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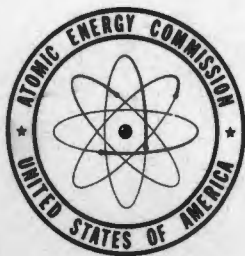
LIQUID-LIQUID EXTRACTION OF MOLTEN URANIUM WITH SILVER

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URANIUM WITH SILVER[*]

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ABSTRACT

In recent years interest in the United States in the nuclear field has been turning towards power reactors. Among the many problems that must be solved before economical electrical power can be produced from nuclear reactors are the problems connected with the processing of spent reactor fuels. The only reactor fuel processing methods available at present, the aqueous processes, are relatively complex, destroy the metallic character of the fuel, require "long-cooled" fuels necessitating high inventories of fissionable material, and leave huge volumes of radioactive waste solutions to be processed and stored.

For these reasons interest has been turning towards other processing methods, including "pyroprocessing" by liquid-liquid extraction of the molten fuel with silver. The purpose of this study was to develop a part of the equipment and technology needed to study the extraction of uranium with silver and to ascertain some of the problems that might be expected in processing of spent reactor fuels with a silver extraction.

A vacuum system was built in which to carry out uranium-silver contacting; induction heating equipment was set up to heat the materials. Temperature measuring methods and techniques for use in liquid metal extraction work also were studied. Chromel-alumel, platinum-platinum rhodium, and columbium-tungsten thermocouples were investigated. Graphite was selected as the best container material for the molten metals and was used satisfactorily in all of this work.

A number of uranium-silver melts were made in which the phase separation and mass transfer were studied. Phase separation was sharp but occasional macroscopic inclusions were found in both phases. Microscopic phase separation was complete. Uranium

was found to crystallize out of the silver phases as they cooled
and to settle towards the interfaces. Mass transfer of the
uranium to the silver appeared to be fairly rapid.

A graphite extractor for passing silver through a pool of
molten uranium was designed and tested. It was found to be
very simple to operate, easy to fabricate, and capable of
transferring nearly equilibrium amounts of uranium to the silver.

A number of recommendations are presented for improving
the equipment and techniques used in this study, along with some
proposals for future work in this field. A pyroprocessing
scheme, based upon a silver extraction of the fuel in the ex-
tractor designed in this study, is proposed as a basis for
further study.

INTRODUCTION

The inherent disadvantages and the high processing costs
of present day aqueous methods of processing irradiated re-
actor fuels have given rise to an increasing incterest in the
"pyroprocesses" or high-temperature, non-aqueous processes.
One of the more promising of these processes is the liquid-
liquid extraction of the molten fuel with silver.

Scouting work was done on the behavior of plutonium and
fission products in metallurgical operations with irradiated
uranium at Iowa State College in 1942-1943. It was found that
plutonium and some of the fission products could be extracted
by metals that were immiscible with uranium in the molten state.
The most promising of these metals was silver (1).

This work was extended in 1950-1955 and a paper summarizing
it was presented by Voigt in 1955 (2). It appeared that the
fission products could be divided into several groups which
exhibited similar behavior. Certain fission products such as
Cs and Sr were removed by volatilization. The non-volatile
rare earths extracted readily into silver. A third group,
Te and Zr, was removed by silver but not as readily as the
rare earths. Finally, there was a group consisting of Ru and
and Mo which remained with the uranium. Plutonium was found
to extract fairly readily into silver.

In a pyroprocessing scheme for spent reactor fuels a
silver extraction of the molten fuel would be only a part of
the overall process. Figure 1 shows a possible pyroprocessing
scheme using a silver extraction step. As can be seen, several
other pyroprocesses would be involved in such a scheme. Most
of these lack the necessary technological development for in-
corporation into a pyroprocessing plant, but it is believed
that these developments are possible if such a scheme continues
to show promise.

In undertaking a study of the liquid-metal extraction pro-
cessing of irradiated uranium, one finds that not only is there
a lack of fundamental data concerning the variables affecting
the removal of various fission products, equilibrium relation-
ships, solubilities, and operating conditions, but a serious
deficiency also exists in the development of facilities
and technology with which to obtain such data. The purpose
of the present investigation is to help to develop a part

Figure 1. Flow Sheet for a Possible Pyroprocessing Plant.

of this equipment and technology and to ascertain some of the problems that might be expected in the processing of molten reactor fuels with molten silver.

EQUIPMENT

Vacuum system

Uranium is highly reactive with oxygen (and nitrogen to a lesser extent) and is discolored in air at room temperatures. At high temperatures it burns readily. Thus, the maintenance of an inert atmosphere is necessary in any pyroprocess for uranium.

A vacuum system was built to maintain an inert atmosphere in the runs of this study. Figure 2 shows a diagram of this system. The system consisted of a quartz tube, two water-cooled brass heads, a Welch #1400 Duo-Seal Vacuum Pump, and a Distillation Products Model TG-02 thermocouple vacuum gauge.

The working pressure of this system was 15 to 18 microns of Hg, obtained with pumping times of 30 to 45 minutes. The leak rate when the pump was turned off was 0.1 to 5 microns of Hg per minute depending upon the pumping time used. Longer pumping times always gave lower leak rates. Although the addition of a diffusion pump would have reduced the pumping time, the metal losses were not large with the system and such an addition did not appear to be justified in this study.

It was noted that the first pump-down of the system each day or after the system had been open to the atmosphere gave a pump-down curve somewhat higher than pump-downs which immediately followed. Thus, it appeared that some material was being adsorbed from the atmosphere by the system when it was open. The variance of the leak rate with pumping time also indicated that some material was adsorbed upon the surfaces inside the vacuum system.

