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PURIFICATION OF REACTOR FUELS USING LIQUID ZINC

by

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I. ABSTRACT

The possibilities of purification of reactor fuel materials by processing in liquid zinc media have been studied. In the course of this work, pertinent information was accumulated on the following:

1. Solubilities in liquid zinc of uranium, zirconium, ruthenium, palladium, barium, cerium, and molybdenum were obtained as a function of temperature.
2. Solubilities of ruthenium, zirconium, barium, and cerium were also investigated in uranium-saturated zinc solutions.
3. The behavior of individual elements in complex zinc solutions resulting from solution in zinc of fission alloys (uranium-"noble"* fission element alloys) was studied.
4. The effects of magnesium addition to zinc solutions were examined.
5. Several of the engineering operations required for full-scale development were demonstrated.
6. Some chemical reactions in liquid zinc media were briefly explored.

Various processing concepts may be envisioned in which separations are effected by fractional crystallization based on solubility and concentration relationships, volatilization, and selective reactions. Because of the considerable promise of liquid metals as processing media, it is recommended that effort in this field be expanded.

* Fission elements more noble than uranium: molybdenum, ruthenium, rhodium, palladium, etc.

II. SUMMARY

Preliminary work* has shown that processing of reactor fuel materials in liquid zinc media is an attractive method for the recovery and purification of uranium, and is worthy of further development. A process based on the use of zinc as a solvent metal may include dissolution in zinc, cooling to crystallize out the uranium as a zinc-uranium intermetallic compound, separation of the uranium precipitate from the supernatant zinc solution, and retorting of the uranium intermetallic compound to volatilize the solvent metal and enable recovery of uranium as metal. Fission product separations are possible because of favorable solubility differences. The process has the advantages of simplicity, ready isolation of uranium as a metal product, and employment of radiation damage-resistant processing media. Choices of construction material are limited; however, graphite, tantalum, tungsten, and several refractory materials appear to be resistant to attack by molten zinc.

Individual solubilities of uranium and several fission product elements in zinc were determined as a function of temperature. These are shown in Figures 3 through 10. The uranium solubility is 5 per cent at 800 C, decreasing to 0.02 per cent at 500 C. Thus, essentially quantitative precipitation of the uranium can be effected by cooling. Zirconium, palladium, and rhodium have higher solubilities in zinc than uranium. The solubility of ruthenium is about 1 per cent at 750 C and 0.01 at 500 C, which is only slightly lower than that of uranium. The solubility of cerium is also slightly lower than that of uranium, whereas that of barium is appreciably lower. The solubility of molybdenum is about 0.02 per cent and is not significantly affected by temperature over the investigated range from 500 to 800 C.

The presence of uranium in zinc solution in general depressed solubilities of the fission products. In the case of ruthenium, this effect would make the separation of ruthenium from uranium difficult. Mutual solubility effects in cerium-uranium-zinc and barium-uranium-zinc systems appear to be due to a coprecipitation phenomenon. This was confirmed in an active run using fission products in tracer concentrations in which rare earth elements and plutonium extensively coprecipitated with uranium. Ruthenium showed no coprecipitation tendencies. Removal of zirconium, niobium, and strontium from zinc solution in the active run appears to have occurred through selective oxidation mechanisms.

All process operations were demonstrated on a small scale. These included metal dissolution, separation of the precipitated uranium intermetallic compound from the zinc supernatant by filtration, and retorting of the intermetallic to recover uranium metal. The zinc concentration in a sample of recovered uranium metal was 80 ppm.

*Over the two-year period from June, 1956 to June, 1958.

Scouting work yielded the following information which is believed to have considerable process significance:

1. Uranium compounds (UO_2 , UO_3 , and UF_4) were reduced by magnesium in a dilute solution of magnesium in zinc.
2. The uranium-zinc intermetallic compound was decomposed by the addition of sufficient magnesium. This decomposition liberates uranium metal which precipitates from the solution.
3. Attempts to separate ruthenium by selective formation of intermetallic compounds with rare earth, alkali, and alkaline earth metals were unsuccessful. It was demonstrated that ruthenium may be separated from a mixture of uranium oxide and fission product oxides by zinc reduction and leaching. Other metals more noble than zinc such as palladium, rhodium, and molybdenum would be expected to undergo a similar separation.
4. Direct reaction of uranium and zinc to form an intermetallic compound was demonstrated.

III. INTRODUCTION

In the past few years interest has grown in the use of liquid metals as solvents for nuclear fuel materials. Fissionable materials dissolved in liquid metals have been investigated for nuclear reactor use, e.g., the Liquid Metal Fuel Reactor (LMFR) in which the fuel is a solution of uranium in bismuth. Liquid metal solutions are also media through which various operations might be carried out to effect the separation of valuable materials from each other and from fission products. Such operations include fractional crystallization, volatilization, selective oxidation and reduction, extraction, and electromigration. The possible application of these methods to nuclear fuels was first discussed by Isserow.⁽¹⁾ The advantages of liquid metal solutions are as follows: liquid metals are not susceptible to radiation damage, so processing of discharged fuel materials may take place with a short cooling period, which makes small fuel inventories possible; valuable fuel materials, such as uranium and plutonium, may be readily recovered in metallic forms; and fission products may be fixed in the solidified solvent metals in forms suitable for disposal or utilization as radiation sources.

