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**THE HERMEX PROCESS FOR METAL DECONTAMINATION
BY MERCURY PROCESSING**

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1.0 INTRODUCTION

Recent work at ORNL has been directed toward the development of a new reprocessing method, the Hermex Process, in which mercury is used as a dissolvent or extractant for purifying and recycling metals. Initial experiments have explored the feasibility of removing fission products from irradiated uranium and the recycle of scrap uranium in feed materials processing. The process will also be applied to thorium, zirconium, niobium, molybdenum, and aluminum as well as their alloys with uranium.

Several criteria have been established which may offer significant cost advantages over the presently used aqueous processing and the proposed pyrometallurgical method. The criteria for aqueous methods are the retention of uranium in the metallic state throughout the process and a more radiation resistant dissolvent and extractant. These criteria for pyrometallurgical methods are a low dissolution temperature, high purification, continuous process, and the use of standard materials of construction. Preliminary investigations indicate that the Hermex Process satisfies all of these criteria.

The basis of the Hermex Process is the solubility of uranium and other metals in mercury. After the mercury dissolution, the impurities and fission products are removed by slagging and washing the metal-mercury solution with solvents, and the purified metal is recovered by volatilization of the mercury and melting or sintering the high melting metal. Initial laboratory work on uranium has established the dissolution rate of solid uranium in boiling mercury. Later experiments showed that significant fission product removal was accomplished by slagging and washing the uranium-mercury solution that was obtained by dissolving sections from 3-year decayed X-10 reactor slugs. Scrap uranium metal from Fernald Feed Materials Preparation Center was shown to dissolve rapidly in boiling mercury without any preliminary cleaning or pickling. The Hermex Process offers considerable promise in the scrap recycle program because it can handle small scrap which is difficult to remelt directly and can probably purify this scrap without the expensive oxidation, solvent extraction, and reduction cycle.

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2.0 SUMMARY

The Hermex Process is a new method for decontaminating irradiated metals and purifying scrap virgin metals. The process as applied to irradiated uranium consists of the following steps (Fig. 1).

1. Uranium is continuously dissolved in boiling mercury (356°C).
2. The hot 0.2% uranium-mercury solution from the dissolver vessel is withdrawn continuously leaving a slag layer containing ~ 87% of the fission products or impurities.
3. The 0.2% uranium-mercury solution is cooled to 25°C and concentrated to 3% U by vacuum filtration. The mercury filtrate is recycled to the dissolver vessel.
4. The 3% uranium quasi-amalgam is washed with dilute HCl to remove ~ 6% of the fission products or impurities.
5. The mercury is volatilized from the quasi-amalgam and the uranium melted to dense metal by slow heating to 1250°C in a single operation.

Rapid dissolution rates of 12-17 and 7-9 mg/min/cm² were obtained on massive unirradiated and irradiated uranium samples, respectively. About 1-5% of the uranium was lost to the slag and 2-3% in the aqueous wash. The uranium loss figures are not particularly significant as yet since they were controlled by the equipment used rather than process principles. Decontamination factors of 100-200 for gross γ and 400-500 for gross β activity were obtained in two experiments using X-10 uranium cooled about 3-years. The uranium product from these experiments had about twice the γ activity and 2/3 the β activity of natural uranium.

3.0 PROPOSED APPLICATIONS

Mercury appears to have many advantages as a metal reprocessing reagent. These include the ability to dissolve, degrade, or amalgamate most metals,

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Fig. 1 Hermex Process

Fig. 2 The System U-Hg Showing Critical Alloys
(From: AERE M/R 1208, B. R. T. Frost)

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work, a continuous dissolving technique was developed for use at the boiling point (see Section 4.1). In this procedure, dilute uranium amalgam is continuously withdrawn from the dissolver, UHg_4 precipitated by cooling, the mercuride recovered by filtration or centrifugation, and the mercury filtrate recycled to the dissolver (see Fig. 1). Insoluble impurities rise to the surface of the amalgam as a slag and are drawn off directly from the dissolver or are flushed away along with amalgam soluble impurities in a subsequent step in which the amalgam is washed with hydrochloric acid. Uranium amalgam is not decomposed significantly by hydrochloric acid in the absence of oxygen. The purified uranium amalgam is then sent to a retort where the mercury is volatilized off and the uranium melted to massive metal.