Induction heating equipment

To allow greater convenience and flexibility in heating the materials in this study, it was decided to use induction heating. An Ajax-Northrup, 220 v., 60 cycle, single phase,
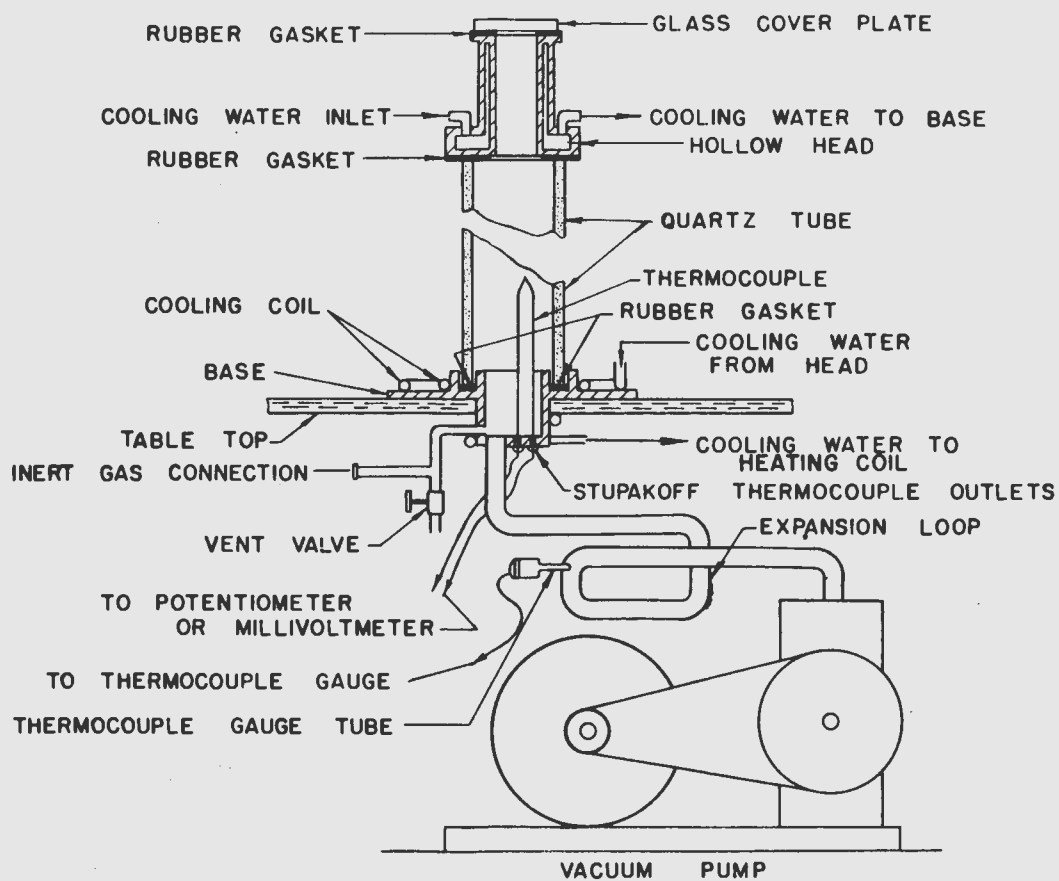
Figure 2. Vacuum System.

6-kw, closed spark-gap converter was used in conjunction with a 2 7/8" I. D. x 3¼" high induction coil purchased with the converter.

Figure 3 shows a diagram of the heating coil and its sliding mount for positioning it around the quartz tube.

To obtain the usual operating temperatures of 1200 to 1350°C with no insulation around the load required a converter power setting of 3.0 to 4.0 kw using 1" O. D. x 2" long crucibles with ¼" thick walls and 3.5 to 5.0 kw for the 1 5/8" O. D. x 5 3/4" long extractors used in later work.

An attempt was made to establish a temperature vs. converter power setting curve for a given graphite crucible. However, the curve was easily shifted parallel to itself by very small variations in the relative positions of the load and the induction coil in different experiments. A family of such curves might be of value for controlling the temperature during a run by controlling the converter power setting, after having first established one point on one of the curves.

TEMPERATURE MEASUREMENT

An optical or radiation pyrometer could not be used to measure temperatures at various locations in this extractor without tailoring the equipment to meet the "black body" conditions required by such a pyrometer. This would have imposed serious limitations upon furnace and extractor design in this study. A pyrometer's view might also be obscured by vapors and gases from the hot metals. The use of some type of thermocouple appeared, then, to be essential.

Three types of thermocouples were investigated. These thermocouples and their published useful ranges were (3) (4) (5): Chromel-alumel, about 1300°C; platinum-platinum rhodium, about 1600°C; columbium-tungsten, greater than 1900°C.

Failure of platinum-platinum rhodium thermocouples was encountered repeatedly at 1450 to 1550°C. Graphite appeared to have a detrimental effect, but even with protection from the graphite the thermocouples were not reliable above 1500°C.

TOP VIEW

QUARTZ TUBE

COIL MOUNT

ELECTRICAL
CONNECTIONS

SET SCREW

COOLING
WATER

INDUCTION COIL
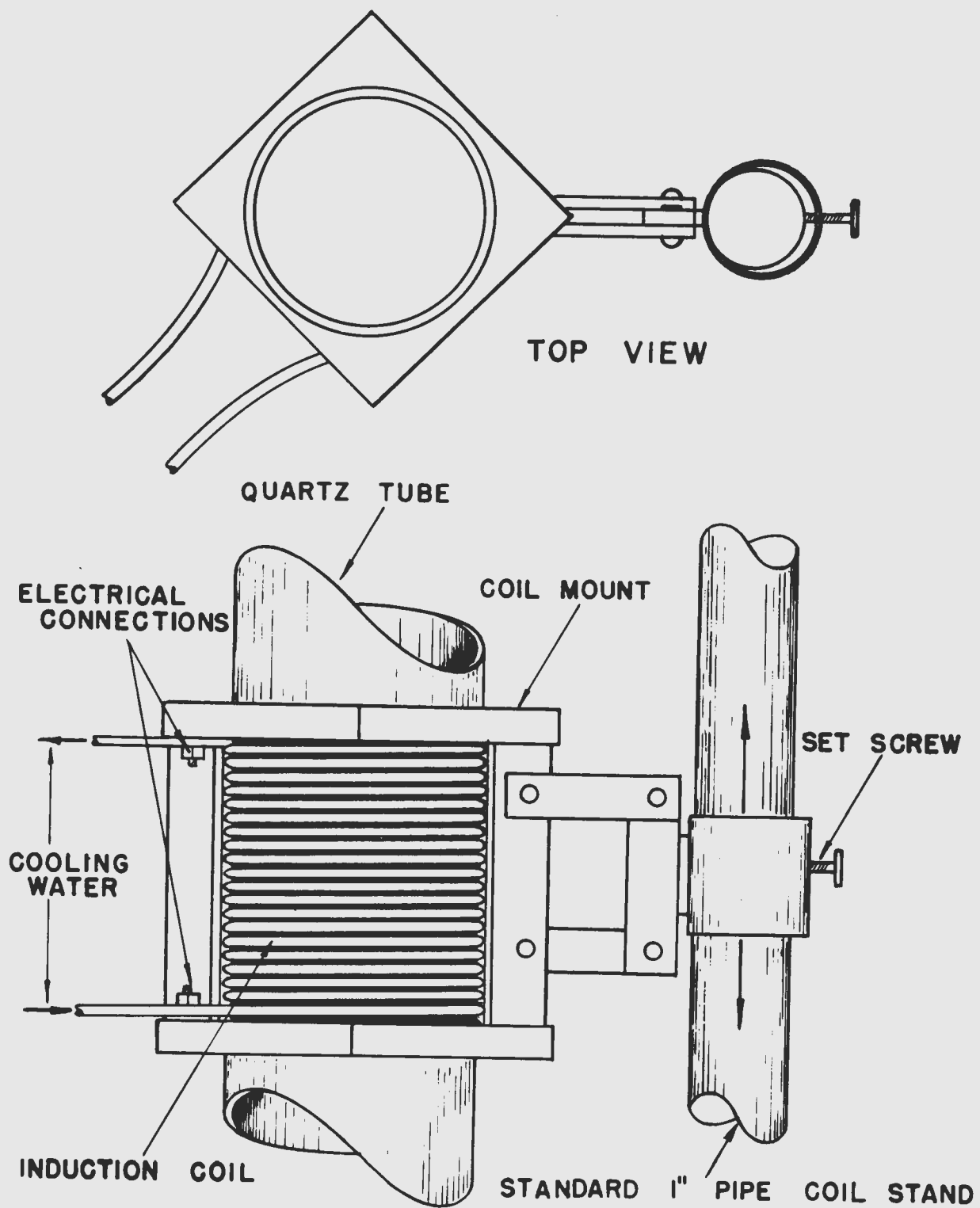
STANDARD 1" PIPE COIL STAND