Various metals might be considered as possible solvents for nuclear fuel materials. These include bismuth, tin, mercury, lead, cadmium, thallium, aluminum, and zinc. Purification of a bismuth-uranium fuel solution by selective oxidation and reduction has been extensively investigated at Brookhaven National Laboratory.^(2,3,4) Teitel⁽⁵⁾ has reported on the purification of uranium effected by precipitation from lead, bismuth, and tin

solutions. At Oak Ridge National Laboratory the use of mercury as a solvent has been under study.⁽⁶⁾ The status of work on various solvents has been summarized through spring, 1958.⁽⁷⁾

This study of the application of zinc as a solvent covers the period from July 1956 to July 1958. A basis for this work was a phase diagram for the uranium-zinc system (Figure 1) reported by Chiotti *et al.*,⁽⁸⁾ of the Ames Laboratory. These investigators showed that the solubility of uranium in zinc at 800 C is about 6 weight per cent, and at 500 C it is only about 0.01 weight per cent. Virtually complete precipitation of uranium upon cooling is assured. The precipitated intermetallic compound, reported as UZn_9 , exerts an appreciable decomposition pressure which reaches one atmosphere at 945 C. Hence, the compound may be decomposed to zinc vapor and uranium, permitting ready recovery of the uranium by retorting. It is noteworthy that the compound is not pyrophoric and is not readily oxidized at ordinary conditions.⁽⁹⁾ These characteristics appeared to the authors to be very favorable for the use of zinc as a processing solvent.

Figure 1

URANIUM-ZINC SYSTEM AT ONE
ATMOSPHERE PRESSURE

[From J. of Metals, 8, 562 (1956)]

In the study reported herein the solubility of uranium in zinc has been determined with greater precision. Investigations⁽⁹⁾ subsequent to those of Chiotti *et al.*, established the formula of the intermetallic compound as U_2Zn_{17} . Subsequently, another intermetallic compound has been identified, $UZn_{11.5}$.⁽³⁰⁾ It is believed that this compound is the low-temperature equilibrium solid phase, while U_2Zn_{17} is the high-temperature (above about 800 C) solid phase.

An important reason for undertaking this work was the necessity for the development of a process for use as an auxiliary to the melt-refining process.⁽¹⁰⁾ The latter is to be used for processing fuel from the second Experimental Breeder Reactor (EBR-II) being developed by Argonne National Laboratory. The melt-refining process does not provide for the removal of metals more noble than uranium, such as ruthenium, rhodium, palladium, molybdenum, and technetium, from the reactor fuel. Consequently, a portion of the fuel must be processed for nearly complete removal of these elements in order to maintain their concentrations in the fuel at tolerable levels.

This auxiliary process was originally envisioned as consisting of the following steps: (1) solution in zinc, (2) cooling to effect precipitation of the intermetallic compounds of uranium and plutonium, leaving the bulk of the contaminants in the supernatant liquor, (3) separation of the intermetallic compounds from the supernatant liquor, and (4) retorting of the separated intermetallic concentrate to vaporize the zinc. It was also realized that additional purification steps might be employed, e.g., selective oxidation and reduction. Such reactions were demonstrated and the favorable results clearly indicated the inherent processing flexibility of liquid metal solutions. It was then recognized that applications to other fuels, to blanket materials, and to feed materials production would also be worth investigating.

This report contains the preliminary results of studies on the use of zinc in processing reactor materials. Most of the experimental work was done by James B. Knighton over the period from June 1956 to June 1958. Since this preliminary feasibility study on the use of liquid metals for processing reactor materials showed considerable promise, the work has been expanded at Argonne National Laboratory. Further studies of solubilities, the accumulation of other pertinent thermodynamic information, and a record of progress in process development are provided in summary reports issued quarterly by the Chemical Engineering Division of Argonne National Laboratory.

IV. EXPERIMENTAL MATERIALS AND PROCEDURE

The solubilities of the heavy metals and of the fission product elements in zinc were required in order to assess the possible utility of the proposed system. It was decided to employ a liquid-sampling technique for the determination of these solubilities because of the known difficulties with thermal analyses of dilute solutions or other techniques.

A. Liquid-sampling Technique

The solutes under investigation were dissolved in zinc or a zinc-rich alloy in a suitable crucible which was contained within a closed stainless steel tube heated by a resistance furnace (Figure 2). The furnace tube was evacuated with a mechanical pump and flushed with argon several times before finally filling with argon. The argon atmosphere was maintained at a slightly positive pressure for the duration of the run. The melt was agitated with a stirrer for at least one-half hour at each temperature to ensure saturation before sampling was begun. In general, saturation was approached from above by successively lowering the temperature to the desired value. On occasion, confirmation was obtained by approaching saturation from below, i.e., by raising the temperature of the melt before sampling.

Liquid samples were drawn by suction through porous graphite filter plugs (33-micron average pore size) into seven-millimeter Vycor tubes. Particles larger than twelve microns were excluded by this filter plug. Suspended particles smaller than twelve microns could, if present, pass through the filter and result in solubilities greater than the true values. However, because of the self-consistency and reproducibility of the solubility data obtained by this experimental method, filtration was considered to be quantitative.