At the present time, recycle uranium metal is dissolved in acid, purified by solvent extraction, converted to salt and reduced back to metal. It appears that many chemical costs could be avoided using the Hermex process since the uranium remains in a semi-metallic state and does not require oxidation and reduction. In the case of irradiated metal, long cooling prior to processing would not be required thus avoiding excessive inventory costs. If the decontamination achieved is high, as is indicated by initial experiments, the subsequent metallurgy step could be classed as semi-remote since U^{237} would be the only significant activity remaining. In the case of other proposed pyrometallurgical schemes, decontamination factors are low and truly remote metallurgy is mandatory. If further decontamination is required by solvent extraction, the uranium can be recovered from the amalgam by oxidative leaching, i.e., treatment with oxygen and hydrochloric acid, and passed into the extraction cycle.

Uranium Alloys

It is expected that U-Zr, U-Nb, U-Mo and U-Al alloys will be dissolved or amalgamated by boiling mercury particularly in the case of alloys with high uranium contents. A dissolution rate of $5 \text{ mg/cm}^2/\text{min}$ for 98% U-2% Zr alloy has been obtained. Zirconium mercurides are known and aluminum is

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readily soluble in mercury. The alloys are expected to act in the same manner as the pure metals. Thus the purification and recovery steps would be similar to those described above for uranium.

In some cases, the separation of macro amounts of metals may be practical. For example, metals such as aluminum, the alkaline earths, and the alkali metals which have relatively high solubilities in mercury at room temperature may be separated from metals with low solubilities, such as uranium and thorium by filtration or by a non-oxidizing acid wash. The insoluble metals are present as colloidal solid mercurides which are not decomposed by hydrochloric acid as are the Group I and II amalgams.

3.2 Metal Extraction

Mercury will be evaluated as a metal solvent for the recovery and decontamination of metals from fused salt solutions or molten metal reactor fuels. Heterogeneous reactor fuels are readily soluble in fused fluoride or sulfate salts. In this case, the transfer of the metals to the mercury phase would involve the simultaneous reduction of the metal; the presence of a reducing agent, such as sodium, in the mercury phase would be required. Extraction of metals from a molten metal fuel would not require a reducing agent, however. Many of the proposed operations would require pressurized containers in order to achieve high temperatures. Fortunately, industry has solved many of the implied operating problems in applications of high temperature mercury equipment in the turbine and oil cracking industries.

3.3 Degradation

Mercury can be used as a degrading vapor at high temperatures and atmospheric pressure to transform heterogeneous fuels to mercurides at elevated temperatures as an initial processing step prior to Hermex or aqueous solvent extraction processing. Experiments have shown that tantalum wire exposed to mercury vapor at 1200°C is degraded and can be readily powdered on cooling to room temperature. Pietrokowsky⁽²⁾ has shown that zirconium mercurides are formed by mercury vapor and zirconium metal at 1000°C . The formation of hydrides prior to mercurization will also be

(2) Pietrokowsky, P., Journal Institute of Metals, Feb., 1954.

explored.

3.4 Reactor Processing

The use of mercury as a solvent for fuels in a fast breeder reactor has been proposed by F. L. Culler. Continuous processing of this type of reactor fuel appears feasible using Hermex Process principles. A schematic diagram of the proposed reactor and reprocessing cycle is shown in Fig. 3. Fuel from the reactor would pass through a clone or centrifuge to remove the insoluble fission products as a slag and the soluble fission products then removed by acid washing. Oxygen could be added prior to centrifugation to aid in slag formation if necessary. In this method of recycle the bulk of the uranium is recycled directly to the reactor and only a small portion withdrawn with the slag for complete decontamination and eventual recycle to the reactor.

The reactor conditions are chosen from phase diagram data and correspond roughly to the uranium concentration present in the Detroit-Edison Breeder reactor. R. A. Charpie has stated that the fast neutron cross section data for mercury must be rechecked before the practicality of the mercury reactor can be judged.

4.0 EXPERIMENTAL RESULTS

A total of four runs were made to study the Hermex Process as applied to uranium metal, two using unirradiated uranium to perfect the equipment, and two with 3-year cooled X-10 slug samples. A brief description of the actual procedure followed in each step of the Hermex process follows.