Figure 3. Induction Heating Coil.

Temperatures of 1300 to 1320°C were measured for relatively long periods (one to two hours) with chromel-alumel thermocouples with no apparent damage to the thermocouples. Temperatures of 1325 to 1350°C were measured consistently for periods of about 30 minutes. However, at these temperatures the thermocouples were often attacked, although little difficulty was encountered from thermocouple failures.

It was concluded from these studies that the additional temperature range afforded by the use of platinum-platinum rhodium thermocouples was not sufficient to warrant their use in view of the expense and extra precautions that would be necessary.

Columbium-tungsten thermocouples were investigated briefly (5). It was concluded that they do not offer much promise for use in this work. The initial brittleness of the tungsten makes thermocouple fabrication difficult and the additional embrittlement caused by heating makes the thermocouples very difficult to reuse. The calibration also changes from thermo-couple to thermocouple (6). A more serious limitation was found in attempting to calibrate columbium-tungsten thermocouples. The calibration apparently shifts with a given thermocouple as it is heated. This calibration shift is presumably re-lated to the crystal changes in the metals which lead to the embrittlement.

Crucibles and refractory materials

After a survey of possible materials to contain molten uranium and silver, it was decided that the only fairly satis-factory material for this study was graphite. Graphite has excellent resistance to thermal shock, has adequate structural strength, is easy to fabricate, and is relatively inexpensive. There is evidence also (7) that zirconium, which is one of the more difficult fission products to remove, can be removed by carbide slagging. Graphite has been used with considerable success in previous investigations (8) (9). The carbon dis-persed throughout the uranium, when using graphite to contain molten uranium, does not appear to be a prohibitive factor.

Type AGR graphite was used in this work. Ash content of this graphite was 0.10 to 0.16% and consisted mainly of Ca

with moderate amounts of Ti and traces of Zr also present.

A disadvantage in using graphite as a container material is the degassing required before each run in order to keep adsorbed gases from contriubting to uranium losses. Degassing of the crucibles used in this study required heating them under vacuum for 1 to $2\frac{1}{2}$ hours at temperatures of 1200 to 1400°C to bring the pressure in the (hot) system down to 30 to 60 microns of Hg. Degassing times were longer for new crucibles; also degassing times for previously degassed crucibles increased as a function of time exposed to the atmosphere. Thus, it appeared that some material was adsorbed from the atmosphere upon the graphite. Higher degassing temperatures also produced faster degassing. The development of a thermocouple to measure temperatures above 1400°C would be of advantage in allowing a crucible to be degassed in place at high temperatures just before a run.

Graphite "pot" crucibles were used in preliminary equipment testing and phase study runs. These were of two sizes, 7/8" I. D. x 2" long with 3/16" thick walls, and 1" I. D. x 2" long with $\frac{1}{4}$" thick walls. In some of these runs graphite lids were fabricated to fit the crucibles.

A uranium-silver contactor was designed for use in later work. Figure 4 shows a full-size section view of this contactor. It was fabricated from a solid cylinder of graphite 1 5/8" in diamter by 3" long with holes drilled in it as shown. Portions of the holes were closed off by force-fitted graphite plugs to form a continuous leg inside the contactor. A threaded graphite plug closed the top of the center leg. Also shown in Figure 4 are a silver holder and lid, a solvent recovery capsule, a condensing lid, and a reclaimed silver collector.

The contactor was used to pass a given amount of silver through a pool of uranium and operated as follows: The uranium and silver legs were filled with pre-cut uranium and silver rods such that the two heads would be equal when the metals were melted. The threaded plug was then put in place. The silver holder (full of silver) was put in place on top of the extractor and the extractor was put in place on top of the silver recovery capsule. The unit was then evacuated in the vacuum system and the center (extractor) portion of the unit was heated. When the extractor temperature was above the melting
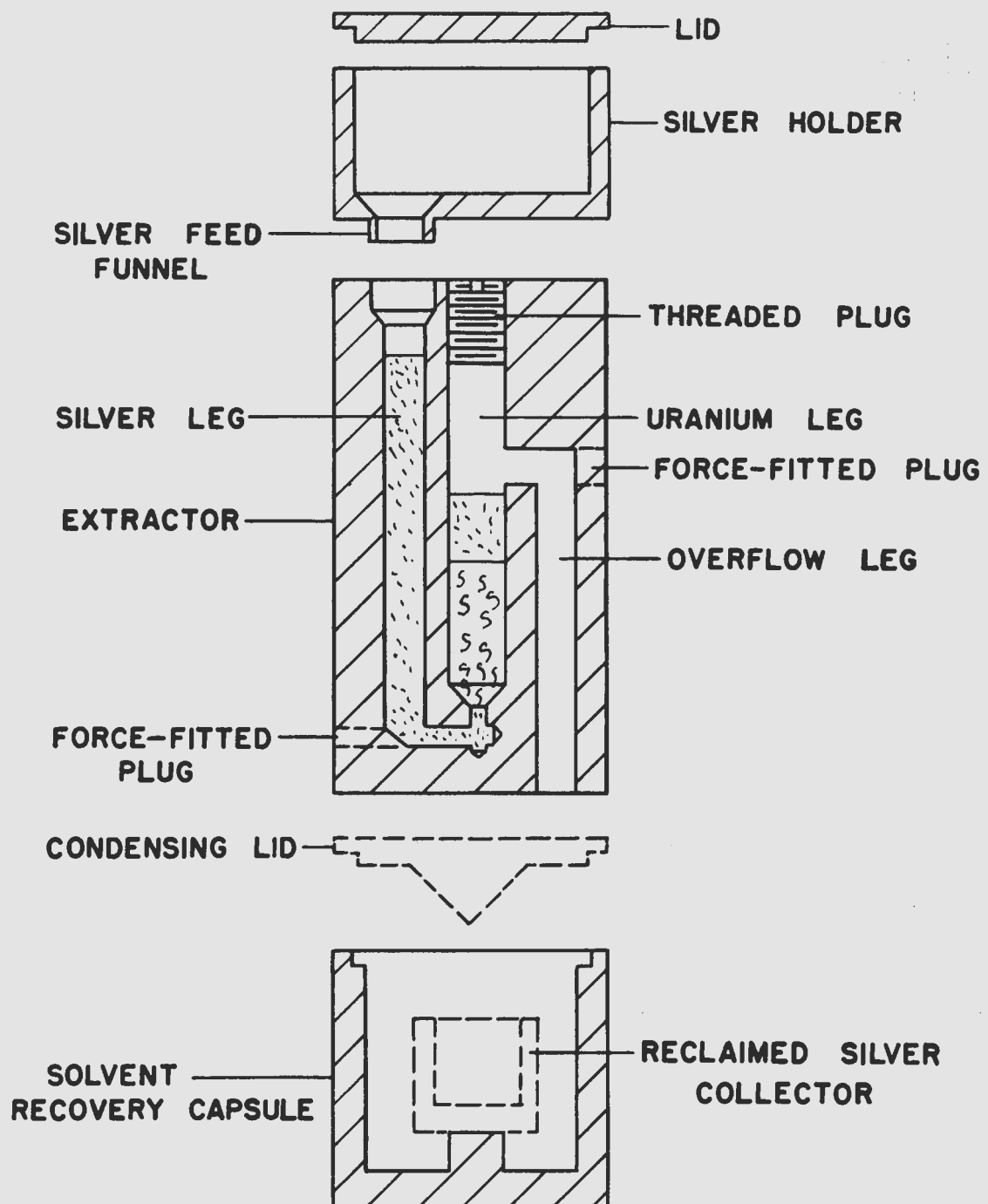
Figure 4. Uranium - Silver Extraction Unit.

