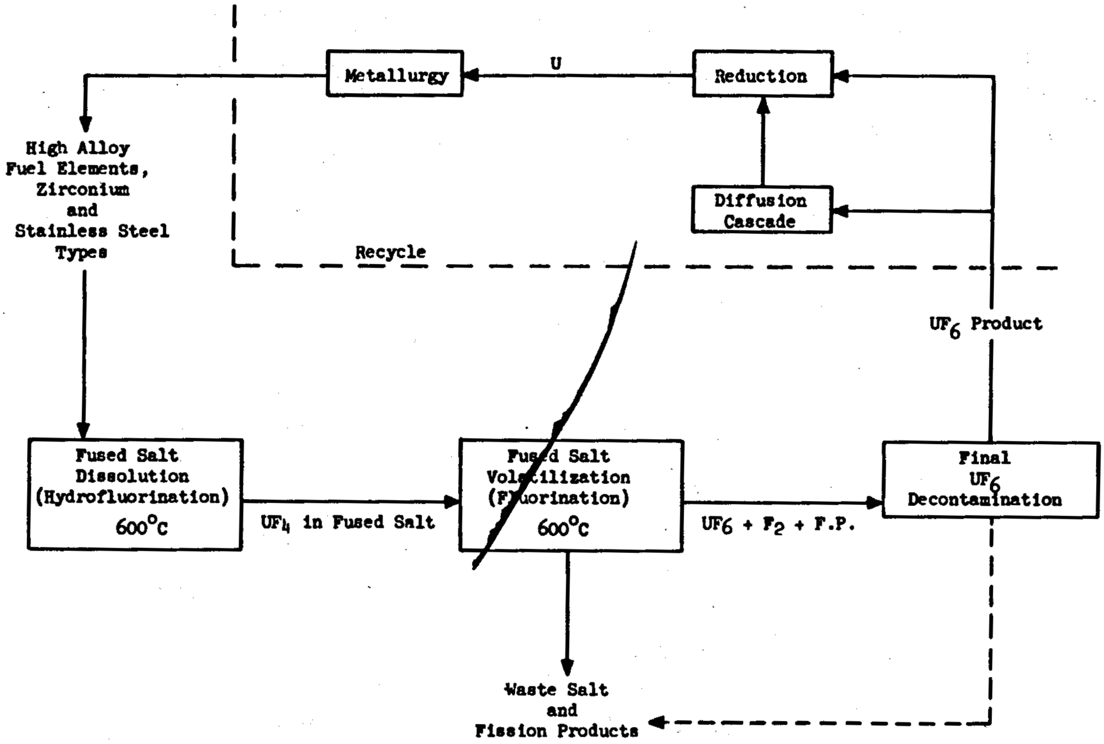


Fig. 1 Fused Salt Volatility Process Cycle

The material presented here is a brief survey of development work on the fused salt--fluoride volatility process being carried out at the Argonne and Oak Ridge National Laboratories. It covers the fused salt dissolution and fluorination work in addition to NaF absorption as a proposed new technique for decontaminating and handling the product UF_6.[5-7] The alternative of distillation has been adequately described.

Process Alternatives

A variety of methods and conditions may be applicable in each of the three major steps of the process. Some of the procedures tested are given in Table 1. In the fused salt dissolution and fluorination steps there is a wide choice in the salt system and fluorinating agent. The essential requirement of the salt system is compatibility with all the fluorides of the fuel element. In early work low-temperature melts, e.g., $NaHF_2$ and KHF_2, were tried with generally unsatisfactory results. Although corrosion is higher, the use of high-temperature binary or ternary melts is preferred in the current work at both Argonne and Oak Ridge National

Table 1. Fused Salt--Fluoride Volatility Process Methods

System		Temperature (°C)
Dissolution		
KHF_2 (HF)		>250
$NH_4F\cdot HF$ (HF)		>125
$KF\cdot BrF_3$ (BrF_3)		>335
$\underline{NaF\text{-}ZrF_4}$	F_2, BrF_5, HF	$\underline{600}$
$\underline{NaF\text{-}LiF}$		$\underline{700 \longrightarrow 600}$
NaF-LiF-KF		>450
KF-LiF		>500
UF_6 Volatilization		
$\underline{NaF\text{-}ZrF_4}$	BrF_5, ClF_3, F_2	$\underline{600}$
UF_6 Decontamination		
Distillation	$BrF_5\text{-}BrF_3\text{-}UF_6$ $ClF_3\text{-}ClF\text{-}UF_6$ UF_6	~ 100
NaF absorption		100-400
Gas filtration		---
Sorption		---

Laboratories, with anhydrous hydrogen fluoride as the dissolution agent. The most attractive melts are underlined in the table.[5,8]

The dissolution procedure is based on the following reaction for uranium (or uranium oxide):

$$U(\text{solid}) + 4HF(\text{solution}) \longrightarrow UF_4(\text{solution}) + 2H_2(\text{gas})$$

with a similar reaction for structural metals and fission products. In the second, or fluorination, step a fluorination agent such as BrF_4, ClF_3, or F_2 is used. In the case of F_2 the reaction is

$$UF_4(\text{solution}) + F_2(\text{gas}) \longrightarrow UF_6(\text{gas})$$

In some work F_2 or BrF_5 achieved both dissolution and UF_6 volatilization. There seems to be little economic justification for this, however, in view of the much lower cost of hydrogen fluoride.

In the third major step of the process, the alternatives for complete decontamination of the UF_6 are distillation, absorption, or gas filtration.

It is probable that gas filtration would always be used in conjunction with one of the other methods.

Flowsheets

Emphasis is being placed on use of $NaF-ZrF_4$ salt for processing fuel elements. The Argonne and Oak Ridge fused salt processing schemes differ in two principal points. Argonne has emphasized the use of BrF_5 rather than F_2 as the fluorinating agent, and Oak Ridge has proposed that the decontamination of UF_6 be carried out by a NaF absorption-desorption cycle rather than by distillation. The two processes are illustrated schematically in Figs. 2 and 3.

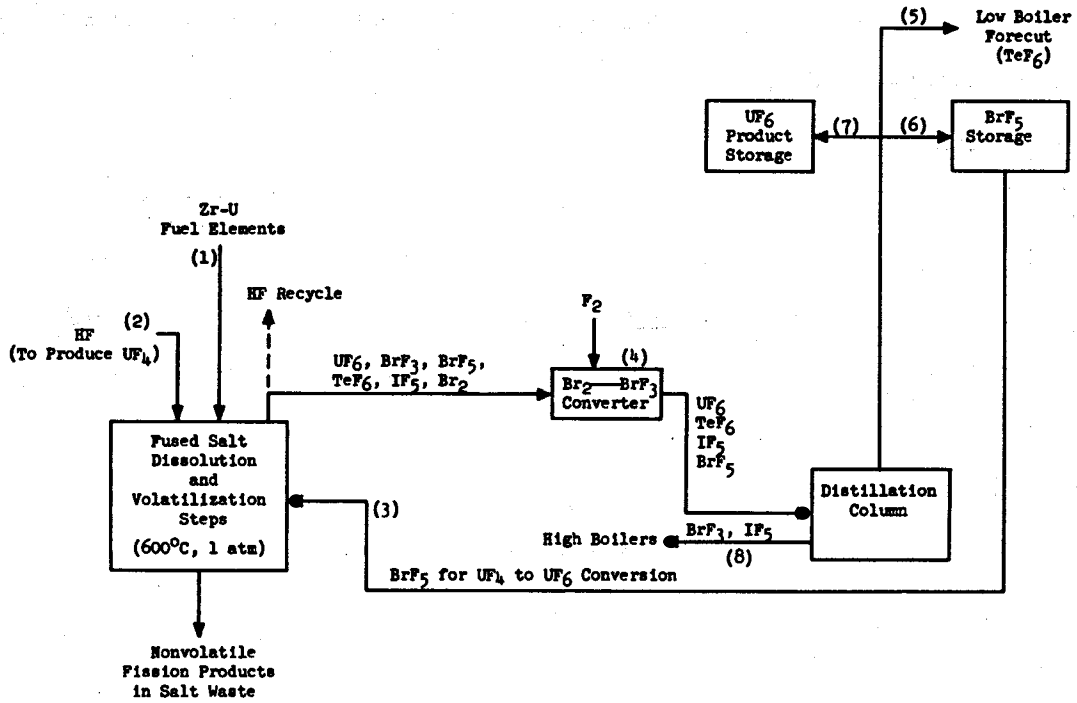
Dissolution Step

Points of interest in the hydrofluorination step include:

1. Geometry and type of gas-salt contactor.
2. Composition of melt
3. HF sparging rate
4. Pressure
5. Temperature
6. Metallurgical variations.

The $NaF-ZrF_4$ melt has been studied the most completely with respect to these variables. It has proved difficult to evaluate the relative importance of these factors owing to their independence. The HF sparging rate, pressure, and temperature are important, possible because of the necessity of keeping the salt saturated with HF. The salt composition is also important since it changes continually during batch dissolutions. The effect of temperature on the dissolution rate is small (Tables 2 and 3).[5,8]

The $NaF-ZrF_4$ system is suited to the dissolution of zirconium-containing fuel elements. A convenient initial salt composition would be 40 or 45 mole % ZrF_4 with the final concentration being 55 to 60 mole %. A



(Numbers in parentheses indicate operational order.)

Fig. 2 ANL Fused Salt Volatility Process Flowsheet

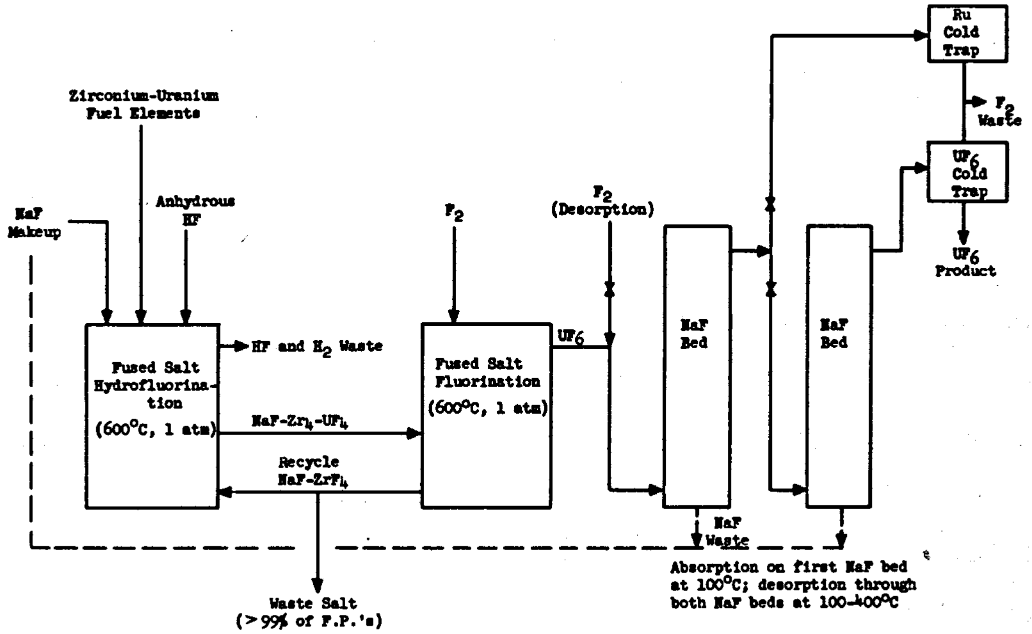


Fig. 3 ORNL Fused Salt Volatility Recovery Process Flowsheet

Table 2. Effect of HF Sparging Rate and Pressure on Dissolution at 600°C in NaF-ZrF_4 Medium

Material dissolved: zirconium-tin-uranium alloy, 1.5% tin, 1% (over-all) uranium, remainder zirconium

Pressure (atm)	HF Rate (g/min)	Penetration Rate (mils/hr)
1/2	0.25	2.8
1/2	0.42	5.6
1	0.70	5.2
1	0.66	7.2
2	0.43	5.6
2	1.14	15.0

Table 3. Dissolution of Zirconium in Fluoride Melts by Hydrofluorination

Melt	Composition (mole %)	Dissolution Rate (mils/hr) 600°C	Dissolution Rate (mils/hr) 700°C
LiF-NaF	57-43	---	48
LiF-NaF-ZrF_4	35-27-38	18	33
LiF-NaF-ZrF_4	26-19-55	0.4	15
NaF-ZrF_4	65-35	30	---
NaF-ZrF_4	50-50	15	18
NaF-ZrF_4	40-60	3	---

second dissolution would be made by taking part of this salt (discarding the remainder) and re-enriching with NaF.

A second attractive alternative is to use a LiF-NaF melt (57-43 mole %) at 700°C to avoid any initial ZrF_4 inventory. There would be no need of salt recycle in this case. Some typical corrosion rates for the LiF-NaF-ZrF_4 case are given in Table 3.

Consideration has been given also to processing stainless steel fuel elements (Table 4) in either NaF-ZrF_4 or LiF-NaF-ZrF_4 mixtures. The use of a higher temperature is desirable in this case to increase the solubility of FeF_2, CrF_2, and NiF_2.

The behavior of radioactive fission products during dissolution of power reactor fuel elements in fused fluorides has an important bearing on the later process steps. Several tests showed that either HF does

Table 4. Effect of Solvent Composition and Temperature on Type 347 Stainless Steel Dissolution Rate

Solvent	Composition (mole %)	Temperature (°C)	Dissolution Rate (mil/hr)
$NaF-ZrF_4$	50-50	600	0.3
	50-50	700	4.2
	50-50	800	5.4
	43-57	700	10.2
$NaF-LiF-ZrF_4$	27-35-38	600	3.0
	27-35-38	700	6.0
	19-26-55	600	0.6
	19-26-55	700	6.0

not form the more volatile fluorides, such as IF_7, MoF_6, TeF_6, and RuF_5, or that complexes are formed between these compounds and the fused fluoride. Data presented in Table 5 show that 0.01% or less of the gross activity was volatilized when uranium metal containing a large percentage of the fission products which form volatile fluorides was dissolved. The volatilization of uranium is completely negligible in the dissolution step. Later data have indicated that niobium is the largest contributor to the activity of the waste HF in long-decayed fuel although accounting only for a small fraction of the total niobium activity present.

Table 5. Volatility of Fission Products during Uranium Dissolution

Uranium dissolved: 6 g
Uranium irradiation: 40 Mwd/ton, decayed 21 days
Fused salt: 67 g of 50-50 mole % $NaF-ZrF_4$
Temperature: 650°C
HF rate: 20 ml/min

Activity	Activity Volatilized (% of Total) Run 1	Run 2
Gross β	1.3×10^{-4}	0.012
I	0.030	0.4
Te	2.0	---
Mo	0.2	---
Ru	0.005	0.026
Nb	0.0015	0.74

UF_6 Volatilization Step

The recovery of uranium as UF_6 by fluorination of fused salt is accomplished with little difficulty. Data with different fluorination agents show that more than 99.9% volatilization is possible (Table 6). However, the chemistry of the fluorination step is probably complicated by the formation of intermediates and the presence of impurities. This is true particularly at higher initial uranium concentration melts where an induction period is evident (Fig. 4).

Table 6. Summary of Data from Uranium Recovery Runs at 600°C

Material	Weight (g)	Charge (moles)		Sparge Gas	Sparge Rate[b]	Time (min)	Pressure (atm)	U Retained in Melt (% of charge)
		Melt[a]	UF_4					
Zircaloy	73	4.0	0.0031	BrF_5	1.0×10^{-3}	15	1	9.9
						30		0.7
						60		0.1
						90		0.4
Uranium	0.96	2.4	0.0040	F_2	13.3×10^{-3}	15	1	0.03
						30		0.01
						45		0.01
						60		0.01
Zircaloy	58	2.6	0.0024	BrF_5	8.7×10^{-3}	15	1	0.11
						30		0.03
						45		0.03
						60		0.03
UF_4	1.06	2.6	0.0034	ClF_3	5.2×10^{-3}	15	1	0.04
UF_4	0.98	2.6	0.0031	BrF_5	1.4×10^{-3}	15	0.5	52.2
						30		0.46
						45		0.02

[a] Approximately equimolar in NaF and ZrF_4.

[b] Sparge rate $= \frac{\text{moles fluorinating agent}}{\text{hour} \times \text{ml melt}}$.

The behavior of activity in the fluorination step is probably not too dependent on the type of fluorination agent. The results for F_2 show that decontamination is high for the nonvolatile fission product fluorides and low for those that are volatile (Table 7). In the case of short-decayed fuel much iodine and tellurium activity is also volatilized, resulting in low gross decontamination.

Final UF_6 Purification Step

There is no doubt that distillation could be used as the last step in the process. In this paper an effort will be given to describe the use of NaF absorption as a basis for decontaminating UF_6 (ORNL flowsheet,

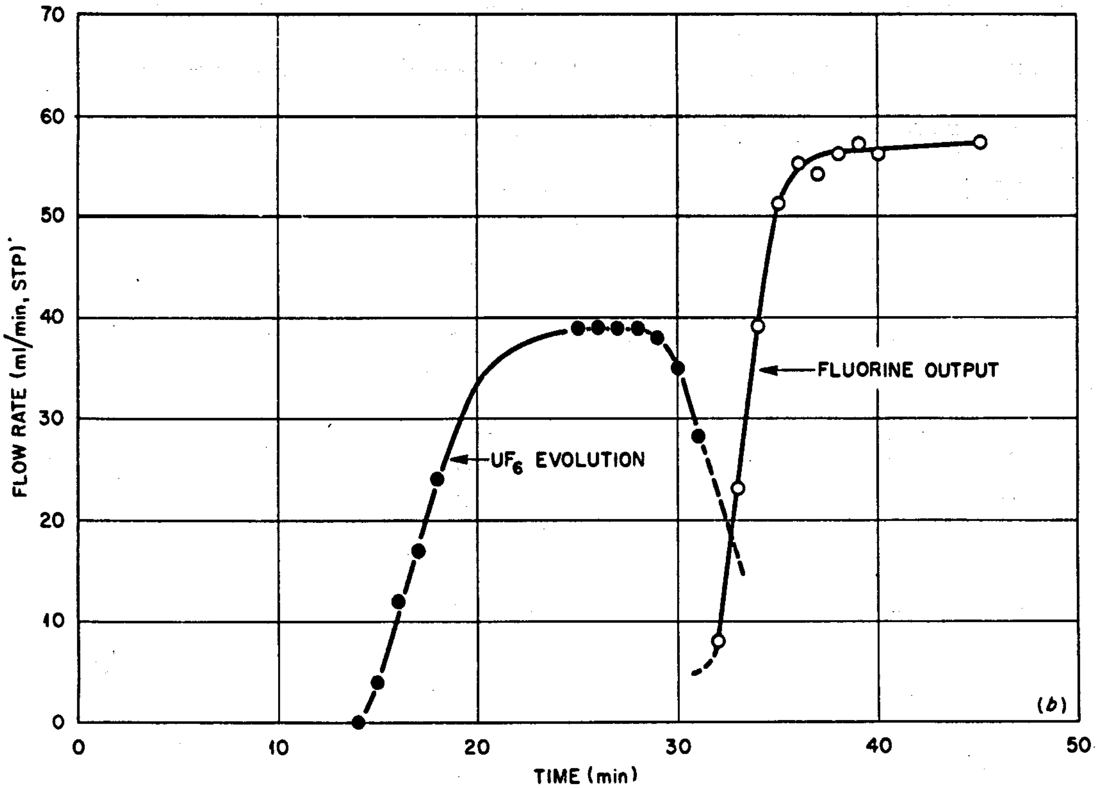


Fig. 4 Kinetics of Fluorination Step Using F_2 With $NaF-ZrF_4-UF_4$ (48-48-4 Mole %)

Table 7. Decontamination of Uranium by Fluorination from Molten $UF_4-NaF-ZrF_4$

Charge: $NaF-ZrF_4-UF_4$ (48-48-4 mole %) with fission product activity level of 10^5 gross beta counts/min/mg U

Conditions: F_2 bubbled through fused salt at 600-650°C in a nickel reactor

Fission Product	Beta Decontamination Factors[a] Run 1	Run 2	Run 3
Gross	260	110	230
Ruthenium	14	6	17
Zirconium	4.2×10^3	1.4×10^3	1.9×10^3
Niobium	13	6	5
Total rare earths	2.1×10^4	3.0×10^4	6.0×10^3

[a] Decontamination factor = quotient of initial activity per unit of uranium and product activity per unit of uranium.

Fig. 3). The reaction is described by the equation

$$\mathrm{UF_6(gas) + 3NaF(solid) \longrightarrow UF_6 \cdot 3NaF(solid)}$$

This reaction is reversible in that an equilibrium partial pressure of UF_6 exists over the complex. The dependence of the equilibrium partial pressure on temperature in the range 80 to 350°C was studied by the transpiration method for a better understanding of the process operation (Fig. 5). The effectiveness of NaF at 100°C in absorbing UF_6 is due to the small equilibrium pressure of about 10^{-3} mm Hg. This corresponds to a UF_6 cold-trap temperature of less than -80°C. At 360°C the equilibrium pressure is approximately atmospheric, which accounts for the relative ease of desorption.[7]

The separation of UF_6 from fission products in the NaF absorption step may be described as gaseous chromatography. A summary of the activity distribution in several runs (Table 8) shows that a three-way split occurs between uranium, ruthenium, and niobium. A large part of the ruthenium activity passes through the first NaF bed when the UF_6 is being absorbed at 100°C. The niobium is also absorbed. Desorption of the UF_6 at 100 to 400°C, however, results in essentially all the niobium remaining on the first bed. The second bed removes any activity carried from the first bed in the UF_6 stream. The effectiveness of the NaF in removing particulate matter in the gas stream is illustrated by the rare earth decontamination in the first bed.

Table 8. Distribution of Activity in NaF Absorption-Desorption Step

	Activity[a] (% of Total)					
	After 4 Consecutive Runs			After 1 Run		
Fission Product	NaF Bed 1	NaF Bed 2	Ru Cold Trap	NaF Bed 1	NaF Bed 2	Ru Cold Trap
Ru γ	1.6	1.1	97	18	0.9	81
Nb γ	98	0.04	2	99	0.04	0.4
Rare earth β	92	4	4	97	0.1	3

[a] Activity found in product, NaF beds, and ruthenium cold trap.

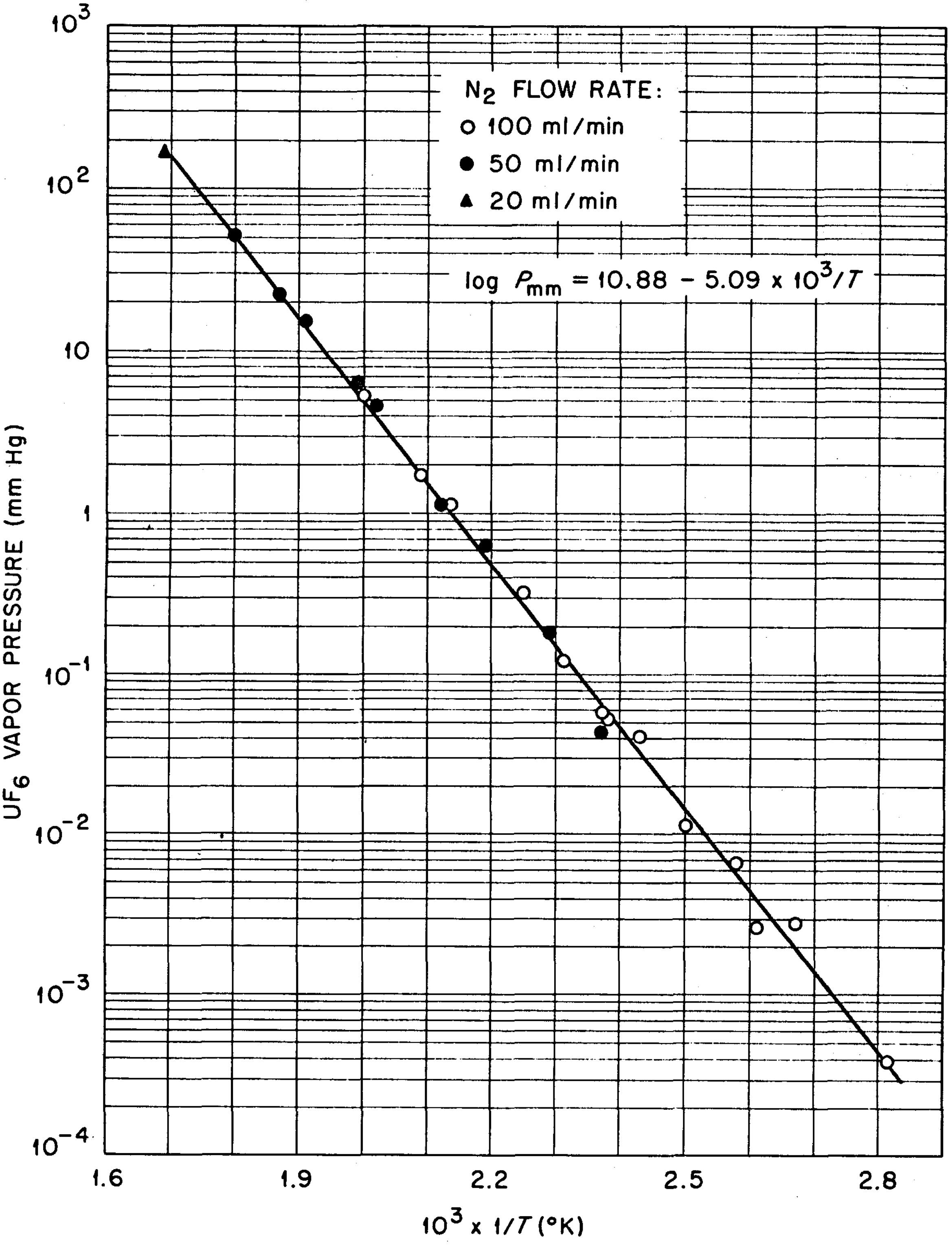


Fig. 5 Equilibrium Partial Pressure of $UF_6 \cdot 3NaF$ Complex as a Function of Temperature

Over-all process testing of the ORNL flowsheet has given the results summarized in Table 9. A difficulty encountered with either the ANL or ORNL flowsheets is that testing has to be carried out at high activity levels to obtain much activity in the product.

Table 9. Decontamination of Uranium in Fluorination and NaF Absorption Steps

Feed: irradiated natural uranium, decayed 120 days

	Decontamination Factor						
Process Step	Gross β^a	Gross γ^a	Ru	Nb	Zr	Cs, Sr, and Rare Earths	I, Mo, Te
Fluorination	10^2	10^2	10	10	10^3-10^4	10^4	1
NaF absorption	10^4	10^4	10^3	10^4	10^3	10^3	Unknown
Over-all	10^6	10^6	10^4	10^5	10^7	10^7	Unknown

[a] For case of long decay period. Gross decontamination is less in presence of iodine or tellurium in case of a short decay period.

Corrosion

Corrosion is the most adverse factor in the fused salt--fluoride volatility process.[5,6] High-nickel alloys are being considered for both the dissolution and volatilization steps. The use of graphite or copper-lined vessels is also possible in the HF dissolution step. Although corrosion is more severe in the volatilization step, the length of time required for dissolution makes this corrosion more serious. Gas impingement effects are especially serious in either case. Since the worst corrosion occurs in the fused salt--containing vessels, consideration is being given to using the salt process vessel also as the waste salt disposal vessel.

A comparison of materials for the HF dissolution step is given in Table 10. In the tests, inconel suffered chromium depletion, showing a weakened and expanded surface layer 8 to 12 mils deep. Low-carbon nickel showed no failures but some intergranular penetration from 2 to 7 mils, which, of course, was much less than for "A" nickel. Hastelloy B showed no attack other than that indicated above. Variations

Table 10. Corrosion of Materials in Dissolution Step Melt of $NaZrF_5$ at 600°C

Material	Approximate Penetration Rate (mils/day)
Graphite	0.1
"A" nickel	0.2-1.2
Low-carbon nickel	0.25
Inconel	0.7
Monel	0.4
Copper (electrolytic tough pitch)	0.1-1.0
Hastelloy B	0.04

in weight loss of copper were due to concentrated local attack in some cases. Monel suffered severe copper depletion to depths of 16 mils and moderate depletion through its entire cross section. Monel apparently was not weakened by intergranular effects. Nickel, unalloyed, suffers greatly from sulfur embrittlement, and there is considerable question as to whether similar effects would not arise from fission products. Embrittlement effects greatly complicate corrosion studies.

Corrosion in the fluorination or volatilization step is in the range of 1-10 mils/day for nickel or nickel alloys, or possibly tenfold greater than in the dissolution step. Since the fluorination step is complete in about 1 hr, it is more pertinent to state the corrosion rate as approximately 0.1-1.0 mil per batch. The corrosion rate in the fluorination step is perhaps dependent on the initial uranium concentration.

Summary

The fused salt--fluoride volatility process appears to be an attractive method of recovering uranium from high-alloy fuels. Both the ANL and ORNL flowsheets have been shown to give high uranium recovery and decontamination from fission product activity. Continued consideration and development of the process are warranted on the basis of these results and some of the more general factors, such as a low solid volume, simple fuel recycle procedures, less stringent criticality considerations with high plant throughput. Consideration could also be given to alternate head-end steps, for example, combination of Zircex (hydrofluorination) head-end treatment with fused salt processing.

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ENGINEERING AND ECONOMIC CONSIDERATIONS OF VOLATILITY PROCESSES

INTRODUCTION

Separations processes based on the volatility of uranium hexafluoride offer two general advantages over the well-established aqueous flowsheets:

(1) The uranium hexafluoride product is closer to the desired end material than that produced by aqueous processes.

(2) The required decontamination is more easily effected, at least potentially, by the use of two unit operations not possible in the aqueous flowsheets, namely, fractional distillation and absorption-desorption.

Processes studied to date fall into two general classes which may be characterized by the temperature range in which the initial dissolution is carried out. In the first of these, nominally called the low-temperature process, natural or slightly enriched uranium containing little or no alloying agent is dissolved in a liquid interhalogen compound at temperatures up to 130 C. The product uranium hexafluoride is subsequently separated from the interhalogen reagent and the volatile fission products by fractional distillation. In the second class, labelled the high-temperature process, uranium (generally enriched) alloyed with significant quantities of one or more other metals is dissolved in a fused fluoride salt bath at temperatures of 600 to 800 C. The dissolution uses hydrogen fluoride to convert the alloy metals to their fluorides and the uranium to the tetrafluoride, followed by fluorine or an interhalogen to convert the uranium to the hexafluoride. The final separation and decontamination may then be accomplished by distillation as in the low temperature flowsheet, or by absorption-desorption. Most of the work on high-temperature processes to date has been in connection with zirconium-matrix fuels.

The chemistry of these two types of processes, together with descriptions of pilot plants and some operating data, has been discussed earlier in this symposium.(1,2) It is the purpose of Part I of this paper to present in greater detail the engineering problems and their solutions, as found by the results of both bench-scale and pilot plant studies. The problems arise largely from the highly corrosive nature of the reagents, thus requiring prudent selection of containing materials. Also, valves, fittings, instruments and process equipment often have to be specifically designed since the ordinary commercially available items are generally not satisfactory nor made of acceptable materials. Also, since the chemicals used are highly toxic as well as corrosive, added precautions are necessary in both the design of equipment and in the selection and use of operating procedures. Considerable emphasis has been placed on personnel safety. It is felt that most or all of the engineering problems can be handled satisfactorily and this paper attempts to convey this confidence in technical feasibility.

In Part II an attempt is made to present the probable economic position of volatility processes. Two hypothetical plants (using a low and an high temperature process) are postulated and the capital and operating costs of each are estimated. It should be emphasized that these are hypothetical plants and the costs are calculated without benefit of data from operating plants of this type.

Part I—Engineering

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May 1, 1957

MATERIALS OF CONSTRUCTION

It was recognized from the beginning of development work on fluoride volatility processes that corrosion would be the predominant consideration in selecting materials of construction. Thus considerable effort has been devoted to studying the corrosion environments in the various process operations of both low and high temperature flowsheets. The two sections below summarize these studies and their conclusions.

A. Corrosion Studies for Low Temperature Flowsheet

1. Dissolution

The original process concept specified a three-stage dissolution involving alternate aqueous and interhalogen environments in the same vessel. An aqueous sodium hydroxide-sodium nitrate solution was to be introduced first to decan the slugs, followed by removal of the residual solution and thorough drying of the vessel. Then the slugs were to be dissolved in liquid interhalogen compounds at temperatures up to 130 C, the step being terminated by taking the volatile uranium hexafluoride and residual interhalogen overhead for further processing. The dry residue of non-volatile fission product and plutonium fluorides was then removed by a second aqueous wash containing aluminum nitrate, the resulting solution being sent to a solvent extraction step for plutonium recovery.

Thus the dissolver would have had to contain successive corrosive environments of interhalogens and aqueous solutions. In exposures involving interhalogens only, nickel, Monel and Inconel have the greatest resistance to attack. These form tenaciously adhering fluoride films that remain intact

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over fairly wide temperature ranges, resulting in very low corrosion rates. Typical rates measured in bench-scale tests are shown in Table 1. The effect of turbulence on these rates is not known quantitatively, however, experience

Table 1

LABORATORY CORROSION DATA OF METALS IN FOUR INTERHALOGEN ENVIRONMENTS AT 125 C

(Data adapted from ANL-5557, page 8)

Separate samples of each metal were exposed to each of the four following environments in both liquid and vapor phases and at the interface.

1. BrF_3
2. 10% BrF_5 in BrF_3
3. 10% Br_2 in BrF_3
4. 10% UF_6 in BrF_3

Metal	Exposure Time, weeks	Maximum Observed Corrosion Rate, mils/yr	
Nickel	11	0.018	<0.05
Welded Nickel	11	0.012	
Monel	11	0.025	
Welded Monel	11	0.033	
K Monel	11	0.036	
Inconel	11	0.046	
Aluminum	4	0.71	<1
Duranickel	4	0.37	
Incoloy	4	3.6	<7
SS 304	1	6.9	
SS 347[a]	1	5.8	
Mild Steel	1	19	
Nicloy 9[b]	1	160	

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[a] Exposed to environment 4 only.

[b] Exposed at interface to environments 1 through 3.

indicates that this would be inappreciable. Table 2 gives corrosion data on some of the same metals exposed alternately to both environments. The penetrations indicated correspond reasonably well with data for aluminum nitrate corrosion alone, thus implying that all of the corrosion occurred during the aqueous exposure and a negligible amount during the interhalogen exposure. This also implies that only a small quantity of metal is consumed in the initial formation of the protective fluoride film.

Table 2

LABORATORY CORROSION DATA ON METALS IN ALTERNATE AQUEOUS AND INTERHALOGEN ENVIRONMENTS

(Data from ANL-5557, page 27)

Cycle: 20 hr in BrF_3 at 125 C; 20 hr in 1 M $Al(NO_3)_3$,
0.05 M Sulfamic Acid, pH 0.5, room temperature.

Metal	mils/cycle	mils/yr (approx)
Nickel	0.005	1
Welded Nickel	0.004	1
Monel	0.004	1
Welded Monel	0.004	1
K Monel	0.005	1
Inconel	0.004	1

Comparison of Tables 1 and 2 shows that, on a bench sacle, the dual environment results in about 20 times the corrosion rates that obtain with interhalogens alone, although the magnitude of the former is still low. However, nickel alloy coupons exposed to alternate cycling in the Argonne National Laboratory pilot plant dissolver showed greater dimensional change than would have been predicted from laboratory data. The results of these tests are shown in Table 3. The time cycle which obtained is not representative of the postulated, dual-environment process, but the approximate penetration rates in mils/yr give at least qualitative indication that other variables are operative in the larger equipment. It is suspected that air in the presence of interhalogen vapor or liquid accelerates the rate of attack, and this may partially explain the higher rate on the pilot plant coupons, although efforts were made to keep the equipment under helium pressure. Data from Brookhaven National Laboratory(3) in conjunction with some dynamic corrosion tests on bromine trifluoride also indicate a possible effect of air. Table 3 also reveals other effects not found in bench-scale tests,

Table 3

PILOT PLANT DISSOLVER CORROSION DATA
IN ALTERNATE AQUEOUS AND INTERHALOGEN ENVIRONMENTS

(Data from ANL-5602, page 50)

Cycle: 600 hr in interhalogen medium (15 to 160 C)
25 hr in aqueous wash and decanning medium
(15 to 60 C)

Metal	mils/cycle	mils/yr (approx)	Comments
Liquid submerged coupons			
Unwelded Monel	0.7	10	Appearance: sound, no pitting
Unwelded Nickel	0.6	9	Sound; some minute pits
Welded Monel-nickel	0.7	10	Small scattered pits
Unwelded Inconel	2.7	40	General attack, pitting
Welded Inconel	8.9	120	Attacked and pitted; particularly the edges
Vapor exposed coupons			
Unwelded Monel and Nickel	0.3	5	Good appearance
Welded Monel and Nickel	0.4	6	Good appearance
Welded Monel-nickel	0.3	5	Good appearance
Unwelded Inconel	6.9	10	Severe attack; edges pitted
Welded Inconel	5.8	8	Attacked and pitted; weld thinned

such as the penetration of Inconel coupons being 3 to 10 times greater than nickel or Monel, and the existence of differences between liquid and vapor environments.

In general, however, the higher rates obtained on nickel and Monel coupons in pilot plant tests are still sufficiently low to make their use reliable.

2. Fluorination

The vapor taken overhead from the dissolution step is condensed and then contacted with elemental fluorine to convert bromine to bromine trifluoride prior to distillation. Thus at least one process vessel and several lines must be exposed to gaseous fluorine.

Nickel and nickel alloys are useful for the containment of fluorine up to pressures of 400 psig (although routine practice is limited to 50 psig) at ambient temperatures. For atmospheric pressure operation, temperatures up to 600 C may be tolerated. However, the inadvertent raising of metal temperature to the ignition point will cause rapid burning of the metal and material failure. Local heating to ignition temperatures has occurred due to reaction of fluorine with organic materials that had not been removed. For this reason screwed connections should be avoided because of the organic substances usually present in pipe compounds. A pipe "dope" of calcium fluoride is recommended if screwed connections are necessary. Sharp bends in process lines, which cause high-velocity impingement of process gases, are thought to be the cause of high local corrosion rates and thus should be avoided if possible. Welded construction is preferred, and heavy-wall piping and tubing will tend to prevent local hot spots and possible ignition.

3. Distillation

The final separation of uranium hexafluoride product from residual interhalogen is performed in a distillation column containing nickel packing. As pointed out previously, the observed corrosion rates in interhalogen environments are low enough so that structural integrity is not threatened. In this operation, however, corrosion is a problem from the standpoint of meeting product specifications. Since the columns contain a very large nickel surface due to the packing, the following type of reaction can occur

$$3\ Ni + 2\ BrF_3 \longrightarrow 3\ NiF_2 + Br_2.$$

The specification for bromine in product uranium hexafluoride is very low and the separation of these two components by distillation is difficult.

4. Miscellaneous Equipment Difficulties

A problem that still exists to some degree is the occasional failure of nickel and Monel bellows and diaphragms in packless valves. The physical integrity of the protective fluoride film on these units is jeopardized by the flexing action of the bellows and diaphragm. To what extent the base metal can be deformed without causing rupture of the film is not known. Additional improvement is needed in this area.

In laboratory experimental equipment, copper and nickel have often been joined via silver-solder connections and leaks have developed at these joints. In most cases preferential attack of the copper was noted. The role of the silver solder at these joints may or may not have accelerated these effects. In earlier experiments, silver solders that were less resistant to corrosive attack were used, and some of the early failures might be attributable to them. Several bi-metallic couples (equal areas) were exposed in the laboratory to interhalogen liquids. Though not conclusive, the metal loss data indicate that nickel is more noble than copper and perhaps slightly less noble than aluminum.

5. Other Materials of Construction

As shown in the preceding paragraphs, most of the laboratory and pilot plant studies on corrosion have been focussed on nickel and nickel alloys. Nickel and Monel are the most commonly used materials in the construction of vessels in three volatility pilot plants built to date. (These are located at Brookhaven National Laboratory, Argonne National Laboratory, and Oak Ridge National Laboratory. The latter pilot plant is no longer in use.) However, other materials have shown good structural integrity and should be mentioned in connection with the low-temperature flowsheet.

a. Copper

In general, the use of copper has been restricted to bromine pentrafluoride, vapor lines, and sometimes to fluorine. The corrosion of copper is thought to be somewhat greater than that of nickel alloys and it is probably more susceptible to ignition with fluorine, but experience in the laboratory has demonstrated it to be a useful material for handling interhalogens. Its physical properties detract from its use where structural strength is desired. In general, the fluoride films formed are heavier than those for nickel alloys, and somewhat less protective. Copper is incompatible with the aqueous aluminum nitrate solution used for decontamination and plutonium removal from the dissolution step. The bi-metallic couple data previously cited indicate that copper is likely to be anodic in contact with nickel and aluminum. Such junctions should be avoided.

b. Aluminum

Aluminum is very resistant to interhalogen solutions, but is quite sensitive to hydrolysis products in the presence of moisture. Aluminum is not usable for the decanning solutions, nor would it be satisfactory with the aqueous decontamination solutions.

The fluoride films formed on aluminum appear to be less tenacious than on nickel, and there have been scattered instances where line plugs have been attributed to loosened fluoride films. In other cases, good protective films have been observed to temperatures of 150 C. The bi-metallic behaviour of aluminum is good; little accelerated attack of aluminum with nickel or copper has been observed.

The structural properties and the melting point of aluminum detract from its use. Local heat-generating reactions bring the temperature of the aluminum up to reaction level, followed by possible melting. The magnitude (although not the cause) of a single incident at Brookhaven National Laboratory can probably be attributed to the use of aluminum. Here a pilot plant distillation column and still pot constructed from aluminum were destroyed, largely because the material did not have sufficient strength, nor could it withstand high temperature without melting (see later section on safety). This limitation of aluminum is a serious one, and also applies to its use with elemental fluorine. The corrosion rate of aluminum in fluorine is low even up to temperatures of 400 C, but the lack of good mechanical properties and susceptibility to ignition are barriers to its use. Aluminum is also susceptible to rapid reaction with bromine which usually is present to some extent in most bromine-containing interhalogens.

c. Mild Steel

Mild steel is used as structural material in the manufacture of crude interhalogens, hydrogen fluoride, and fluorine, and also for the shipping of these materials. In laboratory corrosion tests, the rate of attack of mild steel was several times that of nickel, its alloys, and copper. The presence of moisture accelerates the rate of attack, but in most cases, this rate does not exceed 20 mils per year. Its low cost and ease of fabrication make it attractive as a material of construction in places where high purity is not important. In general, its use for piping is avoided because of its greater susceptibility to ignition in lines containing high-velocity fluid streams.

d. Stainless Steels

The Austenitic stainless steels (types 302 and 347) have some degree of attractiveness as materials of construction for the interhalogen dissolver. From solvent extraction experience, these stainless steels are known to possess the needed corrosive resistance to the aluminum-nitrate solutions used for decontamination and plutonium removal and also for the caustic solutions used for decanning. Some laboratory corrosion experiments were conducted on the stainless steels at all three sites where fluoride volatility pilot plants have existed. Oak Ridge National Laboratory tested stainless steel types 302 and 347 in four different solutions at 80 C for 6 to 10 days. The four solutions consisted of various mixtures of chlorine trifluoride and uranium hexafluoride plus 0 to 15 per cent hydrogen fluoride. The test samples showed no loss in weight (sizes of the samples were not given). At Brookhaven National Laboratory, specimens of the same stainless steels were immersed in boiling bromine trifluoride (technical grade) in an aluminum vessel for a three-month period. The maximum rate of penetration observed was 5 mils per year. At Argonne National Laboratory types 304 and 347 stainless steel were exposed in four different solutions having a bromine trifluoride base, and the maximum corrosion observed was 7 mils per year.

To date no pilot plant evaluations have been made of types 302 and 347 stainless steel. In general, it is felt that these have no particular advantage over the use of nickel or Monel, particularly where the aluminum nitrate used is properly inhibited with sulfamic acid.

e. Non-metals

Fluorothene and Teflon have found much use both in the laboratory and in pilot plants. Teflon is often used as a gasketing material where flange connections are desired. Fluorothene test tubes have been used in experiments up to 150 C and are routinely used for procuring samples in the pilot plant, but it has an aging characteristic that results in embrittlement. Using Fluorothene with uranium hexafluoride seems to accelerate this rate of deterioration. Formerly there had been some difficulty with fluorothene test tubes igniting when samples were procured, and originally this was attributed to fuzzed ends that had not fused completely with the bulk material. (This ignition did not occur when the fluorothone occurred as massive pieces.) The ignitions might also have been due to the presence of acetone in the minute cracks that formed from embrittlement. (All tubes were degreased, prior to use, with acetone which might not always have been completely removed). In general, it appears that fluorothene and Teflon are not quite as satisfactory for use with fluorine as compared to their use with interhalogens, although dilution of the fluorine extends considerably the useful life of these containing materials.

Calcium fluoride is useful for both laboratory and pilot plant where a transparent material of construction is desired. Brookhaven National Laboratory uses calcium fluoride for sight glasses and peep holes in its process equipment. At Argonne National Laboratory this material is used where infra-red analysis is desired and also for determining indexes of refraction.

Alumina is suitable for use with fluorine at both high and low temperatures. Glass and quartz have been used occasionally with interhalogens and uranium hexafluoride at room temperature.

B. Corrosion Studies for High Temperature Flowsheet

While uranium dissolves readily in interhalogen solutions, alloyed uranium--particularly zirconium alloys--does not. The process under study to handle zirconium-uranium alloys consists of immersing the alloy in a fused fluoride salt-bath (50 mole per cent ZrF_4, 50 mole per cent NaF) at 600 to 700 C and sparging the melt with hydrogen fluoride. This converts the zirconium to zirconium tetrafluoride and the uranium to uranium tetrafluoride. When dissolution is complete, the melt is fluorinated (using F_2, BrF_3 or BrF_5), thus converting the non-volatile uranium tetrafluoride to volatile uranium hexafluoride which is simultaneously distilled from the melt. Subsequent cleanup of the uranium hexafluoride may be accomplished by fractional distillation or by an absorption-desorption cycle using sodium fluoride. The selection of materials of construction for both the hydrofluorination and the fluorination steps is quite limited and the problems encountered in the two steps are somewhat different.

1. Hydrofluorination (Dissolution)

Possible construction materials for the hydrofluorination are: nickel, Monel, Inconel, Hastelloy B, copper and graphite.

a. Nickel

The grade of nickel generally referred to as "nickel" is known in trade parlance as "A nickel". "L nickel" is a low carbon modification. The carbon specifications for the two are 0.15 per cent max and 0.02 per cent max, respectively. "A" nickel is heat treated to solubilize the carbon content. However, in the temperature range 500 to 700 C, the carbon tends to come out of solution thus weakening the metal. "L" nickel avoids this graphite precipitation as its carbon content is lower than its solubility in the above temperature range. The ASME pressure vessel code permits design with "A" nickel to 300 C and with "L" nickel to 650 C.

Both "A" and "L" nickel have one severe limitation for use at high temperature, and that is their susceptibility to intergranular attack by sulfur-bearing materials. The sulfur combines preferentially with nickel along grain boundaries to form $Ni_3S_{2\pm x}$. Such effects are additive and irreversible. Once metal has been attacked, there is no treatment of any kind that can restore it to its original condition. The foreign material forms a eutectic with nickel that has a melting point of 645 C. The metal is thus weakened severely at operating temperatures, and leaves a matrix that can be crumbled in the hand at room temperature.

Small quantities of sulfur are known to be present in two of the raw materials used in the fuel-element dissolution step: the fused salt and the hydrogen fluoride. Sulfur in the fused salt can be removed prior to process use by contacting the melt with nickel having large surface areas, such as the various types of column packing, or by passing a strong fluorinating agent through it (F_2, BrF_5, etc) The hydrogen fluoride purification presents more of a problem. As the hydrogen fluoride throughput required for the process is high, a very low sulfur specification must be observed to prevent long range metal deterioration. In small-scale corrosion tests using a 1.5-in. ID nickel can with 0.032-in. wall (600 C), failure of the nickel occurred within 500 hours, although the sulfur content of the inlet hydrogen fluoride at no time exceeded 4 ppm. The results of this and similar corrosion tests that were terminated by metal embrittlement are shown in Table 4.

If sulfur is excluded, nickel may be satisfactory for use in the hydrofluorination step. Laboratory tests have shown that the corrosion

Table 4

EMBRITTLEMENT FAILURES IN HF-SPARGED FUSED SALTS (600 C)

Material and Component	Time to Failure, hr	Relative HF Sparge Rate
"A Nickel" liner	49	1.5
"A Nickel" liner	115	1.0
"A Nickel" liner	117	2.0
"A Nickel" liner	594	1.5
"L Nickel"	408	2.7
"L Nickel" (0.050-in. wall)	629	1.7
Monel	1,188	2.4

All liners began with 0.032-in. wall unless indicated.

rate then is primarily a function of whether the metal contacts only liquid melt, or melt and gas alternately, the latter being more severe. In hydrofluorination tests in which "A" and "L" nickel were exposed to simulated process conditions, typical rates of dimensional change observed were 0.2 mils/day for liquid-phase exposure only and 1 mil/day where exposure alternated between liquid and gas phase. Longer laboratory tests with hydrogen fluoride sparge often produced a hard mealy material which was insoluble in the fused salt and had a high melting point. Chemical analyses of the material revealed a nickel content of 12 to 15 mole per cent and a zirconium to sodium ratio in excess of that present in the clean melt. The material has not been characterized, but its presence could markedly interfere with normal process operations unless provisions were made for it. In larger units having a lower surface-to-volume ratio, the magnitude of this problem should be lessened.

b. Monel

Monel in many respects behaves similarly to nickel. Strength and oxidation resistance are comparable as is the rate of dimensional change. It is somewhat superior to nickel in resisting sulfurous materials. Monel, however, is subject to the preferential leaching of copper leaving a weakened porous structure of nickel.

c. Inconel

Inconel has also been tested for possible use in a hydrofluorinator. Inconel is much superior to nickel in resisting grain boundary attack by sulfurous material, and has good high temperature strength and oxidation resistance. The ASME boiler code gives stress levels for Inconel to 650 C. However, Inconel is also subject to preferential leaching in the dissolution environment, resulting in removal of chromium. This leaves a cellular structure of nickel which tends to spall from the parent metal.

d. Hastelloy B

Hastelloy B has good high temperature strength and oxidation resistance, and, like Inconel, has superior resistance to sulfurous attack. It does have an objectionable age-hardening characteristic in which its tensile strength increases but its ductility decreases to what are probably unacceptable values. Its initial properties may be restored by solution heat treatment. According to manufacturer's information, this metal will fully age harden in 170 hours at 760 C, but Argonne National Laboratory data indicate that 1000 hours at 600 C will not bring about this condition. Little preferential attack was noted in the single test made to date although some intergranular attack was observed.

e. Copper

Because of its poor strength, copper may be used as a liner material only. Precautions must be taken to exclude air and moisture as oxidation progresses rapidly. In corrosion tests at Argonne National Laboratory, difficulty was encountered with mass transfer of copper, to the extent that tests were terminated prematurely. No metallurgical degradation was observed except for blisters that formed in the metal. This was attributed to "hydrogen sickness" in which corrosion product hydrogen reacted with oxide impurities in the metal forming high pressure regions of steam that could not excape. This can be avoided by using oxygen-free copper.

A successful application of copper has been made in fused salt systems at Oak Ridge National Laboratory where the Material Chemistry Division purified salt in batches of 250 lb by alternate hydrofluorination and hydrogen reduction. An oxygen-free copper liner (1/4-in. wall) is placed inside a structural vessel of stainless steel type 316. Treatment temperature is 800 C. The gas rates per unit cross sectional area of the vessel are roughly one tenth that of Argonne National Laboratory rates. The experience to date has been good.

f. Graphite

None of the metals tested to date have given sufficiently reliable performance that the design engineers are willing to accept them as being fully adequate for plant equipment. A material which does appear promising, however, is graphite. The use of graphite is limited to the hydrofluorination step since graphite and the strong fluorinating agents required for uranium tetrafluoride conversion and subsequent volatilization are not compatible.

Graphite is by far the most chemically inert material known for hydrofluorinated fused-fluoride melts. In corrosion tests in which graphite was subjected to simulated process conditions, the rate of dimensional change ranged from < 0.04 mil/day for alternate exposure to melt and hydrogen fluoride to 1 mil/day where hydrogen fluoride impinged directly on melt submerged graphite at a velocity of two to four feet per second. The effects of temperature would be expected to be small, although this has not been confirmed. Unlike metals, graphite is subject to diffusion of melt through it which may be a problem for two reasons: (1) Uranium that is carried into the graphite may be irrecoverable, and (2) thermal cycling of melt-containing graphite may possibly cause some degree of spalling. Bench-scale data to date have not indicated that the latter problem will be serious. Graphite manufacturers have been striving to achieve higher densities and lower porosities in their product, but to date a completely impervious material is yet to be developed.

The biggest limitation in the use of graphite is its lack of impact strength. In the metal dissolvers in use for the aqueous processes at the Idaho Chemical Processing Plant, fuel elements and subassemblies are gravity charged, and the dissolvers are built to withstand the impact. It is questionable whether a graphite dissolver could be designed for such impact. The alternative is to restrain the element in lowering it.

It would appear that graphite is chemically suitable for the hydrofluorination step. It remains to be proved whether or not the mechanical properties are satisfactory, although indications are favorable.

2. Fluorination (Uranium Hexafluoride Volatilization)

Considerably less corrosion work has been done to date on the fluorination step relative to the hydrofluorination step. As was mentioned previously, graphite is unsuitable in a fluorine environment. Nickel appears to be the most promising material. Most of the small scale corrosion work has been done with bromine pentafluoride, but fluorine is expected to show similar behavior. Rates of dimensional change are higher than for the dissolution (hydrofluorination) step and are strongly temperature dependent as shown in Table 5. Intergranular effects have been noted in runs of 80 hours or more, and these are more severe at the higher test temperature. The cause of these effects has not yet been determined.

As some means of storage of the melt is required after volatilization of the uranium, it has been suggested that the fluorinator itself be designed as a disposable unit. This unit would be used for one or two fluorinations and then removed with its charge for disposal. Very high corrosion rates could thus be tolerated for the short overall exposure time involved, and it appeared that an inexpensive material like mild steel might be suitable. However, mild steel is subject to ignition on exposure to fluorine at

Table 5

TYPICAL CORROSION OF NICKEL IN FUSED FLUORIDE SALTS SPARGED WITH BrF_5

Salt: Equimolar $NaF-ZrF_4$

Component	Dimensional Change, mils/day 600 C	 700 C
Liners (two surfaces)	3 to 8	10 to 13
Hole Radii	1.5 to 7	3.5 to 9
Plate Thickness (one surface)	1 to 1.5	6 to 12

relatively low temperatures (400 to 450 C). Although laboratory tests have demonstrated that mild steel surfaces in contact with a liquid fused-salt melt at 600 C will not ignite when sparged with fluorine, the danger of ignition in the vapor phase is too great for mild steel to be considered seriously.

Inhibition of the ignition property of mild steel by a surface coating of nickel may provide a suitable material for a disposable fluorinator. Several commercial processes are now available which chemically deposit nickel films on steel surface (e.g. the "Kanigen" process(4)). Laboratory exposure to bromine pentafluoride of a mild steel sample coated with 1 mil of Kanigen nickel resulted in no ignition, indicating that porosity of the nickel coat was very low. To be suitable for fluorination use, some assurance is needed that (1) the nickel will not be corroded away at any spot during the total exposure time, and (2) the adhesion of the nickel to the mild steel is sufficiently dependable; preliminary observations indicate good adhesion. To be reasonably safe from the corrosion aspect, a coating of 15 to 20 mils would probably be required. Kanigen coatings can be applied to uniform thicknesses of up to 10 mils.

3. Design Considerations for Reducing Corrosion

a. Process Modification

It may be possible to minimize some of the corrosion problems by proper design of plant equipment. A technique that is useful in reducing corrosion of the material of construction is the utilization of a "cold wall". This can be achieved by introducing the heat into a vessel centrally combined with forced cooling of the container wall thus creating a frozen wall adjacent to the outer vessel which would isolate the latter from the corrosive environment. This technique would also reduce the wall temperature of the outer vessel resulting in further corrosion reduction and reducing the probability of ignition (in the case of fluorine on mild steel). However, excessively cold walls would cause more melt solidification with resulting uranium loss.

At the present time, Argonne National Laboratory is having a graphite "cold wall" dissolver fabricated through a subcontract. An inner graphite liner is contained in a nickel or steel shell and the annular space is packed with lampblack. By introducing the heat centrally, a temperature gradient through the graphite and lampblack is obtained that results in a boundary within the liner beyond which the fused melt solidifies. In this manner the nickel is isolated from the environment but still supplies the required structural strength. A sketch of the proposed equipment is shown in Figure 1.

b. Equipment Fabrication

Many corrosion failures that have occurred indicate equipment fabrication that was amenable to local attack, rather than poor selection of material. One of the most important of design criteria relative to corrosion is the avoidance of crevices. Crevices can trap liquid, and because of local effects in the trapped volume, both ionic and dissolved gas concentrations change from that of the bulk fluid (i.e. electrolytic effects) resulting in accelerated corrosion.

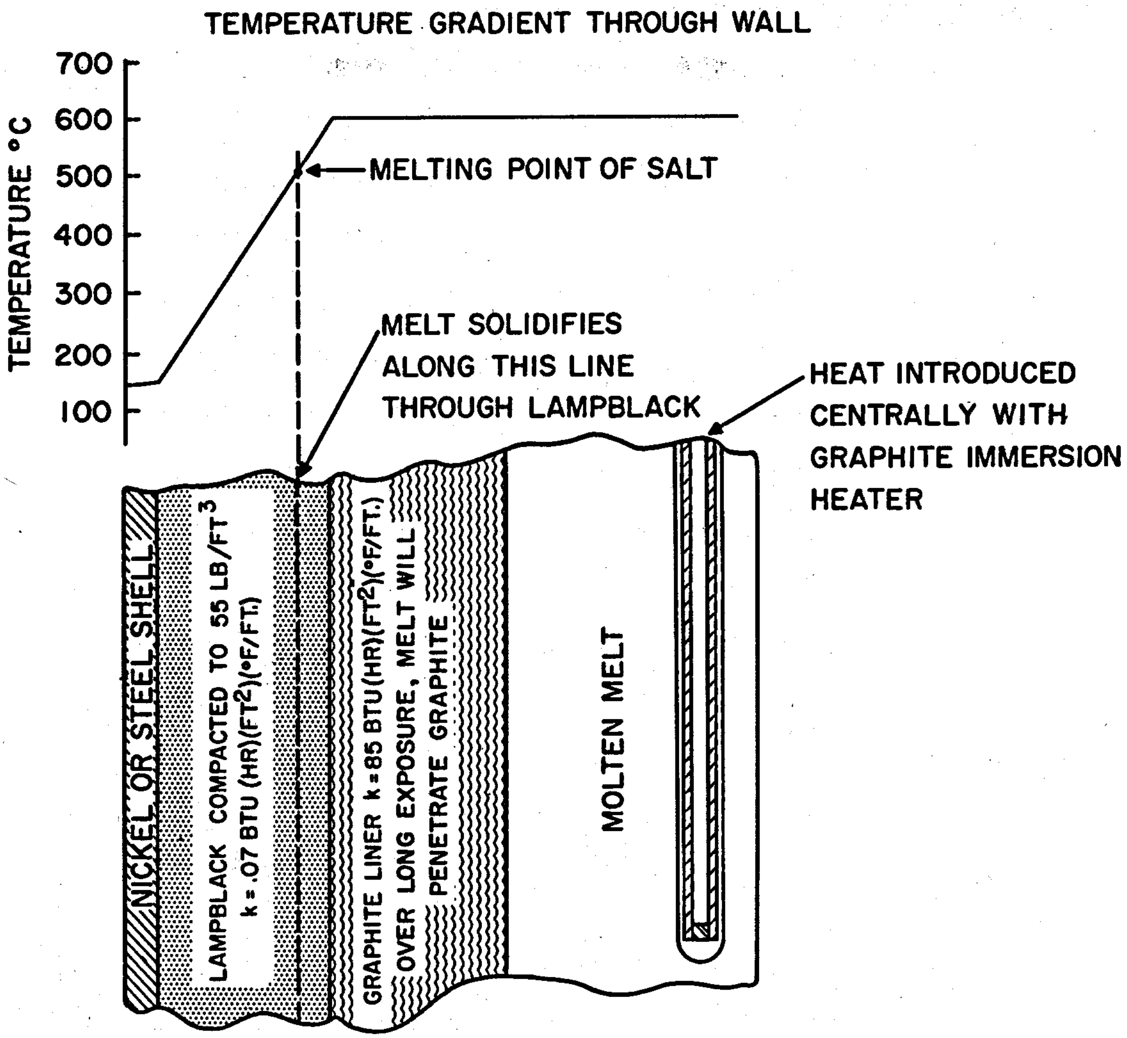

Fig. 1 - Cross section of wall of graphite dissolver using "cold wall" method.