The filter plugs were machined slightly oversize and then force fitted into the Vycor tubes. Since at high temperatures zinc-uranium alloys wet Vycor, it was found desirable to flame spray the outside of the tubes with alumina to prevent sticking of the melt. The sampling tubes were preheated before sampling by holding them above the molten metal for several minutes. The Vycor tubes were broken away from the frozen samples. The entire sample was taken for analysis of the concentration of the element whose solubility was being determined.

Figure 2

APPARATUS USED FOR DETERMINING METAL SOLUBILITIES IN ZINC AND ZINC ALLOYS

B. Source and Purity of Materials

The materials used, their sources, and their purities are given in Table 1.

Table 1

MATERIALS USED IN SOLUBILITY STUDIES

Material	Source	Purity, Percent
Zinc	Mallinckrodt, Baker, Fischer	Analytical Grade, 99.99+
Ruthenium	The American Platinum Works	High Purity, 99+
Zirconium	USAEC	Crystal Bar, 99+
Palladium	J. Bishop and Co. Platinum Works	99+
Rhodium	J. Bishop and Co. Platinum Works	99.5+
Barium	E. H. Sargent	99+
Cerium	Cerium Metals Corporation	99.95
Uranium	USAEC	Reactor Grade, 99.9+
Magnesium	Dow Chemical	99.85

C. Materials of Construction

Most metals are dissolved or attacked by molten zinc at elevated temperatures. Tungsten was not attacked by the zinc solutions which were studied, but it is not readily fabricated into crucible shapes. Tantalum appears to be attacked very slowly by molten zinc. Either tungsten or tantalum was used for stirring rods.

Graphite, because of its high resistance to attack by zinc, its ready availability and low cost, and the ease with which it can be machined, was generally used as the container material in this work.

Many refractory materials, e.g., silicon carbide, alumina, and magnesia, also resist attack by molten zinc and are used industrially for this purpose. However, these refractory materials are sometimes porous and may be penetrated by molten zinc. Therefore, they were not employed in this research. Boron nitride, which became available in the latter stages of the work, also does not appear to be attacked or wetted by zinc and merits further investigation.

In order to justify the use of graphite as a container material, it was important to show that uranium in zinc solution does not react with carbon. A uranium-zinc solution containing 1.2 weight per cent uranium was placed in a well-degassed graphite crucible and held at 750 C for five hours. Analyses of filtered samples taken periodically are given in Table 2.

The essentially constant uranium concentration found indicates that within the accuracy of the analyses there is no reaction of uranium with graphite under the experimental conditions employed.

Table 2

STABILITY OF URANIUM-ZINC SOLUTION
IN GRAPHITE AT 750 C

Time (hr)	Uranium Concentration (w/o)
1	1.26
2	1.17
3	1.26
4	1.26
5	1.21

V. SOLUBILITY MEASUREMENTS IN ZINC AND
URANIUM-SATURATED ZINC SYSTEMS

A. Solubilities in Liquid Zinc

The measured solubilities of individual elements in zinc are presented graphically as a plot of log weight per cent solubility vs reciprocal absolute temperature.

1. Uranium (Figure 3)

The solubility of uranium in zinc is about 5 per cent at 800 C. It decreases sharply with temperature to 0.02 per cent at 500 C. The higher apparent solubilities reported by the Ames Laboratory⁽¹¹⁾ are probably due to the fact that unfiltered samples were taken. Recent personal communication has indicated that remeasurements have resulted in values closer to those reported here.

The uranium-zinc intermetallic compound crystallizing in this system was identified by Makarov and Vinogradov⁽⁹⁾ as having the ideal formula U_2Zn_{17} . * Studies of its crystal structure and the lattice parameters in the hexagonal system have also been reported.

*As noted in the introduction, U_2Zn_{17} has subsequently been found to be the solid phase in equilibrium with melt above about 800 C. At lower temperatures, a solid phase, $UZn_{11.5}$, has been found.⁽³⁰⁾

Figure 3
URANIUM SOLUBILITY IN MOLTEN ZINC AS
A FUNCTION OF TEMPERATURE

Figure 4 is a photograph which shows that large crystals of the intermetallic compound form on the sides and bottom of the crucible on cooling a solution of uranium in zinc. Material similar to that shown in Figure 4 was subsequently remelted and the excess mother liquor was removed by filtration through porous graphite. A photograph of the crystalline mass remaining on the filter and the filtered zinc is shown in Figure 5.

Figure 4
URANIUM-ZINC INTERMETALLIC CRYSTALS
IN SECTIONED INGOT

Figure 5
URANIUM-ZINC FILTER CAKE AND ZINC FILTRATE

2. Zirconium (Figure 6)

The solubility of zirconium was measured over the temperature range from 550 to 745 C. The solubilities found differed markedly from values reported by Gebhardt,⁽¹²⁾ who used thermal analysis to determine the liquidus. A. Martin⁽¹³⁾ has summarized and compared these and subsequent results obtained by others. The results reported here appear to be confirmed over the temperature range investigated. Martin has found that a peritectic occurs in this system at 548 C and that the solubilities below this temperature decrease sharply.