point of uranium, the silver holder was at about the melting point
of silver. The silver was then melted into the silver leg. As
the silver dropped into the silver leg, silver was forced out
the bottom of this leg into the uranium leg where it rose to the
top of the uranium and overflowed through the overflow leg
into the solvent recovery capsule.

A scheme that might be used to recover the silver from
such an extraction was devised using a method similar to a
North American Aviation proposal (10). This is also shown
in Figure 4. Although it was not tested, it would operate as
follows: After an extraction has been made and the extract
has been collected in the capsule, the contactor and silver
holder would be removed and a condensing lid and silver collector
put in place (dotted lines in Figure 4). The recovery capsule
would then be heated and the silver vaporized, condensed on the
condensing lid and dropped into the reclaimed silver collector.
The plutonium and fission products would remain in the lower
part of the capsule while the recovered silver would be removed
in the collector and reused in another extraction.

OPERATING PROCEDURES

The general procedures followed in making the runs were
as follows:

(1) After a preliminary evacuation of the cold system
containing the crucible or extractor to be used, the system
was heated to degas the refractory materials.

(2) The power was then shut off and the system was allowed
to cool to about 150°C.

(3) While the system cooled, the uranium was cleaned
with 1- to -1 or 3- to -1 ratio nitric acid to water and the
metals were prepared for charging to the system.

(4) The cooled system was then opened, the metals were
charged, and the system was reassembled again as quickly as
possible to minimize the adsorbtion mentioned earlier.

(5) The system was reevacuated after the run was completed
and was allowed to cool again.

(6) The melt was then sectioned with a carborundum wheel and cut into samples either to be analyzed for their constituents or to be examined microscopically.

The samples were analyzed for uranium, silver, carbon, and nitrogen. The analytical methods used in these analyses were:

Uranium (high uranium content) - reduced with lead and titrated with ceric ion.

Uranium (low uranium content) - spectrophotometric analysis via thiocyanate complex.

Silver (high silver content) - precipitated as silver chloride and weighed.

Silver (low silver content) - spectrophotometric analysis via silver rhodanine method.

Carbon - burned in an induction furnace, collected as carbon dioxide on ascarite, and weighed.

Nitrogen - Kjeldahl method.

Microscopic examinations and microphotographs of some of the melts were also made. These were made with an American Optical Company Model 2400 Metallograph.

EXPERIMENTAL RUNS

Uranium melting runs

A number of uranium melting runs were made in $1\frac{1}{2}$" O. D. x 2" long "pot" crucibles to check the temperature measurements at the melting point of uranium and to study the effect upon uranium losses of final degassing pressure, leak rate of the system, and heating time of the runs. Uranium losses were determined by the weight difference before and after the runs.

The melting points of uranium measured by the chromel-alumel thermocouples agreed quite well with the Handbook value of 1130°C. Placing the thermocouples in the top of the crucibles

gave essentially the same results as placing them in the bottom.
Thus, the crucibles were apparently at uniform temperature
throughout.

The most important factor in determining how much uranium
was lost in a given run was the length of time that the metal
was hot. Uranium losses ranged from about 0.1% in 10 to 15
minute runs to about 0.7% in 60 to 70 minute runs. The effect
upon metal losses of leak rate of the system and of the final
degassing pressure before the run were masked by the effect
of heating time. The variations of uranium losses due to the
two former effects were apparently small for leak rate variations
from 3 to 18 microns of Hg per minute and for final degassing
pressure variations from 34 to 120 microns of Hg.

Two uranium melts were made to test the flowing of uranium
through graphite holes. The uranium was placed in a 1 3/8"
O. D. x 1 5/8" long graphite crucible with a funnel bottom
(3/8" diameter hole). It was then melted through the hole into
another crucible. No difficulty was encountered in melting the
uranium through the 3/8" hole, except that a metallic scum
was left in the funnel. From a chemical analysis of this scum
its composition was determined to be as follows:

$$U \text{ (metal)} - 79.23\%$$

$$UO_2 - 12.15\% \text{ (estimated)}$$

$$U_3N_4 - 0.81\%$$

$$UC_2 - 8.10\%$$

This corresponded to about 0.7% of the original uranium.
The low nitrogen content should be noted in this and other runs.
This indicated that little air contamination was present in the
system.

Uranium-silver crucible contacting

Uranium and silver were contacted in the "pot" crucibles
mentioned previously to study the rate of mixing of the two molten
metals in an induction field and also to study their phase
separation characteristics.

Number 1 and number 2 of Table 1 show two of these runs.