4.1 Uranium Dissolution

A photograph of the laboratory continuous dissolver is shown in Fig. 4. A 50 gram sample, 3/16" x 1" diam., of uranium was boiled (356°C) in 150 ml of mercury for 30 min under an argon atmosphere. Approximately, 140 ml of mercury containing 0.2 wt % uranium was dropped to the filter where it was allowed to cool to room temperature. A fresh portion of mercury was

(Dotted lines indicate alternate or additional steps.)

Fig. 3 Hermex Reprocessing Scheme for a Mercury-Uranium Fast Breeder Homogeneous Reactor

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Fig. 4 Apparatus for Continuous Dissolution of U in Hg

immediately added to the dissolver from the mercury reservoir. After cooling, the uranium mercuride semi-solid, which formed as a suspension in the mercury phase, was recovered quantitatively by filtration. The mercury filtrate contained ~10 ppm uranium and was recycled from the mercury receiver to the mercury reservoir. A butter like uranium quasi-amalgam containing about 3 wt % uranium was retained on the sintered glass filter. The dissolution-filtration cycle was repeated about five times in each run to provide about 20 g of dissolved uranium for subsequent operations.

A film of black material, probably UO_2 , was always observed on the surface of the mercury in the dissolver vessel after each run. This film was not unexpected because uranium dissolved in mercury is very pyrophoric and traces of air leaked into the system during the manipulations. About 5% of the uranium was lost as oxide in the first run but improved technique reduced this to 1% in the second run. About 4% of the uranium was lost in runs three and four.

Dissolution rates averaged $15 \text{ mg U/cm}^2/\text{min}$ in the runs with unirradiated uranium and $8 \text{ mg U/cm}^2/\text{min}$ in the runs with irradiated uranium (see Table 1). The rate of $15 \text{ mg U/cm}^2/\text{min}$ is in good agreement with the rate of $20 \text{ mg U/cm}^2/\text{min}$ obtained by Wymer in batch experiments. No reason for the lower rate with irradiated uranium can be offered at the present time. However, the mercury dissolution rates are higher than the average rate for uranium dissolution in nitric acid, i.e., $5 \text{ mg U/cm}^2/\text{min}$ in 6 M HNO_3 .

4.2 Acid Washing

The uranium-quasi amalgam retained on the filter was washed with five 100 ml portions of 1 N HCl and then dried with methanol. Efficient contacting was difficult because of the density of the quasi-amalgam. Nevertheless washing was continued until all visible particles of oxide were removed from the amalgam. Uranium losses were 2% to 3%.

4.3 Uranium-Mercury Separation

The uranium-quasi amalgam was loaded into an alundum crucible which

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Table 1

Dissolution of Uranium in Boiling Mercury

Temperature - 356°C

Uranium Sample - 3/16" x 1" diam. section from X-10 slug*

Run No	Type of U	Dissolution Rate (mg U/cm ² /min)	U loss in slag (% of U dissolved)
1	Unirradiated	12	5
2	Unirradiated	17	1
3	Irradiated	7	5
4	Irradiated	9	3

*The Al jacket was removed prior to processing.

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was then suspended in a vertical resistance furnace (see Fig. 5). This furnace was continually flushed with purified argon to exclude air during the heating cycle. The furnace temperature was slowly increased to 1250°C to boil off the mercury and melt the uranium. The condensed mercury distillate contained only one ppm of uranium. After cooling to room temperature a button of uranium was removed from the crucible. Some oxidation of the uranium during the heating cycle was inevitable and from 5-10% of the uranium was converted to oxide during this operation. More elaborate equipment and the processing of larger quantities to increase the volume to surface ratio of the uranium would reduce this oxidation loss. The mercury content of the uranium button was 10-30 ppm.

4.4 Fission Product Distribution

In the 3rd and 4th runs, sections of 3-year cooled uranium from X-10 reactor slugs were processed in the same manner as the cold uranium described above. A comparison of the radioactivity of the uranium before and after processing shows that overall average gross decontamination factors of 160 and 455 were obtained for γ and β activity, respectively. Individual β D.F.'s for run 4 were Cs-220, Sr-1100, TRE-800, Ru-7, and Pu (α)-6 (see Table 2). The Ru, Zr, and Nb D.F.'s are not considered significant due to their low specific activities in the initial sample. The lower D.F. for Pu is interesting since it corresponds to the lower values obtained in oxide slagging experiments on molten uranium metal at Argonne and North American Aviation. The specific gross β and γ activity of the purified uranium metal was about 2/3 and 3-1/2 times that of natural uranium, respectively. (see Table 3).