Dished heads should be used where feasible. Welds should be ground down to present plane surfaces, and all residual welding fluxes (which usually contain fluoride and chloride) should be removed from the surfaces. When welding from the outside of a vessel, a full penetration weld should be used. Fillet welds should be employed liberally. Where temperatures are such as to cause metallurgical changes in the metal, heat treatment may be necessary, either of the solution (nickel requires no solution heat treatment) or stress relieving type.

c. Equipment Layout

Experience in the past has indicated that maximum dimensional change occurs in this system when an impinging gas meets metal surfaces perpendicularly, and this effect reduces in magnitude as the angle of impingement becomes more obtuse. Hence, if gas enters a vessel through a vertical line, any horizontal edges or surfaces should, if possible, be placed beneath the point of gas entry, or if above, should be placed away from the natural path of the gas bubbles. Where horizontal surfaces cannot be avoided, designs that allow for the accumulation of gas under the surface to form a gas cushion are helpful. Horizontal rounds are likely to corrode at the most rapid rate.

The installation of a sacrificial metal draft tube will aid in reducing the attack on vessel walls and other parts. Where a graphite draft tube can be used, it might offer a degree of permanent protection to vessel components.

PILOT PLANT TECHNIQUES

A. Introduction

The purpose of the pilot plant work has been to study further those process salients revealed by the bench-scale work from a viewpoint more representative of the ultimate full-scale plant. As has already been pointed out in connection with certain corrosion problems, a pilot plant test will frequently reveal wholly unexpected results of a phenomenon previously studied on the bench-scale, due to participation of variables that were either overlooked or not operative in the latter. Also the topics of instrumentation, materials handling, operating procedure and safety, which are vital to design of the full-scale plant, could not properly be investigated on the bench-scale. These topics are covered in the ensuing sections.

B. Instrumentation; Measurement and Control

As in most other phases of volatility work, it is often necessary to make some modification of the commercially available instrumentation before it can be successfully applied.

1. Temperature

The measurement of the temperature of interhalogen liquid or vapor is commonly accomplished by the use of a standard thermocouple in a protective well. For the low temperature range (0 to 200 C), either a copper or iron-constantan thermocouple in a nickel or Monel well is used. For temperatures in the range 200 to 700 C, a chromel-alumel thermocouple is employed. For fused salt systems involving hydrogen fluoride, a graphite thermowell is frequently used.

For applications where a conventional thermowell (such as one made of 1/4-inch tubing or pipe) is too bulky or where less lag is required, the needle type thermocouple is appropriate.(5) The unit that is most frequently used in volatility work consists of a 1/16-inch OD Inconel tube inside of which is sealed an insulated (glass fiber) constantan wire. This thermocouple assembly can be used reproducibly to temperatures as high as 600 C.

Normally the output from the thermocouple is merely recorded on a multipoint potentiometer, although for the interhalogen dissolvers a temperature recorder-controller is used. During the bromine trifluoride dissolution of uranium, a maximum temperature of about 150 to 160 C is chosen for the set point on the controller. If the temperature of the dissolver reaches this level, an emergency water cooling valve is opened; the flow of water quickly drops the temperature of the dissolver to a level where the dissolution proceeds at a slow rate. Alternatively, when the dissolver solution is recirculated as is done at Brookhaven National Laboratory, the temperature controller regulates the supply of cooling to the heat exchanger.(6)

Differential thermocouples are used on the distillation columns, and the columns maintained at adiabaticity by adjusting electrical heaters until the output from the differential thermocouples is zero.

2. Pressure

Direct indicating pressure gages with a Monel bourdon tube for the sensing element are used extensively for pressures from 0 to 500 psia.

Pneumatic pressure transmitters are used with either a Monel bourdon tube or a Monel bellows as the moving element. All of these instruments are commercially available with the appropriate receivers or pressure controllers. Also, available are differential pressure transmitters using either Monel diaphragm or bellows seals. Experience with a diaphragm made of Teflon and glass has been unsatisfactory.

A manometer for indicating pressure drop across an orifice through which halogens are flowing can be made from transparent fluorothene tubing, using fluorolube oil as the manometer fluid or sealing liquid.

A precise device for determining pressures in interhalogen systems is an instrument known as the "Booth-Cromer" pressure transmitter.(7) The unit consists of a Monel diaphragm which is continuously kept at or close to the null position by balancing the process interhalogen pressure with an inert gas such as helium. A small electrical contact on the helium side of the diaphragm actuates a light and a self-balancing relay when the diaphragm is not in the null position, a differential of 1/2 mm Hg across the diaphragm being sufficient to cause imbalance. The balancing helium pressure is normally measured with a mercury manometer.

A pneumatic pressure controller is used with the interhalogen dissolver in the same manner as the temperature controller; that is, a pressure above the set-point floods the cooling coils with water. For the control of pressure on the distillation columns, a proportional controller is used to govern the water rate in the reflux condenser. (To prevent freezing of uranium hexafluoride in this condenser the cooling water is preheated to about 65 C.)

3. Liquid Level

For small vessels (up to about 4-liter capacity), fluorothene sight glasses may be used to indicate the liquid level directly. Quartz and calcium fluoride windows are frequently used for observation of liquid level, estimation of bromine concentration, or determination of the refractive index of an interhalogen solution.

The conventional telegage system, which consists essentially of measuring the back pressure from a dipleg through which an inert gas is bubbled, has been used infrequently in volatility work. Most interhalogens are so volatile that there would be considerable loss of material if telegages were used continuously in a vented system. Also, there is the danger of back-up of the halogens to the manometers at the panelboard.

The most reliable method of determining liquid level is by the use of a cylindrical monel float whose buoyant force is continuously balanced pneumatically; a Monel diaphragm seals the instrument inself from the halogens. This commercially available instrument is used at Brookhaven National Laboratory as a liquid level controller.(8)

4. <u>Flow</u>

Flow rates are frequently determined by observing weigh tank readings (see 6 below) as a function of time. Although this method gives an accurate indication of the average rate, it is difficult to use for the initial setting of flow rates or determination of short-term fluctuations in the flow rate.

A thermal flowmeter has been developed for use with any fluorinating gas including fluorine. It consists of a hairpin loop of 1/4-inch nickel tubing passing through two brass blocks. The brass blocks are maintained at a constant temperature difference of 150 C by a proportioning type, pyrometer-controller actuated by a differential thermocouple connected across the two blocks; the pyrometer controls a resistance heater on the higher temperature block. This flowmeter requires calibration for each gas, the calibrations being independent of the bottom block temperature. The unit has been calibrated and used for flow rates between 30 cc/min and 30 1/min with respective outputs of 0.1 and 20 millivolts with an accuracy estimated to be within 3 per cent.(9)

For measurement of the rate of flow of liquid interhalogen streams a magnetic, turbine-type flowmeter with sapphire bearings (commercially available) has been used with success at the Brookhaven National Laboratory.(10)

5. Leak Detection

Each process valve has a leak detector connected between the bellows and the packing gland. The detector consists of a steel spring which is prevented from completing an electrical circuit by a nylon thread; when the valve bellows fails, interhalogens contact the nylon and the thread is severed by chemical reaction. The released spring actuates an alarm circuit at the panelboard. This method of leak detection is extremely sensitive to interhalogens; it has detected bellows-leaks which were not revealed in the initial freon test of the process valves.

Process vessels are individually leak tested in the shop and the entire plant is again freon-leak tested after assembly. Internal leaks can be located by pressurizing an adjacent piece of equipment. After interhalogens are charged, leak testing is carried out by pressurizing a piece of equipment with helium to about 50 psia and observing pressure drop over a period of several days. Potassium iodide-starch paper is generally used for indicating any interhalogen leaks.

6. Weigh Tanks

Weigh tanks are placed on scales which have a remote head operated by a selsyn motor. Direct weights can be taken at the scales by removing shielding plugs from sight holes in the shielding wall, but because of the high accuracy and dependability of the remote reading, this feature has not been used.

C. Materials Handling and Sampling

1. Interhalogens

a. Transfer by Indirect Methods

The volatile halogens are conveniently transferred under their own vapor pressure by heating the vessel to be discharged and cooling the vessel being charged. Transfer lines should be fitted with external heating coils so that residual liquid, if any, may be vaporized. Thus, after transfer, the discharged vessel and transfer line will contain only vapor at a pressure determined by the temperature of the liquid in the charged vessel.

Liquid transfers may also be made by pressurizing the initial vessel with an inert gas. This system does not require the use of an elevated temperature but has the disadvantage that some material is lost with the inerts when they are vented.

b. Transfer by Pumping

A few pumps suitable for use on interhalogens are now available.

Brookhaven has developed a canned rotor pump(11) for liquid bromine trifluoride which uses metal-to-metal bearings and a force balance system on the rotor and impeller. Both diaphragm and piston pumps(12) are also becoming commercially available for use with liquid and vapor interhalogens. A low-capacity piston pump(13) which has been used with vapor interhalogens utilizes a nickel-covered, ferro-magnetic piston material which is machined 0.001 inch smaller than the nickel cylinder. An external alnico magnet moves the piston and gas is pumped in slugs by both sides of the piston, employing gravity-closed disk-type check valves at each end of the cylinder.

c. Valves

The main process valves used are Monel packless type(14), having a bellows seal and pneumatically operated stem. This valve is for simple shut-off operation only and uses a Teflon seating disk with a machined seat integral with the body. Similar, manually operated valves of smaller size(15) (1/4 in.) are used on sampler systems (see below).

For throttling flow-control and for high pressure fluorine systems a Monel, diaphragm-type(16) needle valve was found to be the best of several designs. This valve gives satisfactory flow control down to about 20 cc per minute at a pressure drop of 20 psi.

d. Sampling

Liquid samples are taken by the system illustrated in Figure 2. The vessel whose contents are to be sampled is heated and the sample tank

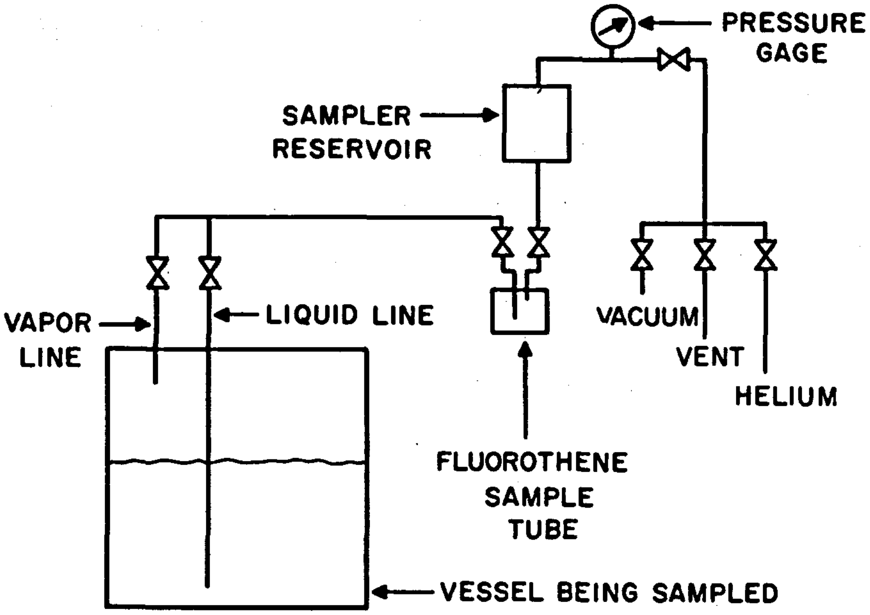

Fig. 2 - Interhalogen sampling system.

cooled, thus forcing liquid into the sample tank through the fluorothene sample tube. Lines are flushed by heating the sample tank and returning its contents to the original vessel via the return line, repeating this procedure several times before isolating the captured sample. The isolated sample is then frozen down with liquid nitrogen to allow its safe removal. Vapor samples can be taken in a similar manner. After the lines are evacuated and purged by venting, the valves are opened a few moments to fill the sample system with vapor. The sample tube is then cooled with liquid nitrogen thus condensing the vapor in the system therein.

The above techniques may be modified to avoid the large losses of material which would occur when a large number of samples are taken and when purge-venting must be extensive due to large changes in concentration between samples. A continuous purge without venting can be effected by adding a vapor pump plus a return line. This will circulate material through the sampler system at all times except when the sample is being collected and no material will be lost except that removed in the sample. A similar, continuously purged sampler(17) for liquids has also been worked out.

The technique used in hydrolyzing the samples should be briefly mentioned since most of the analytical procedures require that the interhalogen sample be put into aqueous solution. Two-quart polythene bottles are used to carry out hydrolyses; machined polythene plugs hold the sample tube in the neck of the bottle and the bottle seal is effected by a rubber O-ring compressed between screwed bottle-cap and plug.

2. Uranium Hexafluoride

For dilute solutions of uranium hexafluoride in interhalogens the comments in paragraph 1 above apply. It should be added that, whenever uranium hexafluoride is handled essentially pure, it must be maintained above 64 C to prevent solidification. Thus all UF_6 transfer lines are traced with asbestos covered nichrome heating wire and insulated with aluminum covered glass wool. The sample boxes are steam heated with a finned tube heater located at the bottom of the box.

3. Fused Salts

a. Transfers

The fused salt must be kept above 600 C to maintain fluidity. Transfer lines are fitted with external Calrod heaters with the interstices packed with steel wool and the assembly wrapped with asbestos insulation. Oak Ridge has employed both autoresistive heating (circa 200 amperes through a 1/2-inch nickel pipe transfer line) and steam heating (through 1/4-inch copper tubing tracing around the transfer lines).

b. Valves

Several freeze-type valves have been designed for use with fused salt transfer lines. A gas-tight design has been developed by Oak Ridge consisting of two loops in a 1/2-inch transfer line. The loops are about 3 feet in diameter and are connected at their tops through a bypass valve. The bypass prevents vapor binding as well as permitting retention of some liquid when the lines are drained. A sketch of this unit is shown in Figure 3.

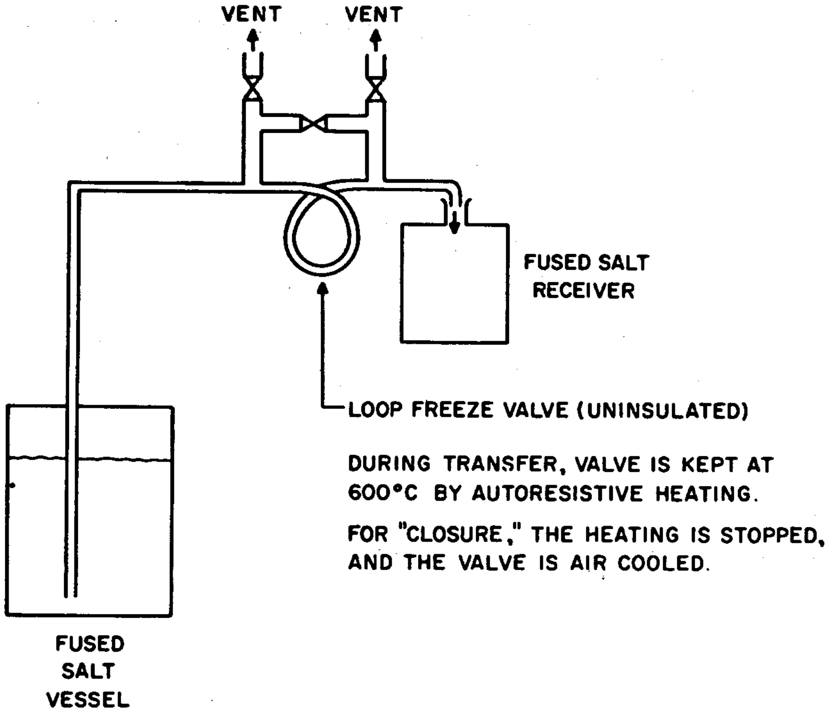

Fig. 3 - Fused salt freeze valve.

c. Sampling

A fused-salt sampler has been designed for sampling the dissolver while bromine pentafluoride or other fluorinating agents are sparging through the melt. The sample is taken in a 5/8-inch nickel-plated brass spoon attached to a nickel leader-rod. The spoon is lowered through a 1-inch pipe with a steel measuring tape and the lowering mechanism is contained in a pressure tight box having a removable window through which the tape can be read and the sample observed. The assembly is continually purged from the top downwards with helium and is sealed from the dissolver during sample removal by closing a 1 inch gate valve. A sketch of this sampler is shown in Figure 4. After lowering the spoon into the melt, the sample is raised and held in the cooler upper part of the dissolver where the salt is allowed to solidify before raising through the pipe. This eliminates any loss of the sample by liquid splashing. After removal of the spoon from the apparatus, the sample is spalled from the spoon by compressing with a pair of pliers.

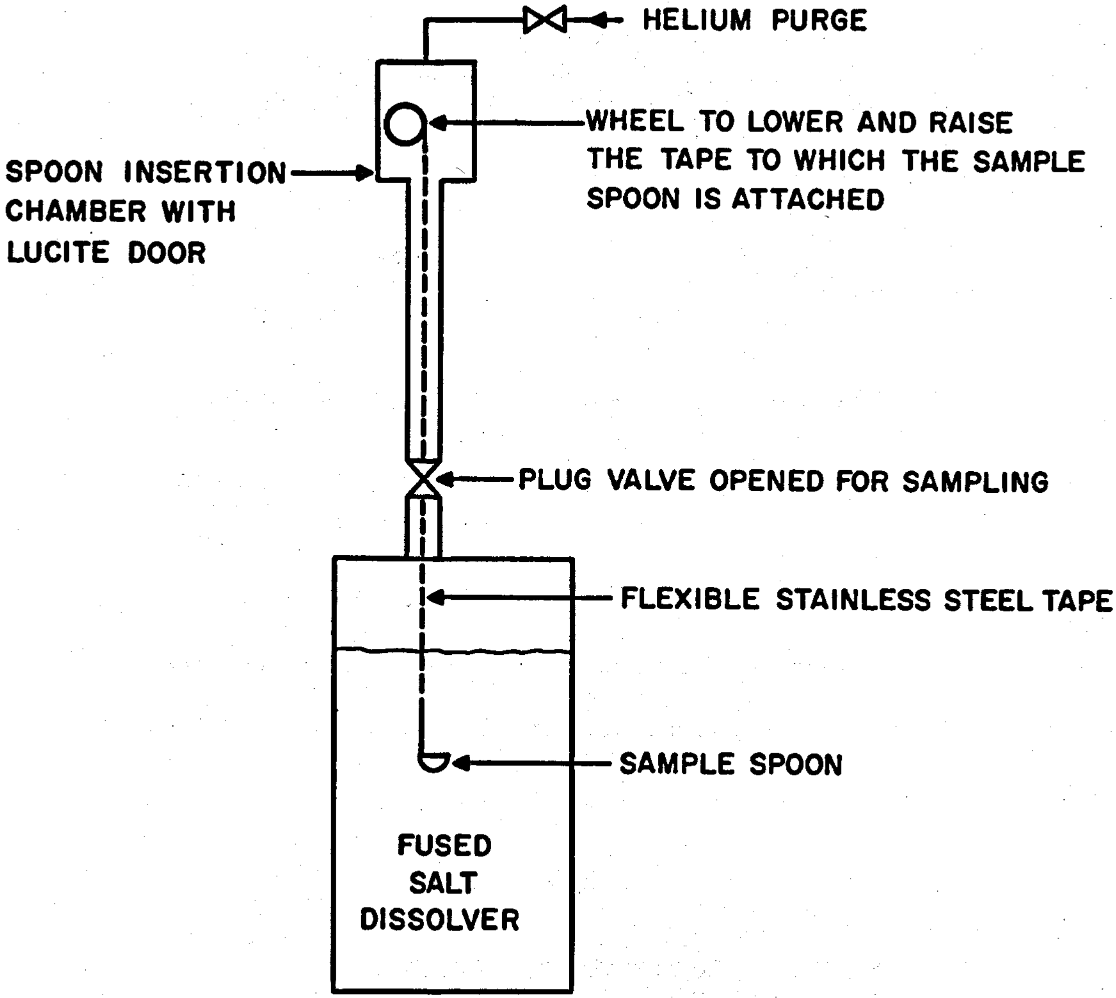

Fig. 4 - Fused salt sampler.

D. Safety

1. Introduction

Volatility separations processes as defined herein normally involve handling the materials and associated hazards listed in Table 6. The combination of radioactive and chemical hazards makes it necessary to perform many of the process operations remotely. A unique problem in the performance of volatility separations is the handling of interhalogen materials under pressure so as to prevent their escape or violent reaction with organic matter and water (including human tissue). An additional problem is the prevention of inhalation of the toxic halogen vapors and volatile fission products. For the former materials, the maximum, allowable concentration for continuous

Table 6

MATERIALS AND ASSOCIATED HAZARDS IN LOW AND HIGH TEMPERATURE FLUORIDE VOLATILITY PROCESSES

State	Material	Hazard
Solid	Zr, NaF, ZrF_4, U, UF_6, PuF_4, fission products	Radioactivity; exposure or ingestion
Liquid	NaF, ZrF_4, UF_6, BrF_3, BrF_5, Br_2, ClF_3, HF	Ignition, inhalation
Gas	UF_6, F_2, HF, BrF_5, ClF_3, PuF_6, TeF_6	Ignition, inhalation, radioactivity

exposure is about 1 ppm in air.(18,19) A lethal dose by ingestion of sodium fluoride is on the order of 5 grams.(20) The allowable concentrations in air of the volatile radioactive metal fluorides of interest are listed in Table 7.

Table 7

MAXIMUM ALLOWABLE CONCENTRATIONS IN AIR OF RADIOACTIVE MATERIALS ENCOUNTERED IN FLUORIDE VOLATILITY PROCESSES

Compound	Microcuries/ml Air [a]
$Pu^{239}F_6$	2×10^{-12}
Natural UF_6	1.7×10^{-11}
$Te^{127}F_6$	1×10^{-7}

[a] National Bureau of Standards Handbook 52, "Maximum Permissible Amounts of Radioisotopes in the Human Body, Air, and Water" (1953).

The procedures necessary to obviate the dangers outlined above and maintain the listed tolerances are described below.

2. Containment of Material

The primary container used for interhalogen materials is usually a nickel or Monel pressure vessel. This vessel is supported on a liquid-tight metal tray of equal or greater volumetric capacity. Several such vessels are normally required for the study of a process and these are located in an enclosed, ventilated area. Each vessel is equipped with a rupture disk which in turn is connected to a large safety vessel. The safety vessel is connected to a process scrub (disposal) tower to permit conversion of any vented halogen compounds to water-soluble fluorides. The safety vessel is also equipped with a drain valve for return of any condensed materials to the process.

Teflon, Inconel, Monel and nickel rupture disks have been used with success. Since the thickness of the rupture disks is only in the order of a few mils, it is common practice to coat the disks with a film of fluorothene to provide additional protection against corrosion.

Thus, by the use of trays, safety vessels and rupture disks primary provision is made for confining both liquid and vapor leaks.

Steel, concrete, or glass enclosed ventilated areas serve as a barrier to protect operating personnel from gas jets or liquid sprays. Entrance into these areas is held to a minimum during operation and is done, if absolutely necessary, with the precautions to be discussed. If necessary, small holes can be drilled in the enclosure to permit insertion of extension handles to reach the valves attached to the vessel. Wherever possible, equipment is remotely operated. Where a pipe transporting halogen materials must traverse an open area, the technique of double piping may be used to insure that there will be no release of toxic materials into an unventilated region. Finally, in any working area containing halogens, it is mandatory that organic and aqueous material be kept to a minimum. Such organic materials as electrical or thermal insulation can be protected by fluorothene film or aluminum foil. Cooling water coils around vessels are made by attaching copper tubing to the vessel with copper spray metal. Condensers on distillation columns are constructed in the same manner. This technique of providing a double wall between the water and interhalogens has been used for several years on various pieces of equipment with complete success in avoiding incidents.

The safety aspects of an interhalogen dissolution of uranium are sufficiently unique to warrant some emphasis. If the dissolution reaction:

$$U + 2\,BrF_3 \longrightarrow UF_6 + Br_2$$

were proceeding too rapidly, one obvious remedy would seem to suggest itself, namely, dump the bromine trifluoride liquid which is reacting with the uranium. However, this dumping of the liquid is the very thing to be avoided, since when metallic uranium is exposed to bromine trifluoride vapors at temperatures at or above 150 C, ignition of the uranium results.(21) Hence, cooling of the dissolver is the most effective way of quenching an errant dissolution.

In the fluorination step of processing fuels by fused-salt volatility methods, it is necessary to contain hazardous materials such as elemental fluorine or bromine pentafluoride at a temperature of about 600 C. Experiments have shown that ordinary 1020 steel ignites when exposed to these strong fluorinating agents at this elevated temperature. Nickel or Monel do not ignite. Also, tests have shown that a 5-mil coating of nickel over the steel is sufficient to prevent the ignition (see previous Section).

3. Handling Escaped Materials

If the primary barrier is breached and halogen materials are released into the cell, it is then necessary to convert the halogens to a non-reactive form. A reliable method of accomplishing this is to hydrolyze the reactive halogens in a spray tower. Tests have shown that about 60 gpm of a 10 per cent caustic solution is adequate to scrub about 5000 cfm of air.(22)

10

The halogens are converted to the soluble potassium fluoride or bromide during contact with a spray of aqueous potassium hydroxide. Potassium hydroxide is employed because of the high solubility of potassium fluoride in water. A cocurrent spray tower, rather than a packed tower, is used because of its low pressure drop. If hydrogen fluoride alone were the contaminant, a limestone bed could be used to convert the gas to calcium fluoride.(23)

Since it is possible that radioactive particulate matter would be present in the leak, both disposal methods outlined above require that standard AEC filters be present in the exhaust system. Tests on the exposure of AEC filters to various halogens in an air stream have shown that a gradual structural weakening results rather than ignition or destruction of the filter. Halogen concentrations in air ranging from about 2 per cent to 20 per cent were used. It was observed that about 3 pounds of reactive halogens could be passed through a filter before the pressure drop across the filter began to decrease appreciably. Small dark spots were observed, indicating localized reaction with either the filter or dust or both. Since several hundred pounds of interhalogens are normally involved in pilot plant operations, it is clear that a device such as a caustic scrubber is required to remove the bulk of the halogens from the air stream to prevent a decrease in filter efficiency and life-time.

In addition to the ventilation scrubber for ambient air, a process scrubber is also available for disposal of waste halogen process streams. The process scrubber consists of an 8-inch diameter Monel pipe with an 8 foot long contacting section. Two spray nozzles are located in series in the upper one-third of the tower. About 15 gal/min of caustic is pumped through the nozzles. This vertical spray tower has been used to dispose of approximately 500 lb of mixed interhalogen wastes from both laboratory and pilot plant operations.

4. Personnel Safety

When it is necessary to come into close contact with equipment containing halogens (such as in sampling or maintenance operations), protective clothing is used. Normally, leather or neoprene gloves and a face shield are worn. However, for some operations involving greater hazards, leather trousers and a leather jacket are also worn along with an assault mask. When it is necessary to work in an area containing high halogen concentrations in the air, a helmet with an independent air supply is worn.

Good safety policy consists of having at least two people present when working with halogens. Safety glasses are worn at all times.

Carbon dioxide fire extinguishers are also available; this is the only type of extinguisher that is acceptable in an area containing interhalogens.

5. First Aid

Each laboratory has safety showers, eye wash fountains, and crocks containing magnesium sulfate solution. Workers are instructed to use these facilities at the slightest suspicion of halogen exposure. In all incidents, the Medical Department is notified immediately; the physician can then give additional treatment, such as calcium gluconate injection, if necessary. The object of both the magnesium sulfate (or oxide) and calcium gluconate treatment is to convert the hydrogen fluoride to the insoluble calcium or magnesium fluoride. A recent development in the treatment of fluoride burns is the use of quaternary ammonium compounds which are believed to function on the ion exchange principle.(24)

The important principle to be followed in dealing with an individual who has been in a halogen-contaminated atmosphere is speed in removal from the area followed by a drenching shower to wash the hydrofluoric acid from the skin. If hydrofluoric acid has entered the eyes, at least a five-minute irrigation with water is recommended. If some of the halogen were taken internally, the individual should immediately drink a large quantity of water.(25)

Materials such as fluorine, chlorine trifluoride, bromine pentafluoride, etc., all require the same first aid as outline above, since during their reaction with body fluids hydrofluoric acid is produced. However, in addition to the chemical effect (reaction with tissues, etc.), thermal damage can occur because of the highly exothermic nature of the fluorination.

All of the first aid facilities in a laboratory are given periodic inspection to insure that they are in working order.

6. Incidents

Most of the incidents which have occurred during the handling of interhalogens have been of a relatively minor nature. A list of those reported is given below, followed by another list of the lessons emphasized by the incidents.

a. A vacuum distillation of bromine trifluoride from a one-ounce sample of a graphite material was being conducted in an aluminum vessel. When the bulk of the bromine trifluoride had been distilled off, a sudden release of gas occurred at about 100 C. The vessel then exploded and the individual performing the operations was injured by fragments from the vessel.

b. A fluorothene tube for interhalogens exploded while being refrigerated with dry ice-acetone mixture in a glass dewar. Some of the glass fragments struck the individual in the eyes and face. The glass dewar was wrapped with transparent tape since the experiment required observing crystals of bromine pentafluoride at -78 C.

c. An open waste container containing liquid interhalogens contacted some combustible material; the individual handling the container was exposed to some drops of the liquid and to the fumes. (The waste container was initially assumed to be empty).

d. While pipetting bromine trifluoride, a drop fell on a nearby dewar flask containing acetone. This small amount of bromine trifluoride reacted with the acetone and ruptured the glass dewar scattering the acetone and glass. Some of the acetone then fell into an open container of bromine trifluoride, which had been left from another operation, causing further reaction and splattering. No personnel injury or equipment damage was sustained other than the loss of the dewar.

e. Preparatory to transferring about 80 cc of bromine pentafluoride a nickel receiver was dried. The receiver was then chilled to minimize vaporization of the volatile bromine pentafluoride during the transfer. About 10 cc of the liquid had been poured from a fluorothene beaker into the nickel vessel when a sharp explosion hurled the beaker from the grasp of the operator into a corner of the hood. Although the explosion was so rapid that the operator had no time to move, the protective clothing and hood ventilation gave protection. The cause of the incident was a reaction between the bromine pentafluoride and water which had condensed in the nickel vessel during the cooling operation. This occurrence took place on a warm, humid day.

f. Ten grams of irradiated uranium was placed in a one-half inch copper tube together with 37 grams of crude bromine trifluoride; the tube was then plugged shut and allowed to stand at room temperature in a lead shield. Two hours later the tube exploded showering the room with halogens and fission products. The copper tube was propelled through the transite roof of the hood. Some pertinent information concerning this incident is as follows:

(1) The incident occurred very early in the history of the volatility program; at that time the autocatalytic nature of the dissolution was not known.

(2) The same operation had previously been done with distilled bromine trifluoride with no reaction noted.

(3) The tube was open to the atmosphere about ten minutes during the charging of the uranium and bromine trifluoride.

(4) The lower end of the copper tube was spun and sealed with silver solder. The other end had a flare nut seal.

(5) There were no casualties from the incident; however, one individual was showered with red fumes (bromine) and about 20 mr/hr of beta-gamma activity.

(6) 90 per cent of the initial beta-gamma activity in the metal scattered; 10 per cent remained in the tube.

g. While transferring an interhalogen dissolver solution under 2000 mm Hg pressure (containing UF_6, Br_2, BrF_3, PuF_4, and fission product fluorides) a leak developed in the transfer line. The exact location of the failure was a connection between a copper and nickel tube which had been silver soldered. About 350 ml of the radioactive solution spilled both into the hood and unto the laboratory floor. The copper-nickel couple had behaved satisfactorily for ten previous transfers. Two hundred grams of irradiated uranium was present in the solution. No injury or contamination to individuals resulted because of their remote location.

h. While charging a bromine trifluoride purification still, a cylinder containing 15 lbs of the crude interhalogen was connected to a metering tank. An operator not connected or familiar with the still, while working with another piece of equipment, inadvertently applied helium pressure to the tank, thus forcing about 13 lbs of the bromine trifluoride out of the vessel. The material was discharged into a hood; the hood doors were immediately closed. No injury to personnel resulted. The helium manifold, with open valves, which serviced several pieces of equipment was contributory to this incident.

i. A section of a fluorine transfer manifold containing lead seated, brass valves ignited during a transfer from a cylinder at 400 psig to a storage tank at 30 psig. The intense heat caused volatilization of the brass and melting of some of the nickel lines. The use of a concrete and steel cell around the fluorine cylinders, manifold, and storage tank gave protection to the operators. Even though about 4 pounds of fluorine was released, only a faint fluorine odor could be detected outside the cell area; 1000 cfm of air ventilated the fluorine storage area which had a volume of about 500 cubic feet.

j. A dissolution of about 1 kg of unirradiated uranium metal with bromine trifluoride in an aluminum dissolver resulted in rupturing the dissolver vessel. One individual received superficial fluoride burns; all personnel involved wore face shields. No rupture disk or blowoff valve was present on the vessel. It is likely that ignition was probably started by exposure of the slug to the vapor phase of fluorine, bromine trifluoride, bromine, uranium hexafluoride. The metal was initially covered with liquid; however, sufficient material was volatilized from the dissolver into a cold trap during the dissolution to expose the slug to the vapor. The temperature just before the ignition was 162 C. This incident occurred before the study of the ignition of uranium in interhalogen vapor had been made.(26)

k. Several ruptures of fluorothene tubes which are used both as sample tubes and as cold traps have occurred. Liquid fluorine and liquid uranium hexafluoride have been in the tubes during most of the incidents. It is known that prolonged exposure of tubes to liquid uranium hexafluoride results in deterioration of the fluorothene. One incident involved chlorine trifluoride which had been frozen in a 3/4-inch fluorothene tube. Upon melting, the interhalogen apparently reacted with some oil in the bourdon tube of an improperly degreased pressure gage which was connected to the tube. The tube ruptured scattering some of the liquid chlorine trifluoride on an individual standing neraby. Some burns on the leg resulted.

l. A small-scale dissolution of uranium metal in a bromine trifluoride-bromine pentafluoride solution in a nickel vessel resulted in sudden discharge of the interhalogens because of a failure which developed in a thermocouple well immersed in the liquid phase. A similar failure of a weld at the end of a thermowell occurred in a still pot containing about 40 pounds of interhalogens under 3 atm pressure.

m. During check-out operations on a distillation column made of 2-inch IPS, type 3SF aluminum pipe, a fire and explosion occurred. The equipment had previously been used intermittently for a period of about 18 months. The interhalogen solution during the incident consisted of about 50 per cent bromine trifluoride, less than 2 per cent bromine, and the remainder uranium hexafluoride and bromine pentafluoride. Other pertinent data on the incident are as follows:

(1) The entire still assembly was contained in an aluminum covered plywood box. This enclosure confined the explosion and most of the fumes so that no hazards to personnel were involved.

(2) Sufficient heat was generated to melt the aluminum in some locations. It seemed likely that a small leak in the feed line developed thus causing interhalogens to contact the Glascol heating mantle on the column and to ignite explosively.

(3) The still pot made of 2S aluminum was ruptured.

n. A copper cold-trap exploded as a result of inadvertantly condensing both water and bromine pentafluoride in the same trap. The water was that amount present in the air in a nickel overhead receiver which was being evacuated. The interhalogen vapors were condensed from the distillation column. Shortly after removal of the liquid nitrogen coolant, the bottom of the cold trap was blown out. Pieces of copper were scattered throughout the room; fortunately, no one was near the tube at the time of the rupture. The cold trap was being used to protect a mechanical vacuum pump.

Of the incidents reported, five resulted in injury such as halogen burns to the individual. The use of ventilated cells or hoods and the wearing of protective clothing prevented halogen attack in all other incidents. It is estimated that the incidents have occurred during a time interval corresponding to about 200,000 man-hours of laboratory and pilot plant work. It is significant that during this long period of handling of halogen materials, only a few events involving hazards to individuals have resulted.

From these incidents one can make the following rather obvious recommendations:

1. Avoid contact of reactive halogens with reactive items such as graphite, wood, skin, paper, grease, acetone, water, etc.
2. Use metal dewars for refrigerating cold traps in halogen systems; however, if glass dewars are used a protective shield is necessary around the trap assembly.
3. Before disposing of vessels, lines, or valves which have contained halogens, one should first blow them out with air and then give them a water wash to insure that there are no residual halogens.

4. Do not allow halogen reactions to take place in a vessel without a rupture disk, particularly if the vessel has no pressure gage or if it will be left unattended.

5. Avoid junction of dissimilar metals in piping which will contain liquid interhalogens since electrochemical corrosion will result.

6. Avoid brass valves in pressurized fluorine systems.

7. Use nickel or Monel for vessels containing interhalogens rather than aluminum.

8. Fluorothene tubes should not be used repeatedly for liquid fluorine or uranium hexafluoride without first checking for evidence of weakening (such as cracking).

9. The operating personnel should understand the experiment they are performing and the equipment they are using.

10. Since cold traps for protecting vacuum pumps are always somewhat of a nuisance and a hazard, it is desirable to minimize their use. For low vacuums steam jets can be used; if high vacuums are needed, fluorolube oil can be used in mechanical vacuum pumps which are nickel plated. The interhalogens can then pass harmlessly through the pump.

Part II—Economics

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The art of volatility processing is not yet sufficiently advanced to warrant assigning firm costs to the various flowsheets. It is of interest, however, to attempt a qualitative comparison with existing solvent extraction processes.

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For the two types of volatility processes which have been discussed in this session (low-temperature interhalogen dissolution and high-temperature fused-salt dissolution), complete processes have been proposed, hypothetical plants designed, and capital and operating costs calculated. These costs should be viewed as indicative only. Comparisons with previous estimates or actual operating figures for solvent extraction plants have been deliberately avoided, as sufficient time was not available to assure that these estimates were made upon bases completely comparable with solvent extraction information.

LOW TEMPERATURE PROCESS

A. Introduction

In this process it is assumed that natural uranium fuel elements are de-jacketed and then charged to a dissolver in which they are dissolved by liquid interhalogens. Volatile uranium hexafluoride is removed and decontamination then completed by fractional distillation. Plutonium and most of the fission products remain in the dissolver. These may be removed together by an aqueous wash and the plutonium subsequently recovered by solvent extraction, or the plutonium may be selectively removed in one operation by fluorination at an elevated temperature. A schematic comparison of these processes with solvent extraction is shown in Figures 5 and 6.

In the uranium cycle (Figure 5), the advantage accruing to the volatility method is a decrease in the number of processing steps which is achieved by replacing the solvent extraction, denitration, reduction, hydrofluorination, and fluorination steps of the solvent extraction process with a single distillation operation. Both the capital investment and operating costs are thus decreased.

In the plutonium cycle (Figure 6), an additional dissolution step is required in the volatility process if conventional solvent extraction methods are to be used to recover the plutonium (Process I). However, if the plutonium can be fluorinated and volatilized away from most fission products and then purified by distillation (Process II), the number of steps in the

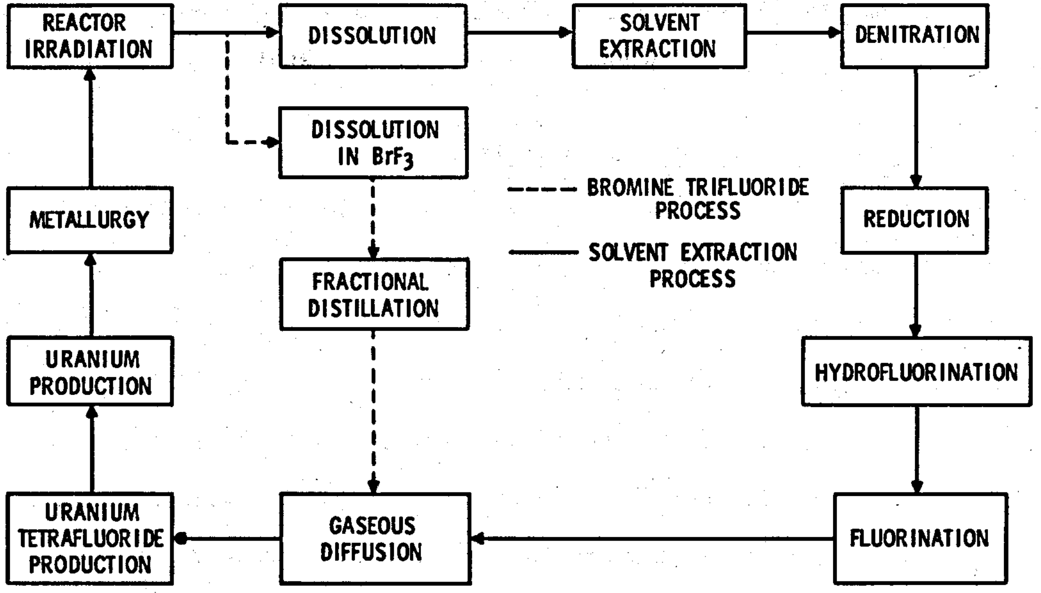


Fig. 5 - Comparison of steps in bromine trifluoride volatility process and the solvent extraction process, uranium cycle.

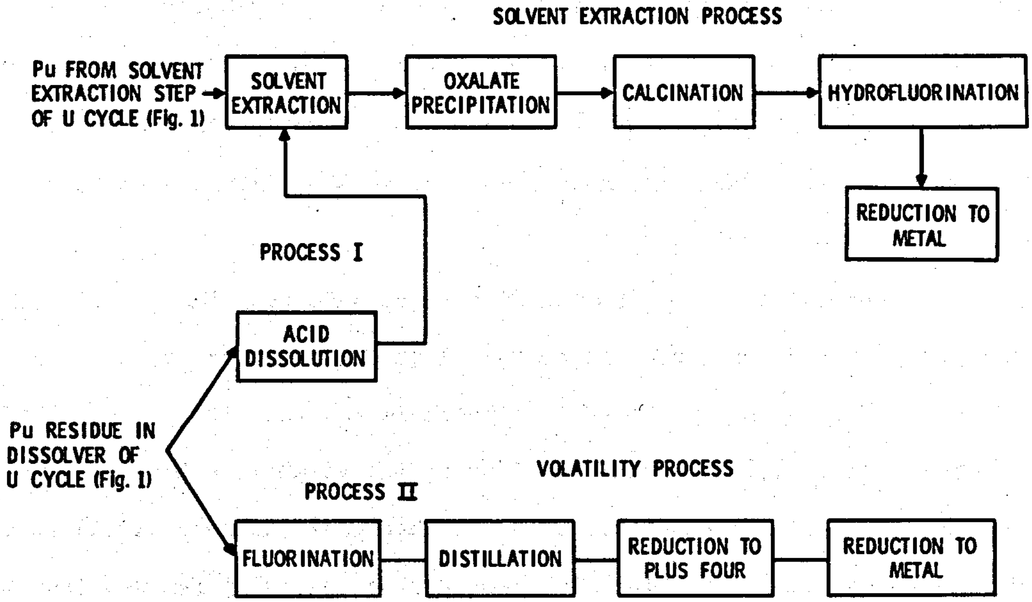


Fig. 6 - Plutonium recovery - Comparison of steps in bromine trifluoride volatility process and solvent extraction process.

process are again reduced compared to the overall aqueous flowsheet.

Disadvantages, however, exist in volatility processing. Generally, the temperatures and pressures are higher than those required in aqueous processing. Most materials of construction must be inert to fluorine, and a greater health hazard is likely because of the higher pressures. And, finally, most of the process streams are more difficult to handle than those found in aqueous flowsheets.

B. Process Description and Flowsheets

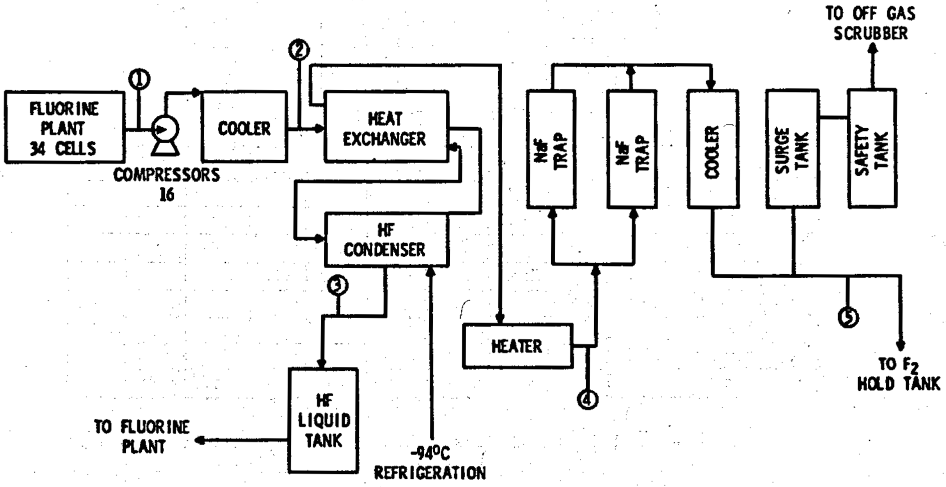
For estimating purposes a process and a plant to handle three metric tons per day of uranium and 2 kg per day of plutonium are hypothesized. The process consists in dissolving the dejacketed slugs in bromine trifluoride thereby forming a volatile uranium hexafluoride, a non-volatile plutonium fluoride, fission-product fluorides of varying volatilities, and bromine. The volatile uranium hexafluoride is removed from the dissolver as a gas along with the bromine, any bromine pentafluoride present, very small amounts of bromine trifluoride (since its boiling point is high), and also the volatile fission-product fluoride of tellurium. Due to its low boiling point, the latter is quantitatively vented as a gas when the remainder of the vapor is condensed. The condensate is then fluorinated, converting the liquid bromine to the trifluoride, and a small amount of the pentafluoride may also form in this step. The uranium hexafluoride in the mixture is then obtained as a pure product by distillation.

The non-volatile plutonium fluoride is removed from the dissolver by a non-aqueous liquid carrier. The carrier liquid is evaporated, leaving a plutonium and fission-product residue which is reacted with elemental fluorine to form volatile plutonium hexafluoride and the volatile ruthenium and niobium fluorides. The plutonium hexafluoride is then purified in a distillation column. Ruthenium and niobium fluorides are occasionally removed from the distillation pot by washing with aluminum nitrate solution. The other fission product residue left in the evaporator after the fluorination is also removed with aluminum nitrate wash. Except for iodine no fission product builds up in the volatility system. The iodine remains with the bromine trifluoride and is recycled to extinction.

Considerable pilot-plant design data on the uranium dissolution and purification have been obtained. No pilot-plant data have been obtained on the plutonium recovery system although bench-scale experiments have indicated that the conservative batch system presented is workable.

1. <u>Fluorine Supply System (Figure 7)</u>

Fluorine gas is produced by thirty medium-temperature fluorine cells operating at approximately 3260 amperes. Four other cells are in maintenance or on standby. Gas from the cells is moved by a blower through the hydrogen fluoride removal system consisting of a refrigerated cooler, in which the major portion of the hydrogen fluoride is removed, and a sodium fluoride absorber for further removal of hydrogen fluoride (the gas originally containing 10 to 14 per cent hydrogen fluoride would then contain less than 3 to 4 per cent). The gas is next compressed to slightly above the process



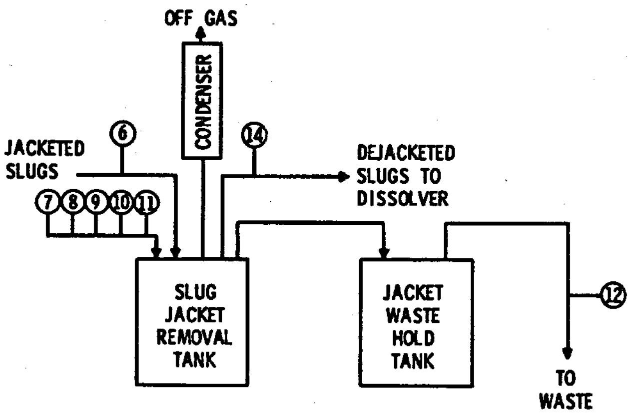
QUANTITY	1	2	3	4	5
F_2 lb/hr	135.7	135.7		135.7	135.7
HF, lb/hr	3.02	3.02	2.29	0.73	0.013
Temp, F	70	70	-94	212	70
Pressure, psia	~15.7	~50	~50	~50	~45

Fig. 7 - Fluorine supply system, flowsheet 1.

dissolution pressure and again put through a similar hydrogen fluoride removal system to remove the last of the hydrogen fluoride.*

2. Dejacketing System (Figure 8)

Slugs shipped to the plant in shielded baskets are removed from the shielding by a remotely-operated monorail hoist which carries the slugs to the jacket-removal dissolver. The aluminum jackets are dissolved by a 10 per cent sodium hydroxide-20 per cent sodium nitrate solution. The dejacketed slugs are then rinsed with a five per cent nitric acid solution and allowed to air-dry. They are then remotely charged to the dissolver.



	6	7	8	9	10	11	12	13	14
NaOH, lb/batch		398.9	398.9						
$NaNO_3$, lb/batch		797.5	797.5						
HNO_3, lb/batch					103				
H_2O, lb/batch		2790	2790	2000	2000	2000			
U, kg/batch	3000								3000
Pu, g/batch	2000								2000
Al, lb/batch	218.1								
Volume, gal		384	384	240	240	240	~1600	~232	

Fig. 8 - Slug jacket removal system, flowsheet 2.

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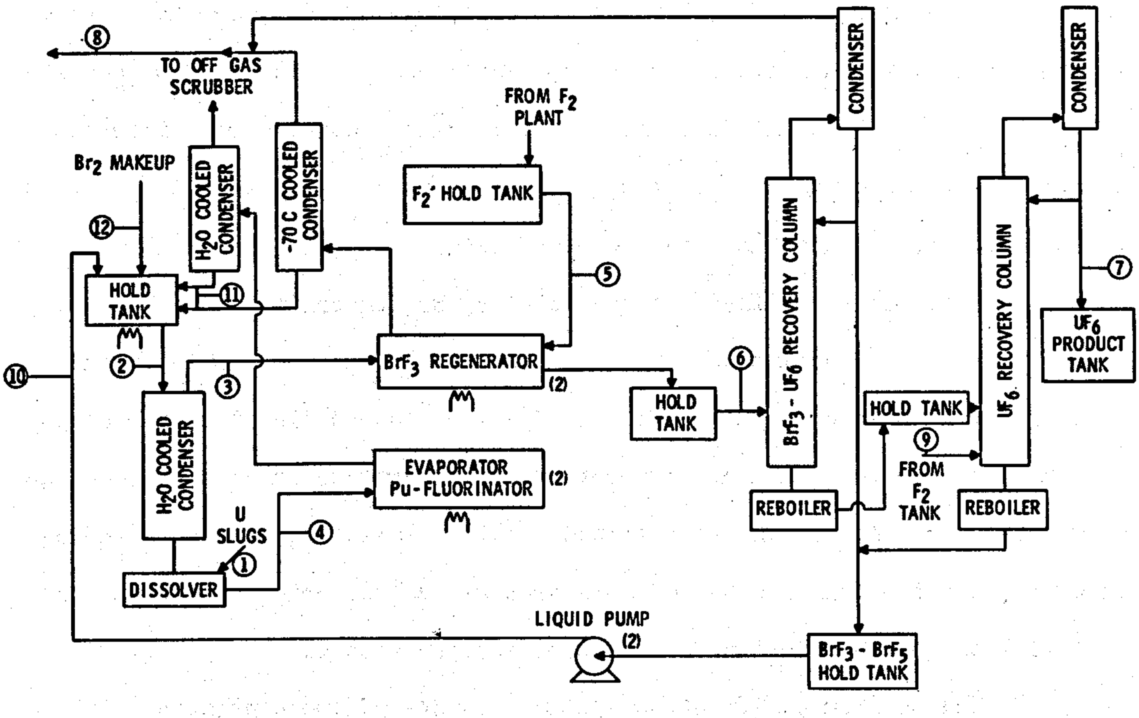
* The hydrogen fluoride removal from the fluorine has been presented as a two-step process, i.e., refrigeration and sodium fluoride absorption to three per cent hydrogen fluoride and then the refrigeration-sodium fluoride treatment again. This has been done because accurate cost data are available for producing fluorine containing a three per cent hydrogen fluoride impurity. In an actual plant the hydrogen fluoride concentration would be reduced to a low amount with only one pass through the refrigerant-adsorber. Amount and cost of equipment would be approximately the same.

3. Dissolution, Bromine Trifluoride Regeneration, and Uranium Purification (Figure 9)

The dissolution system consists of the dissolver and condenser, the evaporator and condenser, and the fluorinating-liquid hold-tank. The dissolution of the slugs in the bromine trifluoride-bromine pentafluoride liquid is semi-continuous. Two material streams enter the reactor--the slugs and the fluorinating liquid; two material streams leave the reactor--the uranium hexafluoride product stream and the plutonium product stream.



QUANTITY	1	2	3	4	5	6	7	8	9	10	11	12
BrF_3, lb/hr		317.0		31.7		308.9		To 1.1 # Br_2		308.9	31.7	
BrF_5, lb/hr			Trace	Trace		10.0				10.0	Trace	
Br_2, lb/hr			185.0	1.95*		0 to Trace					1.95	1.1
F_2, lb/hr					134.6			1.3-2.3*	1.0			
Pu, lb/hr			0.18									
UF_6, lb/hr			407.6	Small Amount		407.6	407.6					
N_2, lb/hr	~30							~30				
U, lb/hr	275.6											
Temp., C				120	Room							Room
Pressure, psia				40	50		45	15		45		145

*Estimated

Fig. 9 - Uranium dissolution, solvent regeneration, and uranium purification, flowsheet 3.

The slugs are added as required to the dissolver through a triple-valve system sealed by inert gas; liquid fluorinating agent is added as required from the liquid hold-tank. A uranium hexafluoride product gas stream is taken periodically from the dissolver-condenser and condensed in the bromine trifluoride regenerator. A portion of the liquid fluorinating agent containing the plutonium and fission products is removed periodically to the evaporator where the fluorinating agent is evaporated, condensed, and returned to the liquid hold tank.

Dissolver liquid is kept at approximately 120 C by cooling water in the coils of the dissolver condenser; system pressure is kept at approximately 40 psi by bleeding the uranium hexafluoride product stream from the dissolver. A dissolution rate of approximately 0.13 lb/(hr)(sq in) obtained in the pilot plant runs has been used for design purposes.

The bromine trifluoride regeneratory system consists of the regenerator tank, fluorine supply tank, and the condenser. Liquid in the regenerator is held at approximately 25 C while fluorinating the bromine to the bromine fluorides in a closed system. Any inert gas is bled through the condenser as required. The fluorinated liquid, consisting of uranium hexafluoride, bromine trifluoride and some bromine pentafluoride, passes to the distillation column hold-tank of the purification system.

The uranium purification system consists of two continuous distillation columns, condensers, hold tanks, and liquid pumps. In the first column a split is made between any bromine pentafluoride present and the uranium hexafluoride plus bromine trifluoride. The latter fraction is separated in the next column. Both distillations are performed at approximately three atmospheres absolute pressure. All bromine fluoride streams from the two columns pass to a common hold-tank from where the liquid is periodically pumped to the liquid hold-tank of the dissolution system. Volatile fission-product tellurium is bled to the scrubber system from the first distillation column condenser.

If the bromine pentafluoride concentration builds up in the system, it may be necessary to divert some bromine pentafluoride from the first column overhead to the solvent regenerator. No additional equipment is required since the liquid can be drained by gravity to the regenerator tank which is at a lower level and also pressure than the distillation columns.

4. Plutonium Recovery (Figure 10)

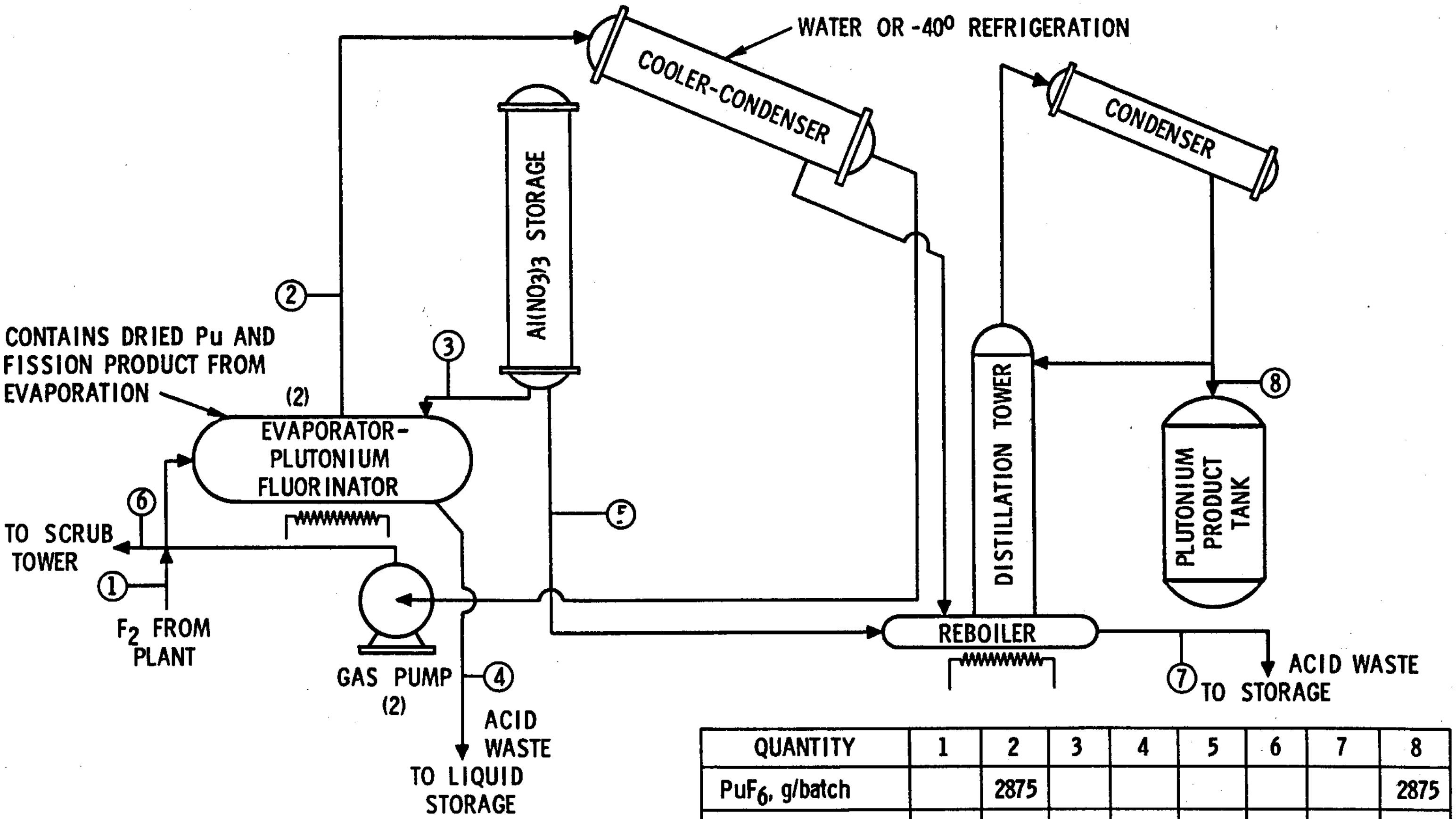
The plutonium recovery system consists of the evaporator of the dissolver system, a cooler-condenser, gas pump, distillation tower, and a wash storage drum. The dry fission product and plutonium fluorides remaining in the evaporator after the evaporation of the fluorinating agent are reacted with fluorine gas at approximately 350 C. The fluorine gas is recirculated by a diaphragm pump successively through the hot reactor, a cooler in which the gas is cooled to 150 C to protect the pump, and then to the pump inlet. When the fluorination is completed the water in the cooler coils is replaced by refrigerated liquid (-60 C) and the plutonium hexafluoride is stripped from the circulating gas. Volatile niobium and ruthenium fluorides are also removed here. Some plutonium tetrafluoride will be present due to decomposition of the hexafluoride although the amount of this component should be small since the operation is carried out in a fluorine atmosphere. The contents of the condenser are liquified and drained to the distillation column where the plutonium is separated from the fission-product fluorides. Niobium and ruthenium fluoride solid residues are removed from the distillation pot by an acid aluminum-nitrate wash as required.