Table 1

Uranium-Silver Contacting Runs

No.	Description of Run	Sample	Uranium	Silver	Carbon	Nitrogen
				Analyses (%)		
1	"Pot" contacting in 1½" O. D. x 2" long crucible	Top of silver phase	5.12	94.49	-	-
		Bottom of silver phase	8.47	90.12	-	-
		Uranium phase	98.28	1.50	-	-
2	"	Top of silver phase	5.01	95.62	-	-
		Bottom of silver phase	8.96	90.48	-	-
		Uranium phase	99.59	0.23	-	-
3	Extractor contacting	Silver overflow	3.60	95.4	0.0103	0.0085
4	"	Silver overflow	3.85	95.22	-	0.0040
5	"	Silver overflow	4.85	94.51	-	-

The uranium was molten for 14 minutes in number 1 and for 4 minutes in number 2. Since the solubility of silver in uranium is about 0.3%, the analysis of the uranium phase in run number 1 is apparently in error. This was probably due to silver inclusions taken with the uranium sample which was used for analysis. Such silver inclusions could be seen in the uranium phase near the sample taken. No uranium inclusions were present near the samples taken from the silver phases and these analyses are believed to be correct. Since the uranium concentrations in the silver phases were nearly identical for both the 14 minute run and the 4 minute run, these were apparently equilibrium values.

The difference in the uranium concentration between the upper and the lower parts of the silver phases is attributed to the settling out towards the interface of uranium which crystallized out of the silver as the molten metals cooled. Figure 5 shows the lower part of the silver phase in one of these crucible runs. A number of dendrites of uranium can be seen. Figure 6 shows the interface in one of these runs.

Figure 5.   Lower Part of the Silver Phase in a
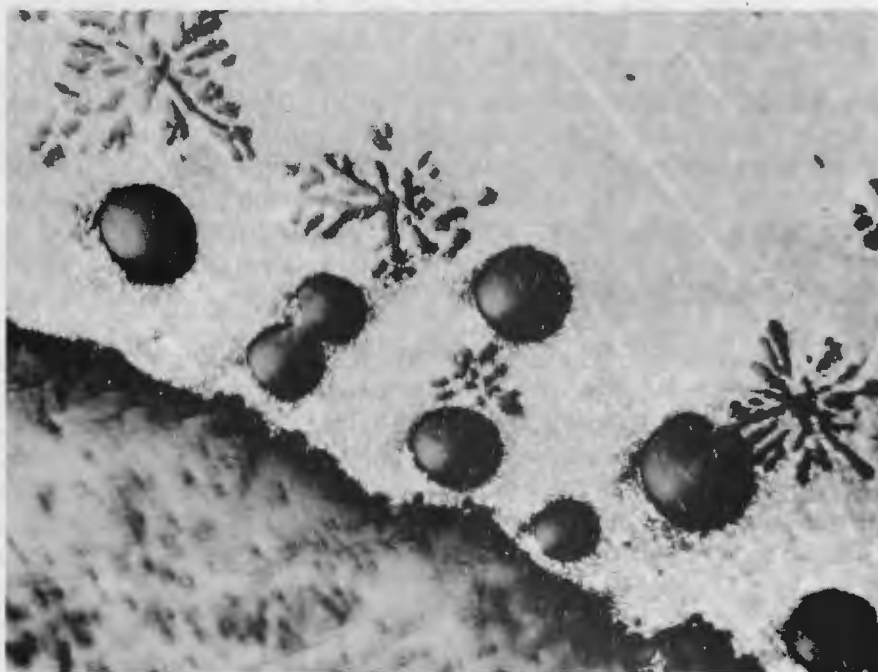   Uranium - Silver Melt. (Magnification - 200X)

Figure 6.   Interface in a Uranium - Silver Melt.
            (Magnification - 250X)

Here, the difference can be seen between the uniform rounded
inclusions found only near the interface and the dendrites found
at some distance above the interface. The rounded inclusions
are believed to be uranium which crystallized out of the silver
while the silver was still above the melting point of uranium.
These apparently had time to settle nearly all of the way out
of the silver before it solidified.

Phase separation was distinct in these crucible contacting
runs, although a few large inclusions could be seen in both phases.
Figure 7 shows the sectioned crucible contacting runs of Table 1.
A large "finger" of uranium can be seen extending up into the
silver phase in one of the runs (number 2 in Table 1). A few
other small inclusions were also noted in both phases near the
interface in each run.

It was concluded from these crucible runs that: (1)
Equilibrium mass transfer of uranium to silver can be attained
with inductive mixing in a comparatively short time (less than
4 minutes) in static melts of this size. (2) Phase separation
is distinct, although care must be exercised in cooling the melts
and in separating the phases in order to avoid macroscopic in-
clusions in both phases. (3) Microscopic phase separation
is complete. (4) Uranium crystallizes out of the silver phase
as it cools and settles towards the interface causing the con-
centration of uranium to be higher in the lower part of the
silver phase than in the upper part. Closer control of the temp-
erature might enable the silver to be maintained just above its
melting point long enough for these crystals of uranium to
completely settle out of the silver. (5) "Oxidation" products
and slags are apparently taken out of the uranium by the silver
leaving a relatively "clean" uranium phase.

Uranium-silver extractor contacting

After the uranium-silver crucible contacting runs were com-
pleted, a number of extractor contacting runs (numbers 3, 4,
and 5 in Table 1) were made with the extractor pictured in
Figure 4.

Figure 8 shows the sectioned extractor unit of run number 5
and an unused unit (extractor-silver holder recovery capsule)
ready for another run. The path of the silver as it was forced
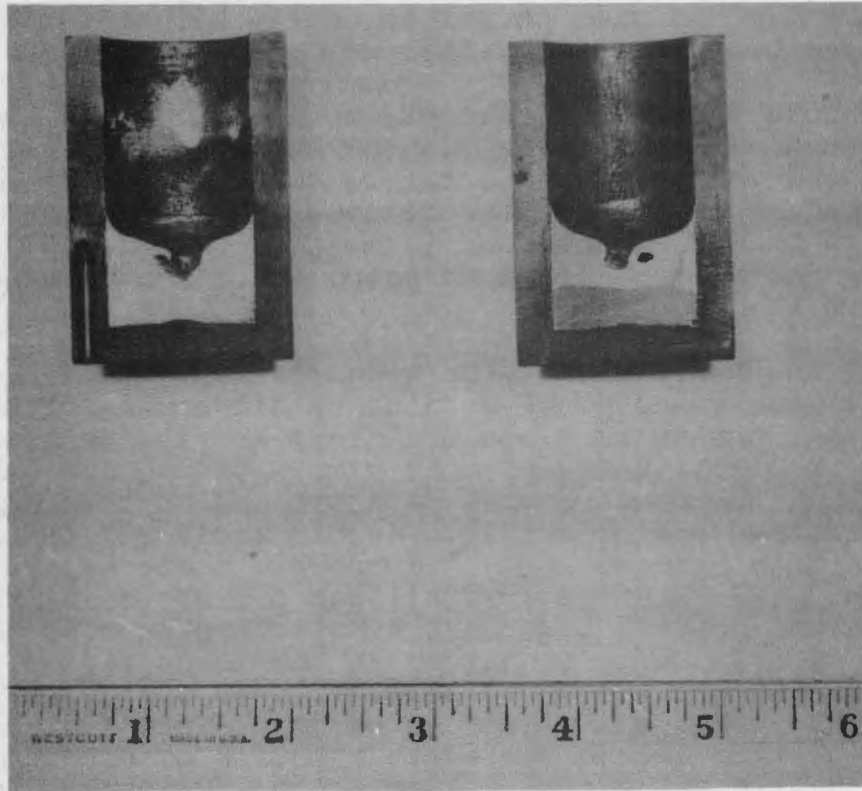over into the uranium (center) leg can be seen, plus a few

