ANL-6243
Metallurgy and Ceramics
(TID-4500, 15th Ed.)
AEC Research and
Development Report

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois

STUDIES OF CORROSION BY MOLTEN
ZINC AND CADMIUM SYSTEMS

by

John P. DeKany, Henry W. Lavendel, and Leslie Burris, Jr.

Chemical Engineering Division

October 1960

Operated by The University of Chicago
under
Contract W-31-109-eng-38

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	<u>Page</u>
I. SUMMARY	3
II. INTRODUCTION.	5
III. GENERAL APPROACH	7
IV. EXPERIMENTAL RESULTS	8
A. Static Corrosion Tests	8
1. Procedure.	8
2. Results of Tests in Cadmium Systems	9
3. Results of Tests in Zinc Systems	12
B. Dynamic Corrosion Tests	21
1. Rotating Capsule Tests	21
2. Thermal Convection Loops.	29
3. Forced Convection Loops.	32
V. CONCLUSIONS.	42
ACKNOWLEDGEMENTS	43
REFERENCES	44

STUDIES OF CORROSION BY MOLTEN ZINC AND CADMIUM SYSTEMS

by

John P. DeKany, Henry W. Lavendel, and Leslie Burris, Jr.

I. SUMMARY

A corrosion program was undertaken in conjunction with development of pyrometallurgical processes employing liquid metal solvents as processing media. The metal solvents under consideration for use as solvents for uranium, plutonium, and thorium were zinc, cadmium, and magnesium, either alone or in various combinations with each other. The objective of the program was to find suitable container materials for the various liquid metal systems encountered.

The corrosion program consisted of 100-hour static tests designed to screen a large number of materials. Promising materials were then subjected to 1000-hour dynamic capsule tests, or used in forced convection or thermal convection loops. The latter enabled an assessment of mass transfer corrosion.

Zinc-base systems were tested at temperatures up to 750 C, the cadmium-base systems at temperatures of 550 to 700 C. Magnesium was generally the other constituent, being used in processes either as a reducing agent or in concentration sufficient to provide certain desirable solubility relationships. The corrosion behavior of dilute zinc-cadmium solutions was also investigated, zinc being used to provide desirable solubility effects.

Cadmium Tests

In view of the previously reported resistance of iron and carbon steels to attack by cadmium at temperatures of up to 500 C, ferrous alloys were selected for testing in the cadmium systems. In 100-hour static tests, nickel-free ferrous alloys were not attacked and were generally unwetted by molten cadmium at temperatures up to 550 C. Nickel-containing stainless steels were intergranularly attacked, probably through leaching of the nickel. The presence of zinc in a 0.2 per cent magnesium-cadmium system did not produce detectable corrosion until a 10 per cent zinc concentration had been reached.

Carbon steel and 410 stainless steel were not attacked by cadmium-magnesium solutions of up to 50 per cent magnesium at 650 C. At 700 C, however, intergranular corrosion by pure cadmium was evident and was strongly accelerated by zinc at a 10 per cent concentration.

Two tests at 650 C were made in 410 stainless and 1040 carbon steel with uranium and fission products dissolved in the cadmium. While metal attack was lacking, a layer which deposited on the surface of the steels indicated interaction with the solute elements. This points out the need for determining the stability of cadmium solutions of various elements held in ferrous alloy containers.

In 1000-hour rotating capsule tests at 550 C, no attack was noted on mild steel by cadmium or dilute cadmium solutions of uranium (2 per cent), zinc (8 per cent), and magnesium (5 per cent). At 350 C and in tests of similar duration in mild and 410 steels, the presence of zinc did not result in detectable corrosion until a 10 per cent concentration was reached.

Two thermal convection loops of medium carbon steel operating in the region of 575 to 730 C with 15 and 30 per cent magnesium-cadmium solutions showed rather low mass transfer corrosion, the maximum thickness of the deposition layer being 6 mils deposited over a 1000-hour period. Two forced convection corrosion loops of $\frac{1}{2}$ -inch medium carbon steel pipe were also operated at 550 C. In the first loop, a nominal 2 per cent uranium-0.2 per cent magnesium-cadmium solution was circulated for slightly more than 1000 hours at 0.8 gal/min. A 0.85 per cent uranium-2 per cent magnesium-cadmium solution containing various fission products in trace amounts was circulated in the second loop for 4800 hours at 0.8 gal/min. Operation of both loops was troublefree. However, the measured uranium concentration in the first loop was only 1.5 per cent instead of the nominal 2 per cent. After shutdown, metallographic examination disclosed uranium deposition in three relatively cold spots, and subsequent interaction with the steel walls may have occurred. No other signs of corrosion were evident.

Through better insulation, more uniform temperatures were realized in operation of the second loop. After shutdown, metallographic examination of this loop did not disclose any evidence of corrosion at any point in the loop. The uranium concentration remained constant at 0.85 per cent for 4300 hours but differed from nominal concentration by 0.12 per cent. This was attributed to the formation of an oxide slag as a result of air contamination during the startup operations.

Zinc Tests

Few materials are resistant to molten zinc, particularly at the elevated temperatures of interest (up to 800 C). Of the metals, only tungsten, tantalum, and molybdenum showed substantial resistance to attack by zinc. Tungsten was completely inert to the zinc system. Tantalum, which may be placed next in order of resistance, did undergo some attack after 100 hours at 750 C to depths of about 1 mil, through formation of a suspected intermetallic compound. However, the presence of magnesium substantially reduced the corrosiveness of zinc toward tantalum and also toward the other metals tested. Molybdenum was attacked to a slightly greater

extent than tantalum by a solution process. Molybdenum was found in the zinc phase to the extent of its measured solubility (ca. 0.02 wt per cent).