5. Off-Gas Scrubbing Equipment

The off-gas scrubbing equipment consists of a vertical scrub tower through which a solution of potassium hydroxide is circulated. Any process gas vented from the process equipment passes through this tower. The scrub liquid is considered an highly active waste.

C. Building and Plant Area

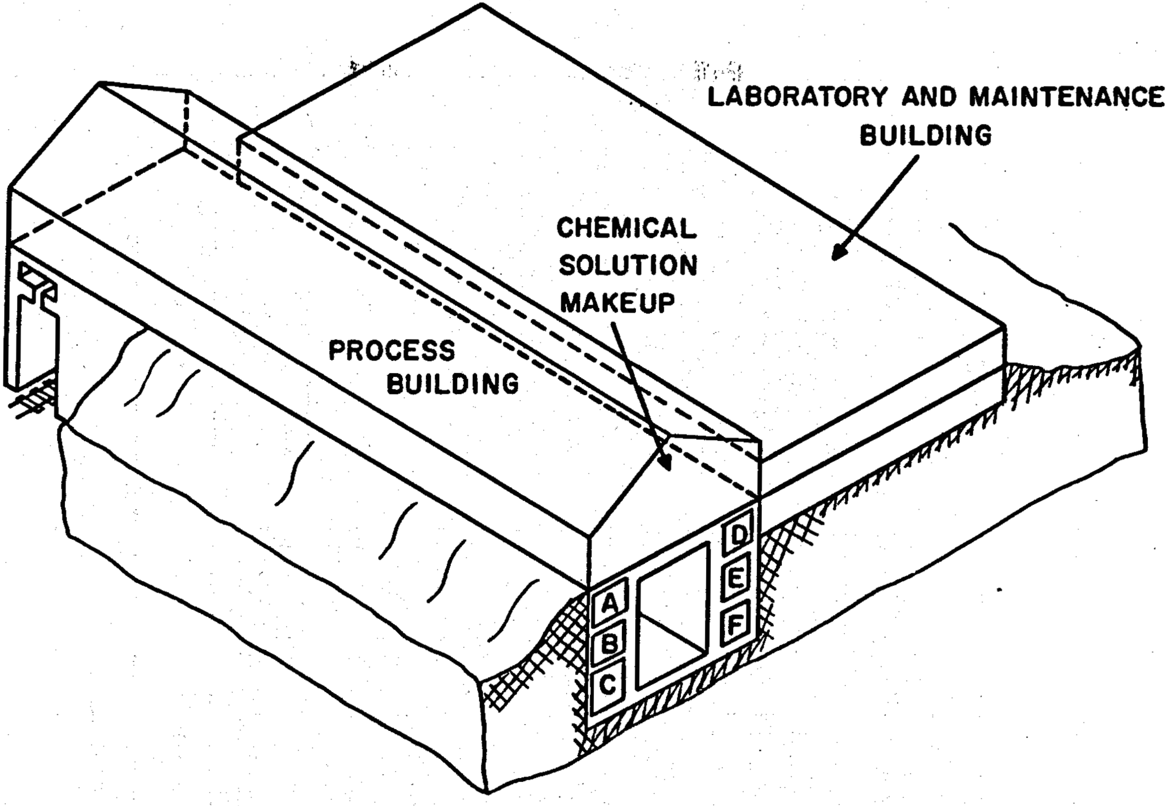
A single building, shown in Figure 11, houses both the processing area



QUANTITY	1	2	3	4	5	6	7	8
PuF_6, g/batch		2875						2875
F_2, g/batch	1089					223		
$Al(NO_3)_3$, lb/batch			31.3	31.3	0.03*		0.03*	
HNO_3, lb/batch			58.7	58.7	0.06*		0.06*	
H_2O, lb/batch			99.9	99.9	0.1*		0.1*	

*Pot washed every tenth day, estimated.

Fig. 10 - Plutonium recovery, flowsheet 4.



A. OPERATING GALLERY
B. COLD SERVICES
C. AIR & ACCESS
D. SAMPLE GALLERY
E. HOT PIPE
F. HOT EXHAUST

Fig. 11 - Diagram of process and laboratory buildings.

and the laboratory and maintenance area. The processing cell block is approximately 65 feet long, 40 feet wide, and 30 feet high. Below ground level the construction is class I (blast-resistant construction) while above ground level the construction is class II (blast-resistant structural frame with friable walls).

The processing section consists of five cells, all lined with stainless steel on the inside surfaces. A layout of the cells and equipment is shown in Figure 12. The aqueous solution make-up and feeding equipment facilities are on the upper level operating deck.

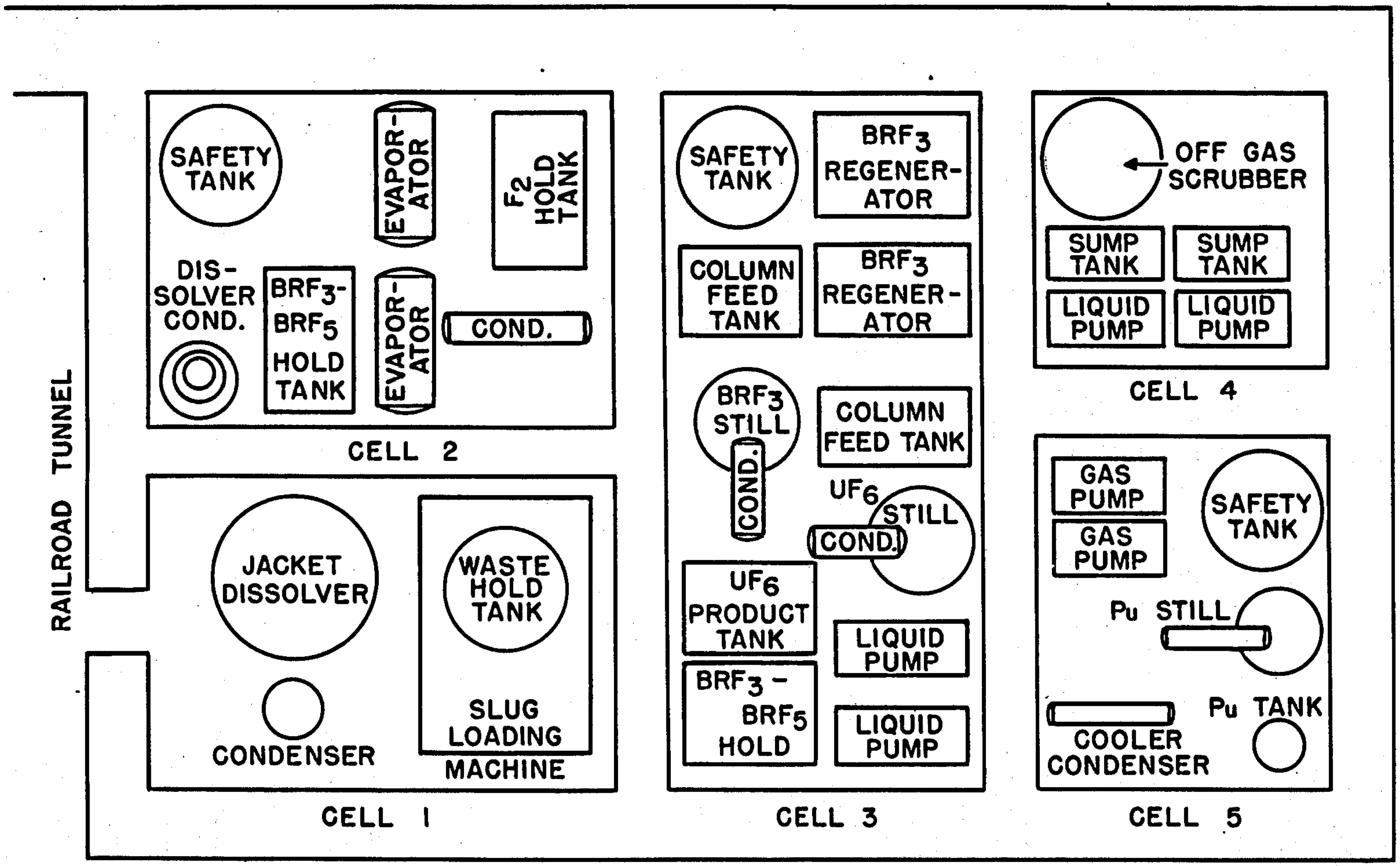


Fig. 12 - Process cells.

The laboratory and maintenance section is a two-story structure running the length of the processing area. It contains the laboratories, change rooms, offices, stores, and shops.

Other plant buildings include a fluorine production plant, a fluorine compression and purification plant, refrigeration plant, chemical storage building, a laboratory-waste evaporator building, steam, water, compressed air plants and an electrical distribution plant. In addition, there are the following areas: retention basin, underground liquid-waste storage, burial ground, waste-burning ground, and a stack filter for gaseous waste.

D. Cost Data

The plant is designed to process three metric tons of uranium and 2000 grams of plutonium per day. The fuel elements are cooled for 120 days prior to processing. Uranium hexafluoride, plutonium hexafluoride, and the fission products in acid solution are the products. Direct maintenance of equipment is considered in all cost estimates.

Processing both uranium and plutonium by volatility methods would result in a total cost of about $15 per gram of plutonium if all costs are charged to the plutonium. The total cost can be broken down as follows:

Annual Cost Summary

Item	Dollars per Year	Dollars per Gram Pu
Fixed investment	4,988,400	6.83
Operating cost	4,192,574	5.74
SF inventory charge	2,016,000	2.76
Working capital	17,400	0.02
TOTAL	11,214,700	15.35

The fixed investment is amortized in 6-2/3 years plus a 1 per cent average interest charge on the investment, equivalent to amortizing at 16 per cent per year. The special materials inventory is taken at 4 per cent.

The estimating methods and bases and sources of costs are detailed in Appendix A. The capital investment is detailed in Appendix B-1; the operating cost in Appendix B-2; the inventory and working capital charges in Appendix B-3.

HIGH TEMPERATURE PROCESS

A. Introduction

Enriched uranium-fueled reactors are likely to be important for such applications as ship propulsion and as the "seed" core for multizone power reactors such as the PWR. These fuel elements are alloyed or clad with zirconium or stainless steel. In this paper are considered the economics of a fused-salt volatility process applied to the processing of high zirconium, highly-enriched uranium-alloy reactor fuel (which cannot be dissolved in liquid interhalogens).

The chief steps of the fused salt process are the following:

(1) dissolution of the alloy in molten $NaF-ZrF_4$ with an hydrogen fluoride vapor sparge at about 600 C and atmospheric pressure,

(2) fluorination of the uranium tetrafluoride to uranium hexafluoride, this product being volatilized from the melt at 1 atm and 600 C with partial decontamination,

(3) final decontamination of uranium hexafluoride by fractional distillation.

A fused-salt process may be used to extend application of fluoride-volatility methods to recovery of decontaminated uranium hexafluoride from high zirconium-uranium fuel alloys. The chief advantages of the low temperature process are retained, namely,

(1) a minimum number of process steps for uranium hexafluoride product,

(2) provision of a liquid phase to remove the heat of reaction,

(3) retention of the bulk of the fission products as a concentrated

non-volatile residue after the volatilization of uranium hexafluoride.

A qualitative comparison of the fused-salt volatility process with established solvent-extraction methods shows two areas of definite potential advantage for the former, three areas where the advantage is equivocal, and a single area of definite disadvantage.

A major contribution to costs in the present solvent extraction process is the large waste volume which must be stored and ultimately disposed of. The waste volume discharged from the fused-salt process is smaller by a factor of more than ten.

Another advantage of the fused salt process is that the equipment and cell size promises to be smaller than for the aqueous process. A general comparison can be made between fused salt and aqueous process as regards equipment and cell size by reference to the several items of major process equipment and the uranium concentrations in the process solutions. These are summarized in Table 8, and the figures show that the fused-salt process requires fewer major items of equipment and less cell space. The saving in heavy concrete shielding is expected to represent a substantial dollar value.

Since nitric acid cannot be used to dissolve high-zirconium alloys, an aqueous dissolution must use hydrofluoric acid. The cost of hydrofluoric acid is about the same, $0.25/lb, in either the aqueous or the anhydrous form. Therefore, this reagent cost is comparable, or may even be in favor of the fused salt process due to the high efficiency of utilization of hydrofluoric acid therein.

The volatility process requires the use of fluorine, or an equivalent fluorinating agent such as bromine pentafluoride or chlorine trifluoride, for formation of uranium hexafluoride. Fluorine costs are about $1.00/lb for large quantities directly from the generating cell or $5.00 to $20.00/lb as compressed gas. This cost may be more than balance in the aqueous flowsheet, however, if the uranyl nitrate product from solvent extraction is subsequently

Table 8

COMPARISON OF FUSED SALT AND AQUEOUS PROCESS
(~6 kg U/day)

Chief Process Steps	Fused Salt	Aqueous Solvent Extraction
Dissolution (Step 1)		
Equipment	1 dissolver	one or more dissolvers
Solution volume, liter/kg U processed	320	~2000
Preparation for final decontamination (Step 2)		
Equipment	1 fluorinator	one or more feed preparation tanks
Solution volume, liter/kg U	180	~2000
Final decontamination (Step 3)		
Equipment	1 distillation column	three cycles, each of 3 extraction columns
Solution volume, liter/kg U	0.28	~330
Primary Process Hot Waste, liter/kg U processed	140 (solid salt)	~2000 first cycle aqueous waste

to be converted to the fluoride for re-introduction to an isotope separation cascade.

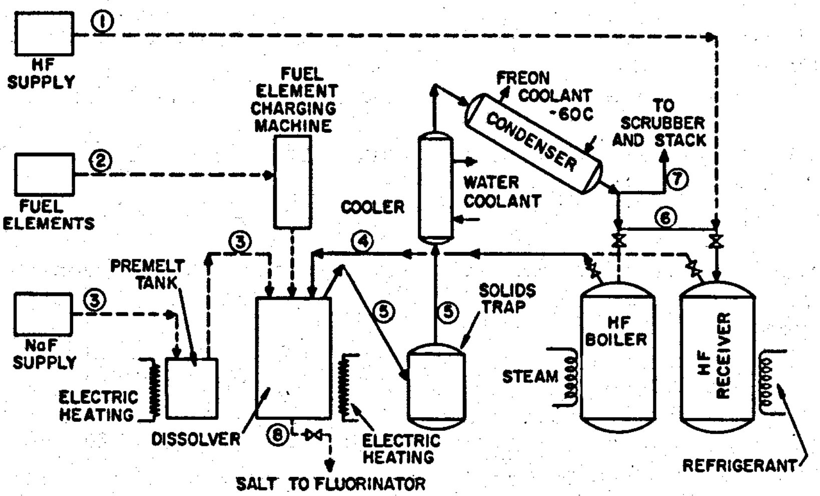
An additional chemical cost for the volatility process is that of the fused salt. The desirable features of a molten-fluoride medium are high fluidity and low vapor pressure at moderate temperatures (together with good chemical properties for dissolution of fuel elements and release of uranium hexafluoride). A NaF-ZrF_4 mixture has these required properties. Economically, the zirconium alloy dissolution complements the use of this salt, since the fuel element furnishes the zirconium fluoride and only make-up quantities of the relatively inexpensive sodium fluoride* are required. Also the raw material cost might be defrayed by using the salt waste in another process for dissolution of other types of fuel elements, e.g., UO_2 clad with stainless steel.

Corrosion of process equipment is a serious problem in the fused-salt flowsheet and it appears that more frequent replacement of vessels will be required than in an aqueous process. To have a process life of as long as a year, a graphite-lined dissolver-hydrofluorinator and a heavy wall (2 inches or more thick) nickel fluorinator are required.

B. Process Description and Flowsheets

Detailed flowsheets for the process are given in Figures 13 and 14.

The dissolution of the fuel elements, assumed to have a Zr/U weight ratio of 120/1, is shown in Figure 13. The fuel elements, previously removed from the reactor core, are charged to the dissolver from a shielded pot with a remote-handling machine. The fused-salt composition is allowed to rise from an initial 42 mole per cent zirconium tetrafluoride to a final 52 mole



PRODUCTION: 2 BATCHES/DAY (4 hr. PERIOD) 365 DAYS/Yr. 2190 KgU ANNUAL PRODUCTION

QUANTITY	1	2	3	4	5	6	7	8
U, Kg/BATCH		3.00						3.00
Zr, Kg/BATCH		360.						351
SALT, Lb/BATCH			333.					1786
SALT, Wt. % NaF			100.					18.8
SALT, Cu. Ft.			2.64					8.95
HF, Lb./BATCH	700			2330	1630.	1617.	13.	
H_2, Lb./BATCH					34.9		34.9	

Fig. 13 - Dissolver and HF system flowsheet.

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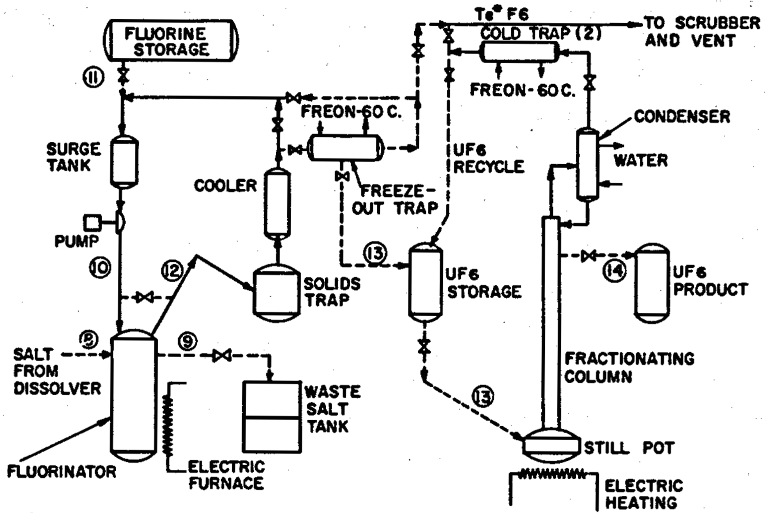
* About $0.12/lb in technical grade.



PRODUCTION: 2 BATCHES/DAY (4 hr. PERIOD) 365 DAYS/Yr. 2190 KgU ANNUAL PRODUCTION

QUANTITY	8	9	10	11	12	13	14
U, Kg/BATCH	3.00	<0.01			3.00	3.00	3,00
SALT, lb/BATCH	1786.	1779.					
SALT, Cu Ft/BATCH	8.95	8.95					
F_2			~10 lb/hr	1.06 lb/batch	~10 lb/hr		

Fig. 14 - Fluorinator and distillation column.

per cent during dissolution. Hydrogen fluoride sparge vapor is introduced from a boiler and the exit gas from the dissolver is put through a solids trap and gas cooler and then a condenser, where the excess hydrogen fluoride is condensed and recovered for re-use. The remaining non-condensibles, which consist largely of hydrogen produced from the reaction, are put through a scrub tower to remove traces of hydrogen fluoride and volatile fission products, since some carry-over of fission product zirconium, niobium, ruthenium and iodine is expected. The former three may be left principally in the solids trap, while the scrubber will remove the iodine and the remaining volatile fission products.

At the completion of the dissolution a portion of the salt equivalent to the metal charge is taken off through a freeze valve to the fluorinator. Sodium fluoride is added for each batch in an amount sufficient to restore the initial melt composition. Two batches per day are scheduled.

The salt (bearing UF_4) in the fluorinator is sparged with fluorine to volatilize the uranium hexafluoride (Figure 14). The off-gas recycles through a freeze-out trap, where the uranium hexafluoride is collected. The stripped waste salt is discharged at the end of the batch cycle, and the uranium hexafluoride is sublimed and routed to a storage tank. Because the plutonium concentration in the enriched fuel is very low, it is not recovered but is treated as waste (the bulk of this plutonium is expected to remain in the salt phase). About 4 hr/batch is required for this overall fluorination step.

The partially decontaminated uranium hexafluoride from the fluorination step is charged to the still pot of the distillation column. After a period of total reflux, the volatile fission products, principally tellurium hexafluoride, concentrate at the top of the column and are removed to a cold trap. The uranium hexafluoride product is then distilled overhead leaving any less volatile fission products in the still pot. Any uranium hexafluoride caught in the waste cold trap is periodically melted and returned to the uranium hexafluoride storage tank for reprocessing. Since tellurium hexafluoride is much more volatile than uranium hexafluoride, the bulk of it can be separated in the cold traps and disposed of in the waste fluorine caustic scrubber. The distillation step will handle 2 batches/day.

The bulk of the fission products, and substantially all of the long-lived ones, are removed with the waste. Waste disposal is achieved by burial in a concrete trench.

Other hot wastes are aqueous: solutions from the process scrub towers, process equipment decontamination, solutions, and laboratory wastes. These aqueous wastes are concentrated in an evaporator and disposed of by storage in large, stainless-steel underground tanks. Because almost all of the fission products in the aqueous solutions are short-lived, storage for 5 years is tantamount to ultimate disposal.

C. Building

The plant building consists of a main process building with three adjuncts: core unloading and handling facility, laboratory and office, and product uranium hexafluoride storage area. The process equipment cells are below grade with operating deck above. A tunnel provides passage for fuel elements from core handling facility to the dissolver process cell. Only the process cell layout is considered in detail.

The process layout shown in Figure 15 consists of eight cells 20 ft high in a block 40 ft wide by 48 ft long, exclusive of the fuel element receiving tunnel and miscellaneous galleries. All cells are lined with stainless steel. The operating deck is enclosed in a blast-resistant steel and transite structure.

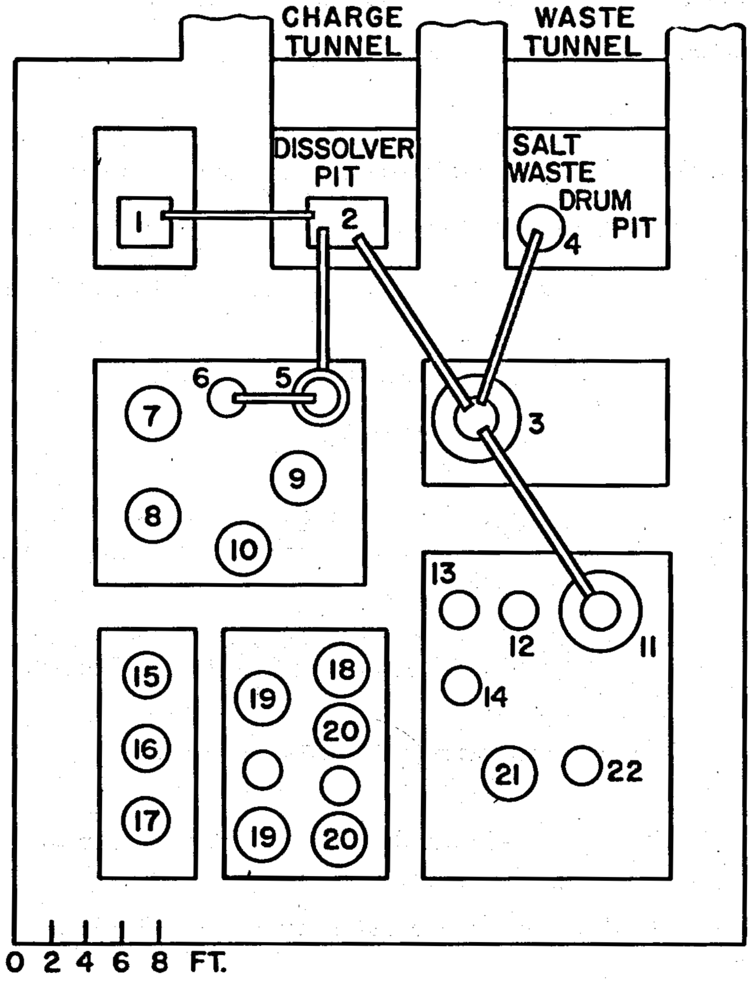
The dissolver and fluorinator high-temperature components are operated and maintained remotely. To avoid difficult and expensive remote operations, major maintenance assumes removal and replacement of an entire unit. The moderate equipment size and the location in individual cells facilitate this method. On the other hand, low temperature components are more readily decontaminated and direct maintenance may be employed. The uranium hexafluoride distillation and product handling is done remotely but maintenance is direct.

D. Cost Data

The plant is designed to process 1750 kg per year of highly-enriched uranium contained in a high Zr-U alloy. The product is uranium hexafluoride decontaminated to natural levels of radioactivity. The processing cost is estimated to be about $2.25 per gram of uranium. This cost can be broken down as follows:

Annual Cost Summary

Item	Dollars per Year	Dollars per g U
Fixed investment	2,210,000	1.01
Operating cost	2,274,000	1.04
Working capital	8,100	0.004
SF inventory	438,000	0.200
TOTAL	$ 4,930,100	$ 2.254



1. PRE-MELT TANK
2. DISSOLVER
3. FLUORINATOR
4. SALT WASTE TANK
5. HF SOLIDS TRAP-COOLER
6. HF CONDENSER
7. HF BOILER-RECEIVER
8. HF BOILER-RECEIVER
9. HF SAFETY TANK
10. AQUEOUS WASH TANK
11. UF$_6$ SOLIDS TRAP-COOLER
12. UF$_6$ FREEZE-OUT TRAP
13. WASTE TRAPS
14. UF$_6$ HOLD-UP TANK
15. F$_2$ SAFETY TANK
16. F$_2$ STORAGE TANK
17. HF STORAGE TANK
18. AQUEOUS WASTE TANK
19. HF SCRUBBER
20. F$_2$ SCRUBBER
21. UF$_6$ COLUMN
22. UF$_6$ PRODUCT RECEIVER

Fig. 15 - Process cell equipment layout.

The fixed investment is amortized in 6 2/3 years plus a one per cent average interest charge on the investment equivalent to amortizing at 16 per cent per year. The special materials inventory is charged at 4 per cent.

The estimating methods and bases and sources of costs are detailed in Appendix A. The capital investment is detailed in Appendix C-1; the operating cost in Appendix C-2; the inventory and working capital charges in C-3.

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* Special Scientific Employee on loan from Union Carbide Nuclear Company.

** Special Scientific Employee on loan from Hercules Powder Company.

APPENDIX A

METHODS OF COST ESTIMATING

Cost data and the methods of tabulating data used here parallel those used in ORNL-1786 in which the costs are detailed for recovering uranium and plutonium by the chlorine trifluoride process.(c)* Data for the chlorine trifluoride process cost study were obtained from Idaho Chemical Processing Plant cost(b,e) and from Hanford Engineering Plant cost(b) as well as from the usual estimating sources in the literature. All data have been checked with existing data from various cost estimating sources to ensure accuracy.(a,d) All construction costs have been corrected to the current Engineering News Record Index of 708 while all equipment costs have been corrected to the current Marshall and Steven's Index of the 211.3. Below are the costs of various items and also an explanation of the factors used in the computation of finished costs.

Equipment Costs

Cost of equipment	Each item was listed separately and either manufacturer's cost was obtained or Idaho Chemical Processing Plant cost data (from ORNL-1786) were used and a size factor of 0.6 applied when necessary. Where data were not available for fluorine-containing equipment the cost of stainless steel equipment was multiplied by a factor of 9.5 to 2.0 for tanks and 4.0 to 6.0 for heat exchangers.(b) This reflects the increased care in equipment construction due to the higher temperature and pressure used.

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* See references at end of Appendix A

Installed cost of equipment—1.14 x equipment cost	This factor was taken from Idaho Chemical Processing Plant data. The factor is lower than usually found but reflects the high cost of equipment for radiochemical plants.
Piping for equipment—(0.6, 1.5, or 2.0) x the installed equipment cost	Three factors were used: (1) 0.6 for non-radiochemical equipment and low temperature refrigeration lines. This number is generally used in cost estimating articles. (2) 1.5 for aqueous radiochemical piping cost. This factor is taken from Idaho Chemical Plant costs. (3) 2.0 for radiochemical fluoride lines. Besides reflecting an increase due to radiochemical operation, the factor also reflects the increase due to the necessity of keeping all lines above 64 C to keep the uranium hexafluoride from condensing.
Instrumentation	
Cost of instrumentation	Instruments and control valves were listed separately to arrive at total total cost. Either manufacturer's cost or Idaho Chemical Processing Plant cost was used.
Panels, piping, and unlisted auxiliaries—1.39 x equipment costs Installed cost of instrumentation—equipment cost x 1.39 x 1.67	The 1.39 and 1.67 factors were taken from Idaho Chemical Processing Plant data. The 1.67 factor is the cost of labor for installation.

0.347 x equipment and piping cost	The factor times process equipment and piping installed cost represents the cost of installed instrumentation for a volatility plant. This factor was taken from chlorine trifluoride volatility plant costs.(c)

Buildings

Process building without laboratory	Volume and area required in the finished building were calculated and unit volume and area costs obtained from the literature and Idaho Chemical Processing Plant costs were applied.
Laboratory building	The laboratory was considered equivalent in cost to the Idaho Chemical Processing Plant laboratory. (For the fused salt process--no plutonium recovery--the laboratory was taken as 50 per cent ICPP).
Service buildings--refrigeration, air, steam, water, electricity	Literature data were used for plant investment costs of the refrigeration facility. Other costs are taken from Idaho Chemical Processing Plant data.

Waste Storage

Liquid high-level waste	This cost was taken from Hanford Engineering Works data.
Burial ground, waste lagoons	These costs were taken from Idaho Chemical Processing Plant data.

Other

Site development and general land facilities development costs	Fifteen per cent of the manufacturing plant cost is the factor for the development costs. This amounted to $1,906,000 which can be broken down as follows:

Administration, etc., 30,000 sq ft at $20/sq ft	$ 600,000
General excavation, grading, roads	301,000
Miscellaneous buildings	138,000

Yard piping	540,000
Fences	106,000
Top soil and seeding	79,000
Communications and alarms	59,000
Sewage disposal plant	57,000
Miscellaneous	26,000
	$ 1,906,000

All costs except the first are taken from Idaho Chemical Processing Plant costs

Engineering, design and inspection--20 per cent of fixed investment Construction and construction fee--22 per cent of fixed investment Contingency--40 per cent of fixed investment	These factors were taken from Idaho Chemical Processing Plant data. This contingency factor reflects the state of the art.
Preoperation and startup	This value was estimated to be one year's operating expense.
Land	This value was estimated roughly since it will vary widely with the plant location.
Operating costs	Unit costs were applied to all labor and raw materials. Factors applied to these to arrive at total operating cost are consistent with estimating practice.
Charge for fissionable material	Under their accounting procedures, the United States Atomic Energy Commission charges a user for the fissionable materials in his possession.

	At the present time this amount is four per cent of the value of these materials.
Amortization of fixed investment	The fixed investment is amortized in 6 2/3 years plus a one per cent average interest charge on the investment. This is equivalent to amortizing at 16 per cent per year.
Plant operating time	For cost estimation purposes, it was assumed that the plant would operate 365 days per year, 24 hours per day.

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APPENDIX B-1

FIXED INVESTMENT

(Low Temperature Plant)

Summary

1. Plant Facilities	
A. Process Building (excluding laboratory and maintenance section)	$ 2,436,800
B. Process Equipment	2,286,000
B1 Slug unloading, jacket removal and charging--$590,700	
B2-B4 Uranium dissolution, solvent regeneration and uranium hexafluoride purification--$1,494,800	
B5 Plutonium recovery and purification--$140,900	
B6 Scrubber equipment--$59,600	
C. Fluorine Plant	2,678,200
2. Waste Facilities	1,979,600
3. Service Buildings and Services	988,600
4. Laboratory Building	2,340,000
5. Site Development and General Buildings	1,906,400
Subtotal	$ 14,615,600
Engineering, design, and inspection, 20% of subtotal	2,923,100
Construction and construction fee, 22% of subtotal	3,215,400
Contingency, 40% of subtotal	5,846,200
Preoperation and startup (one year's operating expense)	4,192,900
Total	30,793,200
Land, 4 sq mi at $150/acre	384,000
Total fixed investment	$ 31,177,200

The fixed investment is amortized in 6 2/3 years plus a 1% average interest on the investment, equivalent to amortizing at 16% per year

Annual capital cost - 16% of $31,177,200 = $4,988,350

Details

1A Process Building

Concrete, 3200 cu yd at $118/cu yd	$ 377,000
Excavation and backfill (10% of concrete cost)	37,700
Operating, sampling, and crane bays, steel and transite, 120,000 cu ft at $0.70/cu ft	84,000
Heating and ventilating equipment at $1.20 cfm, 10 changes/hr	8,000
Stainless steel lining, all surfaces in cells and fluorine cell off-gas tunnel and 2 ft of walls in hot pipe tunnel, 14,650 sq ft at $15.30/sq ft	224,200
Electrical services (same as ICPP)	331,000
Special equipment (50 per cent greater than ICPP)	1,239,000
Painting	41,500
Maintenance crane, 25 ton	59,000
Freight elevator	35,400
	$ 2,436,800

1B Process Equipment

1B-1 Slug Unloading, Jacket Removal, and Charging Equipment

	Item Cost	Instrumentation Cost
Equipment in Cell		
1 Jacket removal dissolver, 4 ft 6 in. diameter by 8 ft high	$ 19,100	$
1 Reflux condenser, 400 sq ft	7,900	5,700
1 Coating waste hold tank, 6 ft diameter by 9 ft 6 in. high	16,500	
1 Slug conveying and pressurized loading machine (estimated)	94,500	19,900
Subtotal	$ 138,000	$ 25,600

	Item Cost	Instrumentation Cost
Equipment Outside Cell		
1 $NaOH$-$NaNO_3$ metering tank, 500 gal	$ 2,800	$ 680
1 Agitator, 1 hp	880	
1 HNC_3-H_2O metering tank, 275 gal	1,830	630
1 Agitator, 1/2 hp	660	
2 Transfer pumps, 50 gpm	1,280	
1 26 per cent $NaNO_3$ solution make-up tank, 500 gal	2,950	590
1 Agitator	1,510	
1 Transfer pump	640	
1 26 per cent $NaNO_3$ storage tank, 3000 gal	9,550	180
Subtotal	$ 22,100	$ 2,080
Total delivered equipment	160,100	27,680
Installation, 0.14 x D. E.	22,400	
Installed equipment	$ 182,500	
Piping, 1.5 x I. E.	273,750	
Equipment and piping	$ 456,250	
Instrumentation installation and piping, 1.39 x 1.67 x D.E.		$ 64,250
Installed instrumentation	91,930	$ 91,930
1 Remote sampler	3,000	
Total process equipment	$ 551,180	
2 Slug transfer buckets	3,540	
1 Slug loading crane	15,950	
2 Periscopes for slug charging	20,000	
Total cost of equipment (B1)	$ 590,670	

1B-2 Uranium Dissolution

	Item Cost
1 Slug dissolver, 175 gal, 15 ft high	$ 14,750
1 Reflux condenser, 150 sq ft	12,250
1 BrF_3-BrF_5 tank, 500 gal	12,750
1 Safety tank, 500 gal	12,750
1 Cold trap, 150 sq ft refrigerent cooled	15,300
1 Bromine storage tank, 10 gal	2,120

1B-3 Solvent Regeneration

2 Fluorinators, 500 gal	25,500
2 Evaporator-Pu fluorinators, 100 gal	9,450
1 Condenser, water cooled, 100 sq ft	11,330
1 Fluorine hold tank, 40 cu ft	10,000

1B-4 Uranium Hexafluoride Purification

1 Safety tank, 500 gal	12,750
1 Liquid hold tank, 400 gal, for BrF_3-UF_6 recovery column	11,150
1 Liquid hold tank B still, 100 gal	4,720
BrF_5-UF_6 recovery distillation column, packed tower, 10 in. diameter by 30 ft high, including a water cooled 100 sq ft condenser and reboiler	57,800
BrF_5-UF_6 separation distillation column, 10 in. diameter by 30 ft high, packed tower, including a water cooled 100 sq ft condenser and reboiler	57,800
1 BrF_3-BrF_5 hold tank, 500 gal	12,750
2 Lapp Pulsafeeder recycle pumps	7,080
1 Uranium hexafluoride product tank, 500 gal	12,750
Total delivered equipment	$ 303,000
Installation, 0.14 x D. E.	42,400
Installed equipment	$ 345,400
Piping, 2.0 x I. E.	690,300
Equipment and piping	$ 1,036,200

	Item Cost
Instrumentation, 0.347 x E. and P.	359,600
11 samplers at $9,000	99,000
Total equipment cost (B2-B4)	$ 1,494,800

1B-5 Plutonium Recovery Equipment

	Item Cost
Fluorinator (included in solvent regenerator equipment	$
2 Gas pumps, Lapp pulsafeeders, 0.1 cfm	4,800
1 Cooler condenser, water cooled and Freon cooled, 5 ft sq	1,770
1 Distillation tower, 1 in. diameter by 16 ft high, batch, including condenser	7,200
1 Plutonium storage tank, product, 10 gal	2,120
1 Safety tank, 500 gal	12,750
Total delivered equipment	$ 28,640
Installation, 0.14 x D. E.	4,010
Installed equipment	$ 32,650
Piping, 2.0 x I. E.	65,300
Equipment and piping	$ 97,950
Instrumentation, 0.347 x E. and P.	33,980
Samplers, 1 at $9,000	9,000
Total equipment cost (B-5)	$ 140,930

1B-6 Scrubber Equipment

	Item Cost	Instrumentation Cost
Equipment in Cell		
1 Off-gas scrubber, 6 in. diameter by 15 ft high	$ 3,540	$
2 Scrubber tower sump tanks, 100 gal	3,540	5,270
2 Scrubber fluid recirculation pumps	3,360	
2 Steam jets	500	

Equipment Outside Cell

1 45% KOH storage tank, 500 gal	1,020	390
1 Transfer pump	240	
Total delivered equipment	$ 12,200	$ 5,660
Installation, 0.14 x D. E.	1,710	
Installed equipment	$ 13,910	
Piping, 1.5 x I. E.	20,860	
Equipment and piping	$ 34,770	
Instrumentation installation and piping, 1.39 x 1.67 x D. E.		13,140
Installed instrumentation	$ 18,800	$ 18,800
2 Remote samplers at $3,000	6,000	
Total equipment and piping (B-6)	$ 59,570	

1C Fluorine Plant

1C-1 Fluorine Generation Plant (including preliminary purification facilities

30 operating cells (installed cost) includes building, electrical services, piping and instruments, blower, refrigeration and absorbers, cells	$ 2,174,000
4 standby cells (installed cost)	36,000
Total cost, installed	$ 2,210,000

1C-2 Compression and Purification Facilities

	Item Cost	Instrumentation Cost
4 pulsafeeder compressors, 1 spare	134,800	1,720
1 F_2 cooler, 20 sq ft, water cooled	4,750	
1 F_2 heat exchanger, 50 sq ft	7,090	2,520
1 HF condenser, 100 sq ft, Freon cooled	11,300	
1 HF collector tank, 10 gal, Freon cooled	710	2,840
1 F_2 heater, 2 kw	885	1,190

2 NaF packed traps, electrically regenerated	5,900	2,390
1 F_2 cooler, 20 sq ft, water cooled	4,720	1,190
1 Surge tank, 20 cu ft	8,420	500
1 Safety tank, 200 cu ft	24,800	1,380
F_2 flow and pressure control		6,230
Total delivered equipment	$ 203,375	$ 19,960
Installation, 0.14 x D.E.	28,470	
Installed equipment	$ 231,845	
Piping, 0.6 x I.E.	139,105	
Equipment and Piping	$ 370,950	
Instrument installation and piping, 1.39 x 1.67 x D. E.		46,330
Installed instrumentation	66,290	$ 66,290
Total Process Equipment	$ 437,240	
Building, 37,500 cu ft at $0.825/cu ft	30,940	
Cost of Compression and Purification Facility	$ 468,180	
Total Cost Fluorine Plant (1C)	$ 2,678,180	

2. Waste Facilities

2A Liquid Waste Storage

The high level waste volumes per day from different sources are tabulated below:

Off-gas scrubber	90 gal/day
Coating removal waste (concentrated in tank)	232 gal/day
Process waste	100 gal/day
Laboratory and decontamination waste	120 gal/day
	542 gal/day

This is approximately 2,000,000 gal per ten-year period. At an installed tank cost of $0.59 per gallon, the capital cost is

	$ 1,118,000
Transfer tanks, condenser, etc.	115,000
Total liquid waste storage cost	$ 1,233,000

2B Gaseous Waste Facilities

A scrubber disposal system consisting of a vertical gas scrubber (KOH solution) and a disposal stack will be used to dispose of gas from the following:

1. gas from the off-gas scrubber in cell
2. the ventilation gas from the process cells

Costs:

Scrubber (estimated)	$ 59,000
Disposal stack, 10,000 cfm capacity, 250 ft high, includes filters and blowers	175,000
Total	$ 234,000

2C Miscellaneous Waste Facilities

Laboratory waste evaporation	$ 269,000
Retention basin for service water	66,100
Burial ground	59,000
Burning ground	29,500
Decontamination facility	59,500
Waste lagoon	29,500
Total	$ 512,600
Total Waste Facilities (2)	$ 1,979,600

3. Services

3A Steam Generation

Process steam (estimate)	10,000 lbs/hr	
Heating and ventilating	4,000	
Peak load allowance	4,000	
Total capacity	18,000 or 20,000 lbs/hr	
Cost of facility		$ 330,000

3B Electricity

Electrical distribution	$189,000	
Emergency electrical services	165,000	
Subtotal		$ 354,000

3C Compressed air

500 scfm $106/scfm	$ 53,000

3D Water

1,200,000 gal/day	$ 115,600

3E Low temperature Refrigeration System

10 ton (estimated size - 60 C)

Refrigeration plant (installed cost)	$ 85,000	
Piping, 0.6 x I. C.	51,000	
Subtotal		$ 136,000
Total Services (3)		$ 988,600

4. Laboratory Building

The laboratory is considered equivalent in cost to that of the Purex Plant Laboratory--$2,340,000.

5. Site Development and General Buildings

Selection and preparation of sites, yard piping, electrical distribution fences, road, railroad spur, warehouses, etc--15 per cent of the plant investment

15% of $12,709,200 = $1,906,380

APPENDIX B-2

OPERATING COST

(Low Temperature Plant)

Summary

1.	Chemicals, except fluorine	$ 140,600/year
2.	Labor, supervision, and overhead	1,949,000
3.	Maintenance material	306,600

4.	Operating supplies	70,000
5.	Steam	124,100
6.	Water	36,500
7.	Compressed air	6,600
8.	Inert gas	19,300
9.	Electricity	87,600
10.	Refrigeration plant	10,200
11.	Fluorine plant	942,400
12.	Control laboratory	500,000
	Total	192,900/year

Details

1. Process Chemicals

Chemical	lb/yr	Dollar per/lb	Dollars per year
Sodium hydroxide (50%)	284,600	0.29	$ 82,530
Sodium nitrate	291,000	0.023	6,693
Nitric acid (70%)	73,500	0.205	15,067
Aluminum nitrate, hydrated	1,150	0.13	149
Ferrous sulfamate	766	1.00*	766
Bromine**	4,774	0.32	1,528
Potassium Hydroxide (45%)	796,800	0.425	33,864
Total chemical cost			$ 140,597

* Estimated

** Assumed yearly loss

2. Labor

	Cost per Year
Operating labor (exclusive of fluorine plant) 18 men/shift at $2.50/hr	$ 394,200
Maintenance labor (exclusive of fluorine plant) 14 men/shift at $2.50/hr	306,600
Supervision, 50% of O.L. plus 25% of M.L.	273,700

	Overhead, 100% of O. L. plus M. L. plus supervision	974,500
	Total Labor	$ 1,949,000
3.	Maintenance material, 100% of M. L. plus maintenance supervision	306,600
4.	Operating supplies, 10% of O. L. plus 10% of M. L.	70,000
5.	Steam, estimated load 340,000 lb/day at $1/1,000 lb	124,100
6.	Water (estimated usage 1,000,000 gal/day at $0.10/1,000 gal)	36,500
7.	Compressed air, estimated load 250 cfm at $0.05/ 1,000 cfm	6,600
8.	Inert gas, estimated nitrogen usage, 400 cfh at $0.55 cu ft	19,300
9.	Electricity (estimated load--1,000 kw at $0.01/kwh)	87,600
10.	Refrigeration plant (10 tons estimated load) $2.80/ton/day	10,200

11. Fluorine Costs

	Dollar per/lb
Materials (chemicals, repairs)	0.3251
Labor (operating, maintenance)	0.1542
Work materials (electricity, steam, water, etc.)	0.0427
Plant expense (overhead)	0.2556
Total	0.7776

Assuming 1,208,000 pounds of fluorine are produced (excess for stack losses), the total cost of fluorine is $ 942,200/yr

12.	Control laboratory	$ 500,000
	Total yearly operating cost	$ 4,192,900

APPENDIX B-3

INVENTORY AND WORKING CAPITAL

(Low Temperature Process)

SF Inventory Charge

The SF inventory charges are based on 120 days' average holdup of materials from the reactor to final product shipping containers and on the assumed dollar values for uranium and plutonium as given:

Uranium:	$ 40/kg x 3,000 kg/day x 120 days	$ 14,400,000
Plutonium:	$150/g x 2,000 g/day x 120 days	36,000,000
	Total	$ 50,400,000

SF inventory charge: 4% of $50,400,000 or $2,016,000

Working Capital

Working capital is considered as a percentage (existing money rates) of the following costs: (1) 30 days' value of raw materials and supplies, (2) 30 days' operating costs, and (3) the value of materials in the plant fill-up. Under Atomic Energy Commission procedures, the finished products are carried in SF inventory and there are no accounts receivable.

Item	Charge
Raw materials and operating supplies	$ 48,000
Materials in plant fill-up	38,500
30 days operating costs	349,400
Total	$ 436,900

4% of $435,900 = $17,436.

APPENDIX C-1

FIXED INVESTMENT

(High Temperature Plant)

Summary

1. Process Building		
A. Building Proper	$ 712,000	
B. Special equipment	520,000	
		$ 1,232,200
2. Process Equipment in Building		
A. Dissolver charging machine	80,000	
B. Dissolver and HF system	559,400	

	C. Fluorinator and UF_6 collection	470,800	
	D. UF_6 distillation	124,100	
	E. Auxiliary process equipment	176,400	
			$ 1,398,100
3.	Fuel Element Handling Facility		250,000
4.	Product UF_6 Storage Facility		100,000
5.	Laboratory building (equipped)		1,000,000
6.	Hot salt burial facility		100,000
7.	Liquid Waste Storage (7 years' capacity)		226,000
8.	Miscellaneous Waste Facilities		272,000
9.	Gaseous Waste Disposal		205,000
10.	Services		
	A. Refrigeration	$ 89,800	
	B. Steam	162,000	
	C. Electricity (including emergency supply)	223,000	
	D. Compressed Air	11,300	
	E. Water	44,000	
			$ 530,100
	Subtotal (a)		5,313,400
	Site development and general buildings, 15% subtotal (a)		800,000
	Subtotal (b)		$ 6,113,400
	Engineering, design, and inspection, 20% subtotal (b)		1,230,000
	Construction and construction fee, 22% of subtotal (b)		1,350,000
	contingency, 40% of subtotal (b)		2,450,000
	Preoperation and start-up (estimated as 1 yr operating expense)		2,274,800
	Land, 4 sq miles @ $150/acre		384,000
	Total Fixed Investment		$ 13,802,200
	Annual capital cost, 16%		2,210,000

Details

1. Process Building

A. Building Proper (See Figure 15)

Concrete (1640 cu yd @ \$100(a)*/cu yd x $\left(\frac{708}{600}\right)$	\$ 198,000
Excavation and backfill (10% concrete)	20,000
Operating, sampling, and crane bays, steel and transite (50,000 cu ft at \$0.60(a)/cu ft x $\left(\frac{708}{600}\right)$	36,000
Heating and ventilating (10 changes/hr in cells, \$1.00(a)/cfm x $\left(\frac{708}{600}\right)$ x 16,000 cu ft x $\frac{10}{60}$	3,200
Stainless steel lining (all surfaces @ \$16/sq ft)(a)	132,000
Elec services	200,000
Painting	27,000
Maintenance Crane	60,000
Freight elevator	36,000
Total Building Proper (1A)	\$ 712,200

B. Special Equipment (selected from similar category at ICPP(b)

Sample station outfitting (4 stations at \$25,000/station)	100,000
Periscopes, tongs, etc. for remote operations	120,000
Electric trucks, lifts	15,000
Activity sample cell handling	180,000
Chargers, carriers for cell sampling	30,000
Radiation detection instruments	50,000
Individual shielding	25,000
Total Special Equipment (1B)	\$ 520,000
Total Process Building	\$ 1,232,200

2. Process Equipment in Building

A. Dissolver Charging Machine (2A) (assumed same as for uranium slugs in ORNL-1786(a))	\$ 80,000

* Letter superscripts refer to references given at the end of the appendix.

B. Dissolver and HF System

Equipment in Cells	Item Cost	Instrumentation Cost
Dissolver, Graphite-Nickel, (27 cu ft salt capacity	$ 30,000	$ 15,000
Pre-Melt Tank, Graphite-Nickel, (6 cu ft NaF capacity)	15,000	8,000
Salt Freeze Valve, (to fluorinator)	1,500	2,000
Salt Sampler (remote)	9,000	
De-Sublimator and Gas Cooler, Monel (100 sq ft, water cooled)	12,400	1,200
HF Condenser, Monel (150 sq ft, Freon cooled)	12,000	8,500
HF Boiler and Receiver, Monel (2 vessels, 400 gal each)	30,000	9,000
Safety Tank, Steel (100 cu ft)	9,000	2,000
Total delivered equipment	$ 118,900	$ 45,700
Installation (14% D. E.)	16,600	
Installed Equipment	$ 135,500	
Piping (2 x I. E.)	271,000	
Equipment and Piping	$ 406,500	
Instrumentation Installation and Piping (1.5 x 1.67 x D.E.-inst)		107,200
Installed Instrumentation	152,900	
Total Equipment, Instruments and Piping for Dissolver and HF System (2B)	$ 559,400	

C. Fluorinator and UF_6 Collection (2C)

Equipment in Cells	Item cost	Instrumentation Cost
Fluorinator, nickel, (2 in. walls, 9 cu ft salt cap)	$ 35,000	$ 9,000
Furance, for above (50 kw)	20,000	2,000
Freeze valve (to waste pot)	1,500	2,000
De-Sublimator and Gas Cooler, Nickel, (12 sq ft, water cooled)	7,700	1,200

Freeze-out trap, Nickel (23 sq ft, Freon cooled)	6,000	2,500
Surge Tank, Nickel (4 cu ft)	800	800
Fluorine pump, Monel (2 cfm)	10,000	2,000
Salt Samples, 2 (remote)	18,000	
Waste Cold Traps (2), Nickel (5 sq ft, Freon cooled)	5,000	2,500
UF_6 Storage Tank, Nickel (10 liters)	1,200	2,800
Safety Tank, Steel (50 cu ft)	5,000	2,000
Total delivered equipment	$ 110,200	$ 26,800
Installation (14% D. E.)	15,400	
Installed Equipment	$ 125,600	
Piping (2 x I. E.)	251,200	
Equipment and Piping	$ 376,800	
Instrumentation installation and piping (1.5 x 1.67 x D.E. inst)		67,200
Installed Instrumentation	$ 94,000	
Total Equipment, Instruments and Piping for Fluorinator and UF_6 Collection (2C)	$ 470,800	

D. UF_6 Distillation (2D)

Equipment in Cells	Item Cost	Instrumentation Cost
Batch distillation column, Nickel (10 liter still pot, 1 in. column, 8 ft high 2 sq ft condenser)	$ 3,000	$ 8,500
Distillate receiver, Nickel (10 liters)	1,200	4,400
Safety tank, Monel (10 cu ft)	2,400	1,200
UF_6 samplers, 3, (semi-remote)	15,000	
Total delivered equipment	$ 21,600	$ 14,100
Installation (14% D. E.)	3,300	
Installed equipment	$ 24,900	
Piping (2.0 x I. E.)	49,800	
Equipment and piping	$ 74,700	

Instrumentation installation and piping (1.5 x 1.67 x D.E.)		35,300
Installed instrumentation	$ 49,400	
Total Equipment, Instrument and Piping for UF_6 Distillation (2D)	$ 124,100	

E. Auxiliary Process Equipment (2E)

Equipment in Cells	Item Cost	Instrumentation Cost
F_2 Off-gas scrubber tower, Monel (6 in. dia x 10 ft high)	2,000	
2 Scrubber tower sump tanks, SS (100 gal)	4,000	3,500
2 Fluid recirculation pumps	4,000	
3 Liquid nozzles and 2 steam jets	1,000	
HF off-gas scrubber tower, SS (10 in. dia x 15 ft high)	3,000	
2 Scrubber tower sump tanks, SS (100 gal)	4,000	3,500
2 Fluid recirculation pumps	4,000	
3 Liquid nozzles and 2 steam jets	1,000	
Hot wash tank for HF boilers, SS (100 gal)	2,000	2,000
Hot wash tank for UF_6 still pot, SS (10 gal)	800	2,000
F_2 storage and addition tank, steel (50 cu ft)	2,500	2,500
NaF absorber for F_2, Nickel (5 in. dia x 6 ft)	1,000	1,000
HF storage tank, steel, (50 cu ft)	2,500	1,000
6 Aqueous samplers	12,000	
Total delivered equipment	$ 43,800	$ 15,500
Installation (14% D. E.)	6,100	
Installed equipment	$ 49,900	
Piping (1.5 I. E.)	75,000	
Equipment and piping	$ 124,900	
Instrumentation installation and piping (1.39 x 1.67 x D. E. inst)		36,000

Installed instrumentation	51,500	
Total Equipment Instruments and Piping for Auxiliary Equipment (2E)	$ 176,400	

3. Fuel Element Handling Facility

To transfer fuel elements from a shielded shipping cask on a railroad flat car to the slug charging machine.

Concrete tunnel	$ 150,000	
Remote crane	50,000	
Auxiliary facilities	50,000	
		$ 250,000

4. Product UF_6 Storage Facility

(For 90 days' production-- est 14,000 cu ft at $0.72/cu ft)	100,000

5. Laboratory Building (equipped)

(~50% that for large natural U-Pu plant, ORNL-1558[c])	1,000,000

6. Hot Salt Burial Facility

(Estimate of transportation and handling facilities, special equipment and area development)	100,000

7. Liquid Waste Storage	226,000

The estimated process high activity waste volumes are:

F_2 off-gas scrubber	2,000 gal/yr
HF off-gas scrubber	24,000 gal/yr
HF boiler decontamination	5,000 gal/yr
UF_6 equipment decontamination	1,000 gal/yr
	32,000 gal/yr

The method is to concentrate the above wastes together with laboratory wastes and store in a large underground tank.

Above process wastes concentrated 5:1 in evaporator	6,400 gal/yr
Concentrated decontamination and laboratory wastes (est.)	18,000 gal/yr
	24,000 gal/yr

Since almost all long-lived fission producst are disposed of the fused salt waste, storage of liquid waste in steel tanks for 5 years is tantamount to ultimate disposal.

The liquid waste storage will use one 180,000 gal underground storage tank which will provide 7 years' storage for all high activity wastes.

1 waste tank 180,000 gal at $0.59/gal in 750,000 gal size.

$$441{,}00\left(\frac{180{,}000}{750{,}000}\right)0.6 = \$\,184{,}000$$

Transfer, tanks, condenser, etc.	42,000
Total liquid waste storage cost	$ 226,000

8. Miscellaneous Waste Facilities $ 272,000

(Estimate of facilities are about 50% of counterpart for large natural uranium plant (ORNL-1558(c))

Laboratory waste evaporation	$ 150,000
Retention basin for service water	24,000
Burial ground	32,000
Burning ground	17,000
Decontamination facility	32,000
Waste lagoon	17,000
Total Misc. Waste Facilities Cost	$ 272,000

9. Gaseous Waste Disposal $ 205,000

Process cell exhaust air (10,000 cfm)

Caustic scrubber, vertical, SS	$ 30,000
250 ft stack, SS for first 20 ft (including fans and filters)(c)	175,000
	$ 205,000

10. Services

A. Refrigeration

4 Tons estimated size, -60 C

$\$72{,}000^{(a)} \left(\frac{4 \text{ tons}}{10 \text{ tons}}\right)^{\$0.6}$ (installed) =	$ 49,000	
Piping, 0.6 x I. C.	30,000	
	$ 79,000	
Building, 15,000 cu ft @ $0.72/cu ft	10,800	
Total		$ 89,800

B. <u>Steam</u>

Steam requirements (max.)

Building heating	3,000 lb/hr
Process heating	600 lb/hr
liquid waste evaporation	2,000 lb/hr
	5,600 lb/hr
or	6,000 lb/hr

Cost of generator unit

$$\$550{,}000^{(a)} \left(\frac{6{,}000}{80{,}000}\right)^{0.6} \times \left(\frac{708}{509}\right) = \qquad \$\ 162{,}000$$

C. <u>Electricity</u>

A total of 1500 KVA estimated for plant and grounds.

Distribution facilities		
$1500 \text{ KVA} \times \$50^{(c)}/\text{KW} \times \left(\frac{708}{477}\right) =$	$ 111,000	
Emergency generator and distribution		
$500 \text{ KW} \times \$150^{(c)}/\text{KW} \times \left(\frac{708}{477}\right) =$	113,000	
Total		$ 223.000

D. <u>Compressed Air</u>

For instruments and miscellaneous,

125 scfm @ 100 psi required

$125 \text{ scfm} \times \$90^{(a)}/\text{scfm} =$ $ 11,300

E. Water

Estimated total maximum usage,
300,000 gal/day

$$\$140{,}000^{(a)} \left(\frac{300{,}000}{2{,}160{,}000}\right)^{0.6} = \$\ 44{,}000$$

Total Services (10)	$ 530,100

APPENDIX C-2

OPERATING COST
(High Temperature Process)

Summary

1.	Chemicals	$ 618,000
2.	Labor, supervision and overhead	876,000
3.	Maintenance material	109,500
4.	Operating supplies	30,660
5.	Steam	21,900
6.	Water	8,760
7.	Compressed air	3,910
8.	Inert gas	30,000
9.	Electricity	64,000
10.	Refrigeration	5,000
11.	Control laboratory	250,000
12.	UF_6 containers	18,000
13.	Salt waste containers	15,000
14.	Salt burial	60,000
15.	Uranium losses (1/2%)	164,000
		$ 2,274,800

Details

1. Chemicals $ 618,000

Chemical	lb/yr*	Dollars per/lb	Annual Cost
F_2	85,600	5.00	$ 428,000
HF	560,000	0.25	140,000
NaF	266,000	0.15	39,900
KOH	4,500	0.16	270
Misc			10,000
Total Chemical Cost			$ 618,170

or

$$\frac{\$618,200}{2190 \text{ kg U}} \cong \$283/\text{kg U.}$$

* Quantities estimated at 10% above stoichiometric. Process losses expected are less than this.