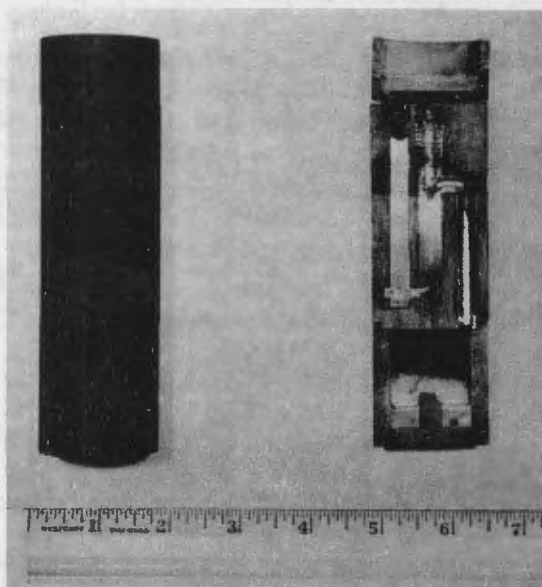**Figure 7. Sectioned Uranium - Silver Contacting Runs.**

Figure 8. Sectioned Extractor After a Contacting Run
and an Unused Extractor, Silver Holder, Solvent
Recovery Unit Ready for Another Run.

"bubbles" of silver that were frozen in the uranium before they reached the silver above the uranium.

The following other points were noted in these runs: (1) As in the crucible contacting runs, the "oxidation" products were swept out of the uranium by the silver. This "slag" formed a thin gold-colored film on top of the silver above the uranium, in the overflow leg, and on top of the silver overflow (Figure 8). This action might offer an important means of decontaminating uranium fuel since fission products are known to concentrate in such slags. (2) The uranium wetted the graphite and caused surface fractures on the extractor in the uranium leg when the uranium contracted upon solidifying. (3) No silver losses through volatilization from the unit were found, although the bottoms of the extractors were covered with silver which was distilled from the silver overflows in the solvent recovery capsules.

Phase separation in these extractor runs was quite sharp, although, as in the static runs, macroscopic inclusions were occasionally found in both phases. Figure 9 shows the interface in run number 3. Small, rounded inclusions in the silver (light) phase near the interface, similar to those discussed in connection with the crucible contacting runs, can be seen in the figure. The dendrites of uranium were also found in the extractor runs. Two silver inclusions can be seen in the uranium (dark) phase in Figure 9.

Figure 10 is a microphotograph of the silver used in run 3 before it contacted the uranium. This silver contained 0.08% uranium. Figure 11 shows a similar picture of the same silver after having passed through the uranium. The uranium-silver eutectic at about 5% uranium (11) can be seen throughout the phase. Two of the dendrites mentioned before can also be seen in the lower left-hand corner of Figure 11. As can be seen, microscopic phase separation was quite good. The uranium-silver eutectic was well dispersed throughout the silver phase and no uranium inclusions were found in the silver besides the "crystals" in the lower part, as mentioned previously.

Run 3 (Table 1) had a $\frac{1}{4}$" leg connecting the uranium and silver legs while runs 4 and 5 had 5/32" legs. It was found that connecting legs smaller than 5/32" would not allow the silver to pass through into the uranium. The head of uranium through which the silver was passed was 3/4" in runs 3 and 5 and $\frac{1}{2}$" in run 4. As can be seen from Table 1, run 4 transferred more uranium to the silver than run 3, although run 3

Figure 9.   Interface Above the Uranium in a Sectioned
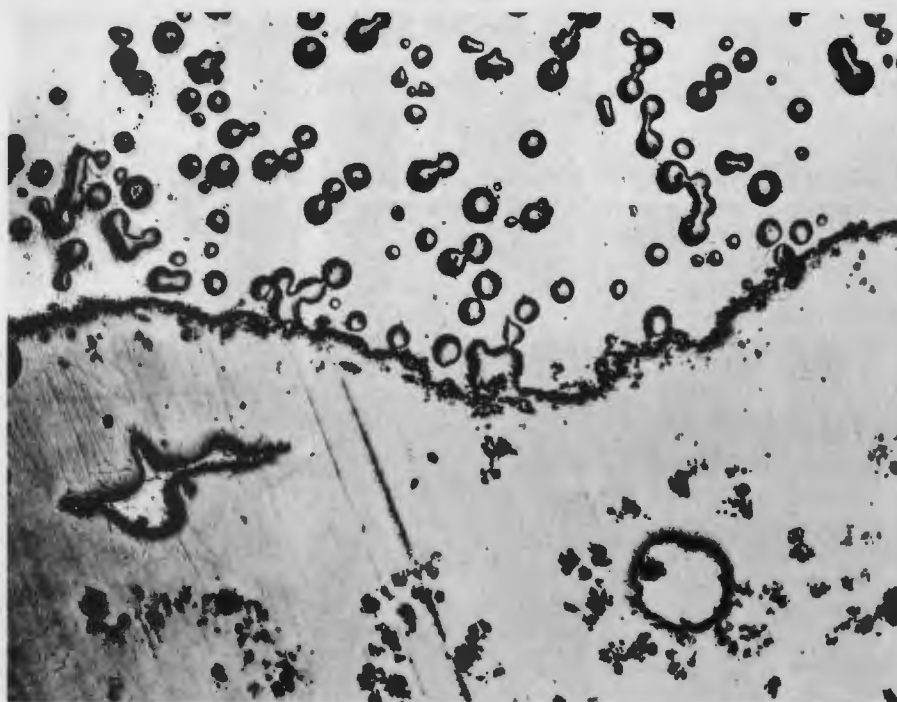   Extractor After a Contacting Run.
            (Magnification - 200X)
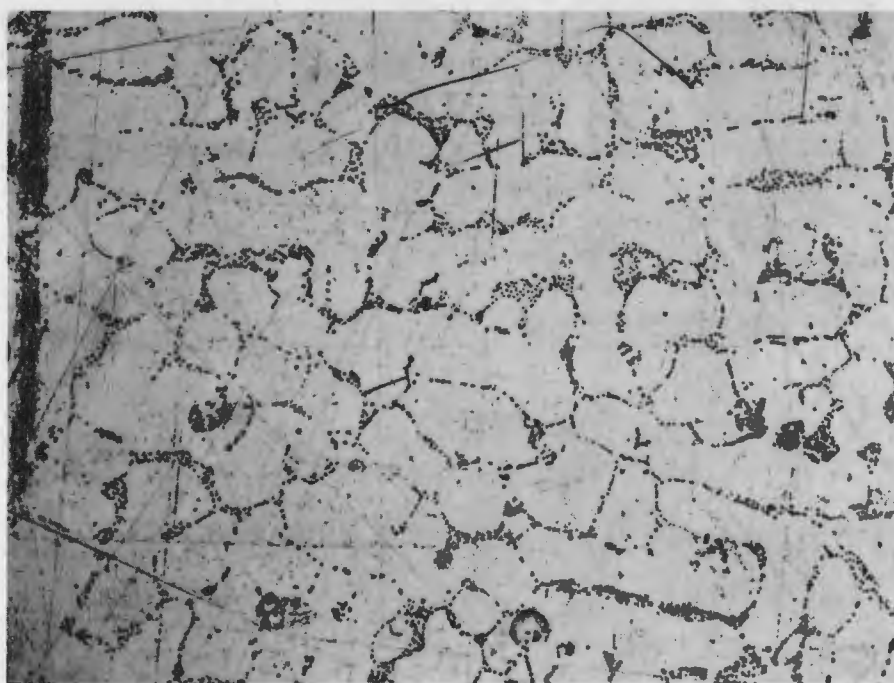