About 86% of the gross activity was removed in the dissolver slag, ~ 6% in the aqueous wash (see Table 4), and 0.4-3.0% in the crucible slag. The conversion of these numbers to decontamination factors per stage is impractical because the activity of the wastes from each stage and not the products was measured. Since the material balances are poor, calculations

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Fig. 5 Equipment for Separation of U and Hg

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based on the difference between the waste activities and the product activities per stage are inaccurate. This method of calculation would show D.F.'s of 4-7, ~ 2, and 1.5-30 for the dissolver slagging, acid wash, and remelting steps, respectively. The most accurate and significant decontamination numbers are the overall values per gram of uranium shown in Table 2.

The mechanism of the dissolver slagging operation is not known but could be the result of insoluble fission products rising to the surface in the molten amalgam or a scavenging of the fission products by oxide impurities or a combination of both.

The efficacy of the acid wash as a separate decontamination step, rather than to merely remove oxide particles not properly separated in the slagging operation, has not been clearly established. However, no significant change in the ratio of fission product activities in the irradiated uranium and in the wash solution was noted. The ratio of Sr:Cs:TRE:Ru was 26:32:42:0.1 in the initial metal and 25:31:43:0.2 in the wash solution (see Table 5). Apparently, no element was selectively removed in the acid wash although this conclusion requires verification on higher activity samples where the accuracy of the results would be more significant. A black, insoluble material was flushed away from the quasi-amalgam in the acid washing step. This material may have been entrained in the dilute amalgam which was drained from the dissolver, or it may have formed by oxidation during the washing step.

Decontamination during the remelting step could be viewed as either a continuation (i.e., a 2nd stage) of the dissolver slagging operation or oxide scavenging as observed in regular pyrometallurgical procedures.

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Table 2

Decontamination Factors for Irradiate Uranium
Purified by the Hermex Process

Activity	Initial U c/min/g U		Decontaminated U c/min/g U		Decontamination Factor	
	Run 3	Run 4	Run 3	Run 4	Run 3	Run 4
gross γ	3.7×10^7	3.7×10^7	4.0×10^5	1.7×10^5	100	220
gross β	2.8×10^7	2.7×10^7	5.6×10^4	6.5×10^4	500	410
Cs β	9.3×10^6	9.2×10^6	6.3×10^3	3.3×10^3	1500	2800
Sr β	7.0×10^6	3.0×10^6	1.6×10^4	2.8×10^3	440	1100
TRE β	1.1×10^7	1.2×10^7	1.2×10^4	1.5×10^4	920	800
Zr γ^*	----	5×10^4	2×10^4	2×10^3	---	10*
Nb γ^*	----	1×10^5	2×10^4	8×10^3	---	25*
Ru β^*	$3.7 \times 10^4^*$	$2.7 \times 10^4^*$	1.4×10^4	2.6×10^4	3*	Nil*
Pu α	1.3×10^6	1.3×10^6	2.9×10^5	2.9×10^5	4	7

*Data not significant due to low specific activity.

Table 3

Comparison of Radioactivity of Natural Uranium and Irradiated
Uranium Purified by the Hermex Process

Material	Gross γ c/min/g U	Gross β c/min/g U	% Difference between Hermex U and Natural U	
			γ	β
Natural U	7.7×10^4	8.4×10^4		
Hermex-Run 3	4.0×10^5	5.6×10^4	+500	-30%
Hermex-Run 4	1.7×10^5	6.5×10^4	+220	-20%

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Table 4

Fission Product Distribution in the Hermex Process

Run No	Activity	% of Total Activity						Total
		Dissolver Slag	Filtered Mercury	Aqueous Wash	Distilled Mercury	Crucible Slag	Product U	
3	Gross γ	87	.3	7.9	.007	.26	1.07	97
	Gross β	85	.2	7.8	.0007	1.1	.18	94
4	Gross γ	86	.01	5.8	.2	1.3	.43	94
	Gross β	76	.07	6.6	.3	3.0	.17	86

Table 5

Distribution of β Activity in Irradiated Uranium and the Acid Wash Solution

Activity	% of Total β Activity per Sample	
	Initial Irradiated uranium	Acid Wash Solution
Sr β	26	25
Cs β	32	31
TRE β	42	43
Ru β	0.1	0.2

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