2. Labor Supervision and Overhead $ 876,000

Operating labor (10 men/shift @ $2.50/hr)	$ 219,000
Maintenance labor (4 men/shift @ $2.50/hr)	87,600
Supervision (50% OL plus 25% ML)	131,400
Overhead (100% OL and ML and supervision)	438,000
	$ 876,000

3.	Maintenance Material (100% of ML and Maint Sup)	$ 109,500
4.	Operating Supplies (10% OL and ML)	$ 30,660
5.	Steam (estimated load: 50,000 lb/day @ $1.2/1000 lb)	$ 21,900
6.	Water (Estimated use: 200,000 gal/day @ $0.12/100 gal)	$ 21,900
7.	Compressed Air (Estimated load: 125 cfm : $0.06/1000 cu ft)	$ 3,910

8.	Inert Gas (est)	$	30,000
9.	Electricity (Estimated load: 600 kw @ $0.012 kwh)	$	64,000
10.	Refrigeration (4 tons estimated load)	$	5,000
11.	Control Laboratory (50% of large natural U-Pu plant(c))	$	250,000
12.	UF_6 Containers, Monel (365 pots, 5 in. diam, 10 in. high)	$	18,000
13.	Salt Waste Containers	$	15,000

Salt is discharged into steel drums. Batch volume of salt 8.74 cu ft = 65.5 gal. Since ordinary steel 55 gal drums cost about $8.00, it is estimated that a satisfactory drum for this purpose could be made for $20.00.

$$\$20/\text{drum} \times 730 \text{ batches/yr} \cong \$15,000.$$

14.	Salt Burial	$	60,000

The drums are buried in a 12-ft deep trench, at first covered with water, and, after 150 days cooling, given final burial with earth. The trench is constructed

Assuming (1) the drums are 20 inches in diameter and 4 feet long and (2) that the drums are laid 4 abreast, the size of the trench is

$$4 \times \frac{20 \text{ in.}}{12} \cong 6.7 \text{ ft inside width}$$

and

$$\frac{4 \text{ ft} \times 600 \text{ batches/yr}}{4} \cong 600 \text{ ft inside length.}$$

Total width of concrete slab

walls	24 ft high
bottom	8 ft wide
	32 ft

Cost of concrete for 8-inch thick section,

$$32 \text{ ft} \times \frac{8 \text{ in}}{12 \text{ in/ft}} \times \frac{600 \text{ ft}}{27 \text{ cu ft/cu yd}} \times \$120/\text{cu yd}$$

$$\cong \$48,000.$$

Excavation and backfill estimated at 10 per cent concrete cost = $4,800. Other costs, including temproary water and final earth fill -- $7,200.

Total -- $60,000.

15.	Uranium Losses (1/2% x 2190 kg/year x $15/g)	$ 164,000
	Total Operating Expense	$ 2,274,800

APPENDIX C-3

CAPITAL AND INVENTORY CHARGE

(High Temperature Plant)

Working Capital

Working capital is cost of money tied up in supplied and cash on hand for one month's operating expenses.

One month's operating cost: $2,274,000/12	$ 189,000
Salt fill-up	13,000
Working capital	$ 202,000
Charge on working capital 4% x 202,000 =	$ 8,100

Special Materials Inventory

The special materials inventory charges are based on 120 days' average hold-up of materials from reactor to final product shipping containers and on the assumed dollar values for uranium. The special materials are leased from the Atomic Energy Commission at a use-charge of 4 per cent per annum.(d)

Uranium, $15/g U x 6,000 g/day x 120 days =	$ 10,800,000
Inventory charge, 4% of $10,800,000 =	$ 438,000

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(a) Nicholson, E. L., "An Economic Study of the Chlorine Trifluoride Volatility Process for Recovery of Uranium and Plutonium from Irradiated Reactor Fuels", ORNL-1786 (1955) (Confidential).

(b) Robertson, P. L. and Stockdale, W. G., "A Cost Analysis of the Idaho Chemical Processing Plant", ORNL-1792 (1955) (Confidential).

(c) Hull, H. L. and Zeitlin, H. R., "A Design and Cost Estimate Study of a Purex Plant", ORNL-1558 (1954) (Secret)

(d) 1956 Financial Report, the United States Atomic Energy Commission.

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THE CHEMISTRY OF PYROMETALLURGICAL PROCESSES: A REVIEW

Harold M. Feder*

May 1, 1957

Historical Introduction

The possibility of separating fissile, fertile, and fission product elements from each other by means of dry reactions of a metallurgical nature was recognized early in the history of the American atomic energy project. In the pioneering effort Spedding and co-workers(1) melted small pieces of lightly neutron irradiated uranium in beryllia crucibles in vacuum for two hours at 1400°C and found that by this treatment the percentage removal of certain fission products was Xe, 99.4; I, 98.8; Ba, 97.8; Sr, 99.5; Zr, 95.4; Ce, 75.5; (La, Pr, Y), 80.4; Mo, <1; Te, <1; Np, <1; Pu, <1; total gamma 7.9. Some of these elements were readily shown to have been removed by volatilization. It was also noted that if a similar experiment was carried out in a graphite crucible considerable concentration of some fission elements, notably Br, Sr, Zr, Ce, La, Pr and Y, into the reaction layer between metal and graphite took place. A U. S. patent by Meister,(2) dating from these early days discusses the purification of uranium by a process of melting it on a perforated graphite disc so as to cause the dross to be left behind as the molten uranium flows through the holes. Thermodynamic reasoning was applied to these processes by Brewer(3) in 1945. A number of subsequent investigations, which will be considered in greater detail later, have, with a few exceptions, verified the predictions of Brewer.

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Between 1945 and 1951 the field under discussion lay more or less untilled. In 1952 a number of institutions, more or less independently, began to re-examine the possibilities of pyrometallurgical processing. It was soon recognized that the field was very wide indeed and that a large number of separate investigations would be needed to fully explore its possibilities. During this period a significant contribution was made by Glassner(4) in the form of readily usable tables and charts of free energy functions. These tables, although they did not pretend to a high degree of reliability, were widely used to estimate the probable direction and extent of high temperature reactions.

The current compilations most likely to be consulted for thermodynamic information on systems of interest are as follows:

(a) Selected Values of Chemical Thermodynamic Properties, NBS Circular 500, Rossini, et al, Washington, 1952, Parts I, II and III.
(b) Heats and Free Energies of Inorganic Oxides, J. P. Coughlin, Bureau of Mines Bulletin 542, Washington, 1954.
(c) The Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics, National Nuclear Energy Series, Vol. IV-19B, Edited by L. L. Quill, McGraw-Hill, 1950.
(d) The Transuranium Elements, Part II, National Nuclear Energy Series, Vol. IV-14B, Seaborg, Katz and Manning, McGraw-Hill, 1949.
(e) High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for Inorganic Compounds, K. K. Kelley, Bureau of Mines Bulletin 476, Washington, 1949.

Supplementary phase equilibrium information is frequently required. The most frequent consulted references (other than standard reference works) are:

(f) Compilation of U. S. and U. K. Uranium and Thorium Constitutional Diagrams, H. A. Saller and F. A. Rough, BMI-1000, Technical Information Service, Oak Ridge, Tennessee, 1955.
(g) Intermetallic Compounds of Pu, Coffinberry and Ellinger, Geneva Conference Paper, P/826.
(h) S. T. Konobeevsky, Equilibrium Diagrams of Certain Systems on Plutonium Bases, Acad. of Sci. U.S.S.R., Session on the Peaceful Uses of Atomic Energy, Vol. III, 362-374 (Moscow, 1955).

In the past five years the experimental investigation of pyrometallurgical processes has proceeded at an accelerated pace at many institutions so that despite the passage of less than two years since the last review of principles(5) a current (May, 1957) review appears warranted.

OUTLINE, DEFINITIONS, AND SCOPE

The following outline of pyrometallurgical operations is (in the author's opinion) suitable for a systematic examination of the field.

I. NON-CHEMICAL SEPARATIONS
   A. Fractional Distillation or Sublimation
   B. Fractional Crystallization
      1. Without added solvent
      2. With added solvent
   C. Liquid-Liquid Partition
   D. Liquid-Solid Extraction

II. SEPARATIONS BY SELECTIVE OXIDATION
   A. Oxides
   B. Carbides
   C. Nitrides and Sulfides
   D. Halides

III. SEPARATIONS BY CYCLIC OXIDATION-REDUCTION
   A. Chemical
   B. Electrochemical

In the above outline the operations are isolable physico-chemical phenomena. The term process will mean a group of operations, either simultaneous or serial, that lead to a desired end. In the terminology used herein the term pyrometallurgical process will be restricted to the use of elevated temperatures to produce a desired result and a product in metallic form. Thus, processes which have as their aim the production of, say, purified uranium hexafluoride or uranium dioxide will not be further discussed even though they may operate at elevated temperatures with substances which are originally metallic.

The scope of this review is judged to be the separation of uranium, plutonium, thorium, fission elements or other unwanted elements from each other in whatever combination they may occur and to whatever extent is required in connection with neutron reaction technology. However, useful examples which are only indirectly connected with such technology will be cited occasionally.

I. Non-Chemical Separations

This section treats of multi-component metal mixtures subjected to a variety of physical treatments.

A. Fractional Distillation or Sublimation

The principles of fractional distillation of mixtures are well understood. Vivian(11) has discussed these more particularly for the special case of interest in pyrometallurgical processing, namely, single stage Rayleigh distillation of metal mixtures. Unless evidence to the contrary is available the assumption of ideal solutions is usually made for calculation purposes.* This must subsequently be checked experimentally. With regard to kinetics it appears to be safe to use the applicable Langmuir or Knudsen equations for distillation at low pressures.

1. Purification and Concentration of Plutonium

A theoretical study(12) of this operation has been made. The results of this study have been expressed as relaxation times, i.e., the time re-

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*If the solute has limited miscibility with the solvent an appropriate correction should be made, e.g., the solubility of lanthanum in uranium at the melting point is about one per cent, hence Henry's Law should be applied and an activity coefficient of 100 assumed for dilute solutions of lanthanum in uranium.

quired for the impurity concentration to fall to 1/e of its initial value, assuming ideality of dilute solutions. The relaxation times calculated are given in Table 1. For reasonable distillation times of the order of 10^4 seconds purification of plutonium from Al, Ca, Li, Mg, Mn and Na should be achievable.

The concentration of a plutonium-magnesium solution by preferential distillation of magnesium at about 10 microns pressure has been demonstrated on a fairly large scale.(44)

2. Separation of Plutonium from Uranium

The theoretical calculations for distillation of plutonium from less volatile uranium have been gathered by Rosser(13) who shows that the significant variables are temperature and the quantity, At/W, exposed area x time/weight of charge. The general validity of these calculations was confirmed by Cubicciotti(14a) for plutonium concentrations up to 0.01 per cent and up to 99 per cent plutonium distilled. McKenzie(14b) has independently verified these results up to a plutonium concentration of 0.24 per cent and similarly concludes that Raoult's Law* and the Langmuir equation are applicable. The completeness of the separation of uranium and plutonium, and the engineering difficulties are pointed out by the latter authors.

3. Separation of Fission Products from Uranium

An experimental study of the vacuum distillation of fission product elements from irradiated uranium contained in refractory crucibles has been reported by Motta and co-workers.(7) At 1680°C and a value of At/w equal to 1700 $cm^2/sec/gm$ the residual fission product activities found were, in per cent of initial activity, Ce, 3; total rare earths, 2; Sr, 2; Ce, 0.2; Te, 2;

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*The extrapolation of this result to higher concentrations should, however, be done only with reservation.

Table I

RELAXATION TIMES FOR IMPURITIES IN PLUTONIUM*

Element	τ (in seconds) ($T = 1073^\circ K$)	 ($T = 1273^\circ K$)	 ($T = 1473^\circ K$)
Al	5.86×10^{7}	3.64×10^{5}	9.09×10^{3}
B	1.32×10^{10}	2.25×10^{7}	3.50×10^{5}
Be	4.08×10^{8}	1.64×10^{6}	2.98×10^{4}
Ca	3.48×10^{2}	2.06×10^{1}	2.65
Ce	8.18×10^{9}	2.14×10^{7}	2.86×10^{5}
Cr	8.28×10^{8}	2.37×10^{6}	3.36×10^{4}
Fe	9.90×10^{10}	$.169 \times 10^{8}$	1.64×10^{6}
La	3.76×10^{10}	9.13×10^{7}	1.15×10^{6}
Li	2.80×10^{1}	2.53	4.40×10^{-1}
Mg	8.03	7.23×10^{-1}	$.127 \times 10^{-1}$
Mn	1.63×10^{6}	2.14×10^{4}	9.24×10^{2}
Mo	6.04×10^{21}	2.50×10^{17}	1.62×10^{14}
Na	6.04×10^{-1}	1.08×10^{-1}	3.14×10^{-2}
Nb	1.02×10^{26}	7.48×10^{20}	1.37×10^{17}
Ni	1.13×10^{12}	1.23×10^{9}	8.58×10^{6}
Ru	1.49×10^{23}	2.25×10^{18}	6.98×10^{14}
Si	1.88×10^{10}	3.21×10^{7}	3.12×10^{5}
U	4.36×10^{16}	9.77×10^{12}	2.17×10^{10}
Zr	5.52×10^{17}	6.92×10^{13}	1.00×10^{11}

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*Taken from Weidenbaum and Ryan, Ref. 12.

Ru, 100. Motta concludes that the evaporation of fission product elements was substantially as expected from their individual vapor pressures, but it was not demonstrated that evaporation was solely responsible for their removal.* At 1200°C and under one atmosphere pressure of inert gas(6) cesium appears in the sublimate to a significant degree, only traces of strontium and rare earths appear and no tellurium is detected. Moreover, mechanisms of fission product removal other than volatilization were shown to be operative for strontium, rare earths and tellurium. A similar contrast is shown by the work of Spedding(1) in which 98.8 per cent of trace iodine content is removed by heating in vacuum for two hours at 1400°C and the work of Ader(16) in which less than one per cent of iodine is removed by heating under atmospheric pressure of helium for four hours at 1250°C. These contrasts are, of course, not contradictory; they simply point up the sharp influence of temperature and pressure on effective volatility and the necessity of considering the deviation of thermodynamic activity of a solute element from its ideal value, particularly for elements capable of forming moderately stable compounds with the solvent. Thus, in the case of iodine for example, it is known that at 1200°C the uranium iodides dissociate to iodine atoms and uranium in high vacuum(17) and that at the same temperature, under pressure, a sublimate having a volatility characteristic of the uranium iodides is obtained.(16) Qualitatively similar situations are to be expected for the uranium selenides and tellurides.(18)

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*The demonstration of cerium and rare earth migration from uranium in vacuum under conditions where only volatilization was likely has been accomplished.(15) Also, Aikin and McKenzie(8) have demonstrated the vacuum distillation of silver (one of the minor fission products) from molten uranium, in connection with the use of silver as a plutonium extractant.

It is evident that further work on the distillation of individual solute elements from solution in uranium, with particular emphasis on the collection of the evolved species in a Knudsen-type apparatus, would be especially helpful for evaluating the possibilities of distillation for practical, as well as scientific purposes.

4. Separation of Uranium or Fission Products from Thorium

Incidental to another investigation Potter(19) has shown that cesium and strontium may be nearly quantitatively volatilized from molten thorium in vacuum at 1700°C. Separation of uranium and thorium does not appear to be feasible.

5. Separation of Polonium from Bismuth

Polonium formed in liquid bismuth by neutron capture may be removed therefrom by taking advantage of the greater volatility of polonium.(20) Both simple and fractional distillation studies(21) have been made in a rather thorough fashion over a temperature range from 450° to 850°C in the pressure range of 1 to 50 microns. Agitation of the melt and de-entrainment of liquid carried in the vapor were shown to be significant factors in obtaining high polonium concentration factors and adequate recoveries.(22) In addition to intrinsic interest in the production of polonium the distillative separation method has been indicated(23) to be of special utility for the continuous separation of polonium from a liquid bismuth fueled reactor.

B-1. Fractional Crystallization Without Added Solvent

By fractional recrystallization without added solvent is meant a separation whereby minor constituents are physically segregated by reason of their unequal distribution between a liquid metal and the solid phase in equilibrium with it. Inasmuch as the operation usually requires repetitive use and zone-melting provides the most well known exemplification of repetitive crystallization attention will be directed toward this operation. The theory of zone-melting as an idealized operation has been rather thoroughly explored.(24,25a,26) The ideal separation of minor constituent from bulk metal can be given as a function of (i) the ratio ("k") of the slopes of the liquidus and solidus lines near the origin ("k") on a temperature-concentration plot for the given element, (ii) the number of passes and (iii) the ratio of the length of molten zone to total length. The situation is not markedly dependent on whether the minor constituent is preferentially soluble in the liquid or the solid phase. The kinetic factors which control the speed of zone-melting are complex, and involve the linear rate of primary crystal growth, diffusive and convective mixing in the molten zone, temperature gradients, etc.(27) No *a priori* theory is applicable to all cases.

1.1 Separation of Ordinary Contaminants from Uranium

Dunworth(26) has studied the purification of metallic uranium from ordinary contaminants that occur in its production. The theory cannot, of course, be applied to contaminants such as carbon, oxygen, and nitrogen which form with uranium compounds essentially insoluble in either phase, i.e., are removed by slagging. Purification from metallic impurities, such as iron, is afforded by this method but the results appear to show that the linear rate of zone travel required for significant movements of impurities are considerably lower for uranium than for more common metals, such as aluminum, germanium and silicon. Hence, the zone-melting method appears to be applicable only to the production of small quantities of high purity metal for laboratory purposes. An interesting development along these lines which has not yet reached print in connection with uranium is the use of a vertical, rather than a horizontal, geometry as in the "floating zone" method.(28) Contamination by reaction with a container material is eliminated by this method.

1.2 Separation of Fission Products and Plutonium from Uranium

This subject has been investigated by three independent groups.(25b,29,30) In these investigations essentially the same conclusion with regard to linear speed of zone-melting was reached as was referred to earlier. In the most thorough of these investigations Burris(25b) determined concentration profiles of appropriate traces in the solidified ingots after normal unidirectional freezing. The concentration profiles found agreed with their theoretically predicted shapes with satisfying accuracy. (Figures 1-3) From the data apparent "k" could be determined for the following solutes: plutonium, 0.60; ruthenium, 0.30; palladium, 0.61; molybdenum, 1 - all at the minimum solidification rate studied of 1/500 inch per minute. These values all appear to be in reasonable agreement with the respective phase diagrams.* The effective "k's" for the first three elements increase toward unity, i.e., separation is very much less effective, when solidification rates are increased.

1.3 Separation of Uranium from Thorium

The separation of uranium (i.e., U^{233}) from dilute solution in thorium would appear to be feasible from inspection of the pertinent phase diagram. This subject is currently being examined by a rather unique technique of zone-melting, i.e., the use of a traveling arc to form the molten zones.(31)

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*Because of the well known difficulties of determining liquidus and solidus lines with high precision by thermal analysis of dilute solutions the ratios determined by unidirectional freezing may, in fact, be more nearly correct.

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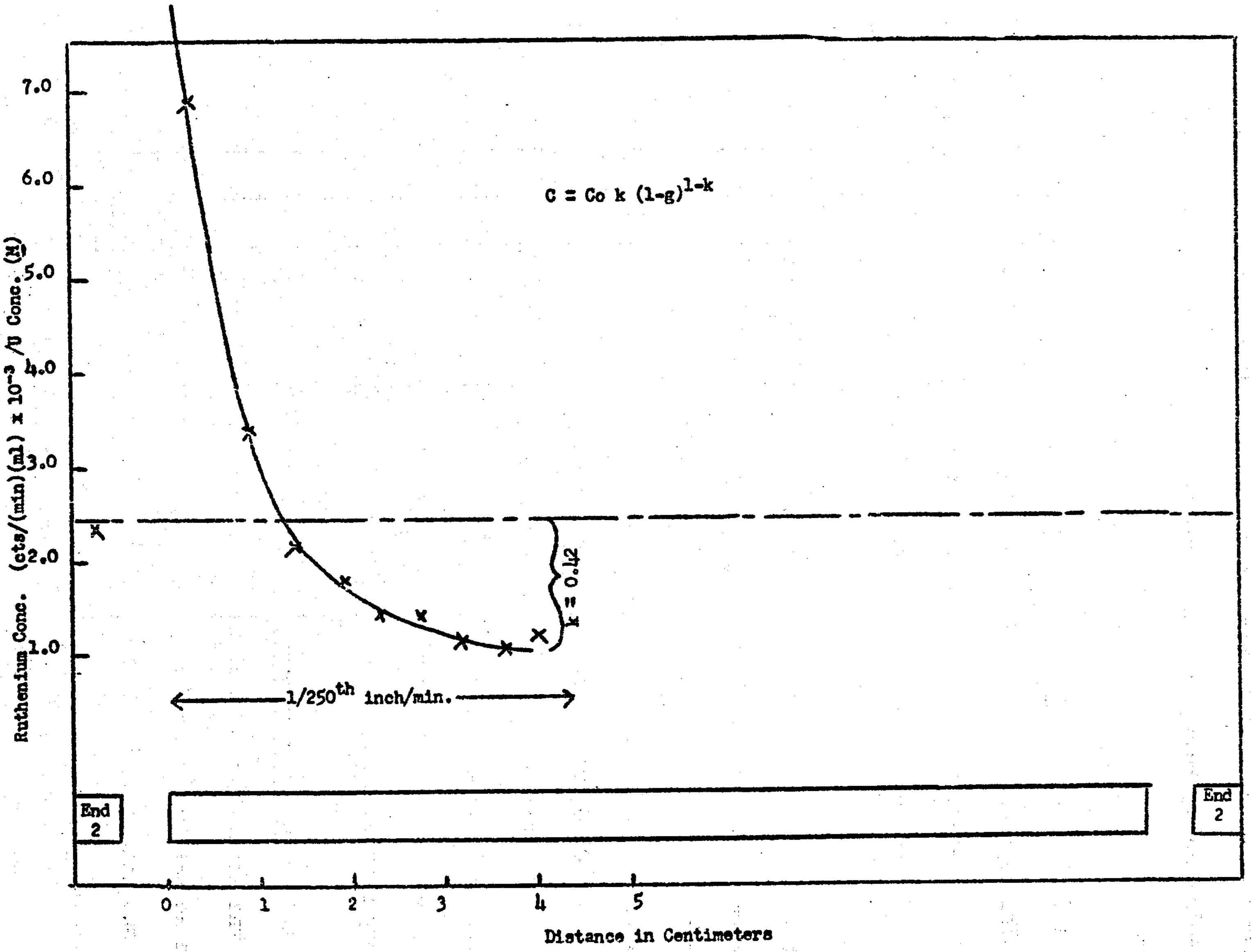

Fig. 1 - Determination of "effective k" for ruthenium by normal freezing.

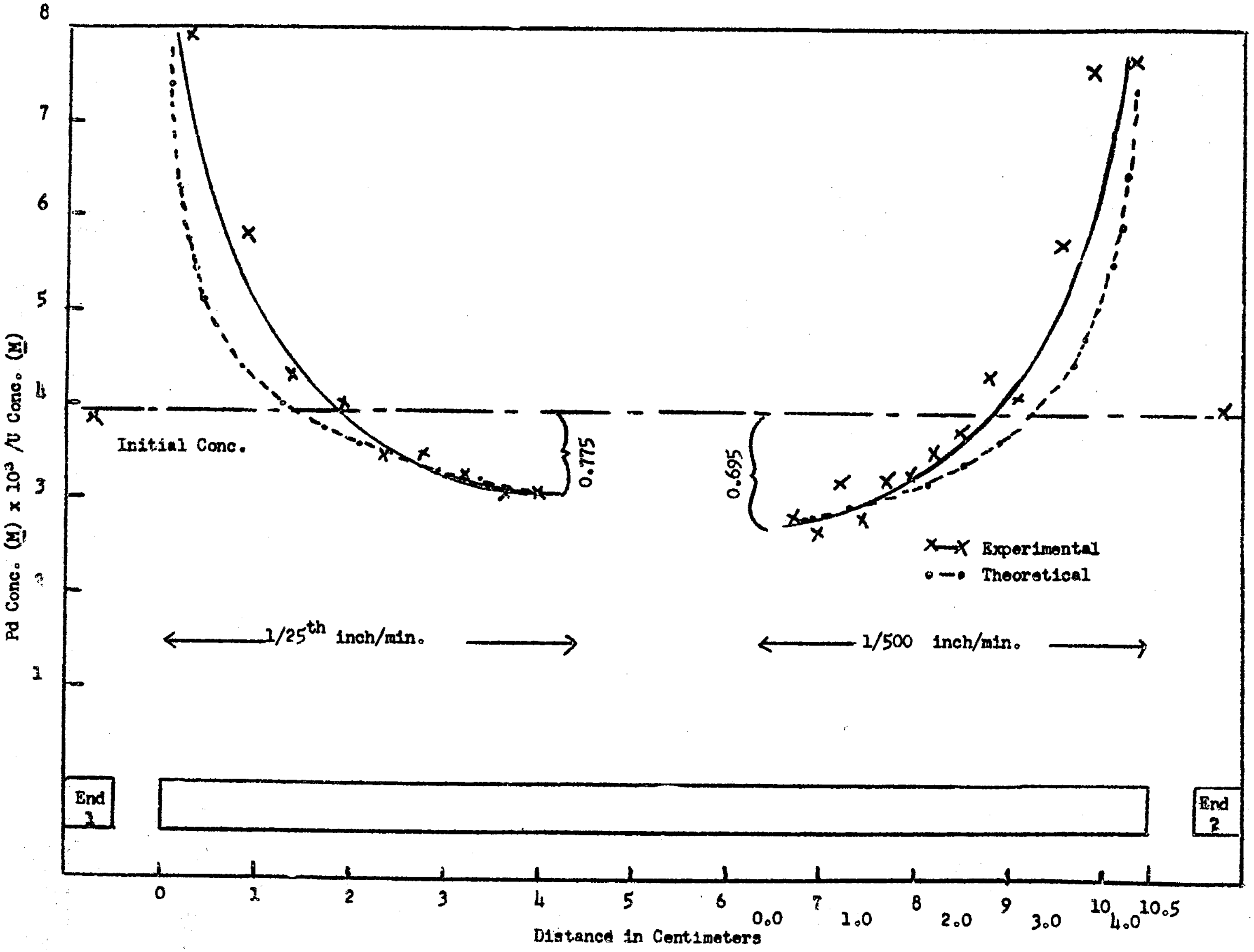

Fig. 2 - Determination of "effective k" for palladium by normal freezing.

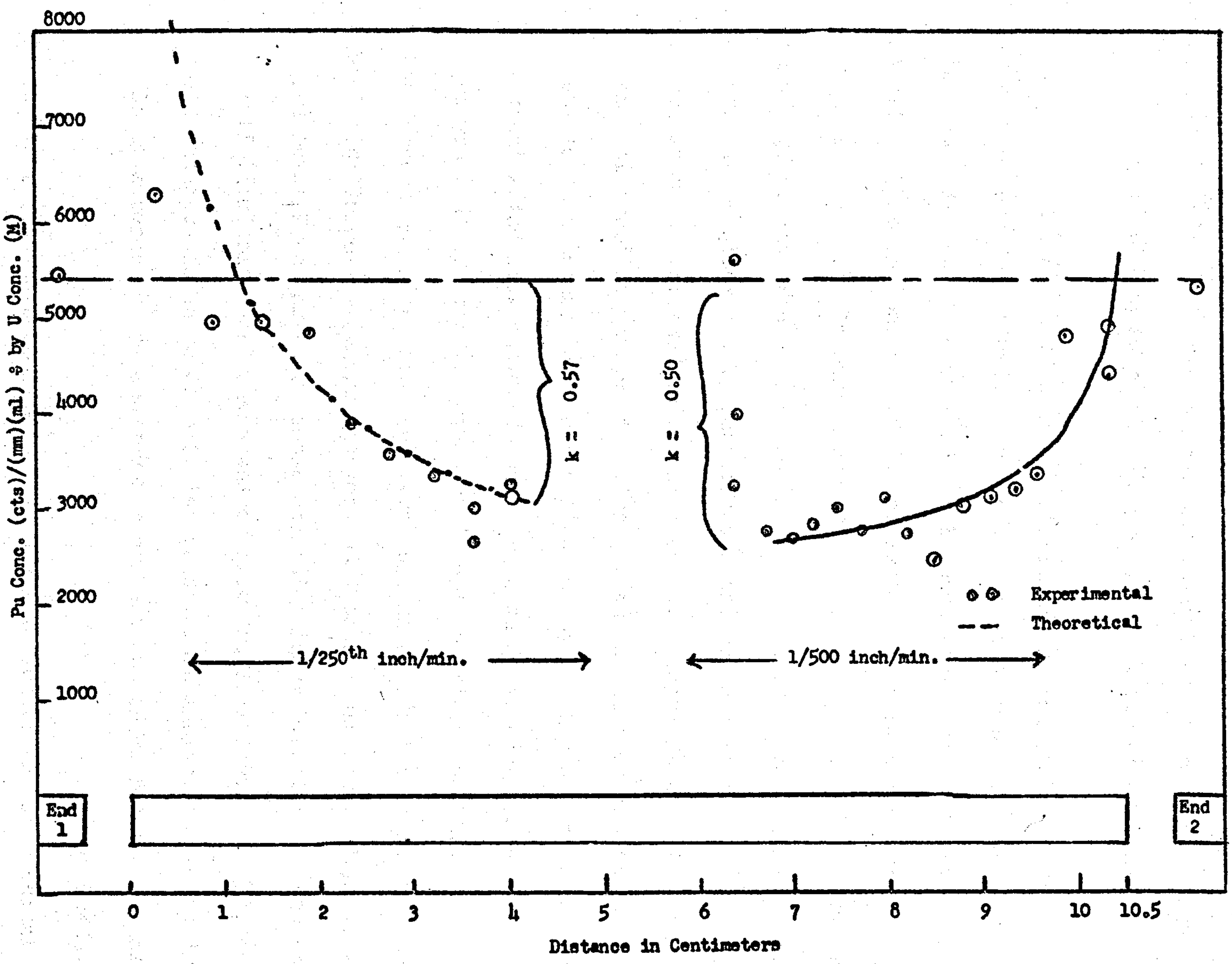

Fig. 3 - Determination of "effective k" for plutonium by normal freezing.

1.4 Purification of Plutonium

No information on this subject is available to the author. From inspection of pertinent phase equilibrium data and the low (650°C) melting point of plutonium it would appear to offer fruitful possibilities.

B-2. Fractional Crystallization With Added Solvent

The separations available by methods discussed in the previous section encounter natural limitations imposed by the nature of the bulk material present. By the addition of a metallic solvent to the system (usually in large excess) the solubility relations, the nature of the phases formed, and the operating temperatures become items which can be varied by the experimenter to enhance the desired separations. The principles of separation by fractional crystallization are well known; mathematical elaborations for the classical cases, e.g., brine crystallization, may be found in standard works. However, in some of the situations to be discussed many of the important constituents are present in concentrations well below their solubilities and the contamination of the crystallizate by them may be called "coprecipitation", as in the analogous case involving aqueous solutions of radioactive substances. No thorough investigation of this interesting aspect of liquid metal solutions seems to be in the literature. Undoubtedly, "coprecipitation" will be the phenomenon which will limit the ultimate separations achievable; detailed study of the responsible mechanisms - solid solution, surface adsorption, etc. - appears to be desirable.

In the sections to follow the material will be discussed in terms of the solvents used rather than the separations desired because of the current organization of the literature. The solubility of uranium in a number of low melting solvents is shown in Figure 4.

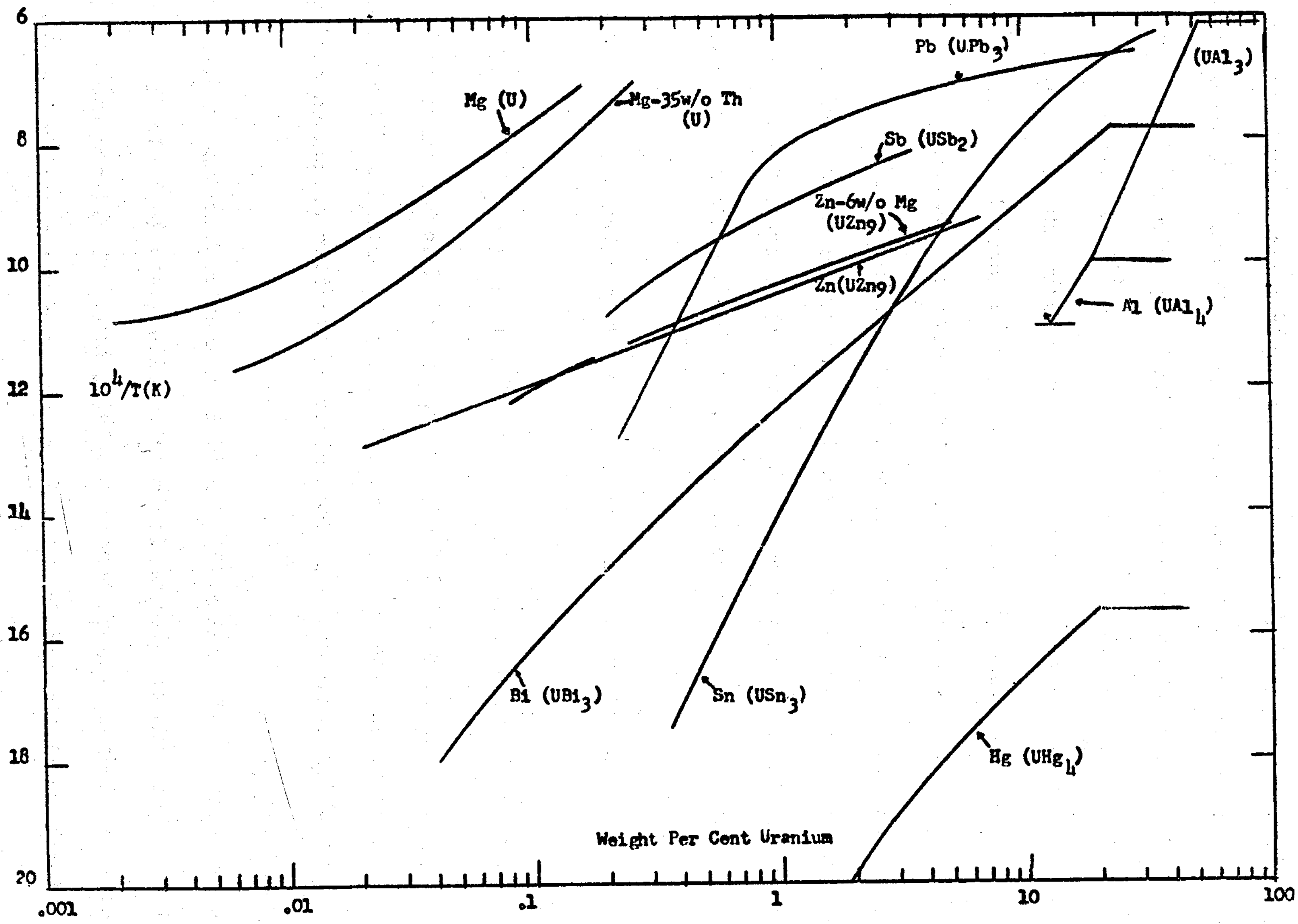

Fig. 4 - Solubility of uranium in different molten metals.

2.1 Bi-Sn-Pb

Fractional precipitation processes from these mixed solvents were the earliest to be investigated(32); the reason for their choice was the proposed use of uranium or thorium dispersions in these solvents for use as nuclear fuels or blankets.(33,34) Teitel's studies(32) consisted of preparation of suitable alloys, heat treatment to bring about complete solution, filtration (through porous graphite) at a lower temperature to remove the uranium intermetallic compound precipitated, and analysis of filtrate and residue. The distribution of rare earth activities between filtrate and residue was determined and the results were expressed mathematically in terms of the ratio, R, of weight concentration in the liquid to concentration in the solid phase. Table II abstracts some of Teitel's results.

The separation of uranium and tracer is readily calculable from the formula:

$$\text{Weight fraction of constituent in liquid phase} = \frac{x}{x + R\ (1-x)}$$

where x is the fraction unsolidified. Teitel found that the value of R_u is simply determined, as expected, by the solubility of uranium. Within the range of variables studied R_{RE} was not a strong function of concentration or temperature.

The separation of uranium-233 formed in a thorium-bismuth breeder blanket was also studied with preliminary results given in Table II.

Teitel's studies, though hardly complete, have established the utility of fractional precipitation from liquid metals as a method of separation even when the choice of solvent is limited to materials suitable as fluid fuels or blankets in a slow neutron reactor.

Table II

DISTRIBUTION OF RARE EARTHS AND URANIUM BETWEEN LIQUID AND SOLID PHASES

Intermetallic Compound	Solution Comp.	$\frac{\text{Weight Conc. in Solid}}{\text{Weight Conc. in Liquid}}$		Filter Temp., (C)
		R_{RE}	R_U	
USn_3	85.6% Pb-9.6% Sn-4.8% U	59	20,000	450
USn_3	"	41	13,000	600
USn_3	58.5% Pb-34.1% Bi-6.4% Sn-1.0% U	25	13,300	457
UBi_2	39.0% Pb-56.0% Bi-5.0% U	38	1,080	450
UBi_2	95.0% Bi-5.0% U	49	114	450
$Th_3 Bi_5$	not given	5,000[a]	5	not given

[a] R_{Th}

2.2 Zinc

When the limitation just mentioned is removed the choice of suitable solvent can be made on the basis of other factors. Knighton, et al(35) chose to study zinc as the solvent for fractional crystallization on the basis of its low cost, availability, some known constitutional diagrams, and its high volatility. The latter point is of considerable importance because of the ease with which the intermetallic compound precipitated from solution - UZn_9, in the case of uranium - may be decomposed to uranium and zinc vapor. The compound, UZn_9, is non-pyrophoric and occurs as large well-developed crystals. The pertinent phase diagram and vapor pressure measurements were obtained by Chiotti and his co-workers.(36)

The work on this system so far reported(35) consists mainly of measurements of the solubility of metals in liquid zinc over the temperature range 450° to 800°C. See Figures 5 and 6. The metals studied were: uranium, barium, cerium, zirconium, ruthenium, rhodium and palladium. In addition, the solubilities of some of these metals in more complex systems containing zinc, magnesium and uranium have been measured.

The possibility for metals separation by re-crystallization from zinc is illustrated by the following example based on these solubility data. An alloy of uranium containing (w/o) 3.4 Mo, 2.5 Ru, 0.5 Rh, 0.3 Pd, 0.1 Zr is dissolved - solution proceeds readily with a little agitation - at 650°C to form a 0.5 w/o solution of uranium in zinc. This is cooled to 500°C and filtered through porous graphite. The filter cake retains 5 to 15 per cent of the zinc, depending on the rate of cooling and the size of the crystals. The filter cake is washed twice with zinc. The filtrate contains 4.3 per cent of the uranium, 57 per cent of the molybdenum, 84 per cent of the ruthenium, and essentially all of the rhodium, palladium and zinc. Zinc may be evaporated from both filtrate and filter cake for recycle.

The small scale recovery of massive uranium metal from the UZn_9 by distillation has been demonstrated. Residual zinc contents of about 30 parts per million were readily obtained.

The solubilities of plutonium, thorium, aluminum, and stainless steel in this system, and the distribution of radioactive materials present below their solubility limits between liquid and solid phases is under current investigation. These data will contribute to an analysis of the possibilities for processing natural uranium or highly alloyed fuels or various metallic blanket materials.

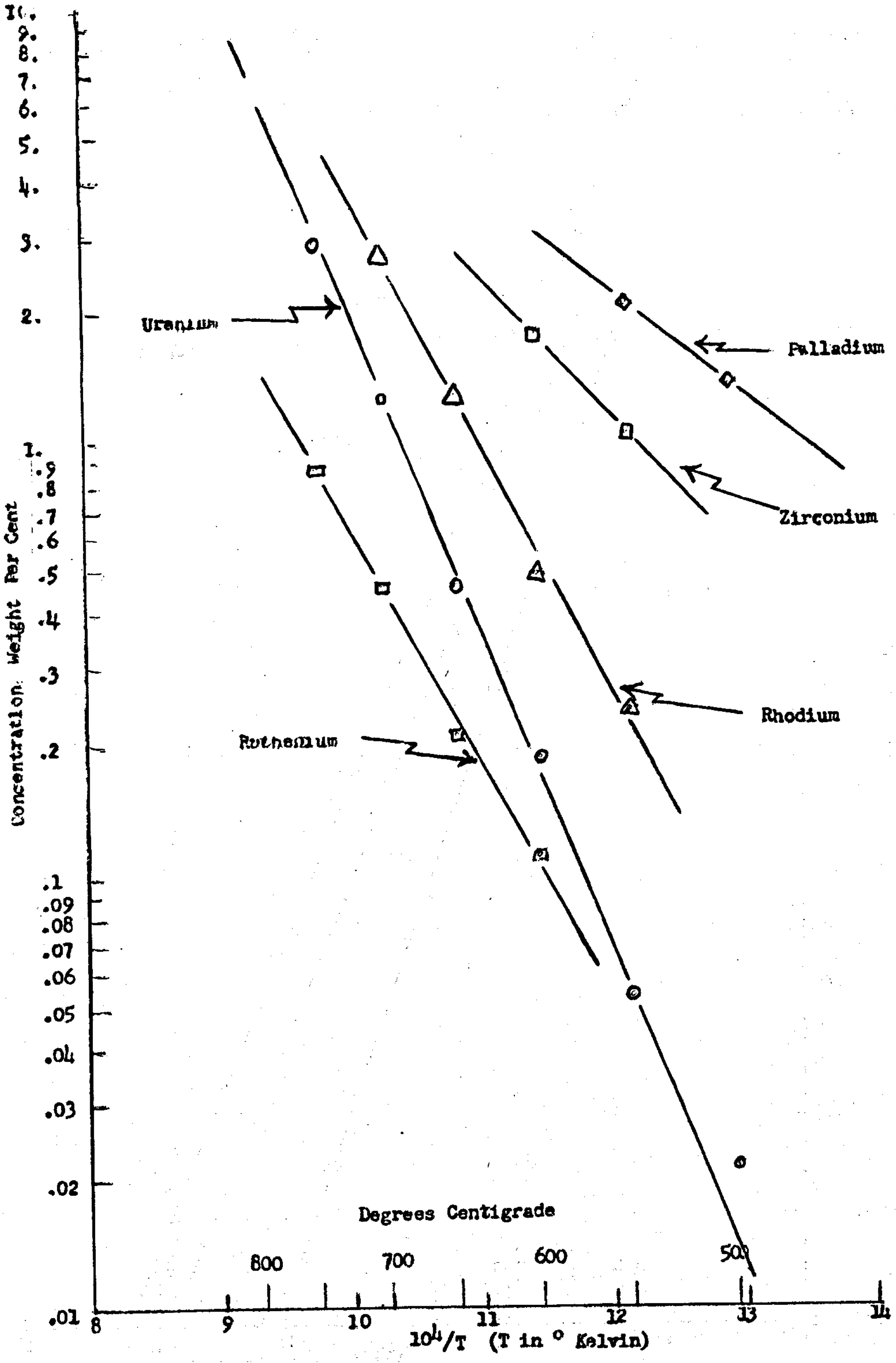

Fig. 5 - Individual solubilities of uranium and noble metal fission product elements in zinc as a function of temperature.

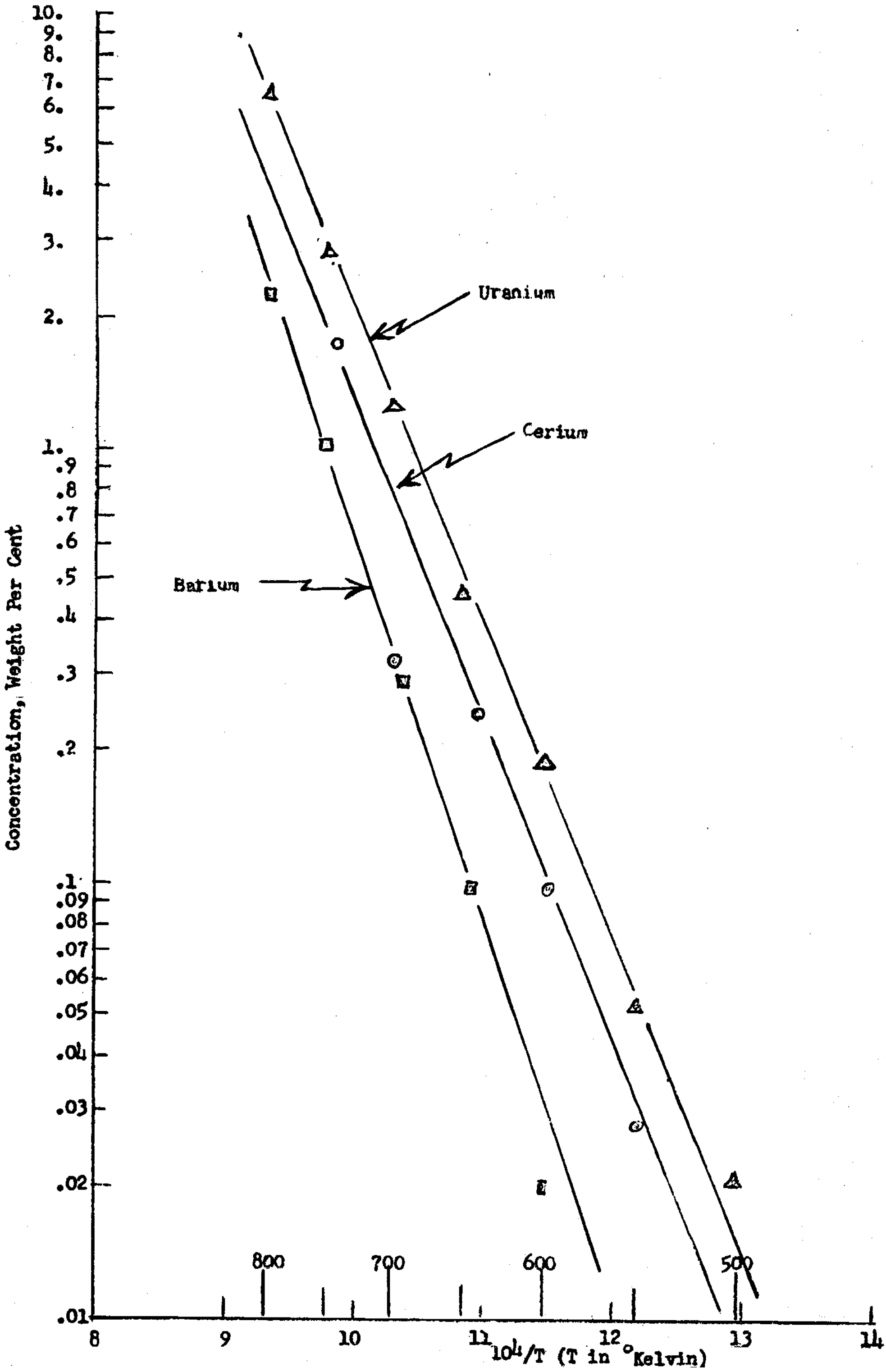

Fig. 6 - Individual solubilities of uranium, cerium, and barium in zinc as a function of temperature.

2.3 Mercury

The use of mercury as a re-crystallization solvent is attractive for a number of reasons. In particular, one may mention the lower temperature of operation, as compared to zinc, and the possibility of using conventional steel equipment.(37) Some obvious disadvantages are the pyrophoricity of uranium quasi-amalgams and the colloidal character of the uranium mercuride (UHg_4) which makes its separation from excess mercury difficult.

The pertinent phase data on the uranium-mercury system were reported by Frost.(38) In studies at Oak Ridge National Laboratory(37) the apparent saturation solubility of massive uranium in boiling mercury was found to be 0.94 mole per cent, in contrast to the equilibrium solubility of 13 mole per cent reported by Frost for powdered uranium. The rate of solution of massive uranium was found to be proportional to the exposed surface area and the fractional departure of the solution from apparent saturation. The room temperature solubility of uranium is about 10 parts per million per million of mercury. A butter-like uranium amalgam containing 3 per cent uranium could be retained on a filter. (The uranium content of the mercuride is 22.9 per cent). Recovery of massive uranium by vacuum distillation of the mercury from a quasi-amalgam has been demonstrated. Residual mercury contents were 10 to 30 parts per million.

Experiments were performed with irradiated uranium. Unfortunately, the fate of the fission product elements was determined only after a sequence of steps which included dissolution, partial oxidation, precipitation, washing, and distillation so that the separation achieved by the precipitation process alone was not determined.

2.4 Magnesium

Chiotti and Shoemaker(39) have studied fractional precipitation from solutions in magnesium. An interesting difference from the solvents discussed above is the fact that uranium itself, rather than an intermetallic compound of uranium, is precipitated. The separation of small quantities of uranium from thorium, as for example U^{233} formed in neutron irradiated thorium, is particularly attractive because of the high solubility of thorium in liquid magnesium and the low solubility of uranium. The solubility of uranium in magnesium, magnesium - 16 w/o thorium, and magnesium - 35 w/o thorium, was determined at various temperatures. At 650°C these solubilities are 20, 80 and 160 parts per million, respectively. The thorium content of the solid in equilibrium with the 35 w/o solution is 0.9 w/o, the balance being essentially uranium.

From this solubility information it can be shown that about 95 per cent uranium-233 contained in a 1 w/o thorium alloy may be recovered by dissolving the alloy to form a 35 w/o thorium solution at 650°C, and allowing the uranium to settle into a relatively small volume. The uranium concentrate could be removed and further separated from the matrix material by heating it above the melting point of uranium to form a liquid phase containing less than 1 w/o thorium. The temperature of separation of a uranium-rich liquid phase might also be lowered to about 900°C by the addition of enough chromium to form the uranium-chromium eutectic. Separation of magnesium from thorium by distillation is suggested by Chiotti and Shoemaker.

2.5 Others

An examination of the literature fails to indicate any investigation of other low melting metals, such as Pb, Cd, Al, Sb, in connection with separation by recrystallization.

C. Liquid-Liquid Partition

The principles of liquid-liquid partition are particularly well known to workers in the field of atomic energy because of their widespread use application to the processing of reactor fuels. These principles are equally applicable to liquid metal partition studies. The technical difficulties of continuous multi-stage contacting of liquid metals makes it desirable to employ systems with partition coefficients for the transferred material which are sufficiently large so that a small number of batch contacts brings about the desired separation.

In theory any pair of immiscible liquid metals might be examined for separation possibilities, e.g., the partition of uranium, plutonium and fission products between unsaturated solutions in zinc and lead. To date, however, with only one exception, systems in which one phase is uranium or a uranium-rich liquid have been studied. The systems to be discussed will be classified according to the major constituents of the immiscible phases.

1. Uranium-Alkali Metals

These metals have very low mutual solubility with the heavy metals. They have not received study on account of the high vapor pressures in the range of temperatures of interest.

2. Uranium-Calcium or Barium

The extraction of plutonium from uranium by calcium or barium has been found to be negligibly small.(40)

3. Uranium-Magnesium

The partition coefficient for plutonium between liquid magnesium and liquid uranium has been determined. At 1150 C a value of 0.23 (in mole frac units) was obtained (7, 42) with initial plutonium concentrations in uranium up to 97 parts per million. In a further study Feder et al(41) showed that up to 1 per cent by weight original plutonium concentration the partition coefficient remained constant at 0.20 ± 0.01 at 1190°C. The substitution of uranium-5 w/o chromium eutectic does not affect the result. Experiments were also carried out at lower temperatures with this eutectic alloy (m.p. 860°C), with equilibrium being approached from either direction. At 930°C the partition coefficient is 0.37. The heat of transfer of plutonium is 9.2 kcal/gram atom.

The partition of trace fission product elements at 1150°C has been examined for the uranium-magnesium system.(7,42) The partition coefficient reported for cerium and rare earths is approximately 2 ± 1. The results for other activities were more in doubt because of possible interferences by the operation of mechanisms other than partition. Elliott(43) has examined the partition of macro amounts of added metals between magnesium and the uranium-iron eutectic alloy (m.p. 750°C). At about 800°C the interesting result was obtained that the partition coefficients could be related to position in the Periodic Table. For the second row transitional metals, Zr, Nb, Mo, and Ru were found to have partition coefficients less than 10^{-3}, while rhodium, palladium, silver and cadmium enjoyed partition coefficients of about 10^{2}. The sharp break between ruthenium and rhodium probably reflects a significant change in available bonding orbitals.

4. Uranium-Lanthanum or Cerium

The mutual solubilities between uranium and these elements are somewhat larger than those already discussed. At 1150°C the solubility of cerium in uranium is 1.2 per cent and of uranium in cerium, 3.6 per cent.(9) The miscibility gap for lanthanum and uranium is about the same. Voigt(9) reports the distribution coefficients (weight fraction basis) for plutonium at 1200°C as 1.0 for cerium and 0.6 for lanthanum, in substantial agreement with Aikin and McKenzie.(8) At about 1100°C, with uranium-chromium eutectic alloy as the heavy phase, the corresponding values were 0.6 and 0.5. In a more detailed study McKenzie et al(45) determined the partition coefficient of plutonium as a function of temperature between 1160 and 1350°C. The heat of transfer of plutonium from uranium was found to be 2.9, 1.1, and 0.0 (all ± 0.4) in kilocalories per gram atom, for lanthanum, cerium and neodymium, respectively.

Some data on the partition of fission products between uranium-rich phases and cerium or lanthanum are also given by Voigt.(9) The most reliable of these data, based on artificial alloys, show partition coefficients into cerium as follows: Zr, 0.8; Mo, 0.04; Ru, 1.0; Nd, 30.

5. Uranium-Silver

Initial experiments with the extraction of tracer plutonium from uranium by molten silver showed that about 90 per cent extracted when equal weights of uranium and silver were used.(8) At 1350°C, 88 per cent is distributed to the silver phase when the uranium initially contained 0.1 per cent plutonium.(47) McKenzie(47) and Voigt(9) agree that the partition coefficient in this case is a function of plutonium concentration but do not agree on the variation. The more detailed studies of McKenzie show that a greater proportion of the plutonium is found in the silver phase at lower total plutonium concentrations. On addition of gold(47) to the system plutonium extraction is increased and passes through a maximum. This maximum appears to be associated with a particular concentration of gold in silver and of gold in uranium. The separation of plutonium and uranium is less efficient than may be indicated by the large partition coefficients for plutonium in this system because the solubility of uranium in silver at 1135°C is about 4 per cent. At 960°C silver in equilibrium with uranium-chromium eutectic alloy contains 2.8 per cent uranium and 0.03 per cent chromium. Some of the subsequent separations required have been considered further.(8) (48)

The extraction of fission products from uranium by silver has been examined.(9) In the most reliable experiments reported macro amounts of several elements were irradiated and alloyed with uranium before equilibration with molten silver. Reported values for the partition coefficients are: Zr, 0.6; Mo, 0.02; Ru, 0.02; Nd, 3.7. It is interesting to compare these values with those quoted earlier with cerium as the immiscible phase. It is quite clear that very specific factors are at work for not only do the ratios of partition coefficients vary on going from silver to cerium but also even on changing from cerium to lanthanum.

6. Aluminum-Bismuth

The distribution of Pu, Am, and certain fission products between molten aluminum and bismuth has been examined.(46) An equal volume of bismuth extracts 78 per cent of the plutonium, 93 per cent of the americium, the majority of the tracer cerium, but essentially no ruthenium or zirconium from the aluminum phase. The fraction of plutonium in the bismuth phase decreases slightly with increasing temperature in the range of 800° to 1050°C but is independent of the plutonium concentration. The heat of transfer of plutonium is 2.68 kcal/gram atom. Since plutonium-aluminum alloys have potential interest for certain reactors this partition may be of value for recovery of the plutonium.

The bismuth-aluminum system is also of potential interest for the purification of bismuth solutions of uranium but no work in this field is known to the author.

D. Liquid-Solid Extraction

Separations based on metal systems in which one phase is a solid insoluble in another liquid metal deserve greater attention than they have received. Clean separations of two liquid phases may require that the interface be accurately located - an operation which is difficult to perform remotely. In the liquid-solid case, however, the solid may be suspended in the liquid and subsequently removed by filtration or, alternatively, a liquid may be percolated through a bed of solids. An operation of this kind will generally be conducted at a lower temperature than the corresponding liquid-liquid extraction.

One of the drawbacks to the use of a solid phase is the rather small diffusion coefficients usually encountered. It may therefore be required that the solid phase be finely divided in order to make the diffusion paths short. Fortunately, in the case of uranium, thorium, zirconium, and plutonium powdering of the metal can be accomplished without great difficulty by the cyclic absorption and desorption of hydrogen under relatively mild conditions.

A separation employing these principles has been described by Feder et al.(41) In this application uranium - 1% plutonium alloys were powdered by hydriding at 250°C and one atmosphere pressure, and dehydrided by pumping off hydrogen at 350°C. The powder produced (about 10 µ average diameter) was readily suspended in molten magnesium by mechanical agitation. Samples of the liquid phase were taken from time to time by filtration through porous graphite or stainless steel. The fraction of the plutonium present in the magnesium was found surprisingly large after rather short times of contact. It appears to rise to a maximum and subsequently diminishes. These results have been interpreted to mean that the hydriding-dehydriding cycle causes some initial phase separation of uranium and plutonium, and that subsequently back diffusion of plutonium into the solid uranium occurs. This interpretation is in accord with information that plutonium hydride requires rather higher temperatures for its decomposition than uranium hydride,(50) and that plutonium has a large solid solubility in uranium.

The behavior of fission products in this system has been cursorily examined. The rare earths are extracted by the magnesium nearly quantitatively, while ruthenium and zirconium stayed nearly quantitatively with uranium.

The action of molten silver or other possible extractants has not been examined. The solubility of solid uranium in molten silver or cerium is considerably less than the solubility of liquid uranium so that some of the difficulties due to the contamination of the extracted plutonium by uranium may be avoided.

II. Separations by Selective Oxidation

If the term oxidation is used in its broad sense of an increase in the valence state of a metal then the initial work in pyrometallurgy, referred to in the historical introduction, is clearly an example of selective oxidation, or more specifically of carbide formation. The selective oxidations which will be treated in this section include reactions to form oxides, carbides, nitrides, sulfides, and halides. In general, the *a priori* discussion of selective oxidations is more readily accomplished than the discussion of physical methods of separating multicomponent metal mixtures. This is so because thermodynamic information on the pertinent metal systems is almost non-existent, whereas the relative thermodynamic stabilities of the compounds which may be formed by oxidation are better, although still incompletely, known. Some of the pertinent data may be found in the reference cited in the introduction and in references 3, 4, 5b and 52.

A. Oxides

The preferential oxidation of certain fission elements in a heavy metal matrix is the most thoroughly studies(6-8,10,19,52,53,54) operation in pyrometallurgical chemistry. There appears to be agreement among all investigators that in a uranium matrix selective oxidation of strontium, barium, thorium, the rare earths, and presumably, yttrium, may occur to a marked degree under appropriate experimental conditions. Under the same experimental conditions oxidation of niobium, molybdenum, the platinum metals, and in fact all elements with atomic numbers from 41 to 50, inclusive, does not occur. The selective oxidation of zirconium and plutonium in a uranium matrix is marginal and may or may not occur, depending on the precise set of conditions encountered. Inasmuch as the results of these investigations are well known it appears most appropriate to deal first with the points of difference among the several experiments and to attempt to resolve them.

1. Mechanism of Oxidation

On the basis of early experiments on the melting of uranium in ceramic oxides Feder et al(6,52) obtained evidence that the main mechanism of preferential oxidation was diffusion of the impurity atoms to the wall of the oxide crucible and subsequent reaction there. Martin and Miles(10) on the other hand, had equally good evidence from their experiments that oxidation takes place in the liquid phase by combination of the electropositive elements with contained oxygen, carbon, or nitrogen. The distinction was discussed(55) without being resolved; the purity of the uranium used, the concentration of fission elements, the degree of mixing, atmosphere purity, reactivity of crucible material, etc ., could all be factors involved. McKenzie and Feder(55) were of the opinion that the purity of the uranium used was the most significant factor at the low concentrations of fission products involve

Since that discussion the rate of reaction of molten uranium with various ceramic oxides has been measured.(56,57) The rate of removal of contained cerium (initially about one per cent) has been shown to be a function of the material of the ceramic used,* the resulting cerium oxide at the crucible-metal interface has been identified, and the rate of removal of cerium has been shown(58) to behave as expected if the mechanism were bulk diffusion from an unstirred liquid.