Figure 10. Silver Containing 0.08% Uranium Before
            Contacting Uranium in an Extractor
            Contacting Run (Etched). (Magnification - 200X)
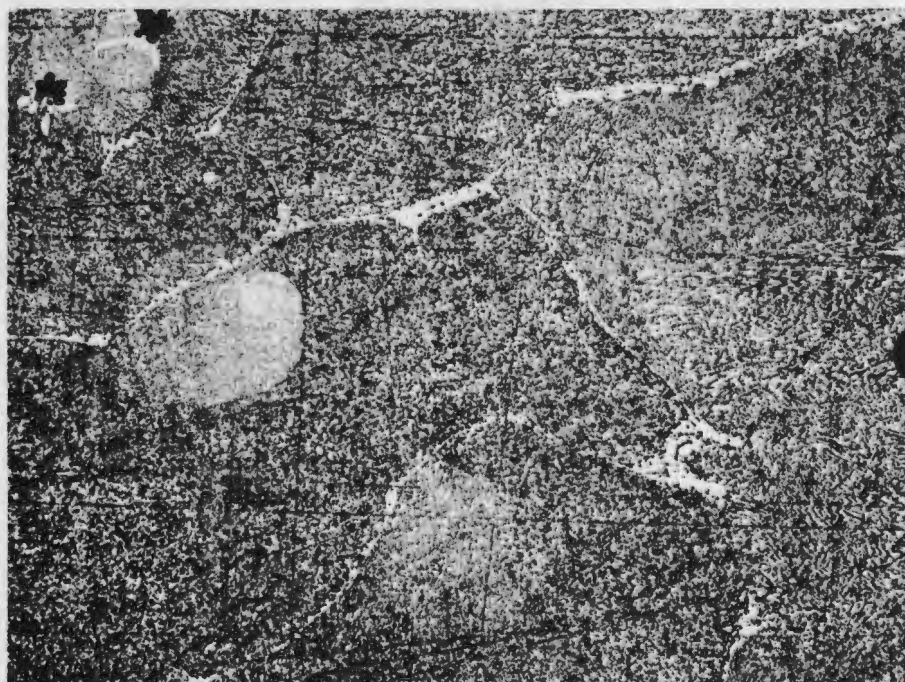
Figure 11. Silver After Having Contacted Uranium in an
            Extractor Contacting Run (Etched).
            (Magnification 200X)

had a longer path of uranium through which the silver was passed. This was because of the smaller connecting leg between the silver and uranium legs; hence, the finer the "bubbles" of silver that were forced into the uranium leg in run 4. Run 5 with a uranium height the same as run 3, but a smaller connecting leg between the uranium and silver legs as in run 4, gave a uranium concentration in the silver overflow approaching that at equilibrium. Equilibrium solubility of uranium in silver at the extraction temperatures is about 5 to 5.5%, whereas, the concentration of uranium in the silver overflow from run 5 was 4.85%.

Mass transfer of uranium to the silver in this extractor was apparently fairly rapid. A considerable improvement in the dispersion of the silver throughout the uranium phase could be accomplished by feeding the silver in a slow, controlled manner during ·the extraction run rather than melting it through as quickly as possible as was done in this study. This slow feeding of the silver and, possibly a longer uranium leg through which the silver is passed, should accomplish equilibrium transfer of uranium to the silver. It is hoped that this will also be true for the fission products and plutonium in processing actual fuel elements.

It was concluded from this study that this extractor offers promise as a contacting unit for uranium and silver in a silver extraction pyroprocessing scheme for irradiated reactor fuel elements.

CONCLUSIONS

The following conclusions were drawn from this investigation:

(1) The addition of a diffusion pump or a purified inert gas supply to the vacuum system is not justified until the small uranium losses become more important.

(2) Some material is adsorbed inside the vacuum system and upon refractory materials (crucibles, thermal shields, etc.) when they are exposed to the atmosphere.

(3) The contamination of the vacuum system during a run comes primarily from the 15 to 20 microns of Hg pressure

left in the system after evacuation and from the materials
adsorbed by the system and the refractory materials while
the system is open to the atmosphere.

(4)   The additional temperature range afforded by platinum-
platinum rhodium thermocouples is not sufficient to warrant
their use instead of chromel-alumel thermocouples, in view of
the additional expense and extra precautions that would be
needed.

(5)   The use of columbium-tungsten thermocouples in this
work does not show much promise. The tungsten becomes very
brittle upon being heated which makes the thermocouples very
difficult to handle and reuse. Furthermore, the calibration
changes from thermocouple to thermocouple and also for a given
thermocouple when it is heated.

(6)   There appear to be no sharp temperature gradients in
graphite crucibles and extractors of varied shapes when they
are heated by induction coils.

(7)   Type AGR graphite contains uranium and silver quite
well and is a satisfactory container material for uranium-
silver contacting. It is easy to fabricate, has adequate
structural strength and excellent resistance to thermal
shock.