Figure 6

ZIRCONIUM SOLUBILITY IN
MOLTEN ZINC AS A FUNCTION
OF TEMPERATURE

3. Ruthenium (Figure 7)

No previous work has been reported on the ruthenium-zinc system. The data for ruthenium solubility have been represented by a single straight line. These data have been subsequently confirmed below 500 C,⁽²⁸⁾ but above 600 C solubilities lower by a factor of nearly two have been measured.⁽²⁹⁾

4. Rhodium (Figure 8)

Four measurements of the solubility of rhodium were made over the temperature range from 550 to 700 C. Nothing is known about the phase diagram of the rhodium-zinc system except for the existence of a gamma-brass-type intermetallic phase.⁽¹⁴⁾

Figure 7
RUTHENIUM SOLUBILITY IN
MOLTEN ZINC AS A FUNCTION
OF TEMPERATURE

Figure 8
RHODIUM AND PALLADIUM
SOLUBILITIES IN MOLTEN
ZINC AS A FUNCTION OF
TEMPERATURE

5. Palladium (Figure 8)

The phase diagram for the palladium-zinc system appearing in Hansen⁽¹⁵⁾ indicates that over the temperature range of interest (from 500 to 800 C) the solubility of palladium is substantial. Two measurements,

which confirmed this high solubility, were made. The published phase diagram indicates that the equilibrium solid phase is a gamma-brass type of intermetallic compound.

6. Barium (Figure 9)

The measurements for barium in zinc made over the temperature range from 550 to 800 C gave solubilities which were considerably lower than those reported by Kornilov.⁽¹⁶⁾ The latter determined the liquidus by thermal analysis. The direction of this disagreement is similar to that for other cases where thermal analysis data are compared with solubility measurements for dilute solutions. The equilibrium solid phase in this range of compositions investigated has been reported to be BaZn_{13} .⁽¹⁷⁾

Figure 9
BARIUM SOLUBILITY IN ZINC AS A
FUNCTION OF TEMPERATURE

7. Cerium (Figure 10)

Cerium measurements were made over the temperature range from 500 to 742 C. Three liquidus points obtained by thermal analysis by Schramm⁽¹⁸⁾ are also shown. As with other thermal analysis determinations, values are somewhat higher than those obtained by sampling the liquid phase.

Figure 10

SOLUBILITY OF CERIUM IN ZINC AS A FUNCTION OF TEMPERATURE

8. Molybdenum

The solubility of molybdenum in zinc was measured from 500 to 800 C and was found to be small and essentially constant (Table 3). Martin⁽¹⁹⁾ has subsequently investigated the system in more detail and confirmed the solubility values found between 600 and 800 C. Below 550 C, however, Martin found that the solubility decreased markedly.

Table 3

THE SOLUBILITY OF MOLYBDENUM IN ZINC AS A FUNCTION OF TEMPERATURE

Temp (C)	Conc (w/o)
800	0.024
750	0.023
700	0.023
650	0.025
600	0.024
550	0.030
500	0.031

B. Solubilities in Zinc Saturated with Uranium

The solubilities of the fission elements in zinc might be appreciably affected by the presence of uranium in relatively high concentrations. Selected systems were cursorily examined to determine the extent of these mutual solubility effects. It is necessary to point out that the concentrations of the elements found in solution are not necessarily equilibrium values because of the possibility that the equilibrium solid phases did not form in the time allowed.

The simultaneous concentrations of uranium and a co-solute were determined for zirconium (Table 4), ruthenium (Table 5), barium (Table 6), and cerium (Table 7).

Table 4

SIMULTANEOUS CONCENTRATIONS OF ZIRCONIUM AND URANIUM IN ZINC SOLUTION AT VARIOUS TEMPERATURES

Cooling Rate: 50 C/hr

Temperature (C)	Conc U (w/o)	Conc Zr (w/o)
700	0.58	2.44
675	0.43	2.13
650	0.26	1.97
625	0.128	1.85
600	0.074	1.59
575	0.018	1.28
550	0.013	0.955
525	0.024 ^a	0.507
500	0.031 ^a	0.291

^aUranium analysis questionable.

By comparison with the solubility data given in Figures 3, 6, 7, 9, and 10, the following qualitative observations could be made.

At temperatures above 550 C some marked effects were noted. Zirconium and uranium together showed a mutual decrease in concentration. The presence of uranium depressed the concentrations of ruthenium found in solution but the uranium concentrations were unaffected. Uranium concentrations were not affected by barium; the barium data were scattered and no definite conclusions can be drawn.

Table 5

SIMULTANEOUS CONCENTRATIONS OF RUTHENIUM AND
URANIUM AT VARIOUS TEMPERATURES

Experiment A. Cooling Rate: 50 C/hr			Experiment B. Cooling Rate: 25 C/hr		
Temperature (C)	Conc U (w/o)	Conc Ru (w/o)	Temperature (C)	Conc U (w/o)	Conc Ru (w/o)
800	4.78	0.199	800	2.87	0.042 ^a
750	2.98	0.145	750	2.94	0.057 ^a
700	1.26	0.054	698	1.41	0.066
650	0.476	0.033	678	0.844	0.033
600	0.239	0.014	652	0.407	0.015
550	0.066	0.013	624	0.281	0.0154
500	0.041	0.011	595	0.229	0.0162
			580	0.120	0.0151
			558	0.021	0.0103 ^b
			528	0.022	0.0087 ^b
			502	0.019	0.0112
			478	0.015	0.0052
			455	0.0058	0.0022

^aNot saturated.