The mechanisms and kinetics of ceramic oxide corrosion by molten uranium is of considerable interest, particularly for the application of preferential oxidation to a large scale operation. The data obtained may be summarized as follows:(56,57) The reactions with alumina or magnesia proceed at a nearly constant rate and are essentially stoichiometric, producing, in the one case aluminum in solution, and in the other magnesium vapor.** The ceramic surfaces are dissolved away and replaced by UO_2 during the course of these reactions. When the aluminum corrosion reaction is conducted in vacuum gaseous Al_2O is also a product. The reactions with beryllia, thoria and zirconia proceed at a rate which accelerates with time. The order of the rates of contamination of the melt are $Al > Be > Th > Zr$. The variation at 1200°C is from about 1 $mg/cm^2/hr$ for aluminum to less than 1

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*In fact, the mode of fabrication, i.e., slip-casting vs. dry-pressing, has a considerable influence.

**Because of the evolution of magnesium vapor which occurs when molten uranium is held in magnesia crucibles the impurity and uranium oxides which form on the crucible wall are dislodged and float to the surface as a scum. This does not occur with the other ceramic oxides.

microgram/cm^2/hr for zirconium. The reactions with thoria and zirconia are non-stoichiometric, that is the quantity of oxygen reacting with the uranium is considerably greater than the equivalent amount of metal dissolved. The ceramic surfaces remain intact during these reactions. The products of these two reactions have been identified by X-ray diffraction and other tests as oxygen-deficient oxides.

A further point of interest is that uranium does not wet any of the five ceramic oxides mentioned above, with the exception of alumina which is wetted when uranium alloys high in molybdenum and ruthenium content are employed. The interior contact angle of molten uranium on the dense packed oxide ion surfaces is 135°. The surface tension of liquid uranium is about 800 dynes/cm.

2. Removal of Cesium, Strontium, Barium, Tellurium and Iodine

Differences between various investigators concerning the removal of these elements during oxidative slagging can be readily resolved in terms of variations in time, temperature and pressure conditions. By examining the sublimates from various experiments more direct evidence about removal by volatilization is available than when only losses from the melt are measured. In an inert atmosphere at temperatures up to 1300°C only cesium, of the above-mentioned elements, is found in the sublimate to any large extent.(58) Considerably less than one per cent of the available iodine is sublimed,(16) and the condensation curve for the iodine activity shows that the sublimate is uranium iodide(s) rather than molecular iodine. At higher temperatures and/or lower pressure appreciable fractions of barium and strontium may volatilize before they become oxidized. The behavior of tellurium accords with that expected from observations on the stability of uranium tellurides to heating in vacuum.(18)

3. Zirconium and Plutonium

The highly variable behavior of zirconium in experiments in which it was present in very low concentration(6,10) led to some confusion regarding the mechanism of its removal. The importance of graphite as a scavenging agent for zirconium has been shown.(6) Subsequent experiments(58) have shown that as the concentration of zirconium increases the effectiveness of its removal decreases, and that at macroscopic concentrations the removal of zirconium by preferential oxidation is very slow. In view of the earlier statements concerning the mechanism of corrosion of zirconia little or no exchange of zirconium in uranium solution with inactive zirconium in zirconium oxide should be expected when the concentration of the former is large.

Selective removal of plutonium has been observed by all investigators. The degree of selective removal when only tracer plutonium was present, however, was found to be small and variable, i.e., concentration factors of 1.0 - 1.4 were usually found. Because side reactions with carbon (as in the case of zirconium) could conceivably play a role and because the thermodynamic stability of plutonium oxide(s) versus uranium dioxide was but poorly known the role of selective oxidation could not be accurately assessed. Recent experiments(58) with initial plutonium concentrations of 1 to 20 per cent in uranium show that plutonium is indeed selectively oxidized, the factor of concentration in the oxidic portion being approximately 1.6.

4. Uranium Monoxide

The possible role of uranium monoxide formation in the oxidative slagging of uranium has been in question for some time. Recent efforts by Vaughan, et al(59) to synthesize this compound in bulk by a variety of methods have failed to produce a pure substance corresponding to this formula. It appears to be entirely unlikely that uranium monoxide is a product of any consequence in the oxidative slagging of uranium.

5. Thorium and Plutonium

Separation of fission products from thorium(19) or plutonium by oxidative slagging has been the subject of recent, incomplete investigations. The discussion must be deferred until more extensive information is available.

B. Carbides

The relative stability scale for the carbides of metals does not differ strikingly from the relative stability scale of the oxides. Relative to uranium the early transitional metals, e.g. zirconium, niobium and molybdenum, became somewhat more stable on going from oxides to carbides. Experimentally, the relative stability of plutonium also appears to be enhanced, contrary to expectation based on estimated free energies of formation.(5b) The relative stabilities of the alkaline earth and rare earth metals are probably slightly decreased. Closer inspection of the free energies of formation of the carbides shows that of the fission product elements only zirconium carbide is much more stable than uranium carbide(s). In accord with expectation it is found(6,52) that zirconium may be selectively removed from molten uranium on a graphite surface. Of course, if sufficient carbon is already dissolved in molten uranium *ab initio* this effect is not observed.(10) No other fission product element appears to be affected as extensively. Plutonium, however, appears to be fairly effectively scavenged by a graphite surface.(52) Even at 900°C, where molten uranium-chromium eutectic alloy reacts with graphite quite slowly, plutonium at low concentrations may be lost to graphite surfaces.(44)

C. Nitrides and Sulfides

On the basis of known or estimated thermodynamic stabilities it would not seem likely that selective formation of nitrides or sulfides would enhance the separation of fission products or plutonium from uranium. The experimental results of various investigators(6,7,10) appear to bear this out. Likewise, the addition of boron or silicon(6) does not enhance the separations of fission elements which occur in oxide slagging.

D. Halides

The relative stability scale for the lower halides of the elements is considerably different from the same scale for the oxides. The stabilities of the halides of the alkali metals, the alkaline earth metals, and the trivalent halides of the rare earth metals, plutonium and the transplutonic metals are all increased relative to the stability of the corresponding lowest uranium, thorium, and zirconium halides.* This has led a large number of investigators to inquire into the possibilities of selective halogenation for the separation of plutonium and the highly electropositive fission product elements from uranium.

1. Separation of Plutonium from Uranium

The first of many investigations of the separation of plutonium from uranium was directed primarily toward finding the location of plutonium trihalides on the stability scale at a time when little was known of their thermodynamic properties. Fontana and Webster(60) examined the distribution

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*An additional factor - not available in oxide or carbide systems - which encourages favorable consideration of halide systems is the possibility of driving reactions in a desired direction by taking advantage of the volatility of one of the products.

of plutonium in a number of systems containing a molten metal in contact with its halide. Their results are shown in the following table.

TABLE III

DISTRIBUTION OF PLUTONIUM IN METAL-METAL HALIDE SYSTEMS

Metal-Halide Mixture	Concn. Pu in Salt/Concn. Pu in Metal
$Ba-BaBr_2$	0.06
$Ca-CaCl_2$	.16
$Sr-SrBr_2$	.21
$Ce-CeBr_3$	.3
$Mn-MnCl_2$	8.7
$Mg-MgCl_2$	17
$U-UBr_3$	40
$Mg-MgI_2$	92
$Pb-PbCl_2$	310

From these results it was then deduced that plutonium trihalides are more stable than the corresponding uranium or magnesium halides, and less stable than the barium, strontium, or cerium halides.

Ader(61) has heated uranium-chromium eutectic alloys containing plutonium with magnesium chloride under inert gas pressure to suppress the volatilization of magnesium or magnesium chloride. Over the temperature range 900°-1000°C the selectivity ratio (= Pu/U in salt phase ÷ Pu/U in metal phase) varied approximately from 100 to 45, in quite fair agreement with values predicted from estimated free energies of formation.

Rosser(62) took advantage of the selectivity of chlorination by allowing uranium containing trace plutonium to react to a small, controlled degree (about 6%) with gaseous hydrogen chloride. The mixed chlorides which were formed were subsequently sublimed in vacuum to produce a sublimate containing all of the plutonium.

McKenzie(8) made use of the similar selectivity of fluorination by equilibrating molten uranium with fused uranium tetrafluoride and subsequently distilling the plutonium-enriched salt phase in vacuum. He observed that the situation is complicated by the fact that uranium and its tetrafluoride react to produce the solid trifluoride in the initial step and that the trifluoride disproportionates during the vacuum distillation. Buyer(63) assumes that the free energies of formation per gram atom of fluorine for uranium trifluoride and tetrafluoride are quite nearly the same at the temperature of his experiments. He has used his selectivity data for the equilibration reaction to calculate a free energy of formation of plutonium trifluoride which agrees within one kilocalorie with Brewer's estimate. The addition of fluxing agents (CaF_2, LiF, BaF_2, $BaCl_2$) to uranium tetrafluoride has been shown(7, 8,10) to be a useful procedure for maintaining the salt phase molten without hindering the selective fluorination of plutonium. Motta(7) reports data on experiments of this kind using about a kilogram of uranium; it would appear that the transfer reaction is kinetically controlled by diffusion.

There appears to be no record of experiments in which plutonium and uranium are dissolved in a low-melting metal prior to selective halogenation. Lower temperature halogenation may well be more selective and technically more feasible than halogenation at higher temperatures.

2. Separation of Electropositive Fission Product Elements from Heavy Metals

In many of the investigations mentioned above(7,8,10,62,63) the selective removal of fission product elements as well as plutonium was examined. There is essential agreement that the alkali metals, the alkaline earth metals, and the rare earth metals are all selectively removed to a greater extent than plutonium, in accord with expectation. Motta(7) reports one experiment using 2 mole % UF_4 - 98 mole % CaF_2 as the liquid phase in which 99% of all these activities were removed from irradiated uranium. Potter(19) also reports selective removal of some fission products from thorium. A rather unique method of contact was used in part of this investigation;(76b) a pellet of thorium was placed on a column of solid powdered calcium fluoride and allowed to melt its way down through the column by inductive heating of the metal.

An elaborate investigation(34,64,65,66) has been made of selective chlorination of fission products from a dilute solution of uranium in bismuth. It was shown(65) at an early stage that the concentration dependence of the partition of a typical fission element between the salt (LiCl-KCl eutectic) and metal phases could be understood in terms of reactions such as

$$Ce_{(Bi)} + 3\ LiCl_{(LiCl-KCl\ eut.)} \rightleftharpoons CeCl_{3(LiCl-KCl\ eut.)} + 3\ Li_{(Bi)}\ .$$

For the subsequent development of this effort in the direction of more precise control of the desired separations by the use of different salt compositions, buffering agents, deoxidants, etc., the reader should consult the references already cited. In the actual application of selective chlorination to circulating bismuth-uranium reactor fuels it appears that the necessary very high degree of selectivity required, i.e. quantitative return of the uranium present to the bismuth stream together with adequate removal of rare earths, can be achieved only by employing at least two distinct sets of conditions in tandem.

Purification of a dilute solution of uranium in aluminum has been briefly examined.(10) Molten potassium chloride was used as the salt phase and the degree of total chlorination was controlled by the addition of gaseous hydrogen chloride. The residual metal was well decontaminated from rare earth activities and, of course, the uranium in the salt phase was well decontaminated from the nobler metals zirconium, niobium, and ruthenium.

The possibility of selective removal of the most electropositive elements from plutonium has been indicated by the earlier discussion, although it is recognized that the situation is not as favorable as for separation from uranium. McKenzie et al(67) have examined the decontamination of plutonium-aluminum alloys using molten cryolite as the fluorinating agent and they have shown that strontium and cerium are effectively removed with little or no loss of plutonium.

III. Separations by Cyclic Oxidation-Reduction

From the preceding discussions of the relative stabilities of metal compounds it is apparent that it is theoretically possible to make a clean separation of any desired constituent from a mixture and to recover it in metallic form by a suitable oxidation-reduction cycle. Thus, to use a hypothetical illustrative example, an alloy of molybdenum, uranium, and lanthanum might be caused to react with a quantity of zinc chloride stoichiometrically equivalent to the sum of the latter two elements. The resulting mixture of uranium and lanthanum chlorides could then be caused to react with a quantity of magnesium stoichiometrically equivalent to the quantity of uranium in order to recover it as metal.

The success of such an operation will, of course, depend not only on the possibility of selecting appropriate oxidants and reductants but also on the completeness of the required phase separations. The necessary conditions are not easy to fulfill, particularly in view of the simplicity usually required of remote operations.

A. Chemical

Two basically chemical methods of carrying out the oxidation-reduction cycle have been investigated. The simpler of these methods is based on the well known van Arkel-DeBoer method of thermal decomposition of metal iodides. The selectivity of this operation is due to physical, as well as chemical, factors. To be transported and deposited as metal on the hot surface a constituent of the metal mixture must (i) react with iodine at the temperature and pressure of iodination, (ii) the resulting iodide must be sufficiently volatile to be transported, and (iii) the volatile iodide must be decomposable at the temperature and pressure conditions at the hot surface. The appropriate conditions have been discussed in detail for uranium(17) and zirconium.(68) Robb(69) has studied the decontamination of irradiated uranium obtainable by this method, and has demonstrated decontamination from both more noble (ruthenium, molybdenum) and more electropositive (cesium, strontium, rare earths) fission product elements. The properties of zirconium and uranium tetraiodides are sufficiently similar that these elements accompany each other and result in the deposition of a uranium-zirconium alloy. By incorporating an additional step, namely the selective condensation and re-evaporation of uranium tetraiodide the separation of these two elements also may be obtained. Robb also discusses the behavior of thorium and plutonium in this system and Milne(70) has examined the behavior of irradiated thorium. Protactinium is transferred more rapidly than thorium, which in turn is transferred more rapidly than uranium.

The kinetics of these reactions are not highly favorable. At the highest iodination temperature tested (625°C) uranium was consumed at a rate of only 0.117 grams per cm^2 per hour, equivalent to a linear penetration rate of about 65 microns/hour. The decomposition rate at the hot surface is limited by the pumping capacity of the vacuum system.

Another chemical method of performing cyclic oxidation-reduction for the purification of irradiated uranium has been investigated by Dawson, Gibson, and McKay. As reported by Martin and Miles$^{(10)}$ uranium and lead chloride react stoichiometrically according to the equation (the "Gibson Reaction")

$$3\ PbCl_2 + 2\ U = 2\ UCl_3 + 3\ Pb \quad .$$

Potassium chloride may be used as a diluent to lower the melting point of the resulting salt phase. The salt phase resulting from the Gibson reaction is separated from the precipitated lead and treated with an amount of magnesium slightly in excess of stiochiometric. The fission product distribution obtained is shown in Table IV.

It should be noted that the electropositive elements accompany the uranium into the salt phase nearly quantitatively and are retained in this phase to a large extent during the reduction by magnesium. The elements more noble than uranium appear not to accompany the precipitated lead nearly as quantitatively as expected. It is reasonable to suppose that because of their very low concentrations elements such as ruthenium occur as a variety of very small sized metallic particles dispersed in the salt. Some of these

TABLE IV

REMOVAL OF FISSION PRODUCTS FROM URANIUM BY CONVERSION TO UCl_3 USING $PbCl_2$, FOLLOWED BY REDUCTION USING MAGNESIUM*

Fission Product Element	% Removal at UCl_3 Stage (After Filtration of Aqueous Solution)	% Removal After Final Reduction to Metal by Mg
Cs	9	68
Ba	3	96
Sr	0	99
Ce	2	76
Rare Earth Metals	0	66
Zr	36	15
Nb	73	31
Ru	77	18

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*After Martin and Miles, Ref. 10.

would pass through the filter and appear in the aqueous solution of the salt phase. This hypothesis is supported by the appearance of these elements in the uranium to a degree which suggests that the particles are carried down with the precipitating metal. Thus, as mentioned previously, the separation problem in this system is likely to be one of phase separation.

One of the ways of overcoming the phase separation difficulty is to provide a liquid metal phase in which the noble metal elements can remain dissolved. (The lead precipitating during the Gibson reaction apparently does not function in the desired manner). This modification was incorporated when the Gibson reaction was carried out on 20% uranium - 80% aluminum alloy.(10) In this case less than one per cent of zirconium, niobium, and ruthenium accompanied uranium into the salt phase. However, the partial chlorination of the aluminum present introduced an undesirable complication into subsequent operations. It would be instructive to examine the net separations afforded by an operation in which the solvent metal is not chlorinated. For example, a zinc solution of uranium may be chlorinated by a $ZnCl_2$-KCl melt, and the resulting UCl_3-KCl salt subsequently reduced with a Zn-Mg solution. Such a sequence might lend itself readily to multicyclic operations.

Beederman(71) has shown that the Gibson reaction may be used with $ZnCl_2$, $CdCl_2$, or $HgCl_2$ as the chlorinating agent, as well as with $PbCl_2$, and Martin and Miles(10) also indicate the use of gaseous hydrogen chloride or anodic dissolution in a fused chloride bath as additional ways of achieving selective chlorination. The last mentioned possibility brings one naturally to a discussion of electrochemical oxidation-reduction cycles.

B. Electrochemical

The electrochemical production of uranium has been reviewed by Katz and Rabinowich.(17) Marzano and his co-workers(72) have demonstrated the purification of uranium from a number of its commonly occurring contaminants by a cyclic oxidation-reduction process carried out electrochemically. In this operation the impure uranium is made the anode in molten LiCl-KCl eutectic containing approximately 20% by weight of UF_4 in solution. The cathode may be tantalum or molybdenum rod. Fused silica ware makes a suitable container and an inert atmosphere must be maintained. Only a small voltage is required to cause anodic dissolution of the uranium and deposition of dendritic crystals of the metal on the cathode. The deposit must be crushed and washed free of occluded salts. A typical analysis of the uranium obtained is in parts per million; C, 16; N, < 10; O, < 8; Fe, 5; Si, 5; Cu, 1; Cr, 1; Mn, 0.5; Mg, 0.5; Al, 5. It was found that operation of this cell could be maintained for several months, after which it was halted by the accumulation of a sludge of impurities and uranium trifluoride at the bottom. The formation of the latter substance could be avoided by substitution of uranium trichloride for uranium tetrafluoride in the melt.

The application of this procedure to the purification of irradiated uranium was investigated by Glassner.(73) The data obtained were not encouraging insofar as the desired results were concerned. The decontamination factor for uranium from the more electropositve elements (including plutonium) was 50 to 100, but the decontamination factor from ruthenium was 5 or less, and zirconium and niobium activities were found to have severely contaminated the uranium deposit. The mechanism of the deposition of zirconium was investigated in separate macro experiments. It was found that zirconium dichloride, a relatively insoluble substance, is stable in the presence of metallic uranium, but the application of only 0.05 volt is sufficient to reduce it to metal on a uranium surface. Because an applied voltage in excess of 0.1 volt is required to achieve a reasonable rate of electromigration the essentially quantitative codeposition of zirconium (and, presumably, also niobium) becomes understandable. Electrophoretic movement of fine, suspended particles is an another possible source of cathode contamination.

Glassner(73) attempted to modify the dendritic nature of the deposited metal in order to simplify its handling. However, variations in temperature, bath composition, voltage, current density, and stirring of the melt were not effective. A quantitative study of the effects of current density and temperature on the deposition characteristics of uranium obtained from mixed chloride-fluoride melts at 725°-900°C has also been made by Kantan et al.(74) In this research, too, no massive metal was deposited.

Niedrach and Glamm(75) have given careful consideration to the problem of selecting cell conditions appropriate to higher specific decontamination, more manageable product, and longer steady operation. They judged the following points to be significant.

(i) The uranium product should be obtained as a liquid. Ideally, the cell should be operated above the melting point of uranium, but the corrosion problems attending such a high temperature operation favor the use of a metal cathode capable of forming a lower melting (750°-950°C) eutectic with uranium.*

(ii) The concentration of the electropositive elements in the molten salt will continually increase as the cell is operated, and the decontamination factor for these elements will consequently decrease. Therefore, the cell contents should be periodically replaced.

(iii) The nobler elements should occur as an insoluble sludge and contamination by them should not increase with time provided that the sludge is retained in an anode basket and is discarded periodically.

The experimental work of Niedrach and Glamm(75) establishes the effect of the significant variables on electrorefining. Their results may be summarized as follows.

(i) Current efficiency is not markedly affected by melt composition or temperature. Increasing current density decreases the current efficiency.**

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*The possibility of using much lower temperatures and a liquid cathode of zinc or mercury is not mentioned by these authors. R. L. Nuttall and H. M. Feder of Argonne National Laboratory are actively considering this development.

**Calculated on the basis of three faradays per mole. At very low current densities this value was approached in this work and also in the research of K. Rohde (privately communicated).

The effect of high current density is believed to be polarization at the anode. When the rate of oxidation at the anode exceeds the diffusional rate for trivalent uranium ions tetravalent uranium ions form in significant amounts. The cyclic reactions between the two valence states consume current inefficiently.

(ii) A minimum concentration of uranium salt must be maintained in the melt. The deposition potentials of uranium ions and, say, calcium ions at the cathode are sufficiently close so that if the activity of the latter far exceeds the activity of the former appreciable amounts of calcium will co-deposit with uranium.

(iii) Both current and temperature have a significant effect on the composition of the liquid alloy which drips from the eutectic-forming cathode. At high current densities the alloy tends to be hypoeutectic and at low current densities hypereutectic. The composition is determined by the rate of uranium deposition and the rate of diffusion of the cathode metal into the deposit. At very high current densities the rate of uranium deposition may exceed the rate of diffusion of cathode metal and a solid dendritic growth results.

(iv) Fission product decontamination factors of from 80 to 260 were obtained after two throughputs.* As many as ten throughputs were made without decreasing decontamination too severely.

(v) Manganese is a suitable cathode material because its selective distillation from the eutectic alloy in vacuum at 1300°C has been demonstrated.

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*One throughput is the dissolution and deposition of a quantity of uranium equal to the amount originally present in the melt.

Hansen(76a) has undertaken investigations of an electrochemical cell for refining irradiated thorium. It operates on principles similar to those expounded by Neidrach and Glamm(75) and makes use of a manganese cathode (eutectic ~20 w/o Mn at 940°C) and a 60 w/o NaCl - 40 w/o $ThCl_4$ electrolyte.

CONCLUDING REMARKS

The last seven years of research on pyrometallurgical processes have been busy and fruitful ones. It is a plausible assumption that the main areas of research have now been mapped out and await only further exploration. The astute observer will, however, remain alert to the chance discovery or new concept which will open entirely new vistas.

In the author's opinion current research in pyrometallurgical chemistry merits three major criticisms. The first, and least, is due to the experimentalist's natural desire to make his apparatus small and uncomplicated. However, it is generally observed that high temperature-high radiation field experiments yield more reliable and more quantitative information when they are carried out on a larger scale in apparatus designed to minimize undesired side reactions and surface phenomena. The second criticism is directed toward the shortsighted policy of the experimentalist who continues to use and to tolerate thermochemical data known to be of inadequate accuracy. The conscientious high temperature chemist will want to add to our fund of accurate thermochemical data in proportion to his withdrawals. The third, and most severe, criticism is of the policy of rushing too rapidly toward the application of pyrometallurgical processes. As a result of this policy some hastily conceived proposals for major innovations in nuclear technology have collapsed because their scientific foundations have been inadequate.

With respect to the future of pyrometallurgical research the author believes that the following may be significant directions.

(i) More attention will be given to obtaining basic scientific data - thermochemical measurements, electrochemical potentials, activity coefficients, diffusion coefficients, solubilities, etc.

(ii) Emphasis will shift toward lower temperatures of operation and to solutions in low-melting metals.

(iii) Corrosion research will burgeon, and the effects of high radiation fields on pyrometallurgical processes and materials will be given more detailed examination.

(iv) Better combinations of well-behaved operations into successful processes will be sought and found.

No claim is made by the author for either the completeness or accuracy of his bibliography. He will appreciate having his attention directed toward any necessary corrections or inadvertent omissions.

The help of colleagues too numerous to mention is gratefully acknowledged.

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PYROMETALLURGICAL PROCESSES: PROCESS AND EQUIPMENT DEVELOPMENT

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INTRODUCTION

Several basic pyrometallurgical extraction methods have been studied and described in the paper on the Chemistry of Pyrometallurgical Processes by Dr. H. Feder. Some of this work has been carried out using somewhat larger equipment which has been built for exploratory engineering experimentation and not primarily designed and developed for industrial use. It is this experimental type of engineering equipment which is described here.

The systems fall into two categories. In one are the various furnaces for extracting fission products or plutonium from molten fuel. In the second category are those systems related to the refabrication into fuel elements of the partially decontaminated and reconstituted fuel alloys. No effort will be made here to relate this equipment closely to specific reactor fuel cycles or to describe every type of equipment which has been used in this work. Some representative types have been selected and are described relatively briefly.

I. PYROMETALLURGICAL DECONTAMINATION AND EXTRACTION SYSTEMS

Two types of equipment used for decontaminating molten metallic fuels may be considered. In one type the molten fuel is contacted with a solid phase which removes some of the fission elements. In the other, a second liquid phase is placed in contact with the molten fuel, and fission products or plutonium are extracted into the liquid phase.

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A. DROSSING FURNACES FOR MOLTEN URANIUM FUEL

Three examples of this kind of system are described. The first is a 1- to 5-kg capacity vacuum induction furnace used inside a dust-tight system or gloved box, which is in turn enclosed in a hot cave to provide shielding from gamma rays. The second is a 50-kg capacity inert atmosphere induction furnace, and the third is a 30-kg capacity vacuum resistance furnace.

1. In-Cell Vacuum Induction Furnace (5-Kg)

A schematic diagram of the basic system is shown in Fig. 1.

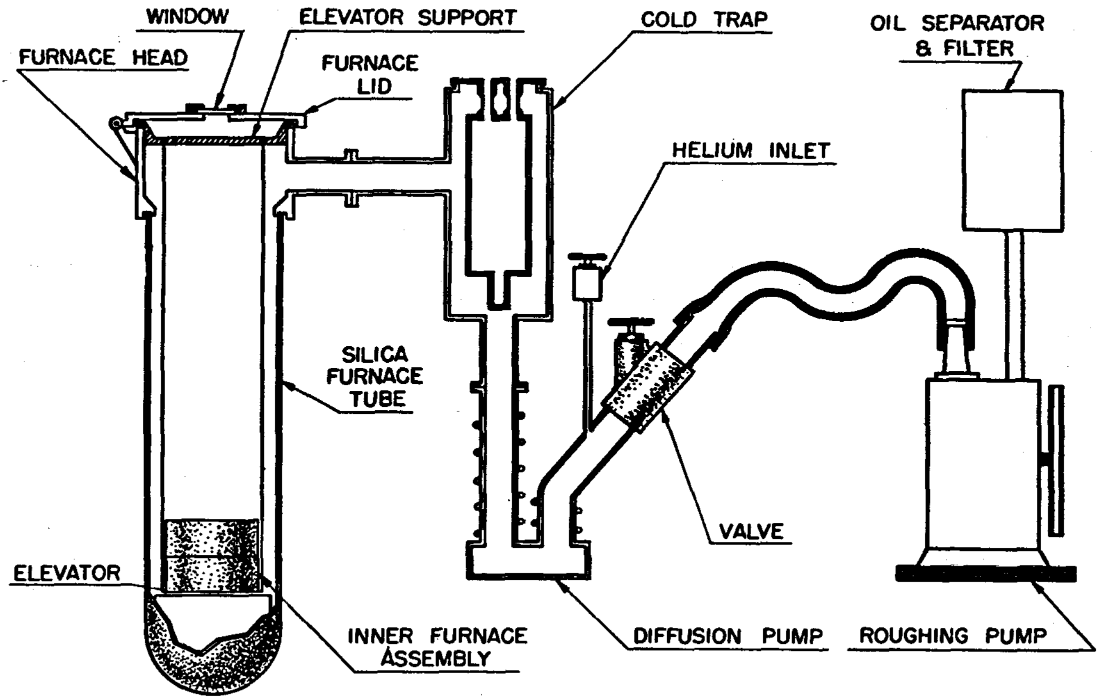

Fig. 1. Induction Furnace System (5 Kg)

The furnace head contains an "O" ring for sealing to the lid and a silicone rubber gasket for sealing to the fused silica vacuum tube. A flanged connection joins the head to the cold trap. Water cooling is provided by means of a copper joint for pressure measurements. Slots were milled into the top of the head for holding the upper part of the hoist. An external flange is connected to the bottom of the head for mounting purposes.

A feature of this system is the remotely operated lid and loading mechanism for the introduction or removal of material. The furnace lid consists of a one-half inch hinged and counterbalanced brass plate. The plate is sealed by atmospheric pressure to the furnace head, using an "O"-ring gasket. Copper tubing, soldered to the lid, is used for water cooling. A Pyrex sight glass is sealed over a hole in the center of the lid by means of neoprene gaskets, and is protected from the volatile materials in the melt by means of a solenoid-operated shutter. An adjustable-lens and prism assembly located on the lid permits temperature measurements with an optical pyrometer.

The liquid-nitrogen cold trap is made of brass and sealed by atmospheric pressure to the system, using an "O" ring. Heat leakage into the trap is decreased by using two thin-walled tubes to support the main body of the trap.

The trap is equipped with a liquid-nitrogen level indicator which actuates an automatic filling device,

A VMF-100 diffusion pump is positioned directly beneath the cold trap. A valve for admitting helium to the evacuated system is placed between the diffusion pump and the vacuum shut-off valve. Both of these valves are operated by the master-slave manipulators with the aid of ratchet wrenches. A thermocouple vacuum gage is installed in the line between the mechanical pump and the diffusion pump. The mechanical pump is equipped with a hoist for lowering it to the floor during operation, thus eliminating vibration of the furnace. The mechanical pump discharges into an oil separator and filter.

Because high-temperature processes tend to produce considerable amounts of radioactive particulate matter, the main operational area is encapsulated in plastic boxes (Fig. 2, 3). One of these boxes is constructed on a removable table and contains all items of process equipment or their access doors; the other box is fastened to the ceiling of the cave and confines the retracted manipulator grips when the cart is not in place. The joint between the two boxes is closed with an inflatable rubber seal. These boxes contain all operational apparatus used in the various processing experiments. A pair of slide-valve plates, located at the open faces of the boxes, permits these plates to be isolated from each other and to be sealed off from the room before removal of the lower box from the cell. Both boxes have blowers and air filters and are maintained at 0.25 to 0.50 inches of water below cell pressure; therefore, all air leakage is into the boxes.

The furnace and vacuum pumps are suspended from the table, and cooling water, electricity, and gases are supplied from a manifold on the inner face of the cave. As a safety measure in case of implosion of the silica vacuum tube, the entire furnace, including the induction coil, is enclosed in a 1/4-in. transite shield.

2. 50-Kg Drossing Furnace - Inert Atmosphere

A schematic diagram of the oxide-drossing furnace is shown in Fig. 4, which shows the various components of this system.

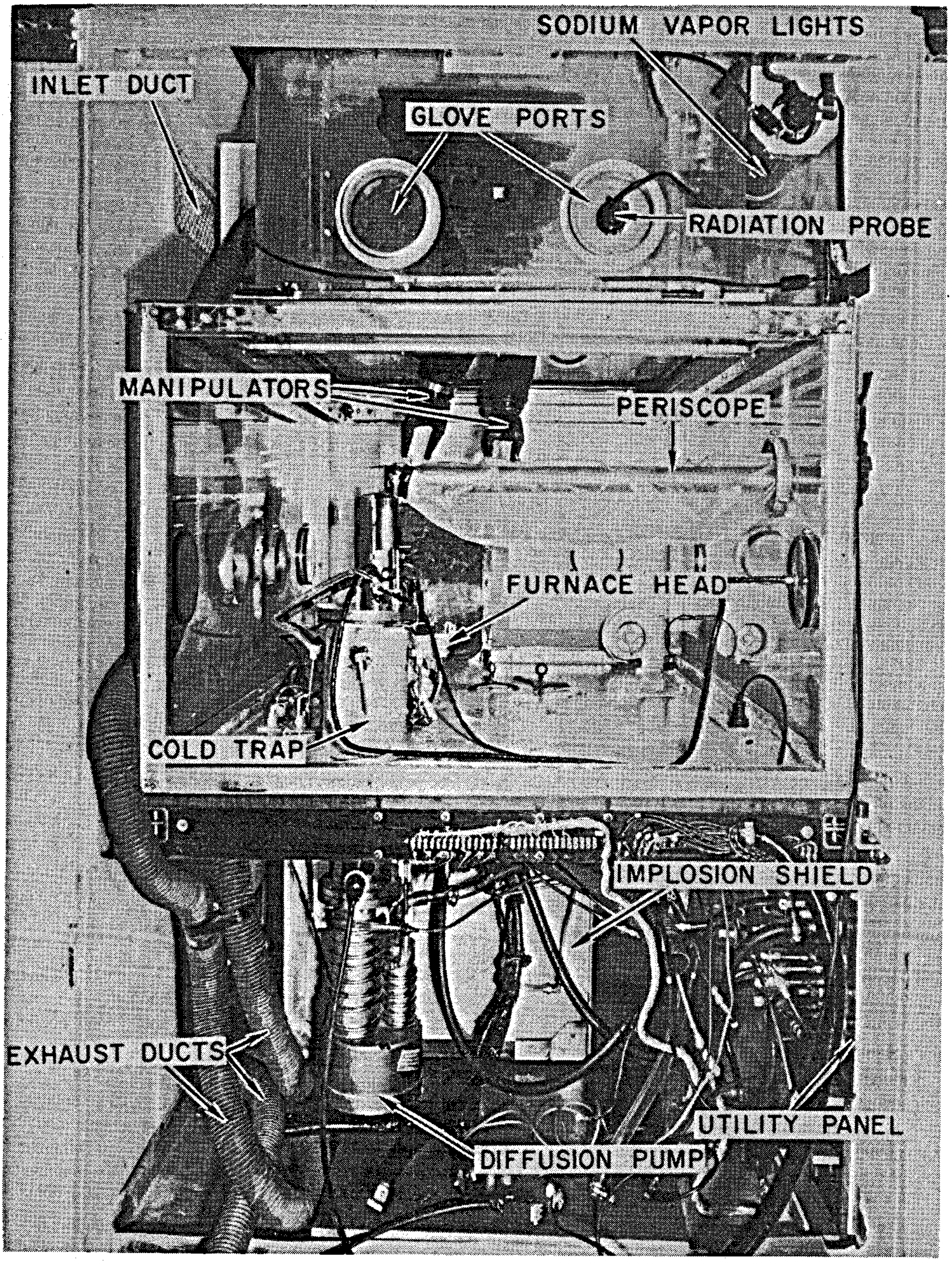

Fig. 2. Induction Furnace Installed in Dust Box and Cell

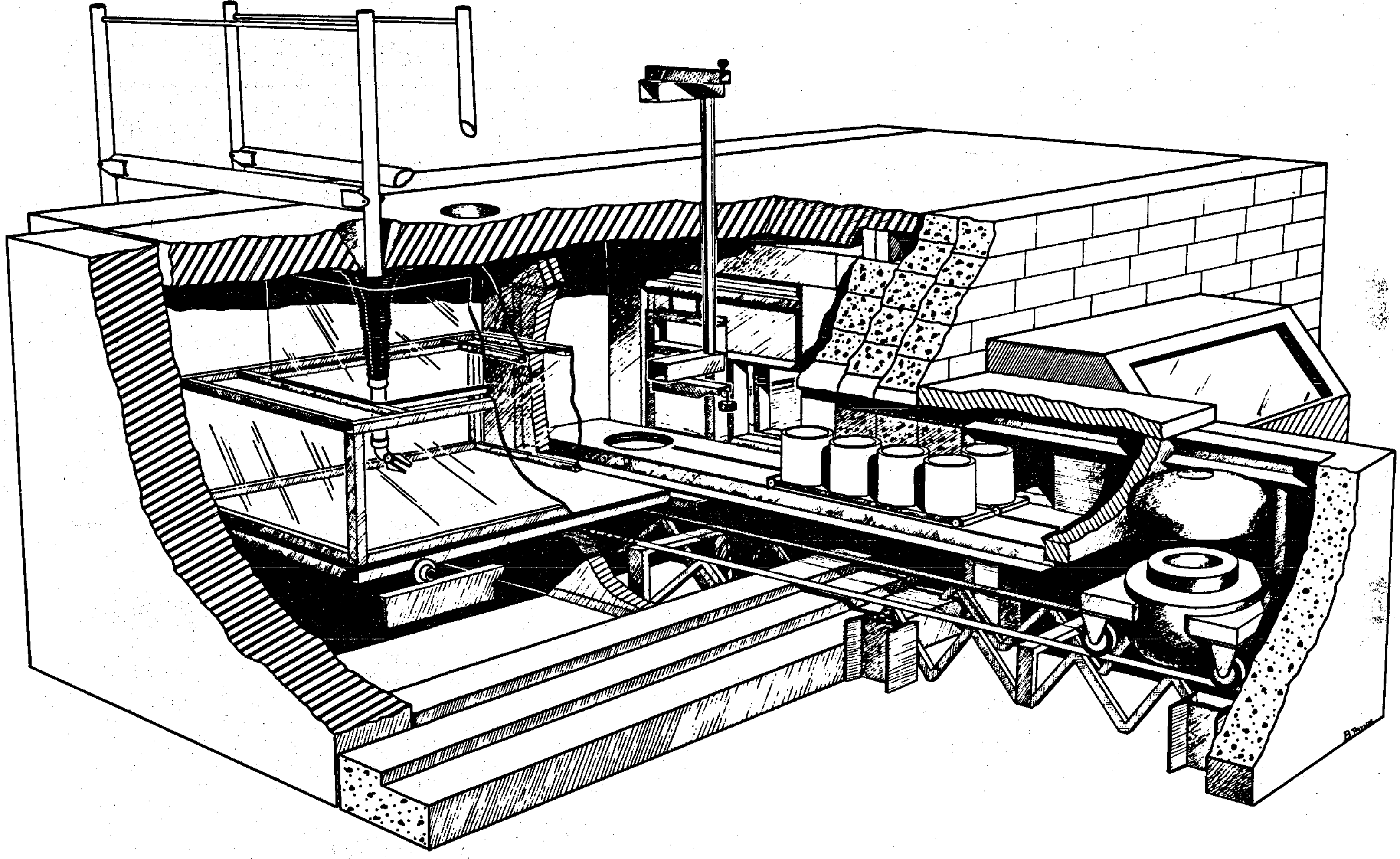

Fig. 3. Hot Cell and Dust Box Arrangement

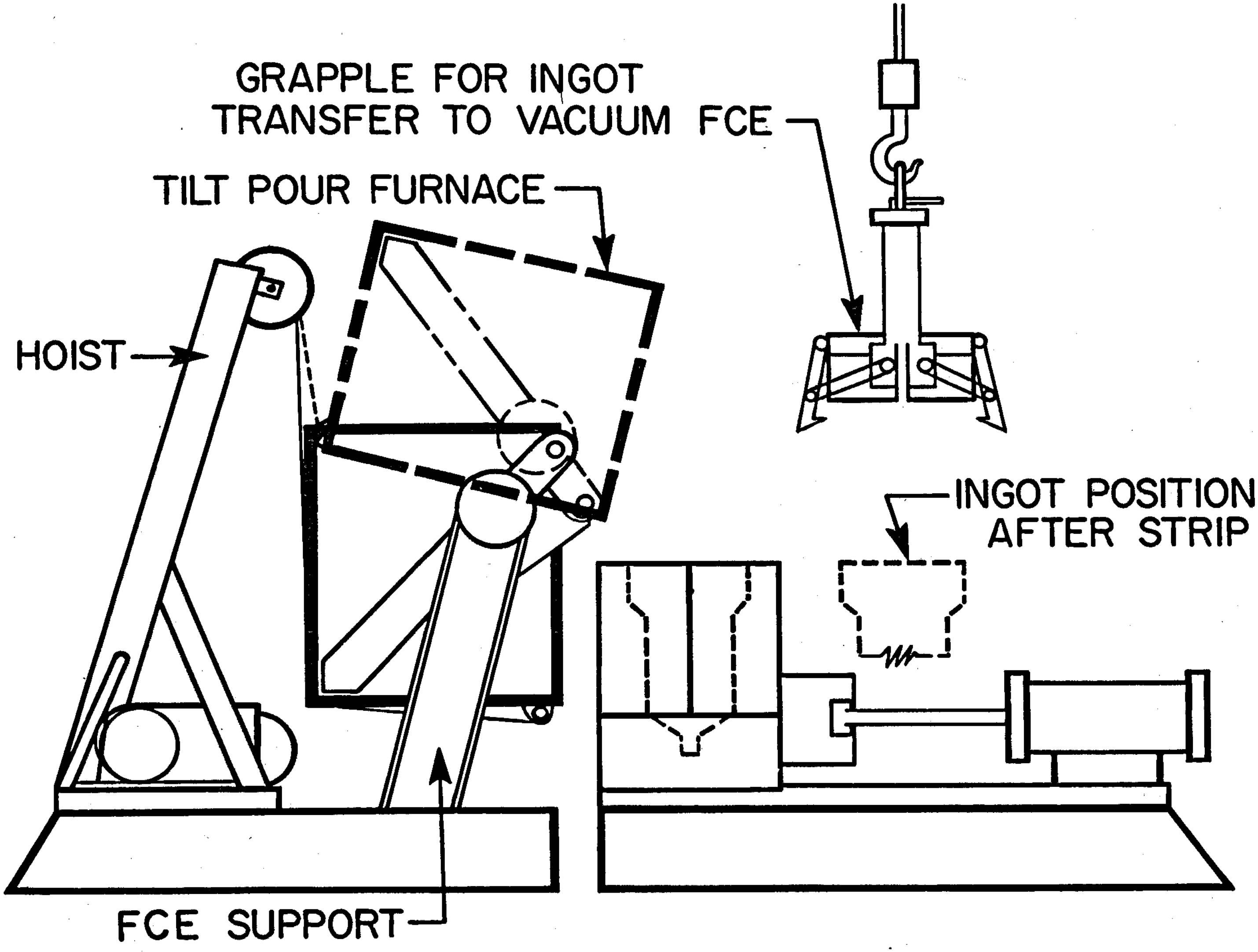

Fig. 4. 50-Kg Induction Furnace - Inert Atmosphere

The magnesia crucible is about 5 in. ID x 10 in. deep. The coil is about 8 in. in diameter and the space between the crucible and coil is filled with alumina. This assembly is supported by a transite box about 24 inches on edge with the crucible lip near the upper edge. A double-trunnion pouring arrangement is used with the pouring-trunnion center line passing through the crucible spout to permit pouring directly over the mold center, even though the mold is about 6 to 8 inches away from the crucible lip in the melting position. This coil-crucible unit is supported about 1 to 1-1/2 ft above the base with the tilting mechanism below and to the rear of the unit.

A ventilation hood carries the temperature-sensing and viewing equipment, and serves as a point of attachment for the electrical precipitator to collect volatile Cs in the furnace off-gas. The hood is movable and is designed for remote maintenance.

The ingot mold receives the molten charge from the oxide-drossing furnace preparatory to being charged to a vacuum-casting furnace. The ingot configuration is accordingly dictated by two considerations – first, the shape and inside dimensions of the vacuum-furnace crucible, and second, the means of grappling employed. The present ingot concept as shown allows adequate clearance in the vacuum-furnace crucible and includes a tapered plug to fill the bottom-pour opening and a head suitable for grappling. Also shown is the mold-casting device which incorporates a split permanent-type mold. In splitting the mold, the ingot is stripped and moved out from under the furnace pouring-lip ready for grappling. The movement is accomplished by means of a gas-operated cylinder actuated in a single motion. Directly above the ingot is a grappling device which transfers the ingot to the vacuum furnace using a crane hook on different rails for pick-up and release.

3. Resistance-Type Drossing Furnace

In this furnace, operations may be conducted in high vacuum or in an inert atmosphere while heating may be accomplished by an electrical resistance heater, and pouring may be done over the lip of the crucible.

The entire furnace assembly (Fig. 5, 6, 7, 8) is enclosed in a large ventilated hood to confine the spread of activity. It is hoped that plutonium-enriched materials, in particular, may be processed. The furnace body itself is shielded with 5-in. thick steel slabs capable of reducing the radiation from irradiated fuel to tolerance level. The top and front slabs are mounted on rollers which permit their ready removal for furnace loading, unloading, and maintenance. A small movable shield plug in one side permits the separate removal of the castings. The inside dimensions of the cave are 33 in. x 28 in. x 33 in. deep.

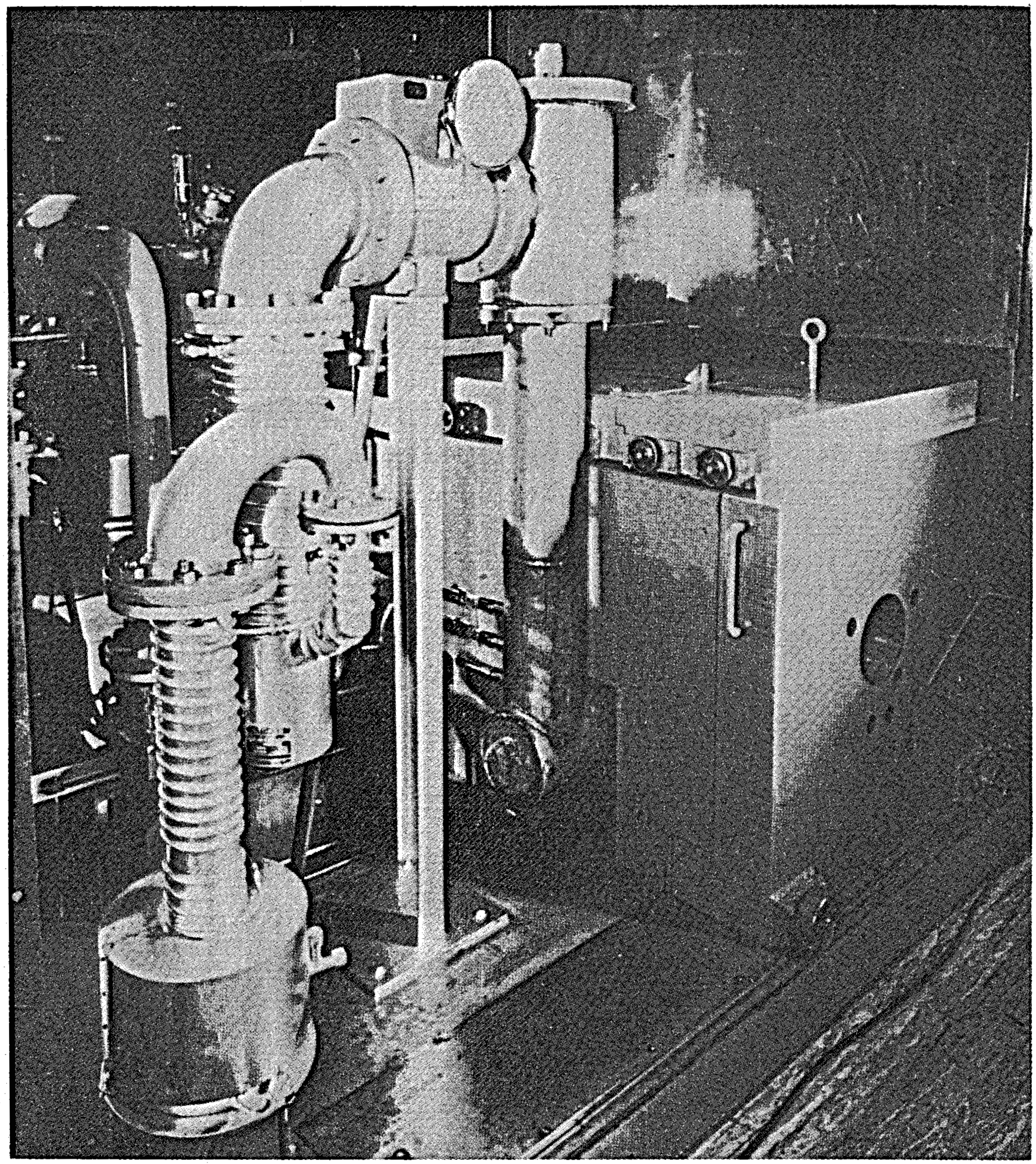

Fig. 5. Pumping System and Movable Shields

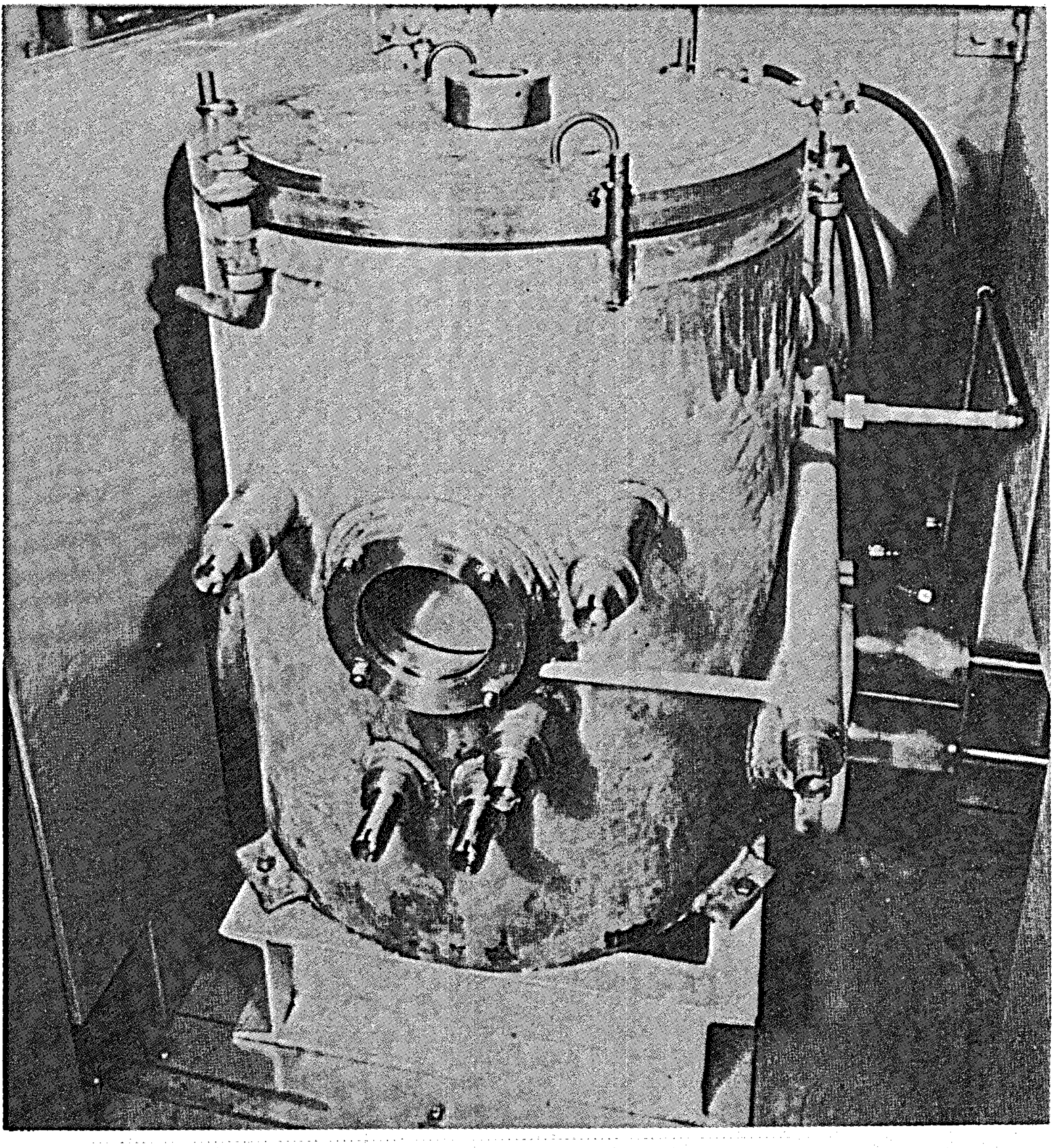

Fig. 6. Exterior Furnace Body

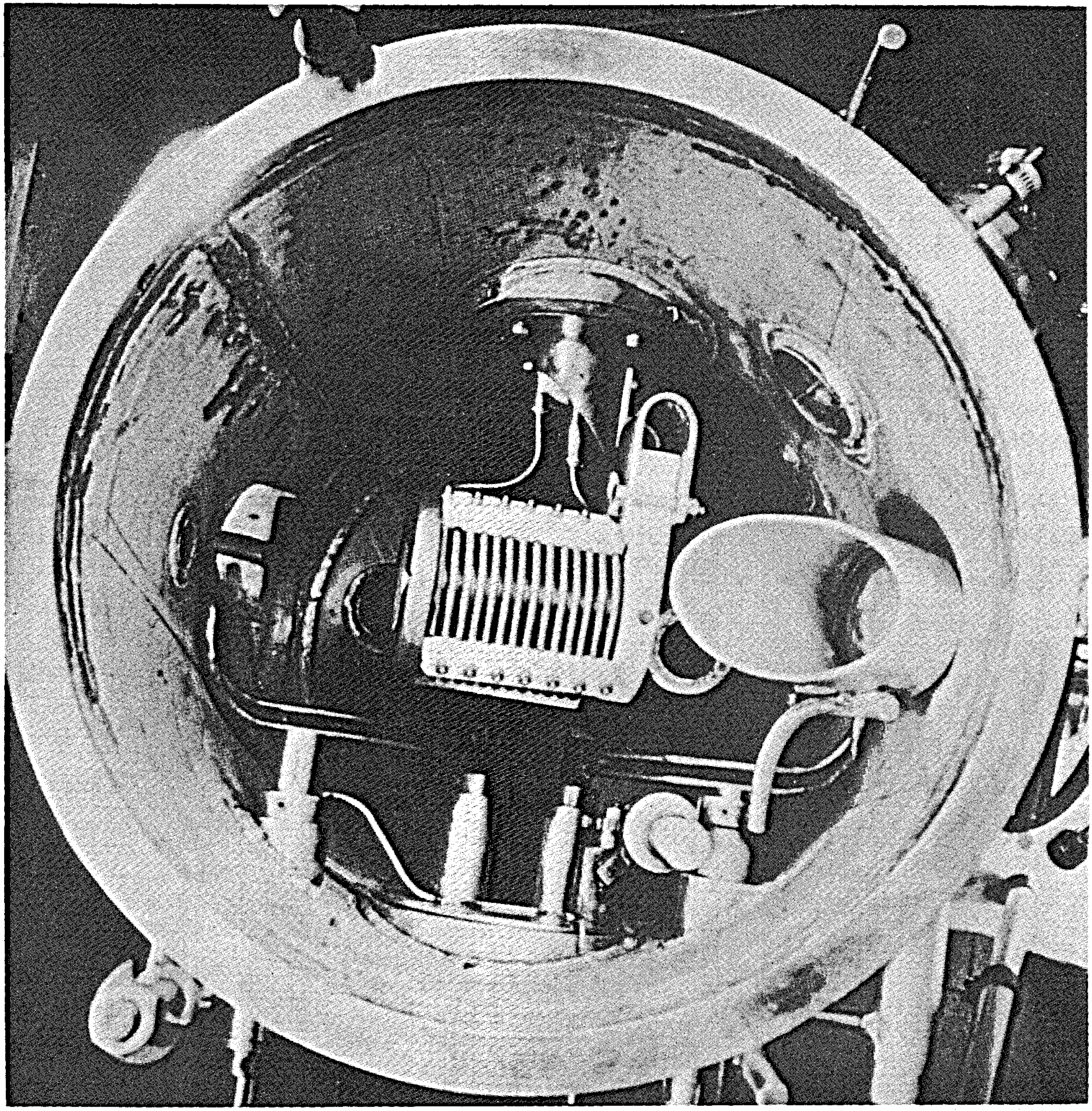

Fig. 7. Crucible and Heater in Position

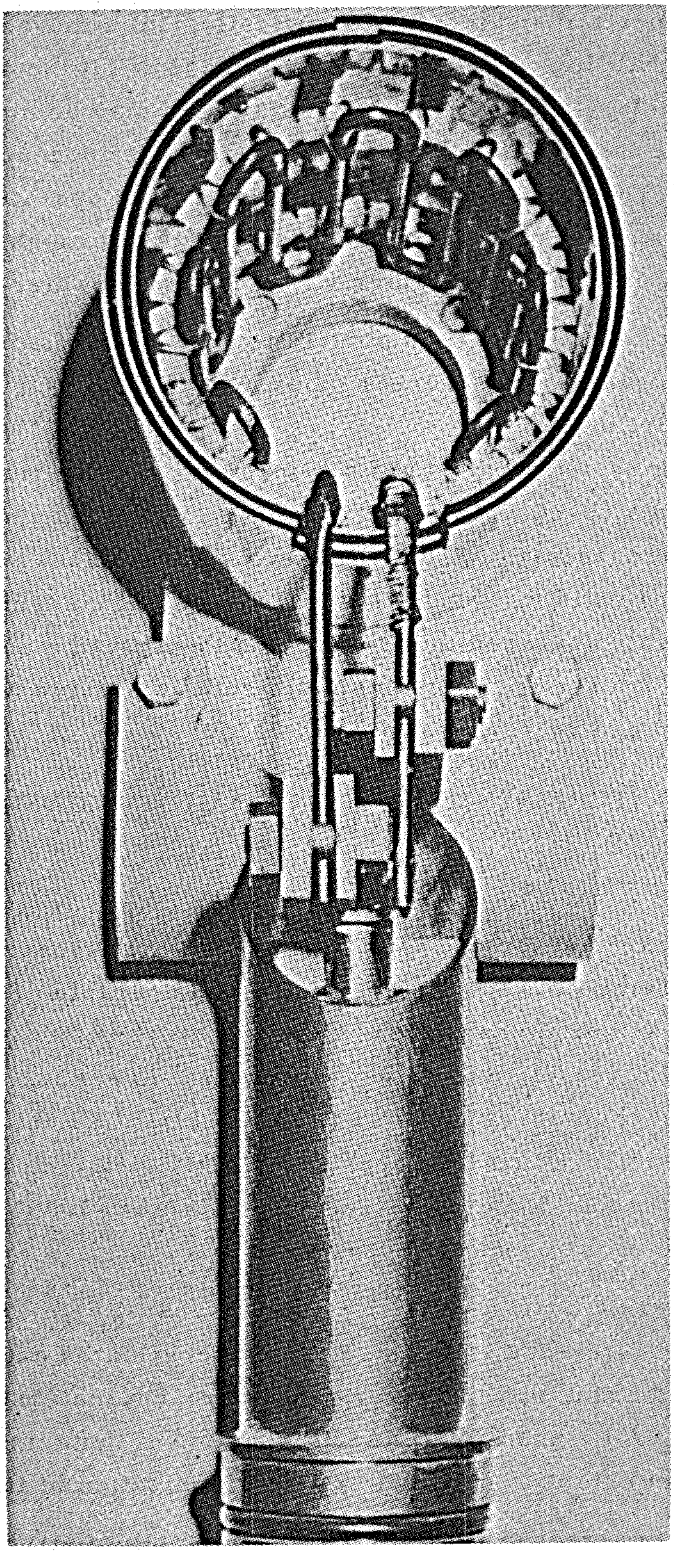

Fig. 8. Molybdenum Resistance-Heater with Shields

The furnace is furnished with the following: (a) a platform which holds both crucible and heating element and which can be tilted 90° from the vertical to each side; (b) movable water-cooled shields over the crucible; (c) a mechanism for positioning a stopper rod and moving it vertically; (d) a movable bucket which may be used for charging while the furnace is closed; (e) top and side windows with movable shields; (f) water-cooled molds which may be moved into various positions while the furnace is in operation; and (g) thermocouple junctions at strategic points. The movable parts of the furnace are operated through "O"-ring-sealed connections by means of lazy handles extending through the shields. The furnace body is 20 in. OD x 28 in. high. It is internally water-cooled.

The resistance heater is constructed from 0.2-inch diameter molybdenum rod and is fed via water-cooled copper tubes by a 10:1 step-down transformer connected to a 208v line.

The pumping system consists of a 6-inch oil diffusion pump, a 4-inch booster pump, and a 60-cfm mechanical pump. The design specifications require a speed of 600 liters/sec at 10^{-5} mm. A second mechanical pump for roughing down or for backing up is included. A stainless-steel liquid-nitrogen trap of the thimble type is located between the furnace and the diffusion pump. A sensing thermistor in this trap triggers an automatic refilling device which draws from a large liquid-nitrogen reservoir tank in the hood.