(8)   The degassing time for graphite equipment is very
dependent upon the previous history of the graphite and upon
the degassing temperatures used. This degassing requires
from one to three hours depending upon these factors and the
extent of the degassing.

(9)   Phase separation in uranium-silver contacting is
quite sharp. However, care must be exercised in allowing
the phases to separate to avoid macroscopic inclusions in both
phases. Microscopic phase separation is complete.

(10)   Uranium crystallizes out of the silver phase in
uranium-silver melts as the metals cool and forms rounded
inclusions and dendrites of uranium. These particles settle
to the lower part of the silver phase before it solidifies
and cause the uranium concentration to be higher there than
in the upper part of the silver phase.

(11) "Oxidation" and slags are removed from the uranium by the silver in uranium-silver melts, leaving a relatively "clean" uranium phase. This slag forms a hard, gold-colored film on top of the silver phase.

(12) Mass transfer of uranium to silver in "static" melts is fairly rapid with inductive mixing.

(13) Uranium will flow easily, in graphite, through legs 3/8" in diameter. Silver will flow through legs 5/32" in diameter, but will not flow easily through smaller legs.

(14) The extractor designed in this study passes silver through uranium quite well. Nearly equilibrium transfer of uranium to the silver can be accomplished. The extractor offers promise as a contactor for uranium and silver in a silver extraction pyroprocessing scheme for spent reactor fuels. It is simple, has no valves, and is easy to operate so that it could be used in a remote pyroprocessing plant. It is easy to fabricate and is inexpensive so that it could be sacrificed at little cost after an extraction run. The combination of high-temperature volatilization of fission products, the affinity of silver for fission products and plutonium, the carbide (and oxide) slagging afforded by the graphite, and the slag removal by the silver should accomplish considerable decontamination of a reactor fuel element.

RECOMMENDATIONS

On the basis of this study the following recommendations are made:

(1) The adsorbtion by the crucibles and vacuum system of materials from the atmosphere should be investigated. Steps should be taken to determine what material is adsorbed, what significance the adsorbtion will have in pyroprocessing uranium, and how the adsorbtion can be eliminated or minimized should it prove to contribute significantly to metal losses.

(2) The relative merits of a high vacuum and a purified inert gas atmosphere in pyroprocessing work should be studied. This should be done to determine which atmosphere should be used in an eventual pyroprocessing plant.

(3)   The possibility of using some type of high-temperature thermocouple in this work should be explored. The measurement of higher temperatures than those which can be measured with conventional thermocouples would be advantageous in determining operating conditions, in silver distillation studies, and in allowing higher temperatures to be used in degassing crucibles in place before a run.

(4)   A means of obtaining temperatures at various points in an extractor (or of obtaining temperature traverses) during a run should be developed. This will be necessary because temperature is such an important variable in metallurgical operations and nearly all phases of any pyroprocessing scheme.

(5)   The establishment of a family of temperature vs. converter power setting curves for a given extractor would be of value. This would allow the temperature to be controlled by controlling the converter power setting for a given extractor.

(6)   A finer power output adjustment should be added to the converter used in this study. This would allow more accurate temperature control.

(7)   A means of feeding the silver in a slow, controlled manner to the extractor used in this study should be devised. A method of measuring the amount of silver fed should be developed at the same time.

(8)   A method of obtaining small samples, periodically, of silver from the overflow leg of the extractor should be developed for use in operating conditions studies.

(9)   Techniques for alloying one or more fission product elements with uranium should be developed to enable actual extractions to be carried out. These elements should be capable of being followed in an extraction and their study should give information applicable to actual fission products.

(10)   The distribution of fission product elements among all of the phases present (graphite, silver, uranium, slags, etc.) in extraction runs should be determined.

(11)   Methods of obtaining and of evaluating data concerning equilibrium relationships, extraction efficiencies, and operating conditions for the extractor should be developed.

(12)   A method of recovering the silver from the extract
after an extraction run should be devised. The solvent re-
covery capsule described in this study should be tested and,
if feasible, developed as a means of recovering the silver.

PYROPROCESSING SCHEME PROPOSED AS A BASIS
FOR FURTHER STUDY

A pyroprocess that uses a silver extraction step and which
might serve as a basis for further study is outlined below.

(1)   The fuel element from the reactor is decanned and
the bonding materials are removed. If the fuel is of a unique
shape it may have to be put into a form suitable for further
pyroprocessing in the plant. (If the fuel must be melted
in this step the volatile fission products could be removed
at the same time.)

(2)   The volatile fission products are then removed (if they
were not in step 1) by melting the fuel and, if necessary,
sparging with an inert gas. This step might be carried out in
an extractor such as the one described in this report by melting
the fuel after charging it to the extractor and before putting
the threaded graphite plug in place. An inert gas could be
introduced into the silver leg for sparging.

(3)   The molten fuel is contacted with silver to remove
most of the remaining fission products and the plutonium.
This might be done with the extractor of this study by putting
the threaded plug in place (after having charged the fuel to
the extractor if step 2 was not carried out in the extractor),
filling the silver leg with silver, and feeding a pre-determined
amount of silver through the extractor at a slow, measured
rate. A multi-stage extraction could be carried out by stacking
several of the extractors on top of one another. The silver
would enter the topmost extractor, contact the uranium there,
overflow into the silver leg of the next (lower) extractor,
contact the uranium there, overflow into the silver leg of
the next extractor, etc. The silver extract would be collected
at the overflow leg of the bottom extractor. The uranium would
be moved from the bottom of the stack to the top by periodically
removing the top-most extractor (containing the most completely
decontaminated fuel) and placing another extractor (containing

a fuel not yet extracted) at the bottom of the stack.

(4) After the silver extraction, the extractor (containing the fuel) is removed from the top of the solvent recovery capsule (containing the silver extract). A condensing lid and reclaimed silver collector are put in place in the recovery capsule (Figure 4) and the silver is distilled into the silver collector and removed.

(5) The plutonium-uranium-fission products concentrate is then processed to recover the plutonium. (This might be done by aqueous processing or by further pyroprocessing.)

(6) The extractor, after being separated from the solvent recovery capsule, is broken open and the uranium and silver removed. The majority of the silver is removed from the uranium mechanically and the remainder is distilled away along with the silver dissolved in the uranium.

(7) The uranium is then reconstituted by adding the proper amount of fresh fissionable material and remotely refabricated into fuel elements for the reactor.

In considering this pyroprocessing scheme, or any pyroprocessing scheme, it must be remembered that all of the processing must be done remotely, and that the techniques, the equipment, and the operational data needed to carry out these operations are in a very embryonic state of development. It is believed, however, that the formidable disadvantages inherent in aqueous processing schemes offer considerable incentive for such development. It is quite possible, if not probable, that the liquid-liquid extraction of molten uranium with silver will play a significant role in the power reactor technology of the future.

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