^bThese points questionable

Table 6

SIMULTANEOUS CONCENTRATIONS OF BARIUM
AND URANIUM IN ZINC SOLUTION AT VARIOUS
TEMPERATURES

Cooling Rate: 50 C/hr		
Temperature (C)	Conc U (w/o)	Conc Ba (w/o)
792	4.3	2.39
742	2.82	1.75
690	1.22	0.238
650	0.596	0.033
599	0.202	<0.007
547	0.057	<0.01

Table 7

SIMULTANEOUS CONCENTRATIONS OF CERIUM AND
URANIUM IN ZINC AT VARIOUS TEMPERATURES

Cooling Rate: 50 C/hr

Temperature (C)	Conc U (w/o)	Conc Ce (w/o)
792	1.1	1.55
741	0.98	1.49
698	0.478	0.803
649	0.242	0.264
595	0.11	0.0809
549	0.016	0.0256
497	0.0086	0.0052

Uranium did not appreciably affect the concentrations of cerium found in solution; cerium appeared to depress the concentrations of uranium in solution. Below 550 C, where concentrations of both solutes in solution were low, the concentrations of uranium and zirconium, or of uranium and ruthenium, did not differ significantly from the equilibrium saturation values for these elements alone in zinc. With the barium-uranium and cerium-uranium systems, however, effects were noted which seem more reasonably treated as cases of mutual coprecipitation than of solubility.

VI. SOLUBILITY MEASUREMENTS IN MULTICOMPONENT SYSTEMS

A. Fissium Alloy

As indicated in the Introduction, one of the major reasons for investigating fractional crystallization from zinc solution as a separations method was the possible application to processing a sidestream from the EBR-II melt-refining process. This sidestream will consist principally of crucible skull and residues containing 5 to 10 per cent of the total fissionable material. This material must be processed for recovery of the fissionable material and for separation of the noble metals (molybdenum, technetium, ruthenium, rhodium, and palladium) which are not removed in the melt-refining process.⁽¹⁰⁾

The single-solute studies were undertaken in order to recognize mutual solubility effects occurring in the complex systems. The uranium-"noble" metal alloy presently planned for the fuel for the EBR-II reactor has been given the generic name of "fissium." Since compositions of this

material can vary widely, it is necessary to specify the composition employed. For this work, the composition employed was the following:

Element	Weight Per Cent
Uranium	91.5
Ruthenium	3.0
Molybdenum	3.7
Zirconium	1.0
Palladium	0.8

Since a method for rhodium analysis was undeveloped, the palladium concentration employed was the sum of the calculated palladium and rhodium concentrations.

This material was dissolved in zinc at 800 C and solute concentrations were determined as a function of temperature on cooling. The solution compositions resulting on cooling over the temperature range from 800 C to 525 C are plotted in Figure 11.

Figure 11
MUTUAL SOLUBILITY EFFECTS
IN URANIUM-NOBLE METAL-
ZINC SYSTEM

In this complex system the ruthenium concentration curve paralleled that of uranium, indicating essentially no separation of ruthenium from uranium. This contrasts with ruthenium behavior in the simpler three-component

(uranium-ruthenium-zinc) system (Figure 12) in which the ruthenium concentrations were affected only at high uranium concentrations (above 0.4 per cent). Below this uranium concentration, the ruthenium solubility was apparently unaffected by uranium. This produced the shift in the ruthenium concentration curve shown in Figure 12.

Figure 12
RUTHENIUM AND URANIUM
SOLUBILITIES IN THE SYSTEM
URANIUM-RUTHENIUM-ZINC

As may be seen in Figure 11, palladium was completely retained in solution. A slight concentrating effect occurred because of the loss of zinc solvent as the uranium-zinc intermetallic crystallized. The zirconium concentration decreased by a factor of two, indicating possibly a coprecipitation behavior. The molybdenum which went into solution corresponded to its saturation concentration of about 0.02 weight per cent. On cooling, the molybdenum concentration changed only slightly.

These results indicate that partial or nearly complete decontamination of all of the "noble" elements except ruthenium is possible, palladium and zirconium by retention in zinc solution, and molybdenum by virtue of its low solubility. Molybdenum separation would have to be effected by a hot filtration.

B. Fast Cooling

Because of indications from laboratory work that fast cooling would reduce coprecipitation,⁽²³⁾ two fast-cooling runs were made. The cooling rates were about 33 C/min as contrasted with a slow-cooling rate of 0.4 C/min. Because of the difficulty of the ruthenium-uranium separation, the concentrations of these two elements were the only ones determined through the entire cooling cycle. As shown in Figure 13, the break in the ruthenium liquidus concentration curve (previously found in the simpler uranium-ruthenium-zinc system, Figure 12) was restored. From the standpoint of achieving good uranium-ruthenium separation, it would be necessary to operate on or beneath the flat portion of the curve.

Figure 13

BEHAVIOR OF RUTHENIUM
SOLUBILITY ON FAST COOLING
OF "FISSION" ZINC SOLUTION

(Cooling Rate - 33 C/min)

A later effort to reproduce the ruthenium behavior described above was not successful. This discrepancy and the rather strange behavior of ruthenium in this system has not been resolved.

C. Effect of Magnesium on Ruthenium Behavior

The knowledge that ruthenium is highly soluble in magnesium (about 20 weight per cent at 800 C)⁽²⁴⁾ prompted an investigation of the effect of magnesium on ruthenium behavior. Magnesium concentrations of 3 and 6 per cent were employed, the lower concentration corresponding to that of a eutectic.⁽¹⁴⁾ The individual solubilities of uranium and ruthenium in zinc were only slightly affected by magnesium at these concentrations. Nevertheless, fission was dissolved in 3 and 6 per cent magnesium solutions and the concentrations of uranium and other fission constituents followed during both fast (30 C/min) and slow (0.8 C/min) cooling. The results were not significantly different from those obtained in the absence of magnesium.