B. HIGH-TEMPERATURE SYSTEM FOR THE MOLTEN-MAGNESIUM EXTRACTION OF MOLTEN URANIUM

1. General

To provide experience in the handling of molten-magnesium and uranium phases, a larger semi-works scale extraction unit, capable of handling 5 kg each of the magnesium and uranium phases, has been constructed. The system includes an extraction vessel, charge vessel, and receivers for the separated uranium and magnesium phases (see Fig. 9, 10, 11). The entire unit is positioned within a 20-kw resistance furnace capable of maintaining temperatures of the order of 1000° C. About 5 hours are required to heat to 1000° C, and approximately 10 hours to cool to room temperature.

The phases are transferred from vessel to vessel by means of pressure and vacuum. Pressure-equalizing lines extend between the extraction vessel and the magnesium and uranium receivers. These prevent material transferring to the wrong vessel. All transfer lines are fabricated of tantalum and these are clad with stainless steel outside the vessel to prevent oxidation of the tantalum.

The phases are mechanically mixed with a tantalum stirrer rotating at 600 rpm. The stirrer packing-gland is located outside the furnace and is water-cooled.

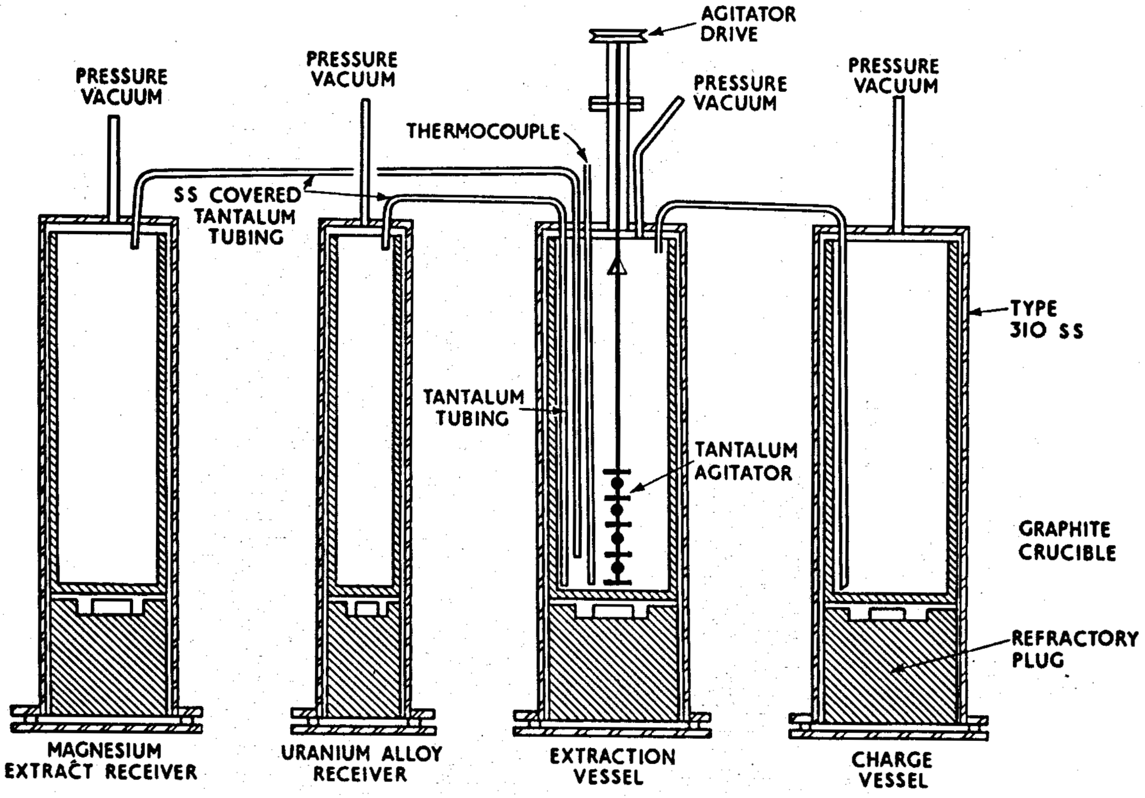

Fig. 9. 5-Kg Scale Magnesium Extraction Unit (Schematic)

The operational sequence involves loading the charge vessel with the magnesium and uranium charges, degassing at 400° C using a mechanical vacuum pump after which an argon atmosphere is maintained in the equipment, heating to 1000° C, transferring the molten-magnesium and uranium alloy phases to the extraction vessel by means of pressure, mixing the phases for one-half hour, and finally transferring each phase to an individual receiver.

Initial experience with this unit has been gratifying. No difficulty has been experienced in transferring the molten phases. Under a pressure differential of 5 psi for magnesium and 18 psi for uranium, the phases transfer in a few seconds.

In initial runs, the heel remaining in the charge and extraction vessel froze to the tips of the transfer lines and prevented the removal of this crucible. To prevent this occurrence, a screw mechanism was incorporated into the bottom flanges of these vessels to provide a means of lowering and raising the crucible within the vessel.

Difficulty has been experienced with magnesium condensation in the vacuum-pressure lines, with the result that these have occasionally become partially or completely plugged. This is being remedied by the use of small vapor traps within

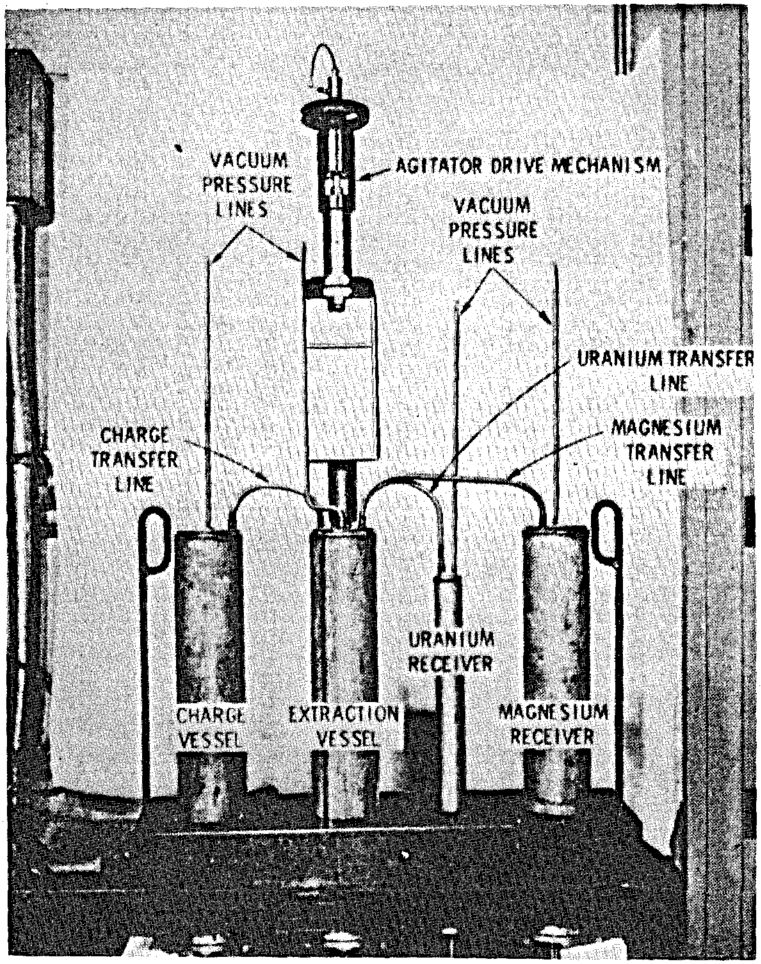

Fig. 10. Pilot-Plant Scale Magnesium Extraction Unit

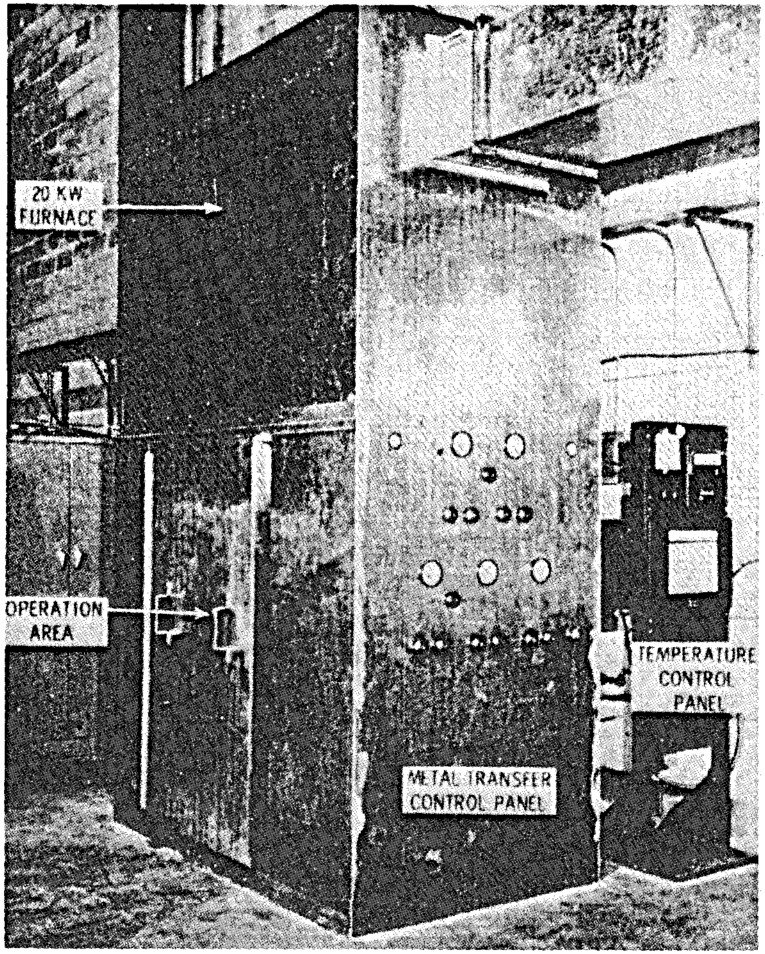

Fig. 11. Hood for Magnesium Extraction Unit

the furnace (see Fig. 12). These traps are maintained at a temperature somewhat below the freezing point of magnesium by air cooling. Any magnesium vapor diffusing into these lines is solidified. On discontinuance of cooling, the traps will heat to above the magnesium melting point, and any condensed magnesium will drain or may be blown back to the vessel.

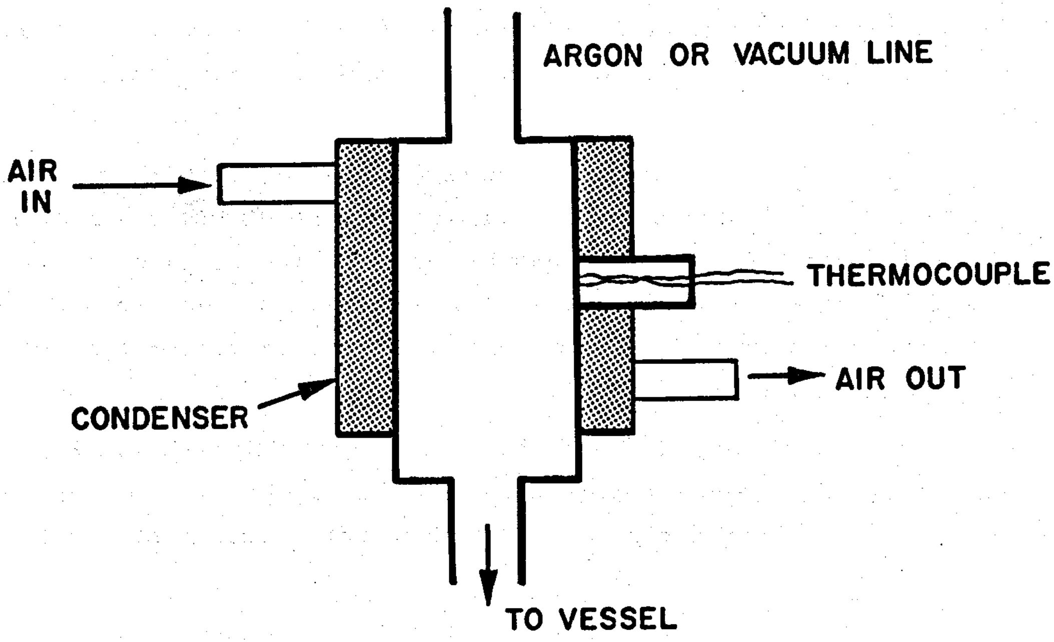

Fig. 12. Magnesium Vapor Trap

Difficulty has also been experienced in removing the ingots and heels from the graphite crucibles. It is apparent that at the high temperatures used, the liquid magnesium penetrates into the porous walls of the graphite. "Graphitite" crucibles, graphite-treated to provide a relatively non-porous surface, have been ordered and will be tested.

In this equipment, an imperfect separation of the phases is effected. The quantity of uranium used is such that the interface is below the magnesium transfer line. Consequently, a clean magnesium product is obtained, but any magnesium remaining in the extraction vessel is transferred with the uranium. In practice, this may not be serious since little plutonium would be present in the final uranium raffinate and magnesium heel. However, consideration is also being given to incorporating a phase-separation vessel.

Data will be forthcoming on successive batch extractions of plutonium-chromium-uranium alloys containing up to 1 w/per cent plutonium.

This is the first relatively large-scale extraction unit to be built and tested. Transfer and handling of the molten phases have not proven to be difficult. Bolder designs of new extraction equipment are being developed on the basis of the experience obtained with this unit.

2. Magnesium Distillation

The objective of the magnesium distillation studies was to develop equipment for demonstrating distillation of magnesium and its condensation and collection as a liquid, since in process use it will be most convenient to handle the magnesium in the liquid state.

To reduce attack of molten magnesium on fabrication materials, the magnesium distillation is conducted under reduced pressure. The temperature of distillation selected is 725° C, corresponding to a magnesium vapor pressure of 10 mm. A condensing temperature of 680° C, intermediate between the freezing point and the temperature of distillation, gives reasonable temperature differences for practical operation.

Fairly successful operation was achieved with the unit shown in Fig. 13. In this unit, the still pot and receiver were heated by resistance elements; the condenser was heated inductively by an 80-turn induction coil from a 15-kw motor-generator unit. An induction coil was used since this provides a method of removal of the heat of condensation by radiation to the coil and surroundings.

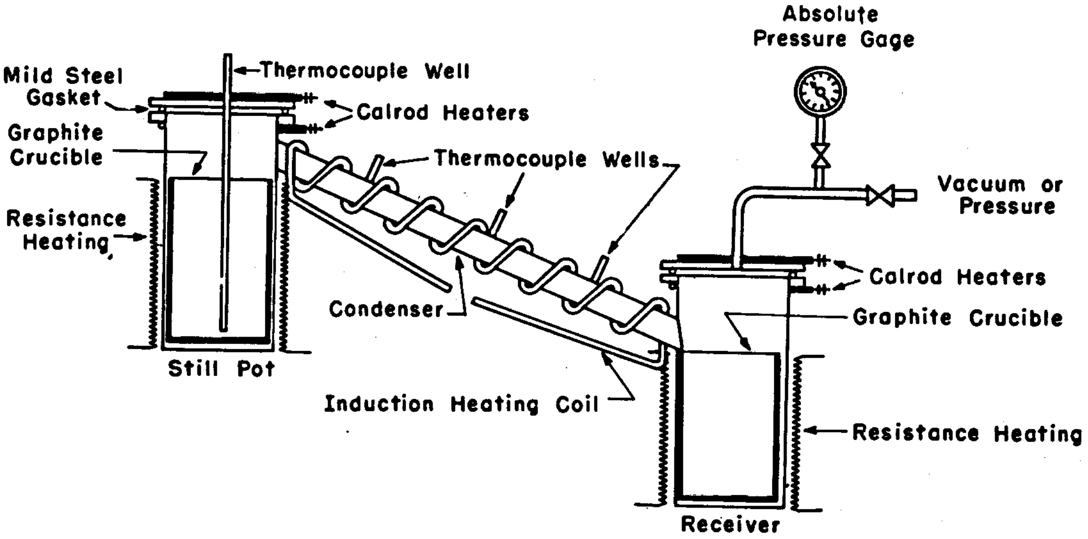

Fig. 13. Magnesium Distillation Unit

This unit was fabricated of type-347 stainless steel. Although this material is attacked by magnesium, it was used because of its resistance to air oxidation. However, attack by magnesium was apparently very slight. Graphite crucibles were used in the receiver and still pot. Mild steel gaskets were used between the flanges and provided a vacuum-tight unit.

The major difficulty with this unit was that large temperature gradients existed along the condenser. While it may have been possible to obtain a uniform temperature along the condenser by adjustment of spacing between coil turns, this was considered an unsatisfactory approach. Resistance heating was tried but this was unsatisfactory because it was not possible to remove the latent heat of the condensing magnesium. As a result, the condenser temperature would rise to that of the still pot.

Consequently, it was decided to jacket the condenser and use liquid sodium as a coolant. Two alternative cooling methods are possible. One is to circulate liquid sodium through the jacket and remove the heat of condensation in an external heat exchanger. The other is to use a static sodium system in which the pressure is adjusted to give a sodium boiling point of 670-680° C, which is about 60 mm of mercury. Heat of condensation boils the sodium until it condenses in an air-cooled reflux condenser (see Fig. 14 and 15). An induction coil is used to heat the sodium to 670° C and maintain it at this temperature. Close control of power input, whether from the induction coil or condensing magnesium, is not required since only the rate of sodium vaporization is affected. The static sodium

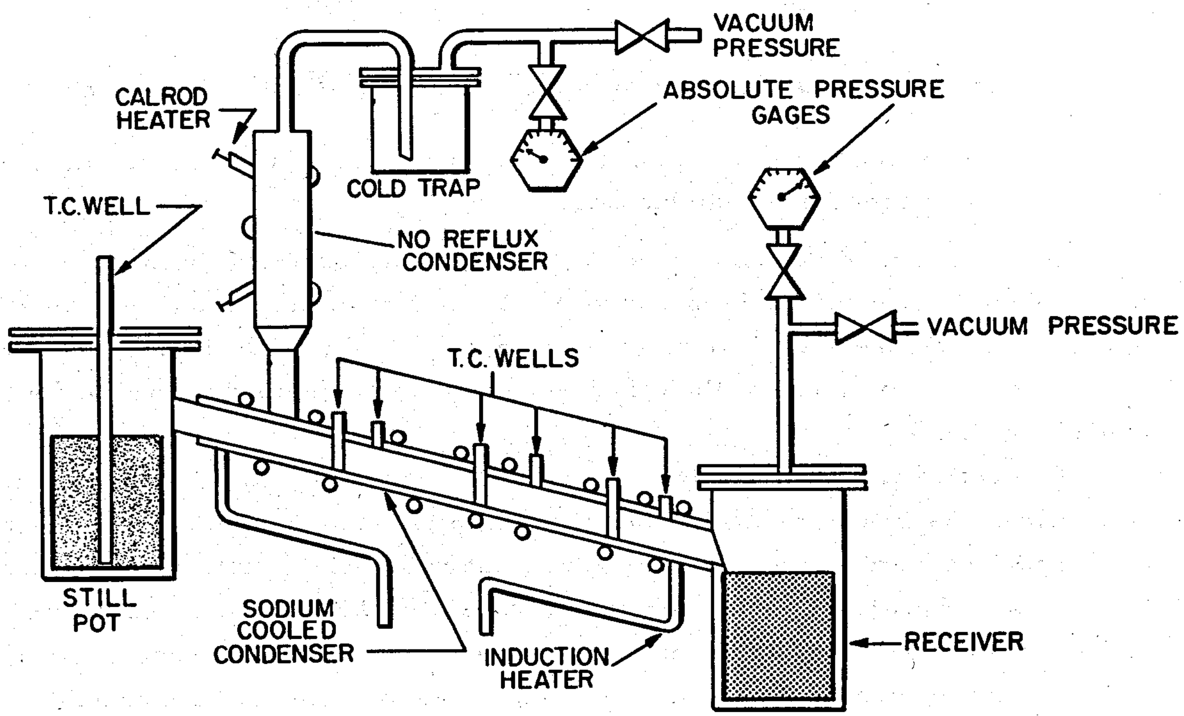

Fig. 14. Magnesium Distillation Unit with Sodium-Cooled Condenser (Schematic)

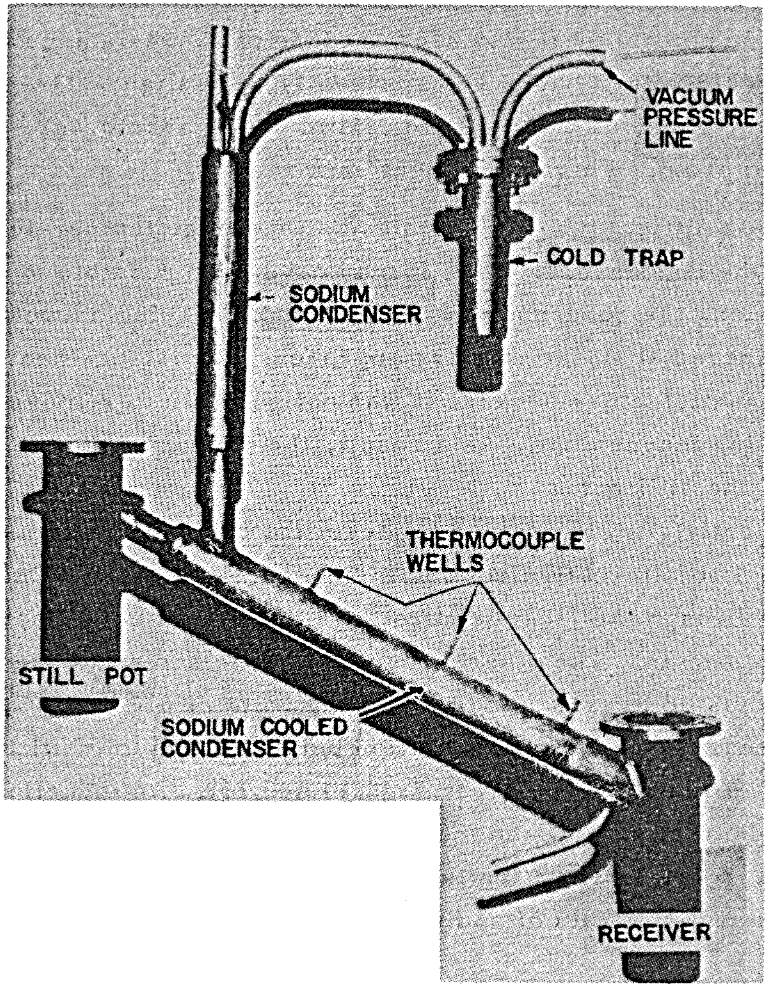

Fig. 15. Magnesium Distillation Unit with Sodium-Cooled Condenser

system is also much simpler than a flowing system, since it eliminates the need of a pump and complicated heat exchanger.

Performance of the sodium-cooled unit has been excellent in the four cold runs and one active run made in this unit. About 2 kg of magnesium were distilled in each run. Temperatures along the condenser varied by only 10 degrees or less, and the temperature of the condenser could be maintained at 670 to 680° C with no difficulty.

One active run involving 1600 gm of magnesium and 3 gm of plutonium has been made. Baffles were used in the still pot to reduce plutonium entrainment since previous work showed them to be necessary to reduce plutonium entrainment to the order of 0.01 per cent. For easy recovery of the plutonium, care was taken to prevent the still pot from running to dryness. This was done by fixing the still-pot thermocouple well about 1/2 in. above the bottom of the crucible, so that the thermocouple temperature would rise when the liquid level dropped below the thermocouple tip.

A still-pot heel of 300 gm of magnesium resulted. The distillate was very clean in appearance and contained 0.5 gm of plutonium. This results in a decontamination factor of 6×10^3 for the distilled magnesium.

II. FUEL-SLUG REFABRICATION EQUIPMENT

A brief description of some of the equipment which has been used in recasting uranium slugs, cutting slugs to size, and checking slug dimensions is presented here. There are alternate approaches to making and finishing uranium slugs. The material presented here covers only a portion of the equipment for refabricating fuel which is under engineering development. It is hoped that the casting, cutting, and measuring systems discussed represent an approach to a low-cost industrial method.

A. FUEL-CASTING EQUIPMENT

Two typical casting systems associated with static and centrifugal casting techniques are discussed here, although there are other methods such as "injection" casting. Both static and centrifugal casting have considerable potential as low cost industrial processes.

1. Static-Casting Furnace

A 50-kg induction-heated, tilt-pour slug-casting furnace is shown in Fig. 16. This furnace is powered by a 4200-cycle, single-phase, 200-v, 30-kw alternator which is directly coupled to a 50-hp motor. A control console allows continuous variation of power input from 0 to 150 per cent of rated power and also permits control of the generator-circuit capacitance and the induction-coil voltage in order to operate the system at a power factor (in the generator circuit) of very nearly unity.

A vacuum is maintained in the furnace enclosure by means of a diffusion pump backed up by a gas-ballast mechanical pump. The charging bucket and thermocouple locks are evacuated by an independent pump. An alphatron and a thermocouple gage are used to measure the vacuum.

The furnace power and cooling water are fed coaxially. This allows the furnace to be tilted for pouring by means of an external hand wheel. The mold table also can be positioned by an external hand wheel. The sight ports allow visual observation of the melt and pour, permitting rapid optical pyrometer temperature readings.

A commercial MgO steel melting crucible, completely outgassed and sintered at 1600° C, serves as the container.

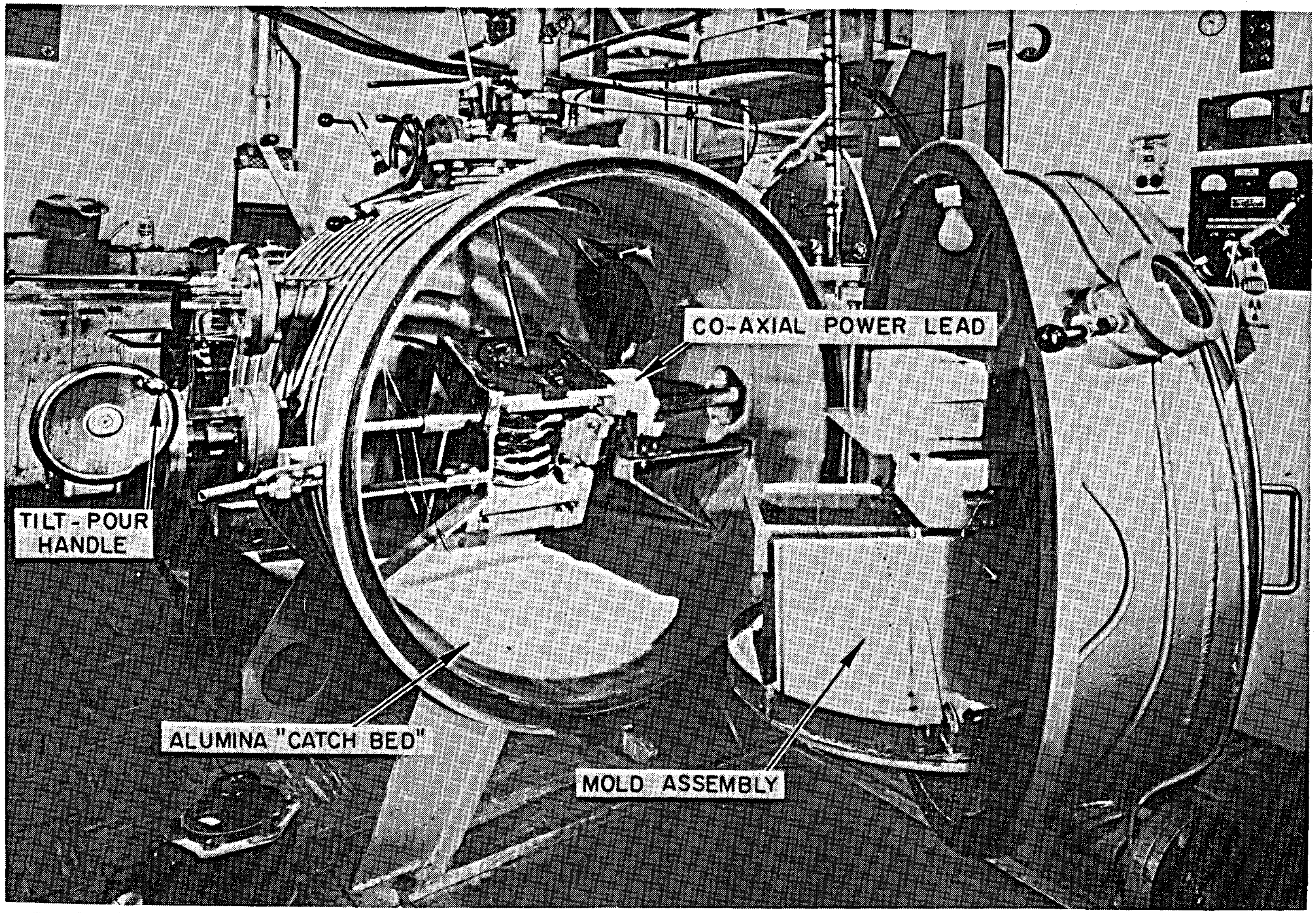

Fig. 16. 4200-Cycle Slug-Casting Furnace

Figures 17, 18, and 19 show the casting mold and a sample casting before and after the separation of individual slugs. The molds are made of graphite.

2. Centrifugal-Casting Furnace

Figure 20 shows an elevation-sectional view of the centrifugal-casting furnace.

The furnace chamber is a stainless-steel shell 42 in. in diameter and 60 in. high. This shell is composed of three sections: (a) the top, 10 in. high, (b) the center, 32 in. high, and (c) the bottom, 18 in. high. Extending from the bottom section about 3 ft is the centrifugal-casting 5-hp direct-drive unit. The center section is fixed in place by means of stationary legs which are attached to the floor. Overall height from floor to the top of the furnace is 8-1/2 ft, allowing about 1 ft clearance from the bottom of the centrifugal drive unit to the floor. This clearance allows the bottom mold section to be dropped away from the center section and moved out horizontally on the tracks to the mold stripping area.

Within the interior of the center section are the crucible and the high-frequency induction-coil assembly. The crucible is roughly 6 in. in diameter by 12 in. high and is designed to hold 50 kg of uranium. A power source of 50 kw feeds the induction coil. The crucible is of coated graphite and provided with a hole in the bottom for bottom-pouring. The hole can be plugged with either a stopper rod or with a fusible uranium plug. The auxiliary induction coil about the pouring spout allows the fusible plug to be alternately cooled and then heated at the time of tapping.

Attached to the top section are the crucible cover and the stopper rod holder mechanism. This mechanism is equipped to apply a positive pressure on the stopper rod during melting and then releasing it when the melt is ready to be tapped.

Directly below the crucible is the centrifugal mold-cone distributor. This graphite distributor sits at the center of the mold insert housing. The mold housing is constructed of aluminum alloy and contains 24 copper mold inserts. This copper insert is 3/4 in. diameter by 7 in. long and receives the molten uranium as it is discharged from the cone distributor. The entire mold assembly rotates at speeds of from 200 to 300 rpm during the casting. A radial log angle of approximately 35° on the copper inserts is necessary to obtain dense castings with good surfaces. The combination of copper and aluminum in the mold is desirable to obtain optimum thermal conductivity during the chill casting.

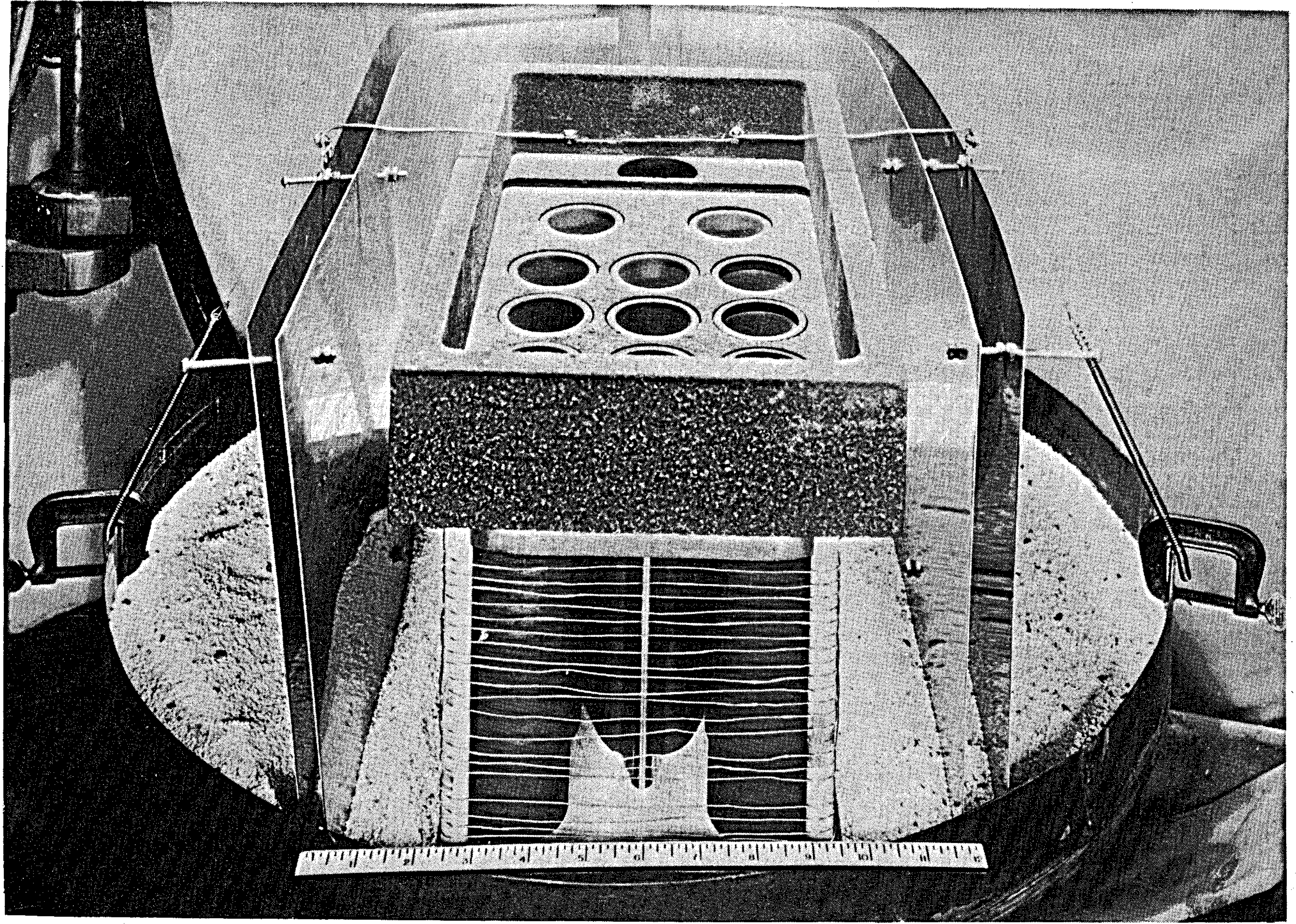

Fig. 17. Graphite Molds

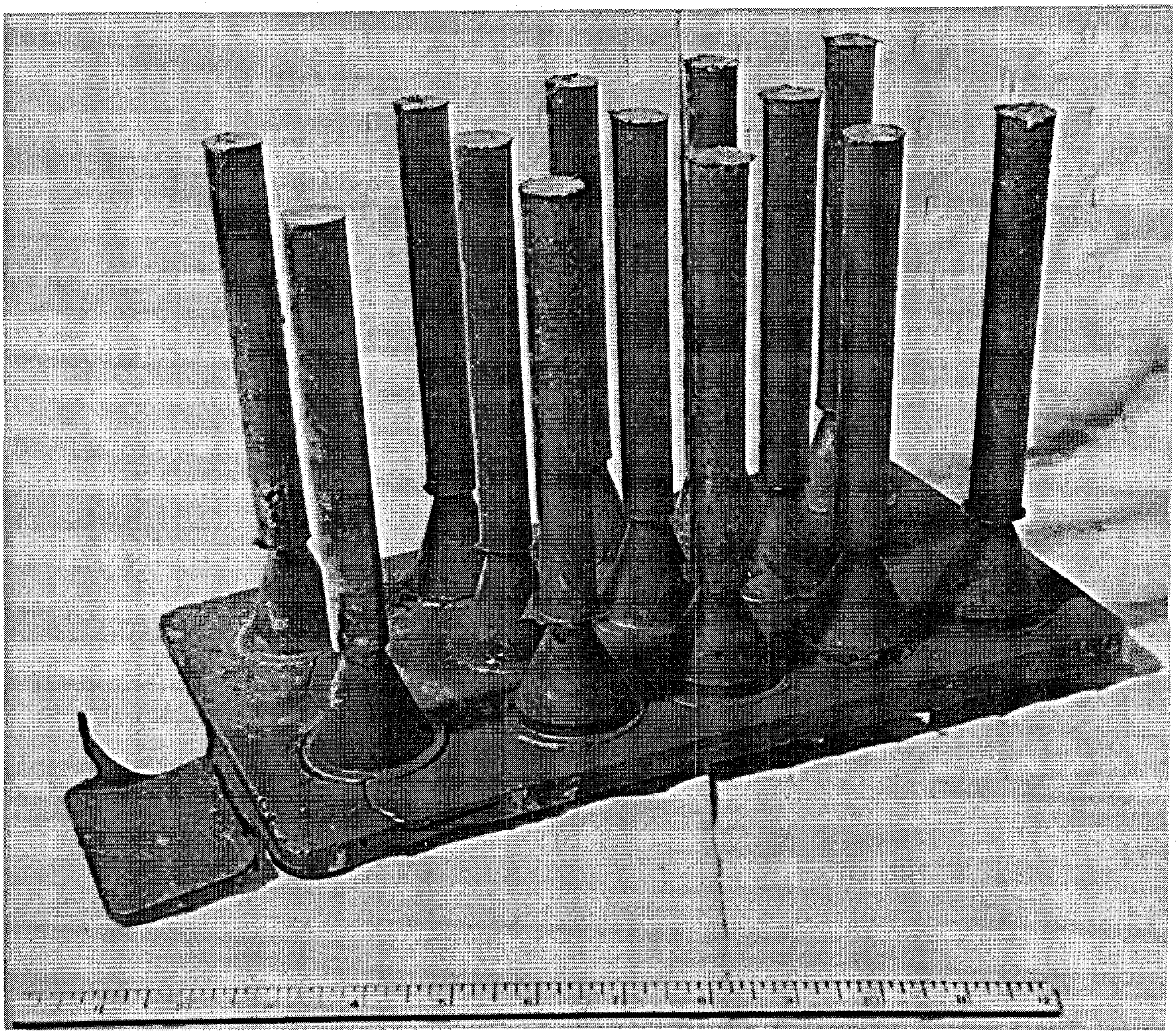

Fig. 18. Sample Casting

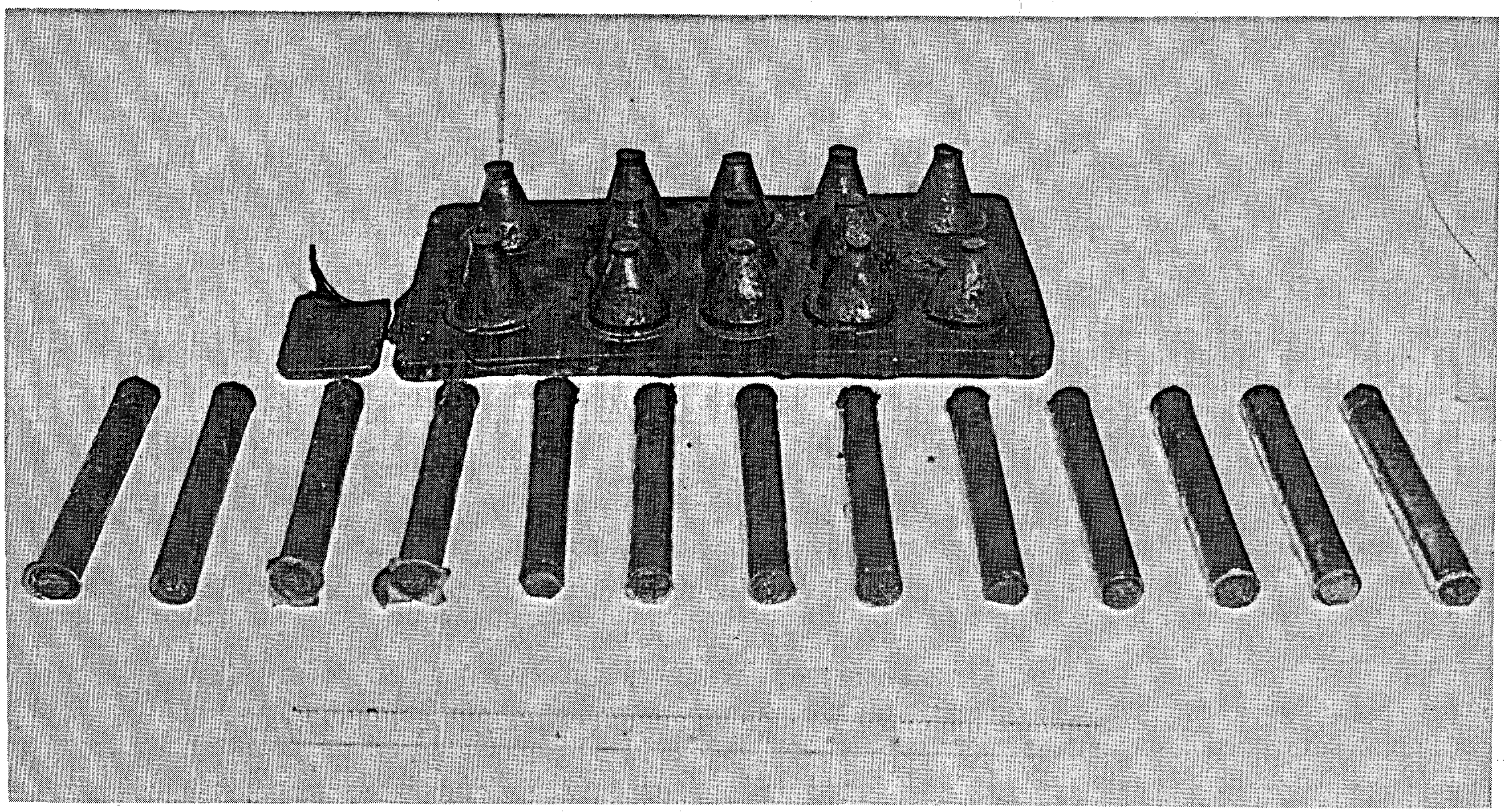

Fig. 19. Slugs Separated from Casting

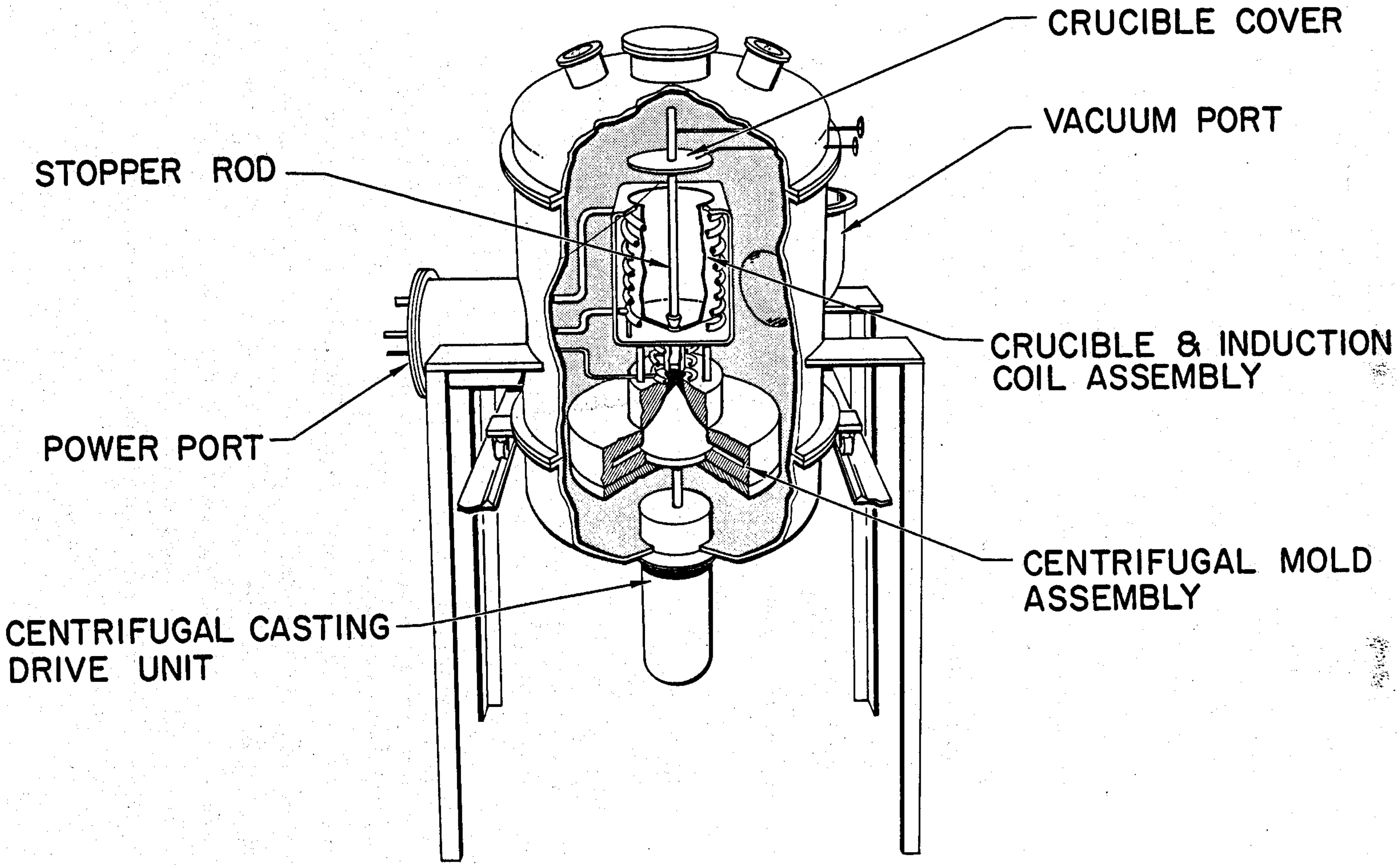

Fig. 20. Centrifugal Casting Furnace

B. ELECTRICAL DISCHARGE SLUG CUT-OFF MACHINE

Electrical discharge machining involves the removal of metal by electrical arcing between an anodic work piece and a cathodic electrode. Electrical discharge machining differs from arc machining in that a high-frequency arc rather than a dc arc is developed during operations. Frequency of the arc may vary from 20,000 to 1,000,000 cps; the load capacitors may be as large as 100 microfarads. The high temperature and pressure of the arc cause machining on all electrically conductive materials tested to date (including tungsten). The high-frequency power supply is rated at 4.5 kva with an input of three phase 220-v ac. The machine is a mill equipped with the Elox M500 head, a horizontal servo-feed, and servo-cross feed. The machine will be used as a straddle mill (Fig. 21). Cut-off discs will be copper, 0.013-in. thick and 8-in. in diameter. Inasmuch as there is no tool pressure during cutting, a simple lever action vise will be used. The entire machining operation must be submerged in a dielectric oil; a metal trough contains the oil. A circulating pump and filter located in the rear of the machine will remove carbon and metal from the oil.

C. FUEL ELEMENT DIMENSION-CHECKING EQUIPMENT

Figure 22 shows a dimensional slug-inspection device. Slug dimensions to be checked are the length 6.000 ± 0.015 in. with readability plus or minus 0.002 in., diameter 0.750 ± 0.0125 in. with readability plus or minus 0.001 in., out-of-roundness ± 0.001 in., and bow plus or minus 0.030 in. with readability plus or minus 0.001 in. The device consists of a special fixture mounted to the cross-feed of a bench lathe in which the slug is supported on 6 cam followers; 2 cam followers are spring-loaded to assure proper centering. One cam is driven so as to rotate the slug. Two dial indicators are mounted on the lathe bed and a third indicator on the end of the slug. All critical dimensions will be held to within 0.0001 in. A standard defect and precision rod will be provided to periodically check the instrument's accuracy. The procedure on each slug will be as follows: the slug will be placed in the device, the middle-section slug will be moved to the dial indicator and rotated so as to locate the plane of the bow; this is the reference plane. The slug is moved horizontally and changes in the dial indicators noted. These readings will note diameter, change in diameter, and bow. The cross-feed will be reversed, the slug rotated, and, as indicated, readings noted around the diameter.

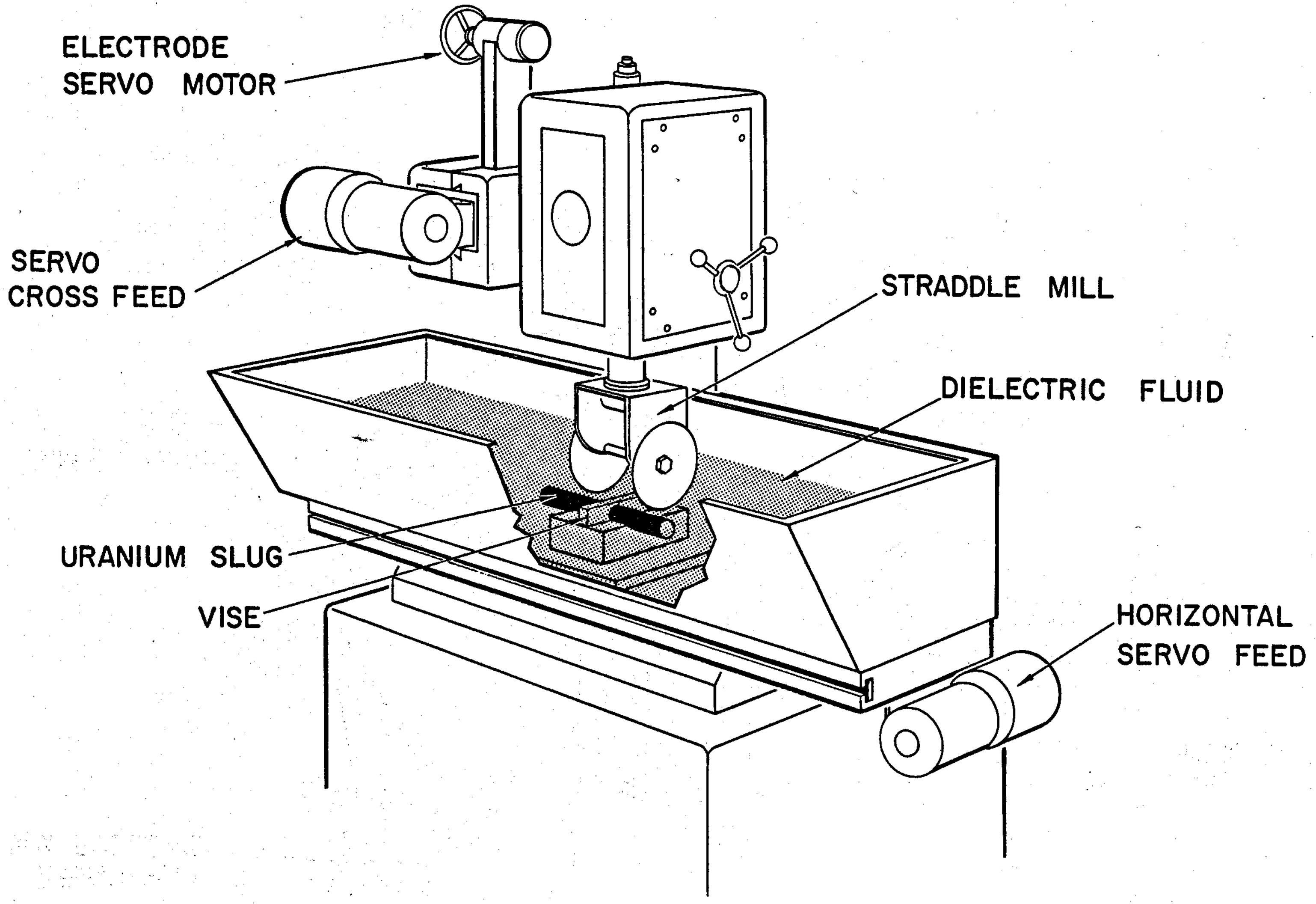

Fig. 21. Electrical Discharge Slug-Cutting Machine

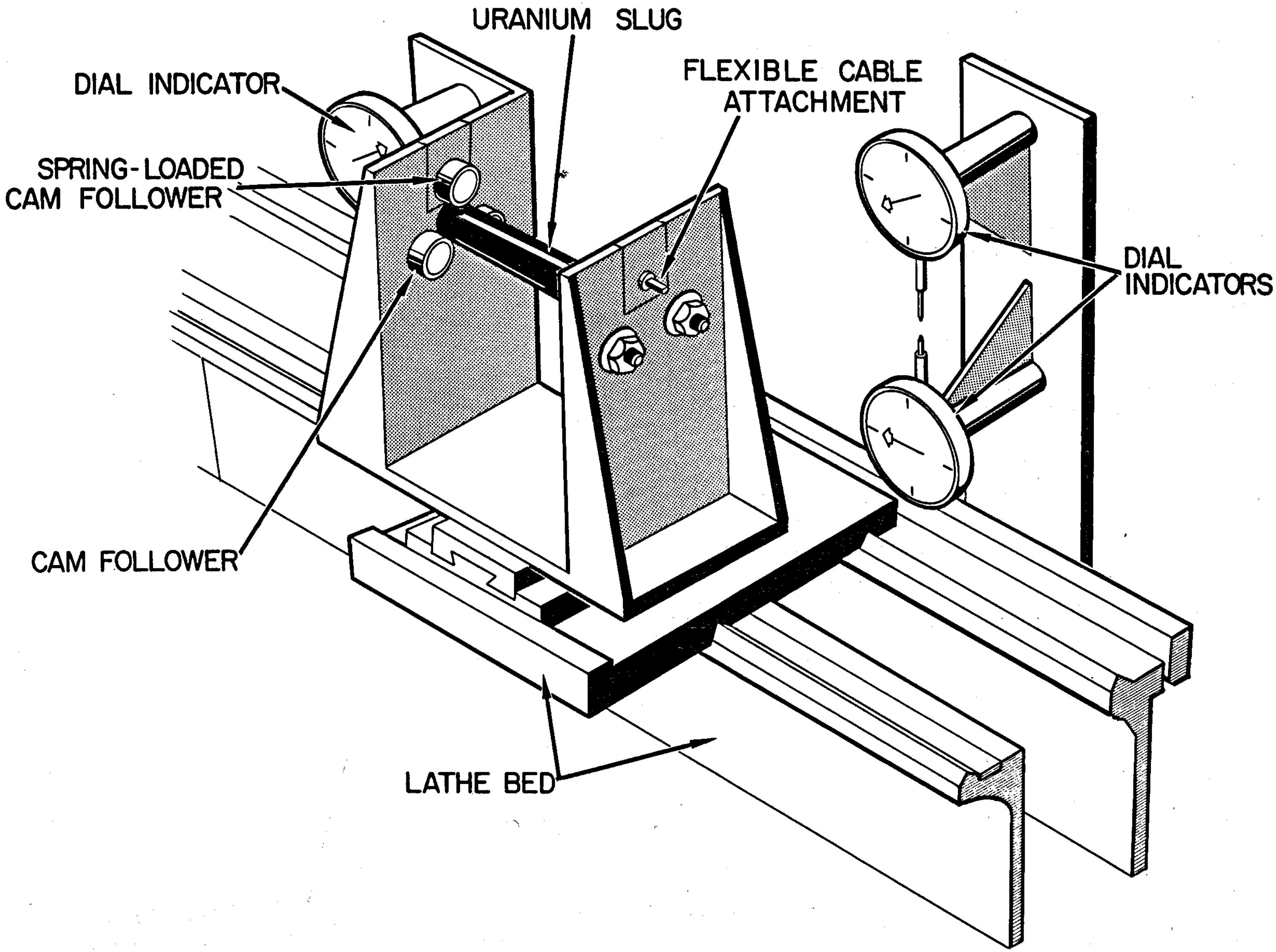

Fig. 22. Slug Dimension-Checking Device

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PYROMETALLURGICAL PROCESSING:
ECONOMICS AND PROPOSED ENGINEERING APPLICATIONS

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May 1, 1957

Several power reactor systems[1,2,3,4] (see Table 1) are now under construction or are planned in the United States in which fuel processing will be carried out by remote pyrometallurgical methods. In these proposed reactors, the fuel is present as a metal, either as a liquid metal or as solid fuel elements. The use of pyrometallurgical processing schemes for metal-fueled reactors is based on the belief that the pyrometallurgical process methods are inherently suited to and will ultimately prove to be the most economical method of processing metal fuels.

The reactor systems shown on Table 1 are pilot reactors designed to provide the technology and operational experience for the construction of large-scale power reactors. The pyrometallurgical processing facilities for these reactors are also pilot plant efforts aimed at the engineering development of the pyro-processing methods and the remote refabrication of fuel into new fuel elements for recycle to the reactor. An important objective of these reactor systems is the demonstration of a closed fuel cycle.

This demonstration program should provide the information required to design industrial plants for reconstituting reactor fuel assemblies from irradiated or discharged fuel materials by these new pyrometallurgical processing methods. The

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ultimate purpose of these power reactor programs is to develop power reactors for central station power application which meet the requirements of both technical and economic feasibility. By economic feasibility is meant the production of power at costs competitive with that from conventional power producing methods.

Table 1

Reactor Systems Employing Pyrometallurgical Fuel Processing Methods

Reactor	Type	Fuel
Experimental Breeder Reactor No. 2 (EBR-II)	Fast Breeder -- Sodium Cooled	Plutonium or Enriched Uranium Alloys
Sodium Reactor Experiment (SRE)	Thermal -- Graphite Moderated -- Sodium Cooled	Slightly Enriched Uranium
Liquid Metal Fueled Reactor (LMFR)	Thermal -- Graphite Moderated -- Heat Removed in Circulating Fuel	Dilute Solution (800 ppm) of U-235 or U-233 in Bismuth

I. Economic Factors Supporting Pyrometallurgical Processing

There is as yet no experience which shows the economics of the pyrometallurgical processing methods. Such experiences will first be provided by the pilot plant operations described above. However, cost estimates have been made (see Table 5) which indicate total fuel processing and refabrication costs of near 2 mills/KWH of electrical output. Potential savings in processing by pyrometallurgical methods are thought to be possible through[5]

1) Reduction of fuel inventory through ability to process short-cooled material.
2) Elimination of chemical conversion, i.e., direct processing of fuel as metal.
3) Ability to utilize low but adequate fission product decontamination in conjunction with remote fuel fabrication.
4) Recovery of expensive alloying agents.

5) Direct production of dry, concentrated fission product wastes.

6) Avoidance of many expensive critical mass problems.

7) Operation of a small compact processing plant at reactor site to avoid shipping costs.

It might be well to point out that processing costs are generally only a small fraction of the total fuel cycle costs, and it is the total fuel cycle costs which are important. The total fuel cycle cost must include chemical processing, reconstitution, and refabrication of the fuel, and the costs assignable to the fuel during residence in the reactor. Thus, the alternative of employing a fuel which can be given a high percentage burnup, and which would, therefore, require only occasional processing, even though this processing were relatively expensive, might very well be superior to frequent, inexpensive processing of a fuel capable of being irradiated to only a small percentage burnup. The support for pyrometallurgical process development will be more clearly evident by the amplification of the above economic factors which follows.

A. Inventory

Aging or cooling of discharged reactor fuel is presently required before reprocessing to permit gross reduction in radioactivity and heat generation, and to permit complete conversion of product intermediates such as neptunium and protactinium. Where high decontamination of the fuel is required in order to permit hand refabrication operations, decay periods of the order of 100 to 200 days may be required in order to allow decay of highly active uranium or plutonium isotopes (such as uranium-237, which cannot be removed by processing). For aging periods of 100 to 200 days, inventory charges become a significant cost item in the total fuel cycle costs. Such decay periods will approximately double the necessary fuel inventory.