VII. COPRECIPITATION BEHAVIOR OF FISSION PRODUCT ELEMENTS

The ultimate separation of uranium from tracer fission product elements by precipitation of the uranium as a uranium-zinc intermetallic compound would be limited only by coprecipitation, since the solubilities of the fission product elements would not be exceeded. A discussion of coprecipitation in metal solutions has been given by Feder and Teitel.⁽⁷⁾ To ascertain the coprecipitation tendencies of fission product elements, an active run was carried out with fission product elements present in tracer concentrations resulting from dissolution in zinc or irradiated uranium.

Equipment - A schematic diagram of the experimental equipment is shown in Figures 14 and 15. A single-stage filtration unit fabricated from graphite was employed. Provisions were made for charge additions, sampling, mixing, and filtering.

Figure 14
SINGLE-STAGE FILTRATION UNIT

Experimental Procedure - A pre-cast zinc ingot was charged to the upper crucible prior to assembly in the furnace. The irradiated uranium was added after the equipment was fully assembled, by dropping the uranium pin through the opening provided for mixing and sampling. The system was then evacuated and flushed with argon. To degas the graphite, the equipment was heated under vacuum to 400 C, which is just below the melting point of zinc (420 C). An argon atmosphere was then maintained in the apparatus for the remainder of the experiment. To dissolve the uranium the temperature was raised to 750 C and the melt was mixed for two hours with a motor-driven tungsten stirring rod. After mixing, samples were taken at 50 C intervals.

Figure 15
SAMPLING ASSEMBLY

Between samples, the melt was cooled for a half-hour and held quiescent for an additional half-hour before sampling. The three-way plug valve was damaged in removing the first sample, and complete control of the atmosphere was not possible from that point on.

At 500 C the bulk of the liquid zinc was filtered by applying an argon pressure of 10 psig to the interior of the upper dissolving and crystallizing crucible. The filtration was effected quickly and without difficulty. An increase in argon flow indicated completion of the filtration.

The filter cake was washed at 500 C with fresh zinc. A filtered sample was taken of this zinc wash solution, after which the remainder was filtered by the application of argon pressure. This filtration completed the experimental cycle. The system was allowed to cool for two days before disassembly.

On disassembly, it was noted that the graphite parts were unaffected. There was no evidence of attack, deterioration, or wetting. The upper crucible showed an activity of about 400 mr and the lower receiver about 20 mr.

Since the atmosphere was not kept as clean as desired, some oxidation had occurred. The oxidized material had floated on the zinc surface, and was retained on the surface of the filter cake and on the crucible walls. The oxidized material on the crucible was separately removed, dissolved, and analyzed. An attempt also was made to separate the dross from the filter cake by chemical dissolution of its exterior surfaces. About 10 grams

were dissolved in nitric acid. No doubt this was an imperfect separation, but it was hoped to eliminate the effects of dross retention.

The filter cake adhered to the porous graphite filter disc. However, the cake was easily separated from the graphite filter by a sharp blow at the interface with a screwdriver.

A visual examination of the ingot confirmed that a wash had been made.

Results - The distribution of the activities that were analyzed is shown in Table 8. Decontamination of uranium from most fission product activities was significant but far from complete. The behavior of individual fission product and plutonium activities was as follows:

1. Plutonium coprecipitated extensively with the uranium. This was in accord with other studies.⁽⁷⁾
2. Considerable coprecipitation of rare earth activities also occurred, which again was in accord with reported information.⁽⁷⁾
3. The high concentration of strontium in the filter cake dross probably resulted from preferential oxidation.
4. Ruthenium quantitatively remained in solution, indicating no coprecipitation tendency. Presumably, rhodium and palladium would show similar behavior.
5. Apparently, a large proportion of the cesium was volatilized.
6. The low material balance for niobium may possibly be due to selective removal as the carbide, resulting from reaction with the graphite crucible.

Table 8
DISTRIBUTION OF URANIUM AND TRACER ACTIVITIES

Conditions: Initial Temp. 750 C; Holding Time, 2 hr;
Cooled to 500 C at rate of 50 C/hr.

Products	Uranium (g)	Activity (Per cent of the activity in solution at 750 C)								
		Pu	Total β	Total γ	Zr	Nb	TRE ^c	Sr	Ru	Cs
Filtrate ^a	0.13	7.7	11.9	9.9	24.5	1.3	4.4	1.0	58.8	2.3
Wash ^a	0.08	1.7	0.9	1.2	2.3	0.4	0.4	0.3	2.2	0.2
Filter Cake	9.12	62.6	60.5	15.8	19.8	5.5	75.2	12.4	1.3	2.7
Dross	3.05	3.2	27.3	15.3	16.4	6.5	26.3	52.5	0.2	9.4
	12.38 ^b	75.2	100.6	42.2	63.0	13.7	106.3	66.2	62.5	14.6

^a Uranium losses in filtrate were about one per cent of that recovered.

^b This represented 87.2 per cent of the total uranium charged.

^c Total rare earths.

In general, the experiment indicated extensive coprecipitation of rare earths and plutonium. Ruthenium showed no coprecipitation tendencies. Strontium, zirconium and niobium may have been removed, largely through formation of stable oxides or carbides. Cesium was largely volatilized.

VIII. DEMONSTRATION OF ENGINEERING OPERATIONS

Several engineering operations must be developed for the success of liquid zinc processes. These are: (1) dissolution of metal phases in zinc or zinc alloys, (2) separation of solid phases, and (3) recovery of the valuable uranium or plutonium by removal of the solvent metal.

Metal Dissolution - Rates of metal solution were not studied. Sufficient agitation was provided with a tantalum paddle and sufficient time was allowed to ensure metal solution. No problem with uranium dissolution was encountered, indicating that this is not likely to pose a problem. However, solution rate data and variables affecting the rate of solution should be obtained.

Solids Separation - An essential part of a process is the separation of solids, either undissolved or deliberately precipitated material, from the bulk of the solution. Procedures commonly employed in chemical and metallurgical fields are filtration, decantation, and centrifugation. The first two of these procedures have been investigated in a preliminary way.

Filtration - Shown in Figure 16 is a schematic diagram of the equipment used by A. A. Chilenskas⁽²⁰⁾ for demonstration of filtration as a separation procedure. Experiments were performed in a graphite crucible with either a grade 60 or grade 40 porous graphite bottom. Grade 20 porous graphite will not support molten zinc.

Figure 16
ZINC-FILTRATION APPARATUS

The procedure used was to dissolve the uranium in zinc at about 750 C. Mixing assisted the dissolution of the uranium. The uranium-zinc intermetallic crystals formed as the saturated uranium-zinc solution cooled. Both large crystals from slow cooling and small crystals from fast cooling could be effectively filtered. The filtration at about 500 C was effected very rapidly by using a pressure differential of 15 psi across the filter. High recoveries of the uncombined zinc have been realized. The analysis of $\text{UZn}_{11.5}$ filter cakes indicated around 20 weight per cent uranium, as compared with a theoretical amount of 23 weight per cent.

High-temperature (~ 800 C) filtrations to remove insolubles from the zinc-uranium solution have also been performed by E. J. Petkus.⁽²⁵⁾ However, the high-temperature filtration has proven more troublesome than the low-temperature filtration, not because the filtration per se is more difficult, but because the high vapor pressure of zinc results in plugging of vent lines.

Decantation - Decantation as a means of separation may also be practicable and, in fact, may be more adaptable to remote operation than filtration, for which difficulties are anticipated in removal of the separated crystals from a filter.

By stirring throughout the cooling, the precipitated crystals can be made to deposit in a dense, well-defined layer on the bottom of the vessel. The decanted zinc has been found to be free of uranium, but the proportion remaining with the crystals has been somewhat higher than in the case of filtration. Alternatively, the crystals may be deposited in a shallow dish which would then be raised out of the solution.

Recovery of Uranium from U_2Zn_{17} Concentrates - Recovery of uranium from U_2Zn_{17} has been effected by A. A. Chilenskas⁽²¹⁾ by retorting in equipment such as is illustrated in Figure 17.

The procedure followed was to degas the U_2Zn_{17} charge and components in place under a vacuum of 10^{-3} millimeter of mercury at 500 C. The zinc was retorted and the uranium coalesced by heating between 950 and 1200 C for 2.5 hours under an atmosphere of purified helium. Analysis of the uranium showed a zinc concentration of 80 ppm. Crucibles of recrystallized alumina, high-purity dry-pressed magnesia, coated graphite and tantalum have been used. Uranium ingots up to 150 grams have been produced.

IX. EXPLORATORY RESEARCH

Scouting experiments were carried out in four areas:

1. The reduction of uranium compounds by magnesium in zinc solution,
2. decomposition of the uranium-zinc intermetallic compound to yield uranium by addition of sufficient magnesium to form a 46.5 weight per cent magnesium-zinc eutectic,
3. removal of macro ruthenium from uranium, and
4. direct reaction of uranium and zinc.

A. Reduction of Uranium Compounds

Chemical reactions which have been effected in a zinc-6 weight per cent magnesium alloy are the following:

1. $UO_2(s) + 2Mg(\text{zinc sol}) \longrightarrow 2MgO(s) + U(\text{zinc sol})$
2. $UO_3(s) + 3Mg(\text{zinc sol}) \longrightarrow 3MgO(s) + U(\text{zinc sol})$
3. $UF_4 + 2Mg(\text{zinc sol}) \longrightarrow 2MgF_2 + U(\text{zinc sol})$

These reactions were verified by metallographic identifications of a uranium-zinc intermetallic compound in the resulting ingots, by analyses of filtered liquid samples which showed uranium to be in solution, and by X-ray diffraction identification of uranium-zinc intermetallic compound in the ingot.

In these preliminary experiments, considerable variation in reduction yields occurred. Maximum reductions realized were as follows:

UO_2	56%
UO_3	24%
UF_4	24%

The incomplete and variable reductions are probably attributable to failure to achieve intimate solid-liquid contact or to inadequate time. Stirring was effected by using a flattened $\frac{1}{4}$ -inch diameter tantalum rod, which undoubtedly provided inadequate agitation. Times were of the order of two hours at 800 C. Approximately 10 grams of 100 mesh powder and 500 grams of a zinc-6 weight per cent magnesium alloy were employed.