Not only are inventory charges important, but fuel which is being stored for decay represents fuel that might be better employed in other reactors. This is particularly important in countries in which the amount of fissionable material available is in short supply.

From the standpoint of the inventory problem alone, serious efforts are justified on the development of processes which can handle short-cooled fuels. A desirable characteristic of the pyrometallurgical processing methods is their suitability for the processing of short-cooled fuels. The incentive of inventory reduction through fast chemical processing is behind a corresponding approach for aqueous homogeneous reactors. A small bleedstream of the reactor fuel contents is continually processed to remove fission product poisons and to keep the level of these in the fuel low enough that they do not result in significant neutron losses.

B. Elimination of Chemical Conversion

Changes in chemical state during the fuel reprocessing cycle are expensive and often lead to complex reactor fuel cycles. The processing of metallic fuel elements by conventional aqueous processes requires the dissolution of the fuel in an aqueous medium, the purification of the fuel in solution, the isolation of the fissionable and fertile salts, and the conversion of these salts back to metal. Figure 1 illustrates the steps which are required in a conventional fuel cycle.[6] Handling the fuel directly as metal within a pyrometallurgical process results in a process such as shown on Figure 2.[6] The simplicity of this process is apparent by contrast with that of the conventional aqueous process.

If fuel is processed directly as metal, the volume of material to be handled daily is very small. For example, for a 1,000 megawatt reactor which burns its fuel elements to 5,000 megawatt-days per ton, the daily processing requirement would amount to only about 2 1/2 gallons of uranium. This volume of material may be handled in small compact equipment in processing facilities that need not be very large. Because of the small volume of material, it seems reasonable that batch processing procedures be employed since remote continuous processing is not very applicable to this volume of material.

C. Fission Product Decontamination

The required fission product decontamination is dependent upon the fuel

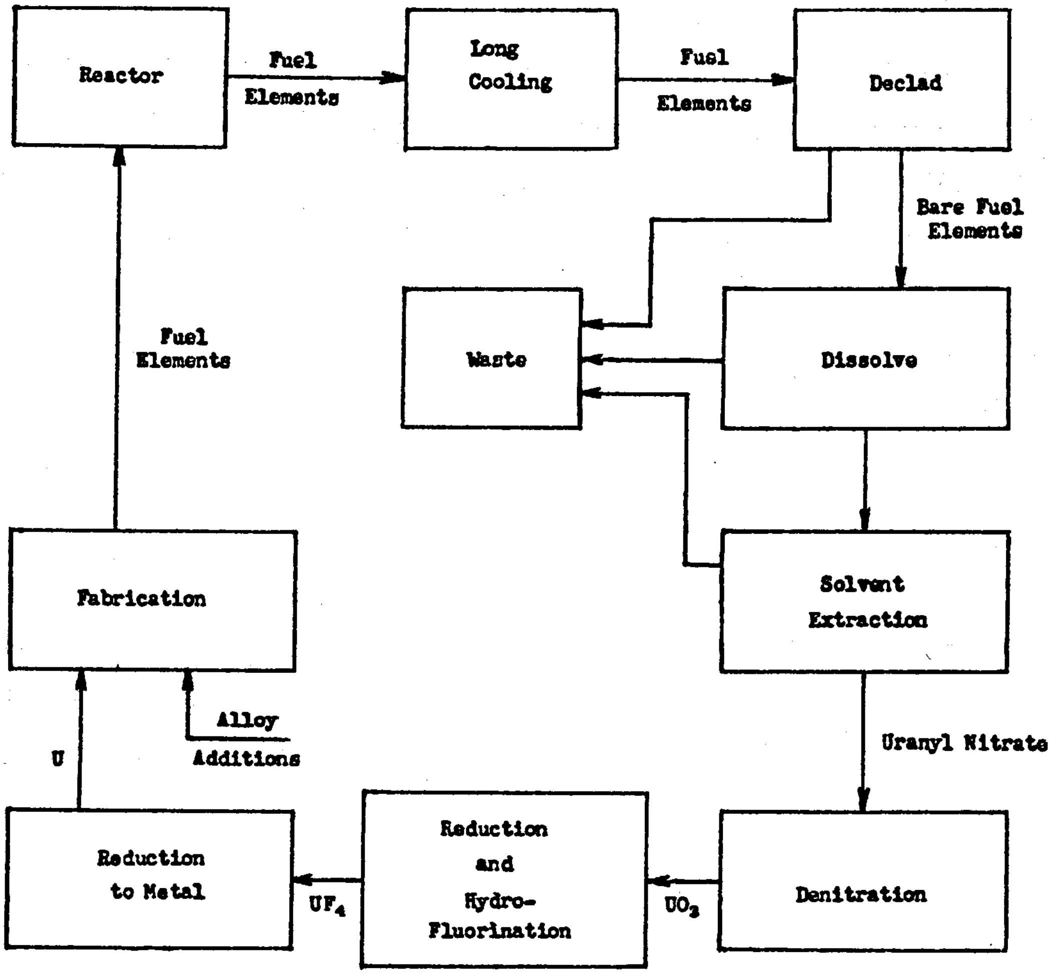

Fig. 1 - Solvent extraction fuel cycle for natural uranium fuel.

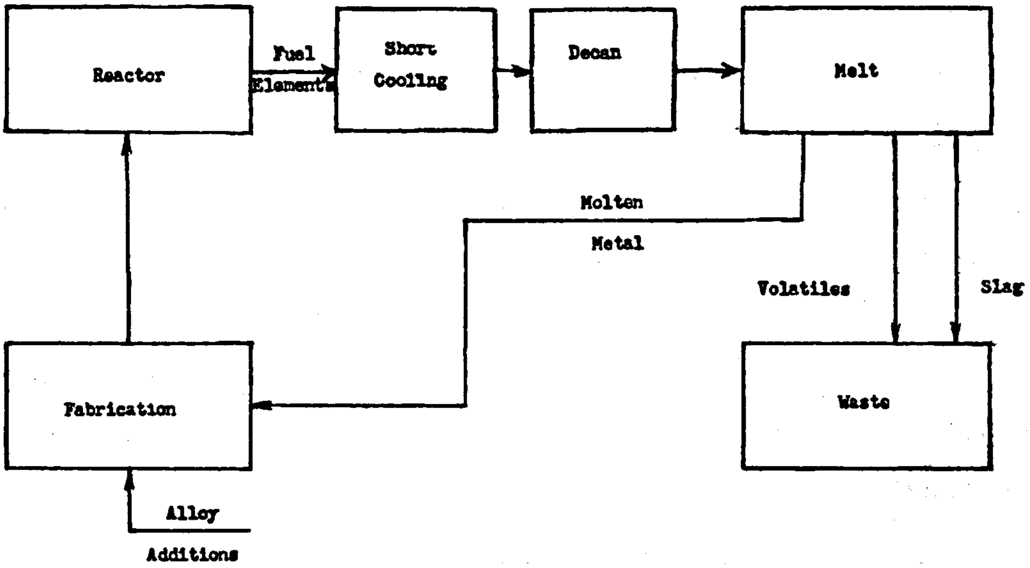

Fig. 2 - Fuel cycle based on pyrometallurgical processing.

cycle which is employed. If hand refabrication operations are required, exceedingly high fission product decontamination factors, of the order of 10^6 to 10^8, are required in conjunction with long cooling periods to provide for decay of short-lived isotopes and for decay of radioactive product isotopes which cannot otherwise be removed. However, if remote refabrication of fuel elements may be performed, then the situation is changed radically. Table 2 illustrates the required decontamination factors dictated by various reasons of fuel processing. For purposes of re-enrichment sufficient fission product atoms must be removed to make room for the addition of new fissionable material, else the volume of the fuel will increase; for purposes of repairing irradiation damage to the fuel element, the gaseous and non-metallic fission products must be removed in order to preserve the metallurgical properties of the fuel which are important in re-fabrication operations; for purposes of removing nuclear poisons, a significant percentage removal of some fission products is required, but this need not exceed a factor of 10; and, as indicated previously, for direct refabrication operations an exceedingly high decontamination of the discharged fuel is required. Decontamination requirements may be seen to be very modest if remote refabrication of the fuel element is possible.

No reactor complex has been constructed to date which employs a closed fuel cycle. As reported by Arnold[7] continued fuel recycle will lead to the accumulation of fissile or fertile material daughter activities, so that even long cooling periods will not, either after or before decontamination, make it possible to produce a product of sufficiently low activity for hand refabrication operations. For example, uranium-237 is produced in the irradiation of U-235 from the intermediate U-236 by successive neutron captures. In a fast power breeder reactor operating on enriched uranium with high fuel consumption per cycle (2 per cent of the total atoms), the fuel cooling time required would be of the order of 100 days. After infinite fuel cycles, the U-237 activity will have increased by a factor of 10, requiring an additional 25 days cooling. In addition, significant quantities of Np-237, Pu-238, Pu-240, Pu-241, Am-241 begin to appear.

Table 2

Required Decontamination Factors

For re-enrichment	~ 1
For radiation damage	~ 1 to 10
For fission product poison removal	~ 1 to 10
For direct refabrication	~ 10^6 to 10^8

Similarly, in the U-233 fuel cycle thorium-234 is produced in the irradiation of thorium-232. Seventy-year uranium-232 is produced from thorium-232 and decays to 1.9-year thorium-228 and its daughters. Figure 2a shows the nuclear reactions involved. The presence of these byproducts leads to a particularly bad situation: a short decay period will lead to U-232 in the U-233 product and allow growth of some thorium-228 into the thorium. The presence of U-232 in the U-233 product makes mandatory remote purification and refabrication of the U-233. Under continued recycle, the thorium product, even under optimum conditions of reactor flux irradiation level and decay time, becomes very much more radioactive than the natural thorium. It is sometimes proposed that semi-remote refabrication of the thorium products be employed. Semi-remote operations are those involving the use of light shielding or distance such that a dose of 1500 mr per week to the hands and 300 mr per week to the body is allowed.* Limited exposure of personnel to higher radiation levels throughout the week may be allowed. Under this latter condition, other work must be found for personnel for the remaining period of time, work in which there is no chance of additional exposure to irradiation.

Existing plutonium fabrication facilities are semi-remote according to the above definition. Despite the use of light shielding (lucite or glass barriers), specialized fabrication and operation of equipment is expensive.

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*These exposure levels may be reduced since the present trend is to lower permissible levels of exposure.

U-232 Production

1. $\text{Th-232} \xrightarrow{n,2n} \text{Th-231} \xrightarrow[26\text{ hr}]{\beta} \text{Pa-231}$

$\text{Pa-231} \xrightarrow{n,\gamma} \text{Pa-232} \xrightarrow[1.3\text{ day}]{\beta} \text{U-232}$

2. $\text{U-233} \xrightarrow{n,2n} \text{U-232}$

3. $\text{Th-232} \xrightarrow{n,\gamma} \text{Th-233} \xrightarrow[23\text{ min}]{\beta} \text{Pa-233}$

$\text{Pa-233} \xrightarrow{n,2n} \text{Pa-232} \xrightarrow[1.3\text{ day}]{\beta} \text{U-232}$

U-234 Production

1. $\text{U-233} \xrightarrow{n,\gamma} \text{U-234}$

2. $\text{Pa-233} \xrightarrow{n,\gamma} \text{Pa-234} \xrightarrow[6.6\text{ hr}]{\beta} \text{U-234}$

The decay chains involved are:

For U-232:

$$\text{U-232} \xrightarrow[70\text{ yr}]{5.3\text{ Mev }\alpha} \text{Th-228} \xrightarrow[1.9\text{ yr}]{5.4\text{ Mev }\alpha} \text{Ra-224} \xrightarrow[3.6\text{ day}]{5.7\text{ Mev }\alpha} \text{Em-220}$$

$$\text{Em-220} \xrightarrow[54\text{ sec}]{6.3\text{ Mev }\alpha} \text{Po-216} \xrightarrow[0.15\text{ sec}]{6.8\text{ Mev }\alpha} \text{Pb-212} \xrightarrow[11\text{ hr}]{\substack{0.3,0.6\text{ Mev }\beta\\ 0.2,0.3\text{ Mev }\gamma}} \text{Bi-212}$$

$$\begin{tikzcd}
 & \text{Tl-208} \arrow[r, "1.8\text{ Mev }\alpha,\ 2.6\text{ Mev }\gamma", "3\text{ min}"'] & \text{Pb-208 (stable)} \\
\text{Bi-212} \arrow[ur, "34\%,\ 6\text{ Mev }\alpha", "60\text{ min}"'] \arrow[dr, "66\%\ \beta,\ 2.3\text{ Mev};\ \gamma\text{'s} - 2.2,\ 1.8,\ 1.6\text{ Mev}", "60\text{ min}"'] & & \\
 & \text{Po-212} \arrow[uur, "8.8\text{ Mev }\alpha", "3 \times 10^{-7}\text{ sec}"'] &
\end{tikzcd}$$

For U-234:

$$\text{U-234} \xrightarrow[2.5 \times 10^{5}\text{ yr}]{\substack{4.76\text{ Mev }\alpha\\ 0.05\text{ Mev }\gamma}} \text{Th-230}$$

Fig. 2a - Side reactions for U^{233} - thorium cycle.

It becomes clear that under conditions of continued recycle of fuel, remote refabrication of the fuel element is likely to be required in any event. The need, therefore, for high decontamination factors in fuel processing is eliminated, and processes which provide small but adequate fission product decontamination, such as the pyrometallurgical type of process, may be considered and may be employed advantageously.

D. Recovery of Expensive Alloying Agents

The development of radiation-stable fuel elements which are capable of withstanding relatively high fuel burnups (of the order of 2 per cent of the total atoms) has been accomplished by the use of alloying elements. Molybdenum, niobium, zirconium, and ruthenium are elements which, when alloyed with uranium, improve its radiation stability. All of these elements are fairly expensive. Zirconium costs around $40 a pound; and ruthenium, several hundred dollars a pound. If these elements are lost in the fuel reprocessing procedure, their replacement in order to reconstitute new fuel elements is likely to be a very expensive consideration. This could easily lead to the situation in which the value of the fuel alloying agents approaches that of the fissionable material. An important consideration in presently conceived pyrometallurgical processes is that these elements are not removed.

E., Waste Disposal

In the United States, present practices of waste handling involve the storage of large volumes of radioactive wastes in specially constructed storage vessels. No solution to the waste disposal problem has been found other than that of concentration and confinement. An economic advantage of the pyrometallurgical processes is that the wastes are concentrated and dry in a form suitable for disposal or for utilization. In fact, they are so concentrated that problems of heat removal may require dilution for storage. This would seem to be easier than problems of concentration which are normally encountered in waste handling.

F Criticality Problems

Problems of critical mass control in processing enriched fuels directly as metal are much less severe than if processed in aqueous solutions where the presence of the water moderator makes critical amounts of U-235 small. Critical mass control, whether by infinitely safe geometry or by batch-size control, has proven costly in aqueous processing plants. If processed directly as metal, batch sizes are such that the daily output of central station power reactor (500 MW as heat) may be safely processed in two, or possibly one batch.

G. Shipping Costs

Proposed pyrometallurgical processing facilities are located at the reactor site in order to avoid long distance shipping costs. Although high capacity plants are desirable from the standpoint of economic processing, pyrometallurgical processing procedures do not lend themselves to use in a large central processing facility because of the multiplicity of fuel element shapes and compositions encountered.

However, use of plants at the reactor site avoids shipping costs to central facilities, which may be some distance away. Shipping costs for highly irradiated fuel are high because of the tons of shielding which must be transported per pound of fuel. According to C. E. Stevenson[8], costs may be of the order of $50-$500 per pound of irradiated fuel. The investment in shipping containers is heavy, perhaps of the order of $15,000/cask. Heat transfer provisions must be provided to remove fission product decay heat. Criticality considerations may impose severe limitations on the amount of fuel carried in a container. Safety and security measures may also have a significant effect on costs. On-site, pyrometallurgical processing alleviates not only the shipping costs but also the inventory costs.

H. Cost Estimates for Pyrometallurgical Processing and Refabrication

Conceptual designs of pyrometallurgical process and refabrication plants were developed by Vitro Corporation[9] and Atomic Power Development Associates[10] as a basis for estimating costs of these facilities. Similar preliminary information has been detailed by Argonne for the experimental processing plant which will be built in connection with the EBR-II experimental reactor. Some of the important design concepts for this plant will be described in the next section.

1. Cost Estimates for EBR-II Experimental Processing Facility

The contractors for the EBR-II experimental facility have made estimates of the construction costs based on preliminary designs. These estimates are for a processing plant which includes processing, refabrication, and fuel re-assembly facilities, and for a separate laboratory and service building. This latter building houses the general administrative offices for the reactor plant in addition to the laboratory facilities. About 70 per cent of the construction costs for this building are chargeable to processing.

The estimated total cost for the processing plant and laboratory building (Feb., 1957) is $6,920,000. Of this, $3,515,000 are construction costs; $3,405,000 are installed equipment costs. A breakdown of these construction and equipment costs is given in Table 3.

Unit operating costs given in Table 4 are of little significance for the required experimental processing rate of 10 kg/day of enriched uranium. Therefore, unit costs are also given in Table 4 for a throughput rate of 50 kg/day, which processing rate could be achieved in the experimental plant. This processing rate is ample for a 200 MW (electrical) reactor operating with a fuel burn-up of 2 per cent of the total atoms. On this basis, unit reprocessing costs are about 1.8 mills/KWH.

2. Cost Studies by the Vitro Corporation and Atomic Power Development Associates

Construction and operating cost studies were made by the Vitro Corp. and Atomic Power Development Associates on the basis of conceptual pyrometallurgical processing plant designs. These designs are based on the oxidative drossing process investigated at Argonne National Laboratory and a processing rate of 18,000 kg/year, or enough capacity to serve a 167 MW reactor at 1 per cent burn-up. The cost estimates were based on processing and refabricating a complicated fuel element. Eighteen fuel element plates, each 30.5 inches long, 2.48 inches wide, 0.04 inches thick, weighing about 2 pounds, were to be fabricated and assembled into a radiator structure or subassembly, with sodium present in each radiator

Table 3

Estimated Construction Costs

For EBR-II Experimental Processing and Laboratory Facilities

Construction Costs*	
Building Construction	$ 439,000
Plumbing, Heating, Vent., Lighting, Fire Prot.	287,000
Process Cell Construction	696,000
Equipment (Exclusive of Process Equipment)	303,000
Yard, Utilities and Services	100,000
General Site Development	100,000
Lab. and Service Bldg. @ 70% of Total Bldg. Cost	560,000
Supplemental Pay	30,000
Total	$2,515,000
Fixed Charges at 40% of Total Construction Costs	1,000,000
Total	$3,515,000
Equipment Costs**	
Process Cell Service Equipment (Windows, Lights, Locks, Etc.)	$1,130,000
Process Cell Equipment (Cranes, Manipulators, Etc.)	720,000
Process Equipment (Furnaces, Materials Handling Devices, Fuel Fabrication, Etc.)	925,000
Supporting Equipment (Laboratory Facilities, Inert Gas Purification, Etc.)	630,000
	$3,405,000
Total Plant Cost	$6,920,000

* By H. K Ferguson Co., Architect-Engineer
**By Argonne National Laboratory

Table 4

Estimated Annual Costs for an EBR-II-Type Processing Facility

	Processing Rate	
Direct	10 kg/day*	50 kg/day*
Personnel	$ 250,000	$ 450,000
Chemicals	10,000	50,000
Utilities	5,000	25,000
Fuel Assembly Structures	20,000	200,000
Maintenance and Materials	50,000	200,000
	$ 335,000	$ 925,000
Indirect Costs (45% of Direct Costs Without Chemicals)	150,000	420,000
Fixed Charges at 25% of $6,920,000	1,730,000	1,730,000
Total	$2,215,000	$3,075,000
Unit Processing Costs	13 Mills/KWH	1.8 Mills/KWH

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*Reactor electrical output rates assumed to be 20 and 200 MW, respectively. Required processing rates are 4 kg/day and 40 kg/day for a 2 per cent fuel burn-up and 300 days of operation per year.

section to provide a thermal bond. Many much more difficult remote refabrication operations are required than for refabrication of the pin-type fuel elements by precision injection casting as previously described by Dr. Lawroski.[11] The refabrication operations for the above studies include: ingot preparation, hot rolling, cold rolling, solid state heat treatment, slitting, straightening, shearing, inspection, assembly, sodium filling, welding, grinding, leak testing, and heat treatment of the complete subassembly. These are much more difficult refabrication operations than are ultimately believed necessary.

The cost estimates, prepared in January 1956 and shown in Table 5, result in a total construction cost for the reprocessing and refabrication facilities of $5,425,600, of which $3,717,000 is for the processing facilities

Table 5

Estimated Construction Costs for Pyrometallurgical Facilities
(By Vitro Corp. and Atomic Power Development Associates)

	Processing Facility	Refabrication Facility
Site Preparation	$ 90,000	$ 1,300
Structures	540,000*	170,720
Tunnel	648,000	
Equipment	1,417,000	498,900
Services	456,000	84,475
Instrumentation	-	59,000
Stack	84,000	20,000
Initial Cell Atmosphere Purge (Argon)	42,000	38,800
Subtotal	$3,277,000	$ 873,195
Indirect Construction Costs	-**	191,005
Subtotal	$3,277,000	$1,064,200
Uninstalled Spares	-**	106,400
Subtotal	$3,277,000	$1,170,600
Contingency (20%)	-**	234,000
Total Construction Cost	$3,277,000	$1,404,600
Design and Engineering (11%)	-**	154,000
Preliminary Operation Costs	440,000	150,000
Totals	$3,717,000	$1,708,600
Total Plant Investment	$5,425,600	

* Includes reprocessing building at $408,000; air compressors building at $6,000; and maintenance shop at $126,000.

**The estimates of the individual items for the processing facility include fringe benefits for labor, spares, contingency, design and engineering, etc.

and $1,708,600 is for the refabrication facilities. These estimates were prepared from vendors' quotes on standard equipment, and cost estimates of non-standard equipment such as the decanning machine, transfer equipment, and induction furnaces. It may be noted that the tunnel, through which fuel elements are transported from the reactor, costs $648,000. Location of the processing cell adjacent to the reactor would eliminate much of this cost. The cost of start-up operations was estimated to be $590,000 which includes the costs for a 6-month operator training period and a 6-month start-up period. Approximately $1,150,000 of the total construction costs is for facilities used jointly by the refabrication and processing facilities.

Estimates of the annual operating costs for both processing and refabrication are shown in Table 6. This amounts to a total of $2,883,900 of which $1,536,000 is attributable to processing, $1,247,900 to refabrication. These estimates result in a unit cost of $154/kg of enriched uranium processed. On the basis of 500 MW heat output and heat-to-electricity conversion efficiency of 33 per cent, the total processing and refabrication cost is 1.90 mills/KWH.

3. Cost Estimates by Atomics International

Cost estimates were also prepared in January, 1956 by Mattern[12] of Atomics International for the remote processing and refabrication of a 75 MW electrical sodium-graphite reactor. In this thermal reactor, the fuel was assumed to be irradiated to 3000 MWD/T. The rate of fuel discharge from the reactor is 60 kilograms/day. At this processing rate, the unit processing and fabrication costs were calculated to be 1.93 mills/KWH. No breakdown to construction and operating costs was given.

A comparison by Mattern of aqueous processing and direct fabrication and remote pyroprocessing and refabrication showed a savings of 0.4 mills/KWH by the pyroprocessing route. For recycled fuel for which remote fabrication becomes necessary regardless of the fission product decontamination effected, this difference would probably increase. Developments in fuel element designs to make them more amenable to remote fabrication techniques may also be expected, with a consequent reduction in fabrication costs.

Table 6

Estimated Annual Costs for Pyrometallurgical Facilities
(By Vitro Corp. and Atomic Power Development Associates)

Direct Costs:	Processing	Refabrication
Personnel	$ 280,000	$ 128,400
Chemicals	75,000	33,300
Utilities	16,000	6,000
Maintenance Materials	72,000	50,000
Total Direct Cost	$ 443,000	$ 217,700
Indirect Costs:		
Labor, materials and overhead for administration, health physics, first aid, fire protection, etc. at 45% of direct cost without chemicals	$ 165,000	$ 83,000
Total Operation and Maintenance Cost	$ 608,000	$ 300,700
Fixed charges at 25% of total construction costs (see Table 5)	928,000	427,200
Subassembly radiator structures	-	520,000
Totals	$1,536,000	$1,247,900
Total Annual Cost	$2,883,900	
Unit Cost	$154/kg of enriched uranium	

II. Proposed Engineering Applications of Pyrometallurgical Processing Procedures

A. Experimental Fast Breeder Reactor No. 2 (EBR-II)

Probably the earliest operation of a pyrometallurgical process facility will be that now being designed for the EBR-II fast breeder reactor. The major objective of the processing unit is to establish the technical, engineering, and economic feasibility of pyrometallurgical processing and remote fuel refabrication.

The technical feasibility will be based on processing and refabricating all of the core material for many reactor fuel cycles and the processing of sufficient blanket material for adequate demonstration of the blanket process.

Technical feasibility must include:

1) Performance, equipment and process-wise, of the pyrometallurgical process and refabrication operations, and auxiliary operations such as waste disposal, slag recovery, and inert gas purification.

2) The effects of recycled fuel on process performance and reactor operation. The build-up and effect of transuranic elements during fuel recycle will be ascertained.

3) The reliability, dependability, and useful life of equipment and equipment components.

4) The operational requirements with regard to caliber and number of personnel required and other factors such as discharge of radioactivity which might affect the locations of these plants.

Economic feasibility includes:

1) Capital investment.

2) Operating costs of fuel and blanket process.

1. Core and Blanket Compositions

It is planned to check the performance of the EBR-II reactor with both enriched uranium and plutonium fuel loadings. The first core loading will be a 60 per cent enriched uranium fuel. The second will be a plutonium fuel, approximately 20 wt per cent in plutonium. The noble fission product elements are not removed by the pyrometallurgical processing procedure employed, and will build up on continued fuel recycle, eventually reaching equilibrium concentrations which are dependent on the per cent of new fuel material added per cycle. To avoid dealing with fuel of changing composition, the equilibrium concentrations indicated in the following table, excepting that of technetium, will be used at the start.

Table 7

Calculated Equilibrium Fission Product Concentrations

(5 w/o New Metal per Cycle)

Element	Wt Per Cent
Zirconium	0.10
Niobium	0.01
Molybdenum	3.42
Technetium	0.99
Ruthenium	2.63
Rhodium	0.47
Palladium	0.30

These elements have been found to be beneficial, increasing markedly the irradiation stability of the fuel elements. Their presence has increased the achievable burn-up so that 2 per cent burn-up of the total atoms is a realistic goal.

The uranium or plutonium fuel employed in the reactor is in the form of small pins, 0.144 inches in diameter by 14.22 inches long. These pins are individually canned in stainless steel cans. An annulus of 0.004 inches is provided between the pin and the can wall and is filled with sodium which acts as a liquid thermal bond for heat transfer purposes. Ninety-one of these pins are present in fuel sub-assembly.

The blanket or fertile material will be depleted uranium. For a large scale power reactor, processing of the blanket elements would be carried out when the plutonium concentration reached 1 per cent. For the EBR-II pilot reactor, only a few of the inner blanket elements will be processed in order to demonstrate blanket processing.

2. General Process Description

The core processing method will be oxide drossing, or perhaps a more descriptive term is melt refining.[13,14,15] It involves melting the fuel in an oxide crucible, either zirconia or magnesia, and holding it molten at a suitable temperature (1200-1300 C) for 2 to 3 hours. During this period, volatile fission products are vaporized from the melt, and fission products more reactive than uranium react with the crucible and are removed in a reaction layer which forms along the crucible walls. The noble fission products are not removed.

The core processing flowsheet is shown in Figure 3. Major steps in this flowsheet are purification, fabrication, and re-assembly of fuel. Auxiliary operations are sampling, waste handling, dross (slag) recovery, and inert gas purification.

After a 2 per cent burn-up and cooling for 15 days, the radiation intensity one meter from a 10 kilogram batch will be approximately 10^6 to 10^7 R. This intensity will be reduced only by a small factor, 3 to 4, by processing. Radiation intensities throughout the processing area will be of the order, 10^5 to 10^6 R/hour, with local areas of more intense radiation.

The maximum fission product heat generation (beta and gamma) has been calculated to be 0.2 watt/gram. Self-absorption of gamma rays will increase with mass. Forced cooling may be necessary for massive quantities or for close packed assemblies of fuel elements, which have poor heat transfer characteristics.

3. Preparation of Discharged Fuel Elements for Processing

On removal from the reactor, the sub-assemblies are held in the sodium bath in which the reactor is immersed until heating by fission product decay has subsided to the point where gas cooling will prevent melting. The subassembly will be disassembled in the disassembly cell of the reactor building. Individual canned pins are transferred to the processing building.

The stainless steel can is removed by forcing the pin element through three fixed knives located radially 120° apart which slit the can

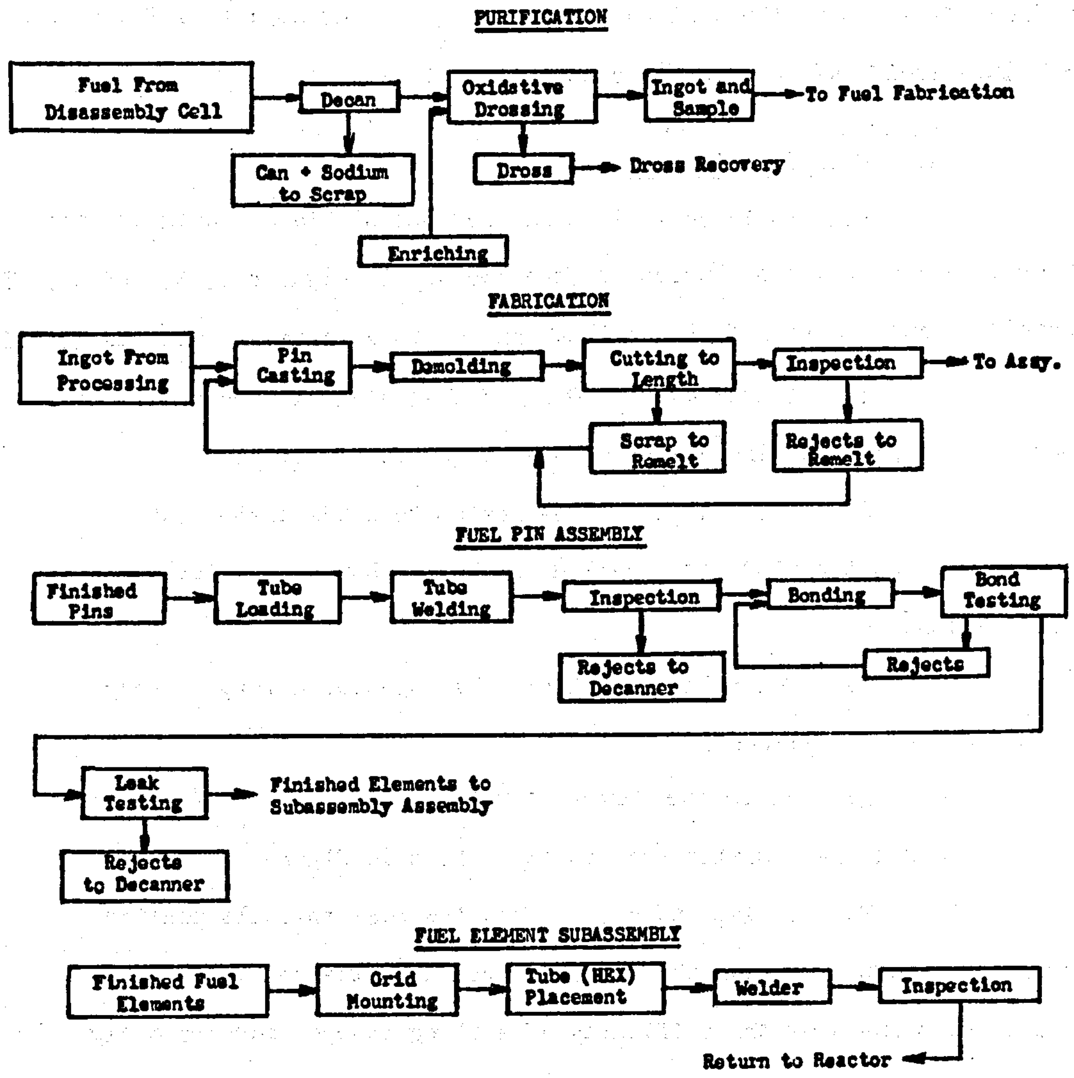

Fig. 3 - Flow sheet for EBR-II fuel processing and refabrication.

axially. The strips are peeled away from the fuel element much as a banana peel is removed from a banana. Part of the sodium remains with the fuel pin.

The pins are then sheared into small pieces for ease of handling and charging. Until they are to be charged into the melting crucible, the pins must be spread out in a tray. If piled together or stored compactly in a container, heat removal from the close packed arrangement of pins is so poor that the mass will heat to a temperature near the melting point. At these temperatures oxidation or nitridation by impurities within the cell gas would be excessive, so a very low oxygen impurity level must be maintained in the inert blanket.

4. Fuel Purification

Melt refining will be carried out within a closed furnace under a very pure inert atmosphere (see mock-up in Figures 4, 5, and 6). The procedure employed to affect purification and metal recovery will be as follows:

1) Approximately 10 kg of fuel element pieces will be charged to a pressed zirconia or pressed magnesia crucible.

2) The charge will be heated to a temperature of 1200-1300 C and liquated for a period of about 3 hours to effect purification.

3) The molten metal will be top-poured into a heavy copper mold and chill-cast.

4) After the furnace is opened the ingot will be dumped from the mold using a device such as that shown in Figure 7.

Top pouring was selected as the most reliable pouring procedure. Bottom pouring through stoppered taps was considered less propitious because of the difficulty of seating stopper rods remotely. The use of a fusible seal in a pouring leg could probably be made to work, but development problems appeared formidable.

a. Description of Mock-Up Furnace

The furnace chamber consists of a metal bell which is sealed to the base plate by means of a fusible metal seal, such as solder. All of the equipment (i.e., crucible and supports, mold, tilting mechanism) will be mounted on the base plate. Services will be brought through the base plate from a service strip attached to the furnace base. Services may be remotely connected or disconnected at the service strip by means of a fusible metal seal (see Figure 8).

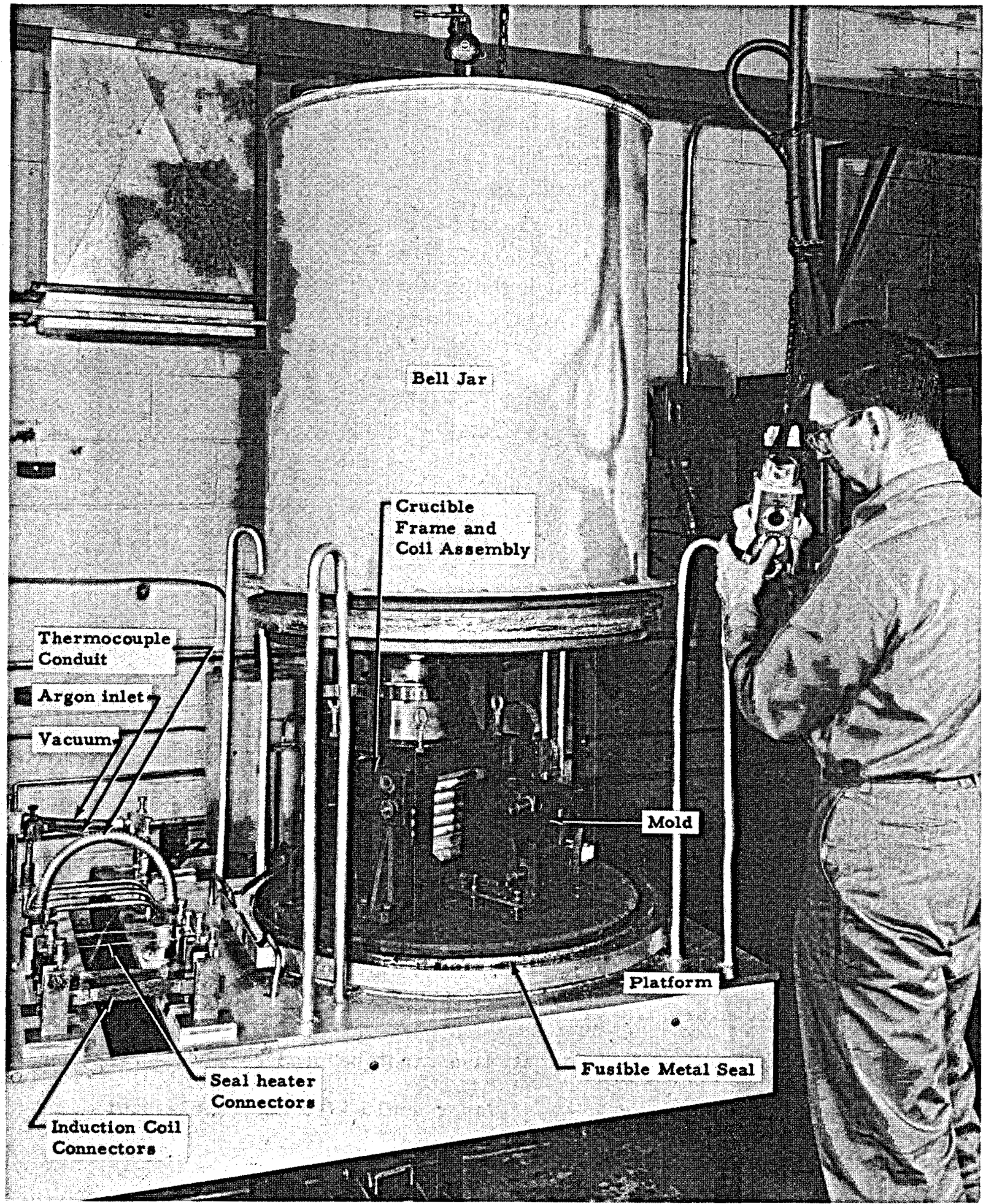

Fig. 4 - Uranium melting furnace - Bell jar partially removed.

Heating is accomplished inductively using uncooled induction coils. For this application, the use of conventional, water-cooled induction coils is considered hazardous. The water provides some moderation reducing the quantity of material which could be processed per batch. Much

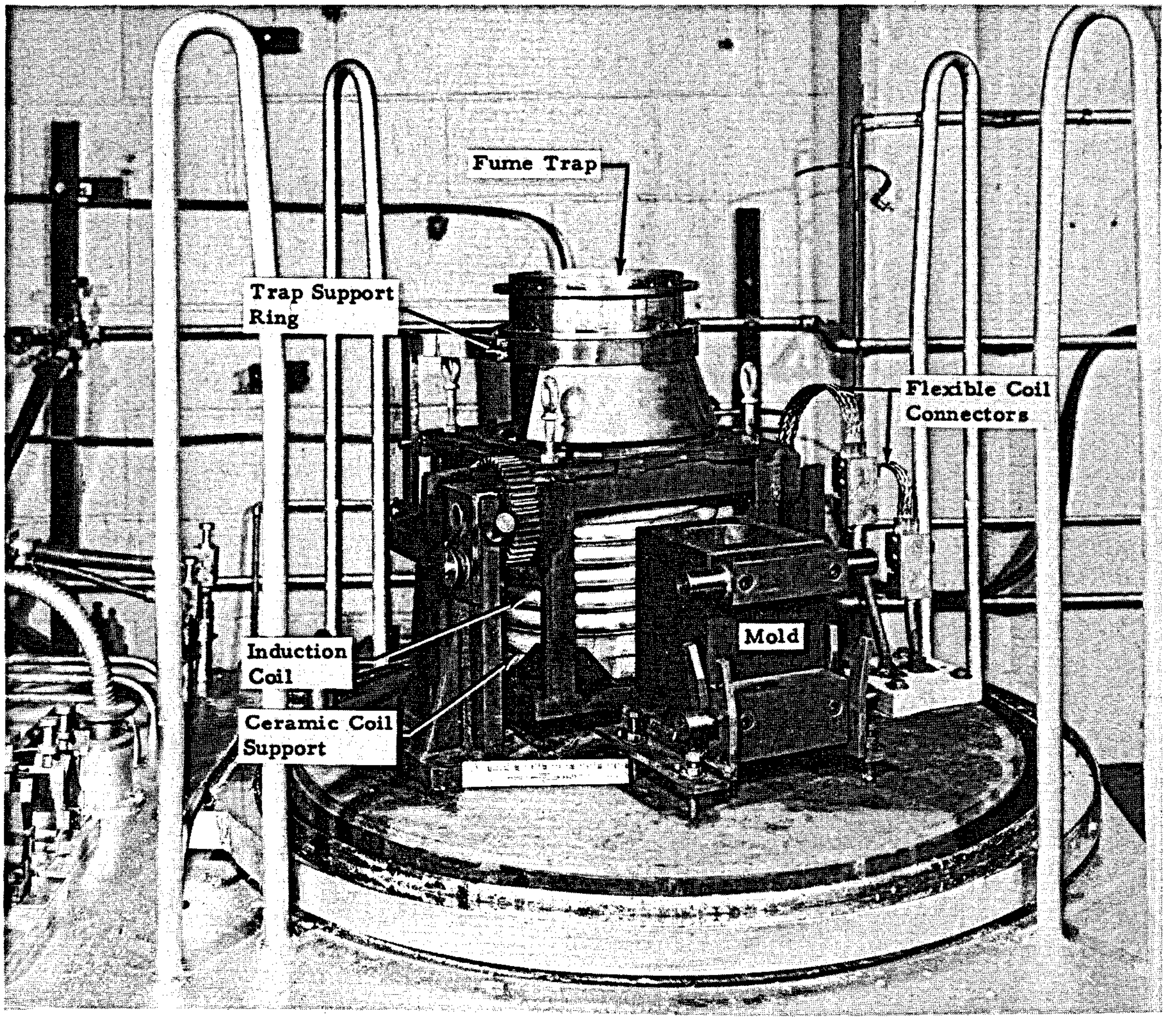

Fig. 5 - Furnace interior.

more important, however, are the severe consequences of a leak. If the furnace filled with water, a critical mass might be produced. The reaction of molten uranium with water or water vapor would also have unpleasant consequences.

Flexible leads are employed in order to accommodate tilt pouring under power. Induction bus bars are brought from the condenser bank through the shielding to the furnace, a distance of about 10 feet. Tests have indicated little power loss and consequently little temperature rise in uncooled bus bar leads of reasonable size (1/2 x 2 inches) if the flat surfaces are in close proximity.

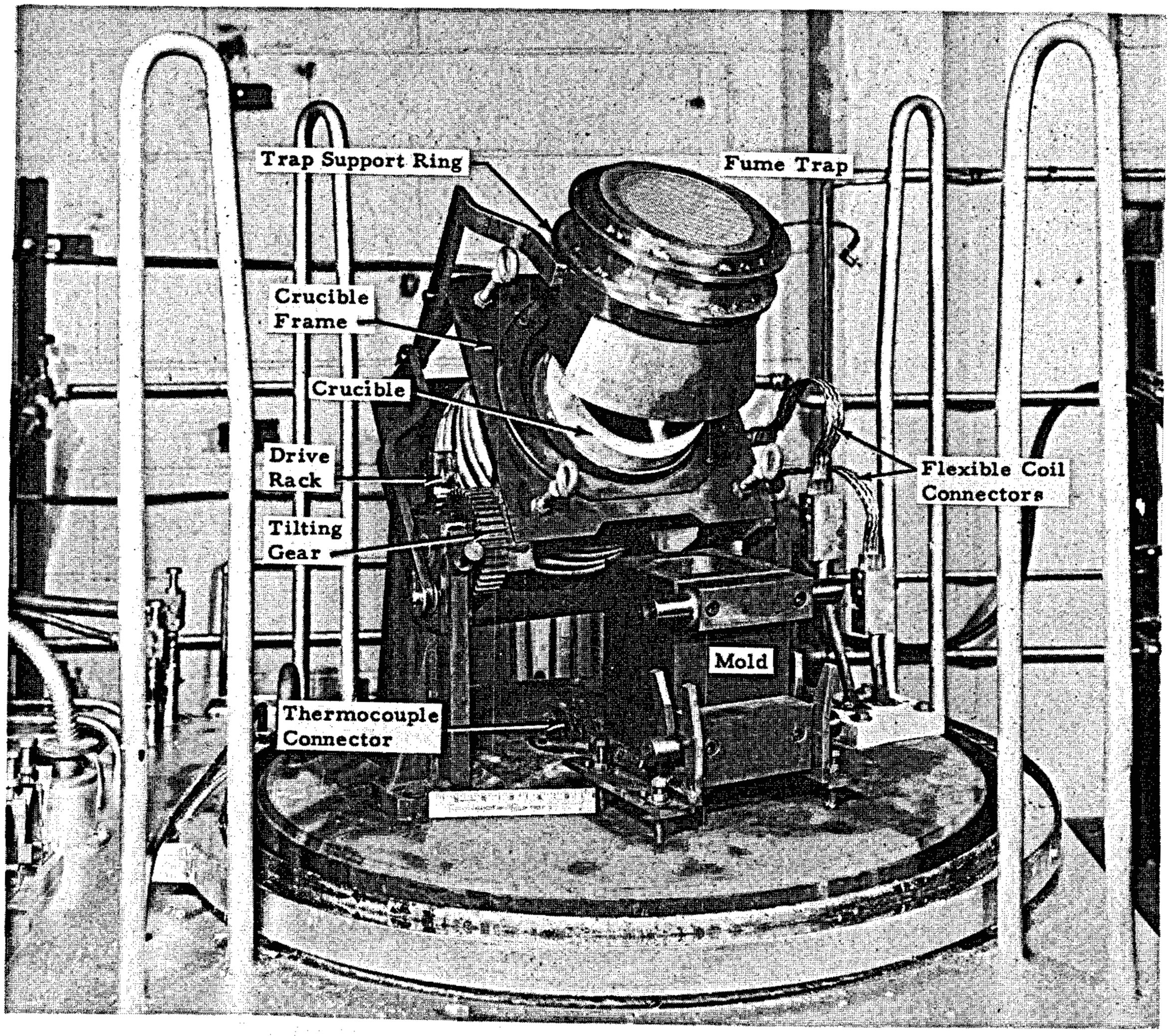

Fig. 6 - Crucible assembly in partially tilted position.

The crucible, susceptor, an insulating refractory sleeve of zirconia, and the induction coil (in the order given from inside to outside) are positioned in a metal framework which is supported on two trunnions. The tilting mechanism consists of a pinion gear integral with the framework and driven by a rack which extends through the base for operation. A solid adsorbent is in the basket which is mounted directly over the crucible for trapping volatilized elements. By a suitable linkage mechanism, the basket is rotated from the crucible during pouring to provide an opening through which the metal can pour.

A componentized assembly is employed so that individual

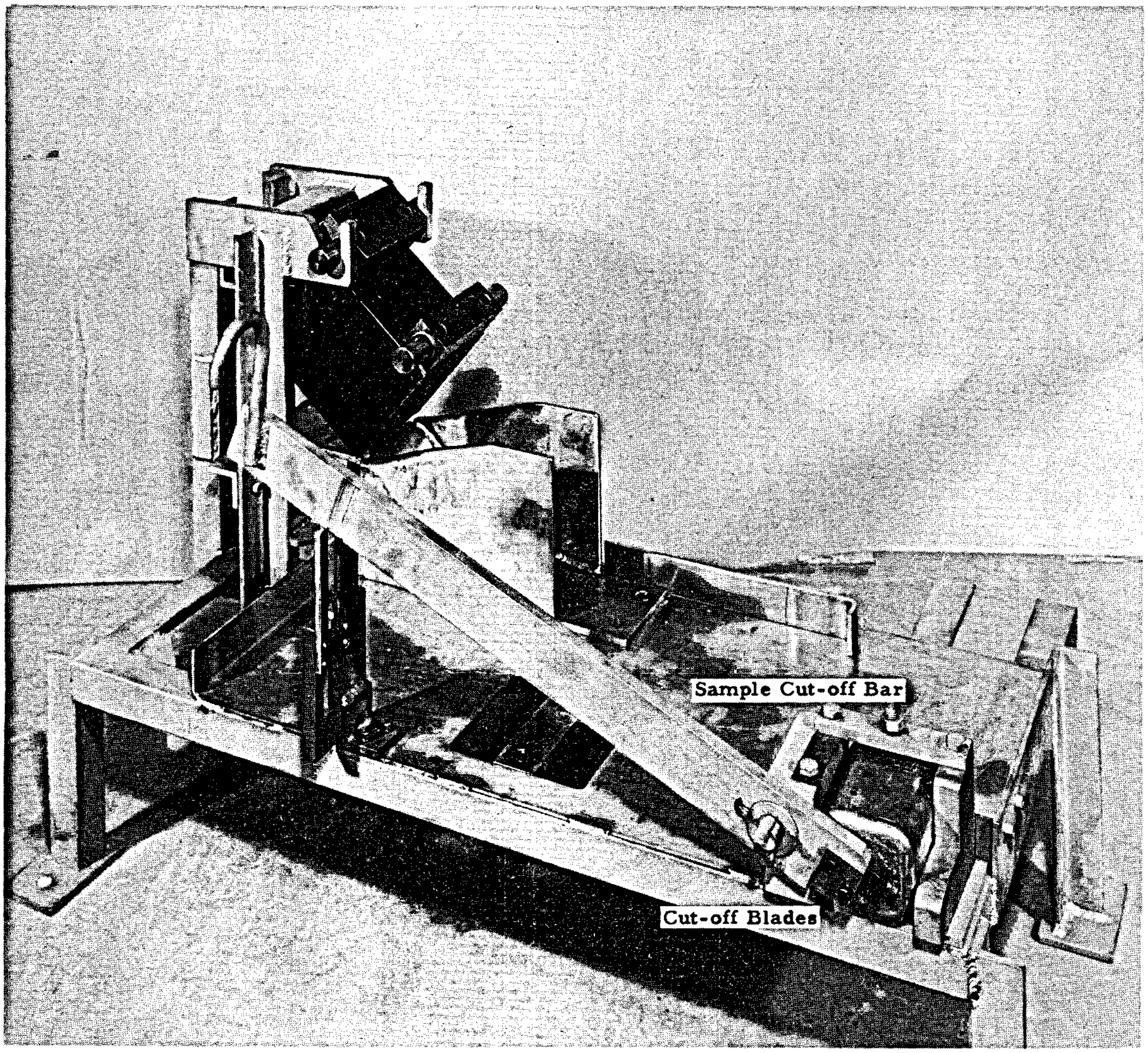

Fig. 7 - Ingot remover and sampler.

components may be replaced. The crucibles, susceptor, supporting framework, and basket of adsorbent may be individually replaced, as can the entire base plate after removal of the service jumpers.

b. Sampling

Two small protrusions, about 1/4 inch long x 1/8 inch in diameter, will be cast on the base of the ingot. These protrusions

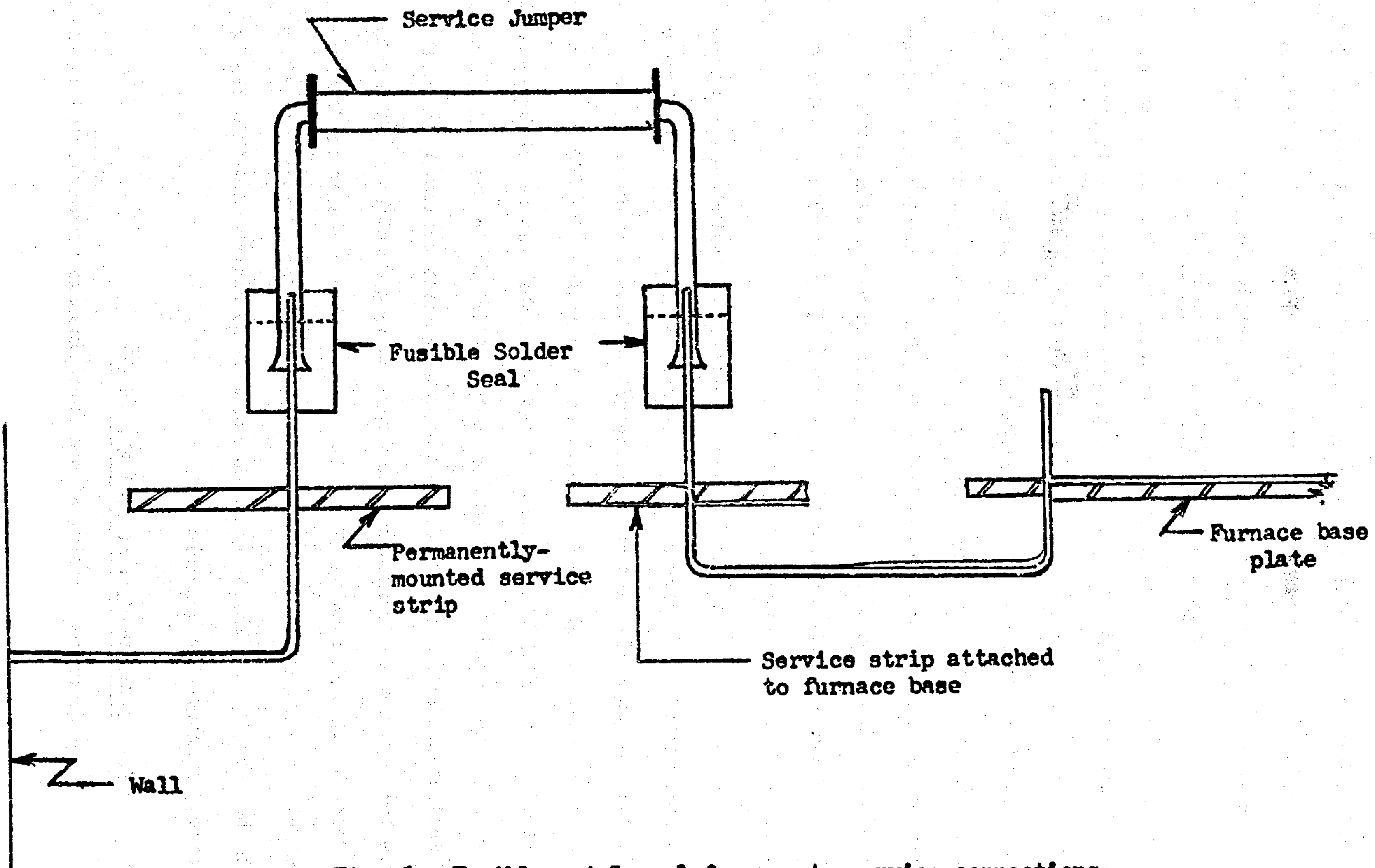

Fig. 8 - Fusible metal seal for remote service connections.

will be sheared off (see Figure 7) and submitted for analyses. Addition of new fissionable material may be made either in the purification furnace on the basis of reactor burn-up data or samples of the original fuel, or may be carried out in the remelt furnace for casting new fuel elements.

c. Trapping of Volatilized Materials

The sodium, which accompanies the fuel pins, magnesium from crucible (MgO) reaction, and several fission elements volatilize. The noble fission gases, xenon and krypton are retained in the furnace and are later pumped to storage and subsequently bled to the atmosphere. Other fission products which are vaporized are cesium, small quantities of strontium and barium, and fission products, probably cadmium and antimony. The indiscriminate deposition of these fission products along with relatively considerably amounts of magnesium (~50 g/10 kg charged) and sodium (~30 g/10 kg charged) is undesirable.

Two surface-active materials, activated charcoal, and a material called "Molecular Sieves,"* composed mainly of calcium aluminum silicates and generally used as a drying agent, have been found to be effective sorbents at elevated temperatures for sodium. At 800 C, and a gas flow rate of 15 ml/(min)(sq cm), these have exhibited remarkably good efficiencies up to loadings of 20 per cent/unit weight for Molecular Sieves and activated alumina and 40 per cent/unit weight for activated charcoal. These loadings before breakthrough are apparently a function of flow rate, and decrease with increasing flow rate. Tests are continuing to determine more fully the characteristics of these sorbents. One of these materials will, however, eventually be selected and will be contained within the bed located just above the crucible.

5. Refabrication of Fuel Elements[16]

Precision casting of the fuel pins has been selected as the

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* Product of Linde Air Products Co.

method having greatest promise and adaptability to remote operation. An injection casting process is employed in which the pressure of an inert gas (helium or argon) plus the inertia effect of the moving metal serves to fill inverted evacuated molds. The method consists of the following steps:

1) A shallow crucible of metal is melted under vacuum in a vacuum-pressure furnace. A cluster of tubular molds with the top ends closed is suspended above the crucible in such a manner that the sprue or gate ends are pointed down toward the metal bath.

2) The crucible is raised, immersing the lower ends of the tubes in the liquid metal bath, and the furnace is simultaneously pressurized with inert gas to several atmospheres.

3) The gas pressure forces the molten metal into the mold cavities.

4) The filling of the cavities is further implemented by the ram inertia effect of the molten metal as the mold is filled.

A schematic drawing of the equipment designed for this operation is shown in Figure 9. The furnace chamber consists of the metal bell which is sealed to the furnace bottom by means of a solder-freeze seal. The crucible is mounted on a vertically acting ram, which, in its lower position, centers the crucible in a solid conductor induction coil, and which may be raised to immerse the tips of the molds.

The molds consist of precision bore (±0.0005 in. diameter tolerance), high silica glass (Vycor) tubes coated on the inside with a colloidal graphite wash. The Vycor tubing has a disadvantage of low resistance to mechanical shock and the pressure and temperature of the metal must be very closely controlled to prevent the rupturing of the tubes as the metal is rammed into them in the casting operation. The colloidal graphite wash serves to separate the metal from the silica. Where the wash coating is imperfect, a reaction layer forms between the silica and

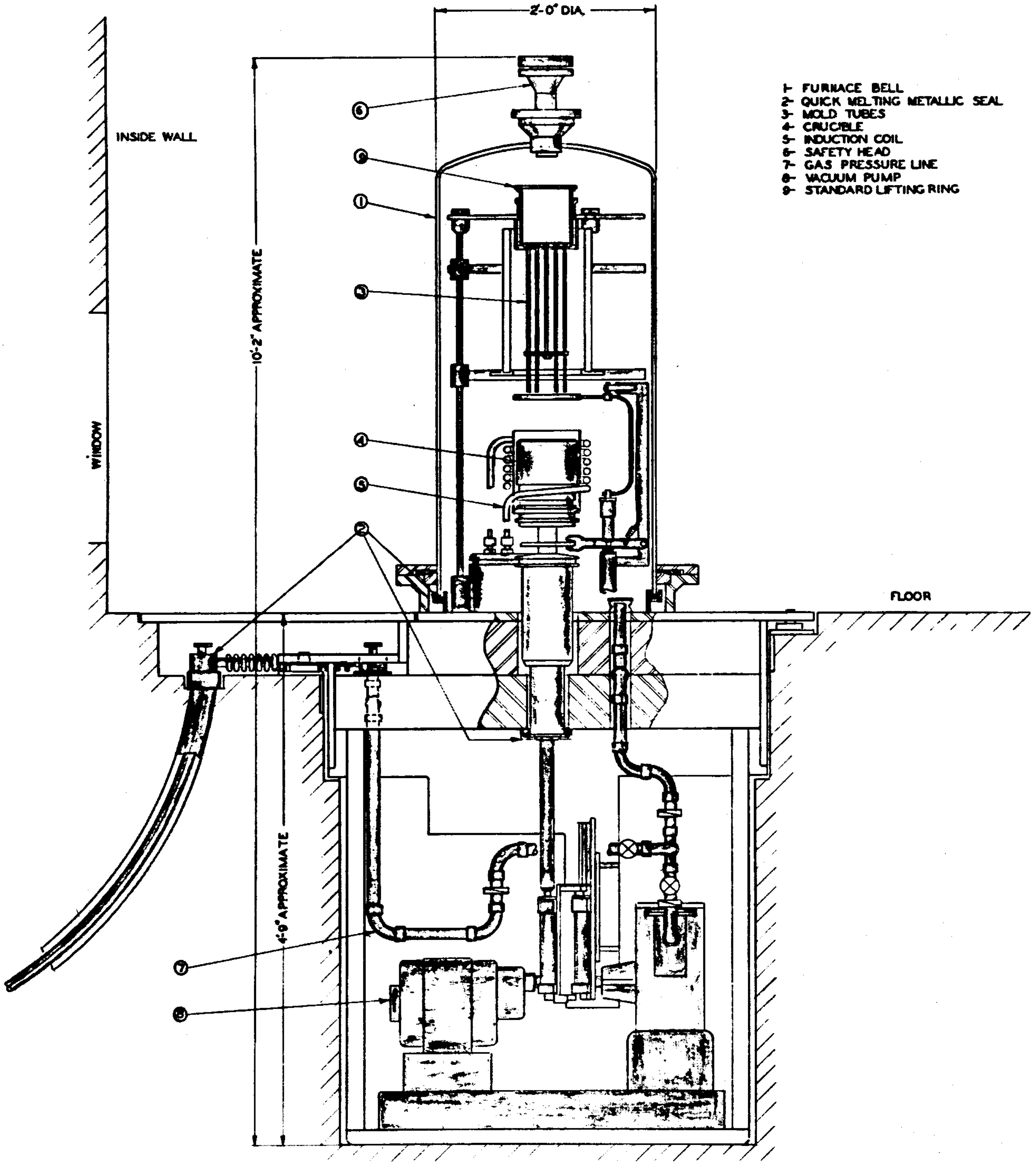

Fig. 9 - Schematic of injection casting furnace.

the metal which causes a slight roughening of the surface of the casting. Where the coating has been applied uniformly, the cast surface is extremely smooth and glasslike. Tolerances of ±0.001 in. diameter are produced in approximately 96 per cent of the castings. Figure 10 shows castings which have been produced by the injection casting technique.