The possibility of reducing uranium compounds in liquid metal media disclosed by the above experiments should have important applications in pyrometallurgical processing of nuclear fuel materials and in the preparation of uranium feed materials.

B. Decomposition of Uranium-Zinc Intermetallic Compound by Magnesium Addition

Decomposition of uranium-zinc intermetallic compound with liberation of uranium metal by addition of sufficient magnesium to form a 46.5 weight per cent magnesium-zinc eutectic alloy has been demonstrated. Figure 18 is a photomicrograph which shows the liberated uranium in the bottom of the ingot. It may be noted that the uranium agglomerated into small globules, the largest being about $\frac{1}{16}$ -inch in diameter. The eutectic composition was employed in this work, but it is now known that, at magnesium concentrations above 20 weight per cent, uranium metal rather than uranium-zinc intermetallic compound is the solid phase in equilibrium with the melt.⁽²²⁾

The ingot shown in Figure 18 was prepared by contacting a uranium-zinc intermetallic filter cake with sufficient magnesium to form the eutectic at 53.5 weight per cent zinc. The melt was mixed at 800 C. Metallic uranium was precipitated and coalesced as the uranium-zinc intermetallic filter cake decomposed.

The phases present were as follows:

1. eutectic matrix,
2. magnesium-zinc intermetallic crystals distributed throughout matrix, and
3. metallic uranium coalesced into small lumps at bottom of crucible.

This experiment shows that by changing the melt composition the composition of the solid phase in equilibrium with the melt may be changed. Coprecipitation of impurity elements may thereby be altered drastically. As an example, plutonium and rare earths coprecipitate nearly quantitatively with the uranium-zinc intermetallic compound, but do not coprecipitate with

the metallic uranium precipitates from a concentrated magnesium solution. The separation of plutonium from uranium provided by this phenomenon may possibly provide the basis of a liquid metal blanket process.

Figure 18
PHOTOMICROGRAPH OF INGOT FROM MAGNESIUM-
ZINC EXTRACTION
(25 X)

C. Separation of Macro Ruthenium from Uranium

In Table 5, page 19, it was shown that the solubility of ruthenium was lowered by the presence of uranium, which resulted in precipitation of the ruthenium along with the uranium (see Figure 11, page 21). Fast cooling was indicated to be beneficial (see Figure 13), but may be difficult to perform from an engineering standpoint. Consequently, other approaches to the problem of removal of ruthenium were sought.

1. Ruthenium Drossing Studies

The object of the ruthenium drossing studies was to determine if the reactive metals barium, sodium, cerium, strontium, and calcium could be added to uranium-fission element solutions in zinc to form selectively intermetallic compounds with the noble metal ruthenium. This might then be separable from the bulk solution either by a hot filtration or by differences in specific gravity.

The results from drossing runs using about one weight per cent ruthenium in zinc and adding equivalent amounts of the desired addition were negative. There was no apparent interaction of the added metals and ruthenium at 800 C.

2. Cyclic Oxidation-Reduction

An experiment was performed to determine if the noble metals could be selectively reduced or leached by zinc from mixtures of uranium dioxide and noble metals (or noble metal oxides, if formed) with subsequent uranium recovery by magnesium reduction of uranium dioxide in zinc.

A small quantity (9.5 grams) of EBR-II fissium was hydrided, dehydrided, and oxidized. (It should be noted in passing that fissium was considerably more difficult to hydride than normal uranium.) Zinc was added and the system mixed at 750 C to take the noble metals into solution. A filtered sample showed that 34.3 per cent of the total ruthenium and 0.4 per cent of the total uranium went into solution. At this point magnesium was added. After mixing, a filtered sample was taken, which showed 96.3 per cent of the total ruthenium and 77.1 per cent of the total uranium to be in solution.

Although, in this single experiment, ruthenium removal was not as high as would be desired, results show the feasibility of removing the relatively noble metals from uranium oxide powder and of uranium recovery by magnesium reduction in zinc solution.

D. Direct Reaction of Uranium and Zinc

The preparation of U_2Zn_{17} from essentially stoichiometric quantities of uranium and zinc was carried out successfully by A. A. Chilenskas⁽²¹⁾ to provide a source of U_2Zn_{17} for retorting studies. The apparatus is shown in Figure 19.

The uranium (weighing 454 grams and charged as small segments of $\frac{5}{16}$ -inch rod) and zinc bar slightly in excess of the stoichiometric quantity required were enclosed within the graphite crucible by means of a threaded graphite cap. The graphite (CS type) was sufficiently porous to permit gases to pass through but retains molten zinc.

Figure 19
 APPARATUS FOR DIRECT REACTION
 OF URANIUM AND ZINC

Powdering the uranium rod was accomplished by hydriding the uranium at 1 atmosphere and 240 C, and dehydriding at 360 C under vacuum. The powdered uranium and zinc charge were then held at 800 C for five hours with occasional agitation provided by rocking the reactor.

Metallographic examination of segments of the product ingot showed crystals assumed to be U_2Zn_{17} with some unreacted zinc constituting a second phase. No evidence of unreacted powdered uranium was found, although several large lumps of uranium which apparently had not hydrided were discovered in sectioning the ingot.

It may also be possible to react uranium and zinc at low temperatures and thus avoid some of the corrosion difficulties present at 800 C.

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