The molds are shielded from direct heat radiation from the crucible by a tantalum shield which automatically swings out of the way as the crucibles rise. Power for melting is supplied by a conventional high-frequency generator outside the shielded area through the induction coil around the crucible assembly. As in the melt refining furnace, the induction coil is uncooled. The charge is melted under high vacuum and since the molds are within the vacuum chamber, they are also evacuated.

After immersing the molds, pressure is supplied from a pressure tank to a pressure of 1 to 2 atmospheres. In order to provide sufficient heat removal to cause the metal to solidify in the central tubes, forced cooling may be supplied by circulating the pressurized furnace atmosphere down across the tubes and up over the furnace shell.

After cooling, the castings are removed and fed between two concave roughened mills which causes the glass to break away from the castings, in small fragments. The castings will then be inserted into the spindle of a double-collet lathe where they will be notched exactly 14.22 inches apart and the ends broken away by pressure rolls. It is believed that the rods can be fractured with sufficient accuracy so that it will unnecessary to face the ends.

The fuel element castings will then be loaded into prefabricated stainless steel tubes with a 0.008 inch wall and 0.008 inch larger in bore diameter than the fuel elements into which a measured volume of sodium metal (ca. 1 ml) has been previously extruded under an inert atmosphere. The sodium is subsequently melted allowing the uranium to move down into the tube and the level of the melted sodium to rise above

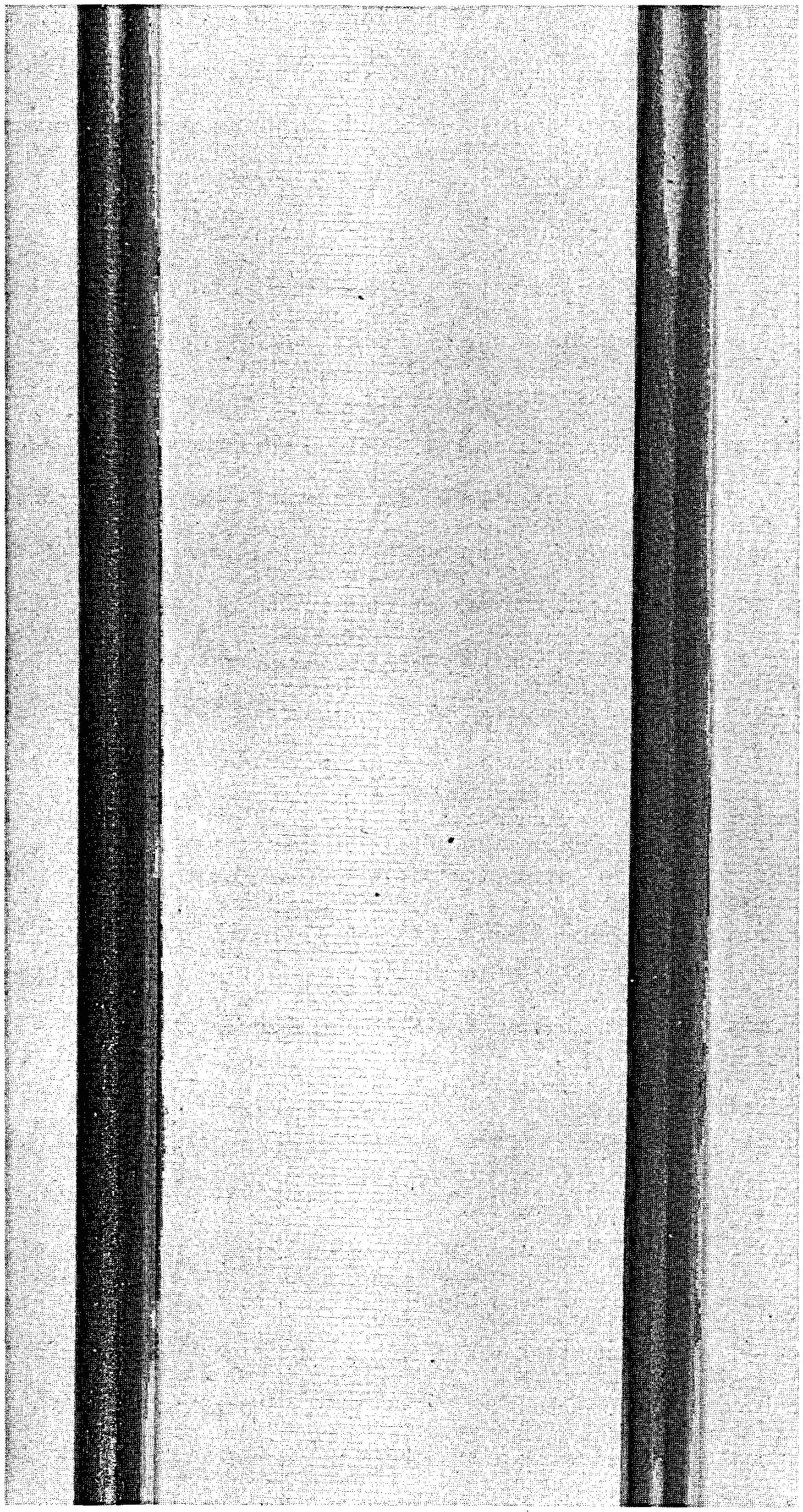

Fig. 10 - Photograph of injection-cast fuel pins showing smooth surface conditions (3 X actual size).

the fuel pin. The end cap is welded on by an arc welding process. The tubes are then centrifuged to eliminate bond separations and are passed through an inductive current scanning device which indicates voids in the sodium bond.

All other parts of the fuel element subassemblies except the active fuel elements are assembled outside of the cell so that only incorporation of the active fuel elements in the subassembly is required within the cell. Each subassembly is leak-detected by the mass spectrometer leak-detection method. Ninety-one of the fuel subassemblies are assembled into the hexagon-shaped major assemblies which are the fuel elements for the reactor.

6. Auxiliary Process Operations

a. Dross (Slag) Recovery and "Dragout" Processing

In order to prevent buildup in the concentration of the noble fission products which are not removed in the melt refining process, some provision must be made for their removal. Physical removal of a portion of the fuel material ("dragout") and replacement with fresh fissionable material which does not contain the noble fission elements will serve to limit the buildup of the noble fission products. After many cycles of fuel through the reactor they will reach an equilibrium concentration which is dependent upon the fraction of material removed and on the percentage burnup of fuel in the reactor. These equilibrium concentrations are given in Table 7 for the 5 per cent metal removal which has been selected.

Some fuel is removed as dross and if this removal amounts to around 5 per cent of the total fuel material, there is then no necessity of further removing more material from the fuel recycle stream. If, however, the dross constitutes only 1 or 2 per cent of the charged fuel material, it will be necessary to remove additional material from the fuel recycle stream. This dragout material and the slag remaining after the melt refining process must be processed to remove the noble fission product contaminants in order to return the contained fissionable material to the reactor fuel cycle.

As presently conceived, equipment will be installed for demonstrating slag or dragout metal recovery and noble fission product separation. Investigation of processes for this purpose are now underway. The most promising process involves the use of zinc as a solvent for the uranium metal from which a uranium-zinc intermetallic can be precipitated by cooling (see paper by H. M. Feder[14]). Separation of the uranium-zinc intermetallic from the zinc solution which contains, by appropriate selection of conditions, the bulk of the fission products may be accomplished by filtration through a porous graphite filter. Subsequently, the UZn_9 may be decomposed, the zinc vaporized, and the residual uranium coalesced into a metallic button for return to the process.

b. Blanket Processing

Blanket processing in the EBR-II facility will also be carried out on the demonstration basis. Sufficient blanket material will be processed to demonstrate the technical feasibility of this operation and to provide for estimates of the cost of blanket processing. The process will probably consist of extracting the plutonium from a molten uranium 5 w/o chromium alloy with molten magnesium and subsequently distilling the magnesium away from the plutonium.[17] The magnesium will then be available for recycle. Considerable laboratory and semi-works experience has been accumulated on this process and has been reported in the papers by H. M. Feder[14] and E. E. Motta.[18] Adaptation to plant scale has not been carried out.

c. Inert Gas Purification

The fuel material, which will be at a relatively high temperature as a result of fission product heating, is exposed to the cell atmosphere in numerous operations, such as the decanning, storage, and transfer operations. Under the conditions of high burn-up and short cooling, it is expected that the temperature of this material may be kept down to 600 C by suitable storage procedures. At this high temperature, uranium will effectively getter the atmosphere of oxygen. The reaction rate with nitrogen at this temperature is negligible in comparison. In order to prevent severe oxidation of the uranium, it is necessary to maintain a low-oxygen atmosphere within the cell. Argon has been selected as the inert blanketing gas. The choice of argon rather then helium was based on the fact that the movement of relatively large quantities of gas through purification equipment and the containment of gas are much more easily effected with argon than with helium. In order to prevent severe oxidation of the uranium in the cell atmosphere, the maximu tolerable oxygen concentration in the blanketing gas has been set at 100 parts per million. Since nitridation of uranium at 600 C occurs very slowly, the nitrogen specification has been arbitrarily established at the relatively high value of 5 volume per cent.

The cell gas must be continuously purified in order to maintain the low oxygen concentration level. While chemical procedures may be employed to control the nitrogen concentration, the least expensive and most convenient method involves simply purging occasionally and replacing with fresh argon. The reprocessing rate for removal of oxygen will be dependent on the leakage rate of air into the cell. It is difficult to estimate this leakage rate, but on the basis that high standards of fabrication and construction will be met and that careful operating procedures will be followed, an in-leakage rate of 0.01 cfm has been assumed for the sizing of purification equipment. This leakage rate requires a processing rate of only about 20 cfm to maintain the oxygen impurity concentration below 100 parts per million, and an argon purge rate averaging 0.16 cfm to maintain the nitrogen concentration at 5 volume per cent.

The oxygen purification procedure selected involves the catalytic conversion of the oxygen to water over a palladium catalyst and removal of the water from the gas stream using a drying agent. A material called "Molecular Sieves,"* which is a dehydrated zeolite, has been selected as the drying agent. This material is capable of adsorbing up to 20 per cent by weight water and its efficiency is such that for a linear flow of 2 ft/sec and a bed length of 3 ft the concentration of the effluent gas is less than 1 ppm in water.

A flowsheet for the inert gas purification operation is shown in Figure 11. The palladium catalyst is 0.5 weight per cent palladium-on-alumina catalyst. It has the very desirable characteristic that it can function as an efficient hydrogen adsorber up to a hydrogen loading of 0.47 ml/ml of. This hydrogen is also available for reaction with oxygen in the gas stream to form water. The catalyst then can function as a hydrogen reservoir as well as a hydrogen adsorber. This allows some flexibility in the operation in that if the hydrogen loading on the catalyst is maintained at a fraction of saturation, small deviations from stoichrometry caused by rate fluctuations or changes in the oxygen content will be neutralized by the catalyst. The effluent stream will be constantly monitored for nitrogen and oxygen.

The major equipment items of the inert gas purification unit consist of a compressor having a capacity of 100 cfm against a head of 5 psi, a palladium catalyst chamber, and a single drying unit containing 100 lbs of "Molecular Sieves"* drying agent. For an in-leakage of 0.01 cfm, regeneration of the "Molecular Sieves"* drying unit will be required once every three months and will be accomplished by heating them to 350 C and stripping the water off with air. After regeneration the air is evacuated from the dryer.

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* Product of Linde Air Products Co.

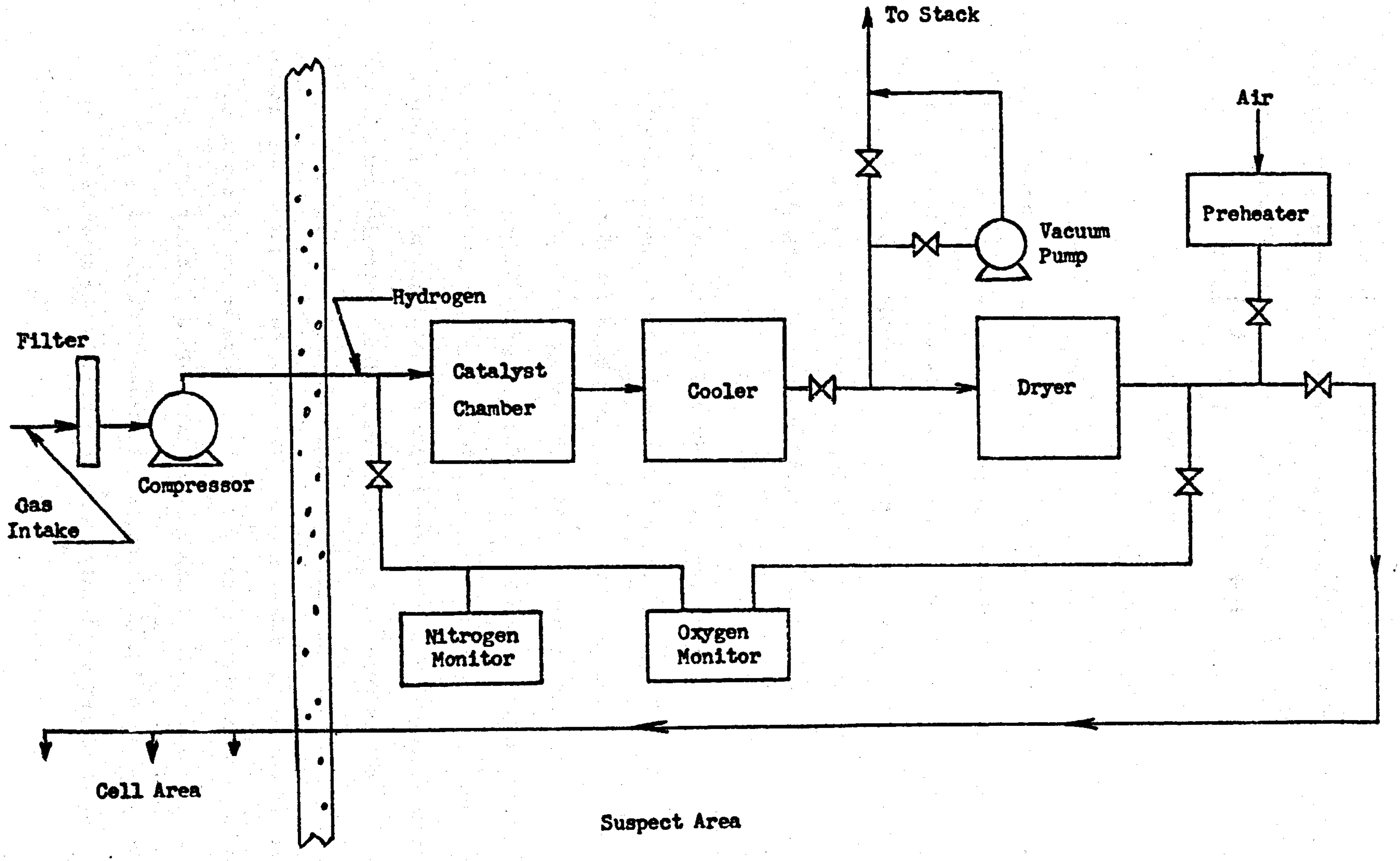

Fig. 11 - Purification scheme for argon blanketing gas.

The gas purification unit will be located in a lightly shielded enclosure outside the cell where it may be operated and maintained semi-remotely. Delivery of purified gas within the cell will be to special locations where high purity gas will be especially beneficial, such as storage of decanned pins or processed metals.

d. Waste Handling

The major high activity wastes produced in pyrometallurgical processing are the gaseous wastes liberated during the melting, and the solid wastes comprised of slags, crucibles, and used equipment items. Liquid wastes are expected to be of low level and result from analytical and decontamination operations. Conventional procedures (evaporation and storage of concentrate) will be employed for disposal of liquid wastes. The gaseous and solid wastes will be handled as follows:

Gaseous Wastes. Xenon and krypton are liberated during the melt refining operation (Table 8) into the inert atmosphere blanketing gas within the furnace. They are pumped out of the melt refining furnace and stored for a time sufficient to alloy decay of the 5.3-day xenon activity to a level safe for disposal. Storage for a time of approximately 3 weeks is required. Two storage methods are presently being considered. One involves the simple detention of the gas within a large storage tank from which it may be removed in controlled amounts for dilution and disposal up a stack to the atmosphere. The second method involves retention on activated charcoal at room temperature. This latter method looks attractive in that a relatively large volume of the xenon and krypton gases may be retained by a small volume of adsorbent. Initial batches of material deposited on the adsorbent are displaced by the succeeding batch and eventually would be eluted to the atmosphere. By proper sizing of the adsorbent tower and control of the total volumetric

Table 8

XENON AND KRYPTON IN DISCHARGED EBR-II FUEL

Burnup: 2 per cent of total atoms in 135 days

Cooling: 15 days

Element	Total Volume at STP/10 kg of Fuel (cu ft)	Curies per 10 kg of Fuel
Xenon	0.15	1.35×10^4
Krypton	0.02	97

flow of gas through the tower, it is possible to retain the xenon and krypton on the bed sufficiently long to allow decay of the xenon activity.

Solid Wastes. Solid wastes are expected to consist mainly of used crucibles, slags, stainless steel cans, the broken vycor molds from the pin casting operation, and equipment items which are being replaced. The slags will constitute an intense source of both radioactivity and heat. Although concentrated in a form convenient for utilization, methods are being sought for immobilization of the activity. One possible method consists of immersion in zinc. Central metal temperatures have been calculated to be of the order of 350 C which is below the melting point of zinc.

7. Processing Cell Description

The processing cell will be cylindrical in shape having an internal diameter of approximately 62 feet and an internal height of 16 ft (see Figures 12 and 13). For the activity levels within the cell, 5-foot wall thickness of heavy aggregate concrete (density: 200 lbs/cu ft) must be employed to reduce radiation along the outside

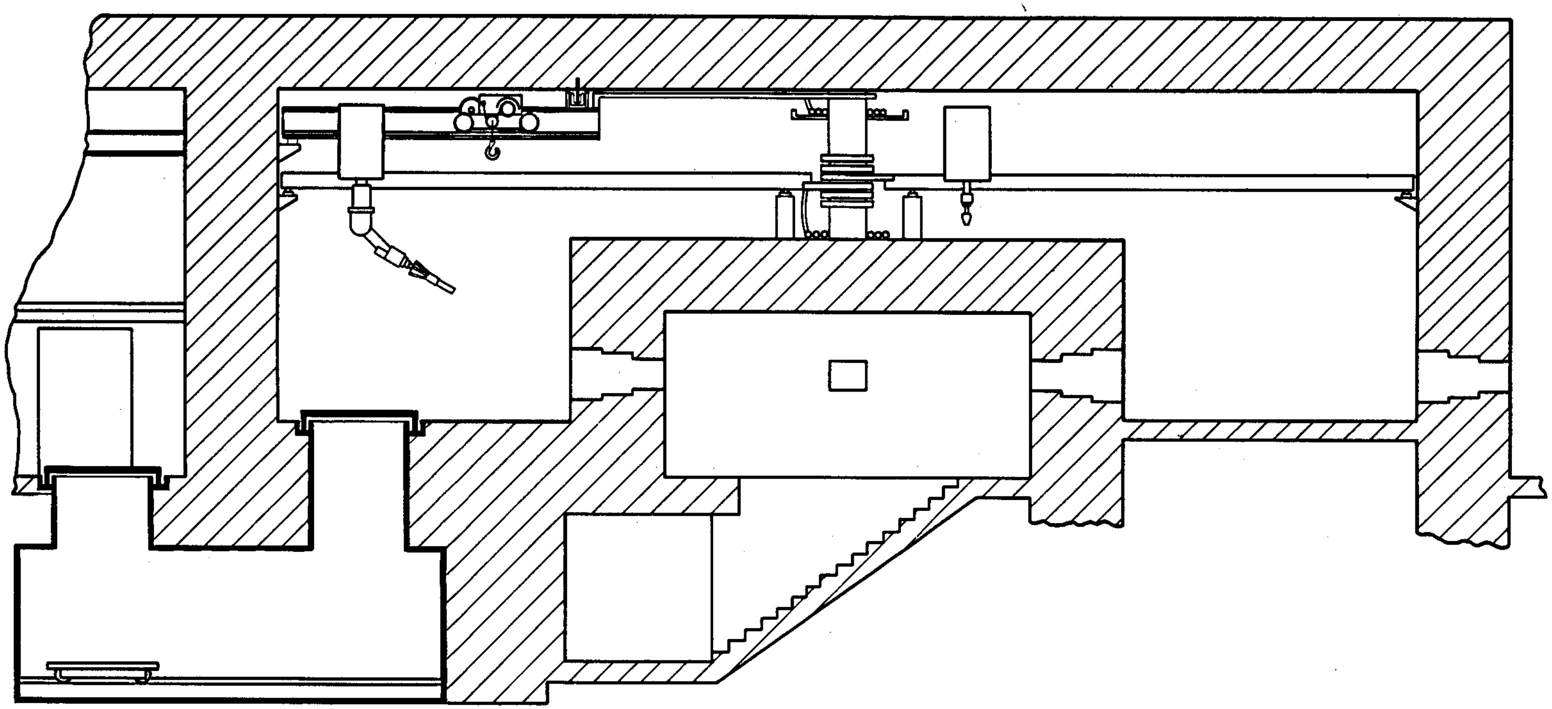

Fig. 12 - Inert atmosphere processing cell (elevation).

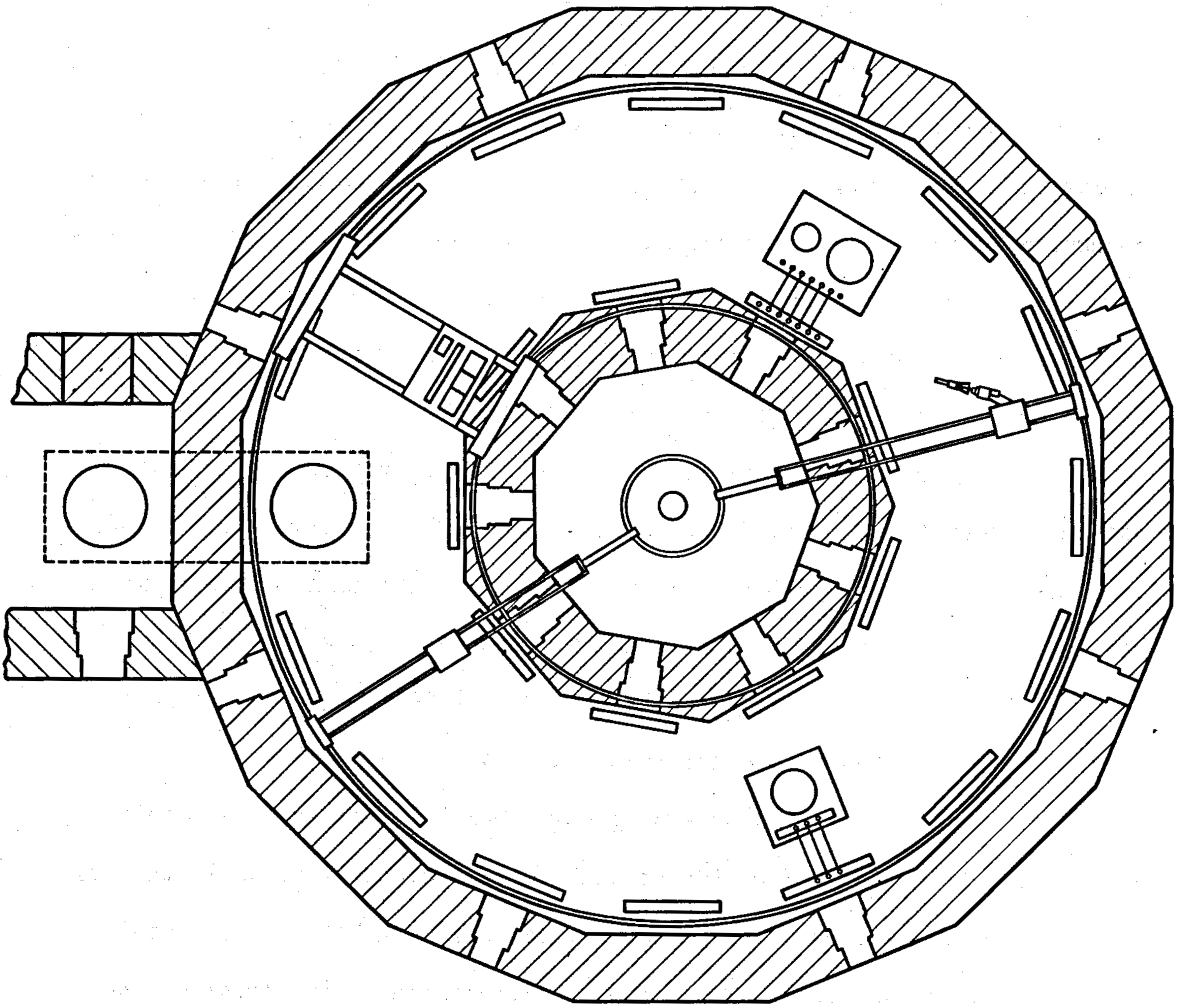

Fig. 13 - Inert atmosphere processing cell (plan).

wall to 1 mr/hour, giving an outer diameter of 72 feet. A shielded room (5 foot thick walls) for general supervision and operation is located centrally within the cell and extends up into the cell a distance of 10 feet, leaving a free height of 6 feet above it which constitutes a relatively low activity area into which cranes and manipulators may be moved when not in use. The operating annulus remaining is 16 feet in radial width. Floor levels of the interior observation area and the external operation areas are 3 foot lower than that of the hot cell, which places the cell floor flush with the lower edge of observation windows and brings most equipment operation to about eye level.

Several cell configurations were studied before a cylindrical cell was chosen. Its major advantages are the excellent visibility of all operations afforded by the interior supervisory area, and the considerable reduction in height over rectangular configurations made possible by a more compact vertical array of cranes and manipulators. The one obvious disadvantage is that its size cannot be increased. Consequently, adequate provision for expansion must be provided initially.

Operations may be viewed through windows located in both the external and internal walls of the cell. General viewing of all operations is convenient from the interior area. However, individual equipment items may be located along either the inner or outer interior walls of the annulus, and the specialized operations for individual equipment pieces will be made from the most convenient location.

Nine windows are equally spaced in the inner shielding wall; 13 in the outer. The windows will consist of thick (4 to 10 inches) plate glass laminations. The glass will be cerium-stabilized to resist darkening under radiation. The windows will be stepped to increase the viewable area, to eliminate straight-through radiation beams, to provide inner shielded gasketing surfaces, and to reduce cost.

Services will be brought into service strips located both around the exterior and interior cell walls. Services will be jumpered from these strips to service strips on the particular equipment items.

Two cranes and six manipulators will be employed. The manipulators will operate on two sets of tracks (below those for the cranes). The problem of power supply to the manipulators is considerably simplified over that for a long rectangular cell. Power will be distributed from an axial post. Two alternative methods are being considered: (1) the use of slip rings and (2) the use of fixed connections through cables which are allowed to wrap themselves around the central post up to a maximum radial motion of 270 degrees (see Figure 14). The cranes will be used to move heavy equipment and are in a position to replace the manipulators. Two types of manipulators will be employed. One type provides articulated motions (elbow, wrist, and gripping); the other provides only rectilinear and gripping motions for various routine lifting and transfer operations. In addition to the manipulators and cranes, special purpose equipment will be used in many materials handling operations.

Introduction of equipment and materials will be through inert gas locks, the covers for which are made leak-tight by solder freeze seals. Several sizes of locks will be provided. Attached to the processing cell will be a heavily-shielded air cell through which all material transfers are made and in which are performed those operations not requiring an inert atmosphere. A high-purity argon blanketing gas will be used in the circular cell (see discussion of inert gas system in Sec. 6c). In order to prevent air in-leakage to this process cell, which will be slightly negative with respect to the operating areas, a steel membrane will line the inner cell walls. High integrity of this membrane is required. This leads to special design requirements for sealing around windows and service inlets. The membrane will be cooled in certain areas for heat removal from the cell.

A basement area beneath the process cell provides access to the central operating room. Auxiliary processes and equipment items are also located in the basement. These include an inert gas purification system; heating, ventilating, air filtration and refrigeration units; induction heating equipment; cooling systems; etc.

General Considerations. In a remotely operated cell, both the processes and equipment must be greatly simplified. Each detail of equipment must be scrutinized to determine its suitability for remote operation. The highly radioactive environment must be considered in design of process equipment.

Organic materials such as rubber, neoprene, polyethylene

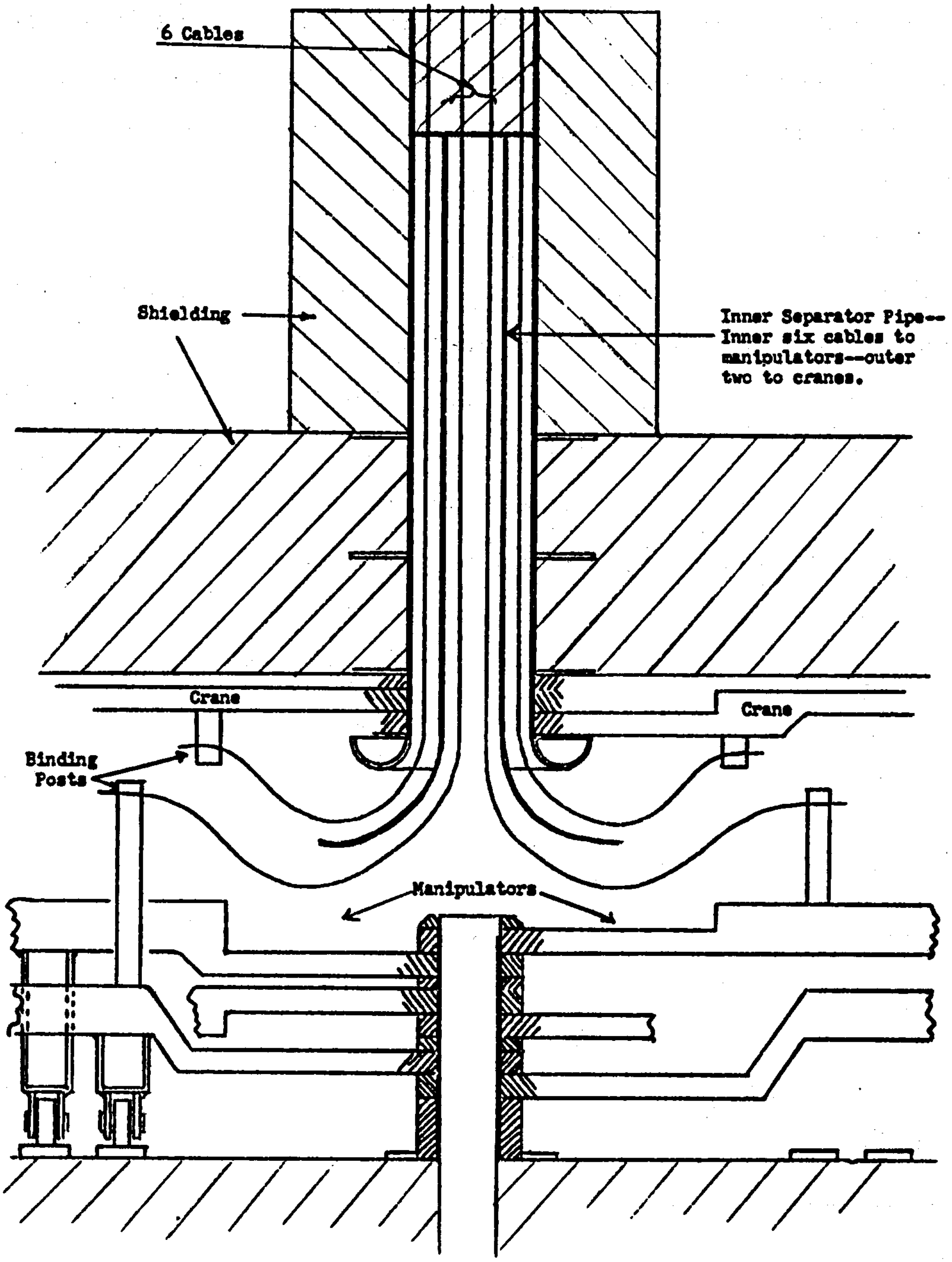

Fig. 14—Schematic Layout of Central Power Distribution System to Cranes and Manipulators.

oils and greases are damaged at from 10^7 to 10^8 roentgens and in our process cell, with 10^6 r/hour background, will last only a few hours. Plastic seals on vacuum equipment, bearings, gasketing for pipes and vessels must, therefore, be avoided or provision must be made to replace them at intervals not exceeding that for minimum damage.

Even the best non-browning optical glass will lose transparency in short periods of time. Optical systems exposed to the fuel, for example, inspection periscopes and microscopes, should be mirror optics. It may be necessary to equip windows with shield shutters to prolong the useful life or to make the front layers of windows replaceable. Conventional electrical insulation will be damaged in a few hours in the high radiation environment. Mineral insulated conductors and cables of the type using a compacted magnesia insulation in a swaged copper or steel jacket are satisfactory, provided a way may be found to seal the ends without the use of organic materials. Conventional electrical motors are not satisfactory unless they can be shielded.

Design and construction of this cell is scheduled to be completed in 1958; hot operations should commence late in 1959.

B. Pyroprocessing Refabrication Experiment (PRE)

The pyroprocessing-refabrication experiment is an engineering development program based on the remote pyroprocessing and refabrication of irradiated uranium metal fuel discharged from the SRE reactor. SRE are the code letters for Sodium Reactor Experiment which is a reactor of the thermal type, graphite-moderated and sodium-cooled. The pyroprocessing refabrication experiment is a part of the research effort supported by the U.S. Atomic Energy Commission for the development of new fuel processing systems such as the pyrometallurgical processes which offer promise of reduced fuel cycle costs. The proposed program involves the initiation of a series of mock-up engineering experiments on cold or unirradiated uranium, the construction of a shielded PRE facility and the carrying out of a group of processing and refabrication experiments using highly radioactive metallic uranium fuel which has been irradiated in the SRE reactor.

Since a very detailed description of this experiment has been written as a document which will become part of the Belgium Conference literature,[19] only a brief description of this experiment will be given here. In some respects the pyroprocessing refabrication experiment is similar to the program for the EBR-II reactor.

However, in the PRE facility, it is necessary only to process and refabricate fuel elements on an experimental basis. A closed fuel cycle will be carried out with the refabricated fuel elements. It is the goal of this demonstration program to provide information required for the design of large scale plants using the pyrometallurgical process approach.

The basic process for SRE uranium fuels as conceived at this time consists of the following steps:

A. Disassembly of SRE fuel clusters and decanning of the irradiated uranium fuel slugs in the SRE fuel rods.

B. Melting, oxide slagging or drossing, and re-enrichment of the uranium.

C. Casting the uranium back into slug form.

D. Inspecting the slugs.

E. Canning good quality slugs into SRE rods and assembling these rods into SRE fuel clusters.

In-cell cold process operations are scheduled to begin in 1960. Hot process operations will be undertaken about one year later.

The basic PRE flowsheet is shown in Figure 15 . The fuel is slightly enriched uranium. It is expected that a burn-up of approximately 0.3 per cent of the total fuel items will be achieved. Because of the high thermal cross-sections of some of the fission products, notably the rare earths and xenon, it is important that these elements be rather well removed from the SRE discharged fuel. For the activity level resulting from 0.3 per cent burn-up, a shielding wall thickness of 3 1/2 feet of heavy aggregate concrete is required to reduce the radiation level of the operating face of the cell to about 1 mr per hour.

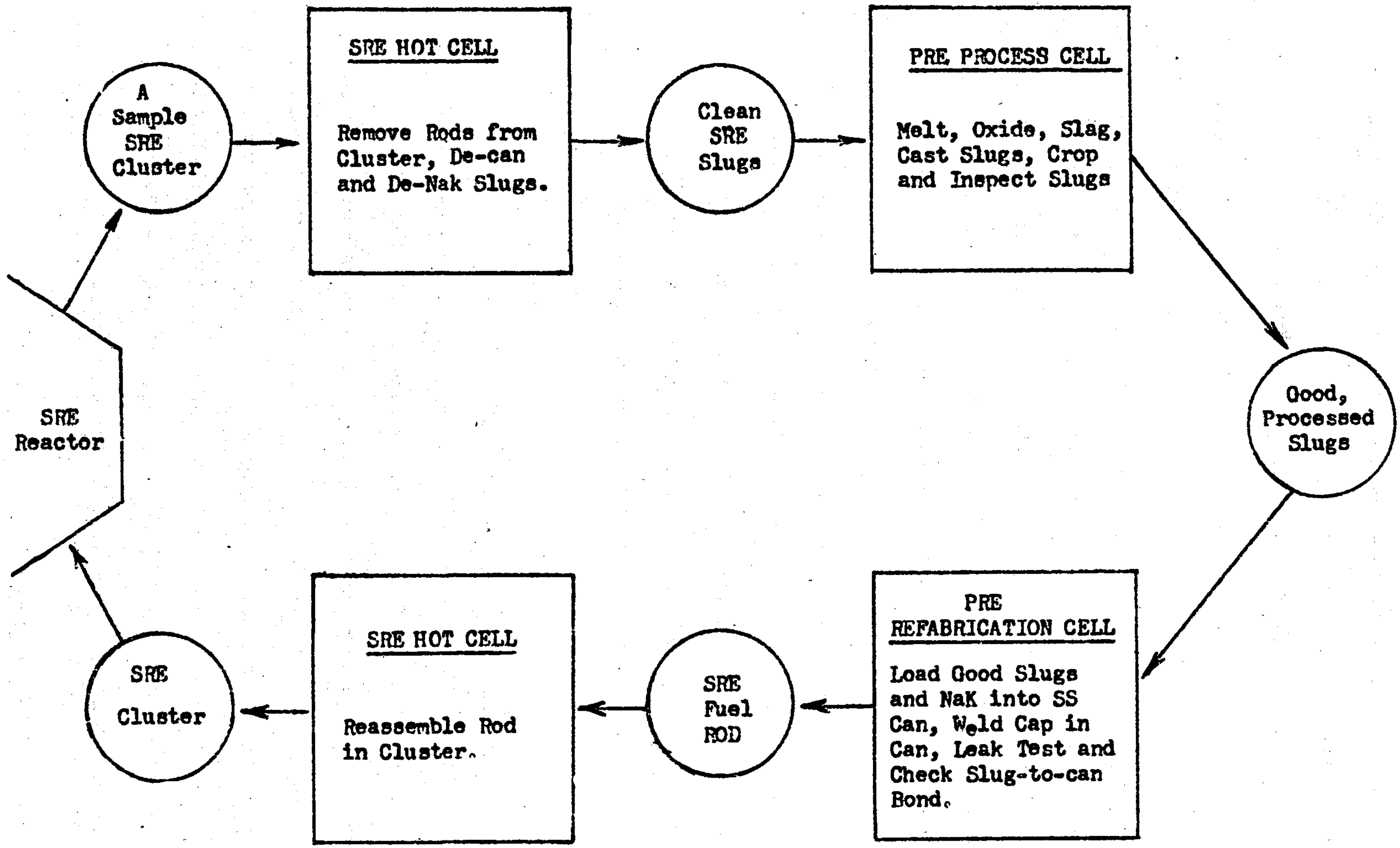

Fig. 15 – Basic pre-process flowsheet.

1. Fuel Processing and Refabrication

As in the EBR-II facility, purification of the irradiated fuel material will be effected by a melt refining operation in which the fission gases are liberated to the furnace atmosphere and the active elements such as the rare earths are removed in a reaction layer along the walls of the crucible. Two types of furnaces will be tested: a tilt-pour furnace (Figure 16), in which the melt is poured into the mold, and a bottom-tap furnace (Figure 17), using either a stopper-rod plug or a frozen metal seal. The fuel slugs will be cast directly into 6-inch long by 0.75-inch diameter slugs from the melt refining furnace.

Considerable equipment development and testing is required for materials handling within the cell, materials transfer into and out of the cell, and slug inspection. These include cranes, manipulators, special mechanical devices necessary to remove the fuel can, transfer mechanisms, vacuum locks, shielded caskets for transfer of material into and out of the cell, visual equipment including windows and periscopes and closed circuit TV systems, inspection devices, and decontamination equipment.

2. Inert Atmosphere Purification

As in the EBR-II facility, it will be necessary to maintain an inner atmosphere in the fuel processing and refabrication cell. Xenon and krypton fission product gases evolved in the melt refining operation are allowed to escape and mix with the inert cell gas. These fission product gases will be subsequently trapped in a charcoal adsorbent at liquid nitrogen temperatures which is part of the inert gas purification system. After the xenon has decayed to a safe activity level, the fission product gases will be vented to the atmosphere.

3. Hot Waste Disposal

The solid radioactive waste (crucible liners, skulls, and

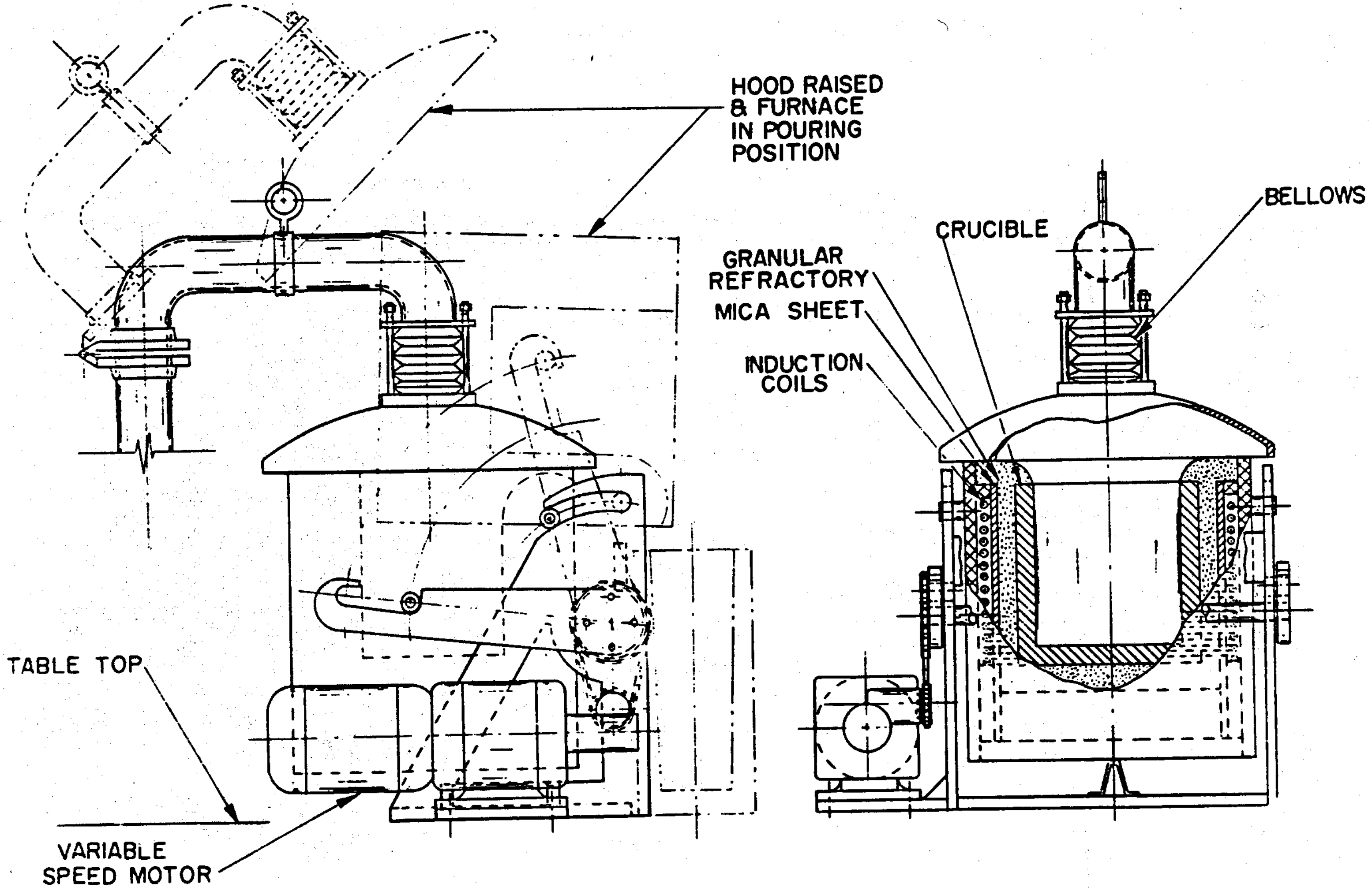

Fig. 16 - Tilt-pour furnace.

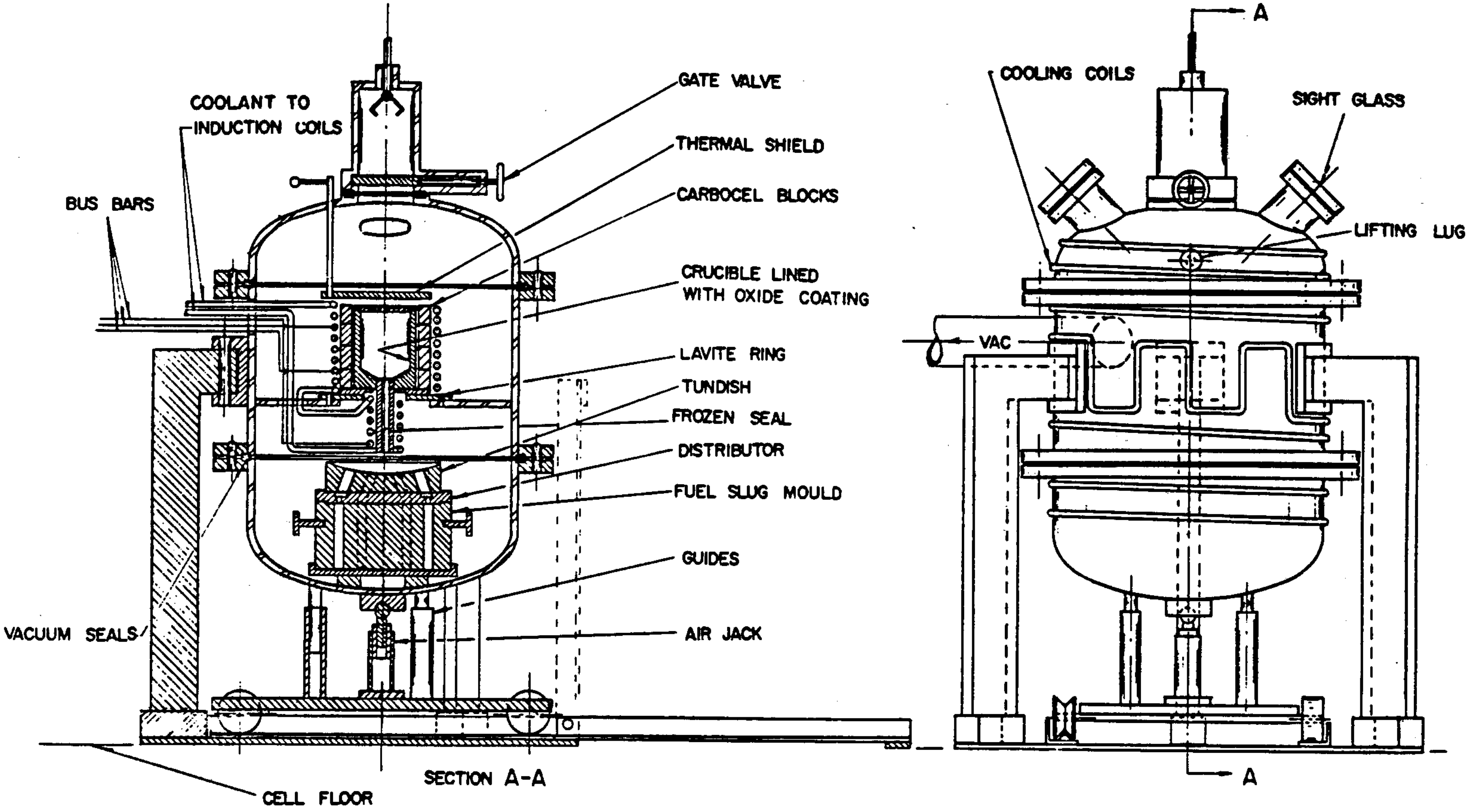

Fig. 17 - Vacuum furnace, bottom tap - frozen seal.

small pieces of contaminated equipment which are no longer useful) will be ram packed in steel cans and sealed for cooling and/or storage. Highly radioactive waste may require temporary cooled storage in a water reservoir before permanent land burial is possible.

C. Processing of Uranium Bismuth Reactor Fuels by Fused Salt Extraction

The liquid metal fuel reactor (LMFR) under development at the Brookhaven National Laboratory uses a fuel which is a solution of U^{233}, magnesium, and zirconium in liquid bismuth. The bismuth fuel solution also functions as the coolant and is continually pumped through the reactor and through heat exchangers for the removal of heat. The LMFR is a thermal breeder reactor in which the breeding is carried out in a blanket, the most promising blanket material being a thorium-bismuthide slurry in bismuth.

Since the neutrons-per-fission value for U^{233} at thermal energies is only 2.31, it is necessary to maintain very low concentrations of fission product poisons in the fuel in order to breed with a breeding ratio significantly greater than 1. For the low fission product concentrations desired in the LMFR, the rate of fuel processing is necessarily high in terms of the pounds of fuel which must be handled per day. However, under conditions of continuous operation, the bleed stream which must be removed continuously for fission product removal amounts to less than one gallon per minute for reactors having heat generation as high as 1,000 megawatts.

The process development work has been thoroughly documented in the open literature[20-27], and consequently will be discussed only briefly.

As in the melt refining operations, the fission products can be divided arbitrarily into three groups:

a) Those elements or compounds formed from fission product elements which are appreciably volatile at operating temperatures.

b) Non-volatile elements which form chlorides more stable thermodynamically than uranium chloride and elements which as anions form salts.

c) Non-volatile elements which form chlorides less stable than UCl_3.

In the first two groups are the elements which constitute by far the worst reactor poisons. These are xenon and the rare earth elements, with their very high thermal cross sections. The noble fission elements, owing to their low poisoning effect, can be allowed to build up to considerably higher concentrations in the fuel with less frequent processing of the fuel being required for their removal. It is proposed to remove the volatile fission products by a volatilization process consisting either of gas sparging or a simple desorption, the latter carried out under low pressure conditions if necessary. The stable fission products comprising the rare earth poisons can be continuously removed from the fuel by salt extraction with alkali and alkaline earth fused salt mixtures.

Two approaches have been proposed for the salt extraction process. The first, called the stoichiometric method, involves the use of a relatively strong oxidant in the salt mixture such as UCl_3 or $BiCl_3$ in concentrations just sufficient to remove the greater portion of the fission products from the fuel stream without oxidizing an appreciable amount of the uranium. A proposed carrier salt for the chloride oxidant is KCl-$NaCl$-$MgCl_2$ in the respective proportions of 18-24-58 weight per cent. The use of UCl_3 as the oxidant has the advantage that as the fission products are removed, uranium is simultaneously added to the fuel. The second proposed system is the buffer system in which the salt is again a mixture of KCl-$NaCl$-$MgCl_2$. In this case, the magnesium chloride salt is reduced by the rare earth fission products. The buffering effect results from the use of a magnesium salt in conjunction with magnesium metal in the fuel alloy. The magnesium in the metal phase serves to buffer the uranium and prevent its being oxidized. Although magnesium is introduced into the metal phase by reduction of magnesium chloride, the oxidation-reduction potential of this type of system is not affected by small changes in the concentration of the magnesium chloride in the salt or the magnesium in the metal and therefore can be easily controlled. However, the magnesium concentration in the metal should be held to around 100 parts per million.

At Brookhaven National Laboratory, both the austinitic Type 347 and the ferritic 400 series stainless steels have been used with good success, as long as the systems are oxygen-free. Zirconium and magnesium in concentrations of about 100 parts per million are added as corrosion inhibitors. It is believed that the zirconium functions as a corrosion inhibitor by forming a protective layer on the stainless steel surface. Magnesium serves as an oxygen getter. Its principal function, therefore, is to prevent the oxidation of uranium, and the subsequent loss of uranium from the solution by deposition on the surfaces of piping and equipment. Pretreatment and conditioning of equipment before use includes such operations as electropolishing, degassing under high vacuum at temperatures in the neighborhood of 800 C and contacting with magnesium-bismuth solution.

The corrosion aspects and system stabilities have been investigated in out-of-pile and in-pile test loops. An in-pile loop was operated in conjunction with external process equipment (Figure 18) for approximately 4,700 hours without incident until leakage developed with one of the electromagnetic pumps. In this time the concentration of uranium remained at 800 ppm ± 7 per cent. The salt mixture employed was the $MgCl_2$-NaCl-KCl buffered system containing 250 parts per million zirconium and about 20 parts per million magnesium. By the use of magnesium and zirconium inhibitors, corrosion has been reduced to small values, as indicated by constant concentrations of magnesium, chromium and iron, 17 ppm, 32 ppm, and 75 ppm respectively. However, the nickel concentration in the bismuth rose slowly (4 ppm/day for a weight of 110 kg

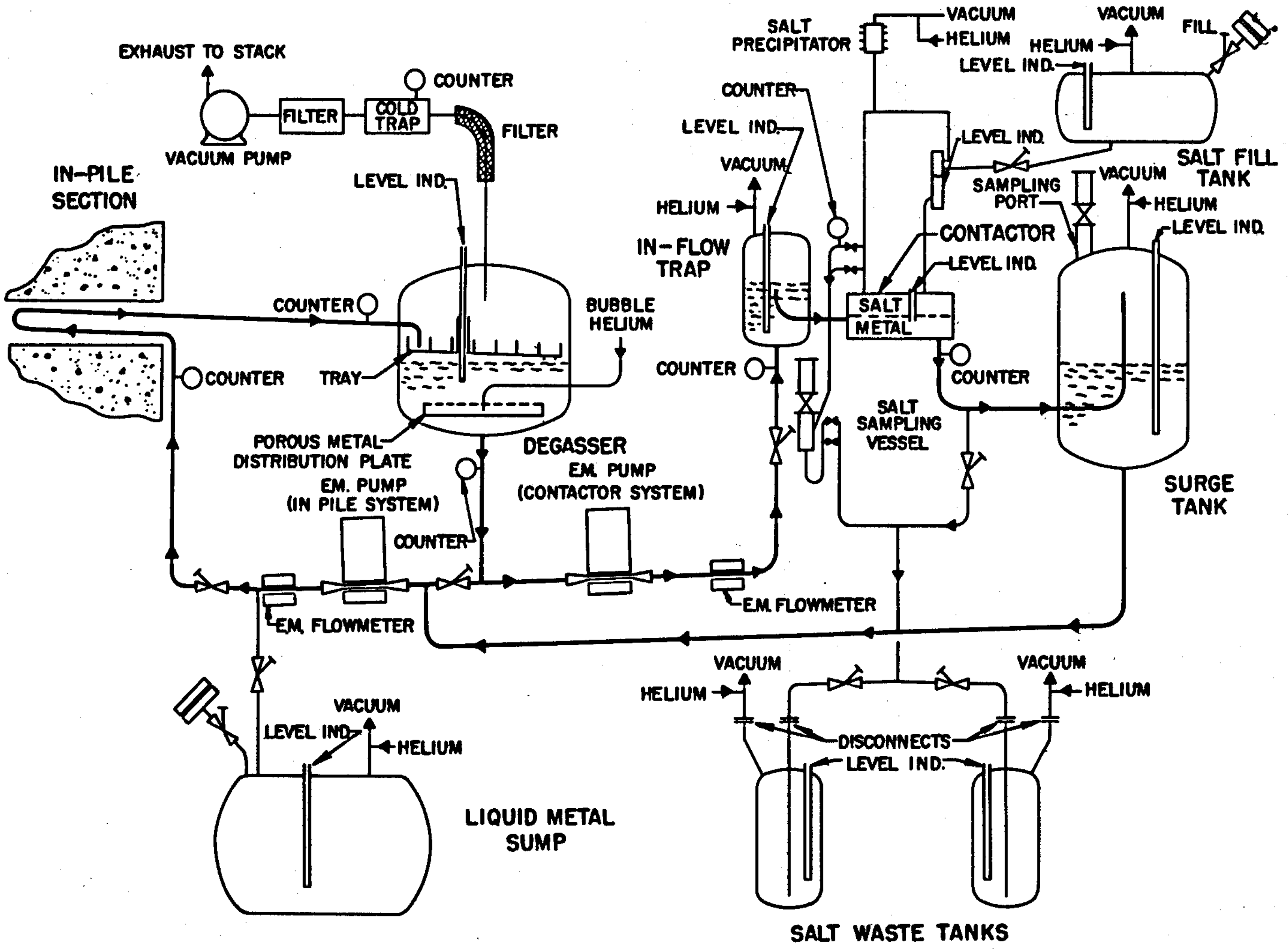

Fig. 18 - Flow diagram of in-pile processing loop, liquid metal fueled reactor.

of bismuth). The use of iron-chromium-molybdenum alloys is now being tested. All of the necessary components of the system were present in the in-pile loop, and various engineering operations have been carried out. These include sampling, salt-metal contacting, pumping, vacuum degassing, etc.

The failure of the electromagnetic pump cells indicates the need of a change in cell or mounting design to improve their reliability and to make the cells readily accessible for replacement.

A proposal for blanket processing consists of partial dissolution of the thorium-bismuth intermetallic by pulsed heating. This liberates bred U-233, and the undissolved intermetallic compounds are the seed crystals for growth of desirable equi-axed crystals formed on cooling. Thorium-bismuthide platelets crystallize from an unseeded solution, giving a non-Newtonian suspension which is difficult to handle.

D. Summary

Development of pyrometallurgical processes for fuel processing and refabrication was stimulated by the need for reducing fuel cycle costs for competitive nuclear power production. Although these are low decontamination processes, low decontamination is sufficient for reactor purposes, and is of minor consequence under continual fuel recycle conditions where the inbreeding of isotopes of the fissionable and fertile elements makes remote processing necessary even when fission product decontamination is high. Savings are expected by reduction of fuel inventory through rapid processing, use of simple, compact processes requiring no chemical conversion, recovery of expensive alloying agents, and simplification of waste disposal and criticality problems. Preliminary economic evaluations indicate fuel processing and refabrication costs of around 2 mills/electrical KWH.

To provide the necessary experience for large scale plants, three pyrometallurgical facilities are presently planned for integral operation with a reactor. These are the EBR-II fast breeder and the Sodium Reactor Experiment, for which the recovery process will be oxide drossing, and the Liquid Metal Fueled Reactor employing a dilute solution of uranium in bismuth to be purified by salt contacting. The engineering and economic feasibility of the remote pyrometallurgical fuel processing method, remote fuel fabrication and direct fuel recycle will be determined with these facilities.

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