All iron or nickel alloys were completely disintegrated by zinc attack. Titanium suffered a similar fate. Alumina, silicon carbide, silicon nitride, zirconia, Vycor (a commercial silica), and graphite were unaffected by runs at 750 C. When magnesium was present, Vycor and silicon nitride were severely corroded. Several of the above ceramics were applied as coatings on steel, but in no case was protection provided, the coatings being rapidly penetrated.

The above work represents only a start in investigating the corrosion behavior of zinc, cadmium, and magnesium systems. The work is continuing, particularly with the zinc systems, whose severe corrosiveness requires the development and testing of new container materials.

II. INTRODUCTION

Several processes employing liquid metals as processing media are currently under development at Argonne National Laboratory for recovery of uranium and plutonium from reactor core and blanket materials. These processes generally utilize various combinations of zinc, cadmium, and magnesium as the solvent media and have certain features in common:

- 1) Dissolution of the material in a suitable liquid metal alloy. Oxides may also be accommodated by employing magnesium as a reducing agent.
- 2) Crystallization of uranium or plutonium as free metals or as intermetallic compounds with the solvent metal. Retention of impurities in solution may take place because of favorable solubility or concentration relationships.
- 3) Phase separations by decantation or filtration to remove the supernatant liquor from the precipitated phase.
- 4) Retorting of the uranium or plutonium precipitates to volatilize the solvent metal and enable recovery of the valuable material in a convenient metallic form.

Temperatures in these steps may range up to 800 C.

Various materials may be selected and are frequently proposed as possible container materials. A corrosion or materials testing program was therefore set up to evaluate these container materials. An overall corrosion program would include developing the following information:

- 1) Extent and type of attack on container material.
- 2) Effects of corrosion on product purity.
- 3) Interactions of container material with uranium or other solutes in liquid metal solution, i.e., effect of container material on solution stability.

The work reported herein was concentrated largely on the first objective inasmuch as it was necessary to screen a large number of materials in order to select materials for more detailed tests. The selection of materials for testing as possible container materials was dictated by several factors:

- 1) the solubility of the container material in the various liquid metal systems to be studied;
- 2) the phase diagram of the container material-liquid metal system, i.e., the existence of intermetallic compounds between container material and liquid metal;
- 3) previous corrosion experience; and
- 4) availability, fabricability, and purity of container material.

The first and second factors determined to a large extent whether a particular material was selected for testing. A great deal of information concerning the solubilities and phase diagrams of possible container materials was found in a book by Hansen.⁽¹⁾ When a material was reported to have low solubility and not to form intermetallic compounds with the liquid metal system, the literature was searched for previous corrosion experience.

For the case of liquid cadmium, the ferrous metals met the above requirements very well. The solubility of iron was reported to be 0.0002 to 0.0003 weight per cent.⁽²⁾ Also, Hansen mentions the results of several unsuccessful attempts to form iron-cadmium intermetallic compounds.⁽¹⁾ Other investigators^(3,4) observed that liquid cadmium did not diffuse into mild steel at temperatures up to 1200 C and under stress. DeLattre⁽⁵⁾ mentioned that cadmium was essentially inert with respect to mild steel. Since nickel is soluble in molten cadmium, nickel-containing ferrous alloys should not be inert to liquid cadmium systems. Such was the case found by Van Ewijk.⁽⁶⁾ The inertness of non-nickel-containing ferrous alloys toward molten cadmium is best summarized by Eldred.⁽⁷⁾ For the above reasons, the ferrous alloys were chosen for extensive testing in liquid cadmium systems.

Owing to the great interest in galvanizing operations, much corrosion information had been compiled on molten zinc systems. An excellent discussion and bibliography on this previous effort may be found in Eldred's report.⁽⁷⁾ Unfortunately, these investigations did not uncover a single

common metal or alloy that could resist indefinitely the alloy action of liquid zinc. Therefore, the attention of this study was focused on metals and new alloys for which reliable zinc corrosion information was not reported. The most promising materials were tantalum, tungsten, tungsten alloys, and molybdenum. Koster and Schmid,⁽⁸⁾ reported that zinc did not alloy with tungsten or molybdenum. Hodge, *et al.*,⁽⁹⁾ reported that a tantalum specimen disintegrated in molten zinc, but this result was contrary to preliminary findings at ANL on the zinc-tantalum system.

III. GENERAL APPROACH

The primary objective of the liquid metals corrosion program was to find suitable container materials for the handling of the following liquid metal systems: zinc, cadmium, zinc-magnesium alloys, cadmium-uranium-magnesium alloys, and cadmium-fissium*-magnesium alloys. Initial experiments were static in nature and designed to screen a number of materials. Particular emphasis was placed upon testing conventional, commercially available materials whenever these materials indicated possible application as containers. The criterion of rejection in the static corrosion tests was the inability of the material to resist attack when exposed to the particular liquid metal or alloy system for 100 hours at the test temperature. The test results were evaluated on the basis of metallographic examination and spectrographic analyses.

The materials successful in passing the static tests were then subjected to two stages of dynamic testing. The first stage consisted of fabricating the materials into capsules, filling the capsules with the molten metal media, and then testing by end-over-end rotation inside a furnace. The most desirable of the materials surviving the rotating capsule tests were then admitted to the second stage of dynamic testing. In this, the materials were fabricated into forced and thermal convection loops in which the molten metals were circulated. The forced convection loops were operated at near isothermal conditions in order to reduce mass transfer effects. The thermal convection loops, of course, operated under large thermal gradients and were used to investigate the possibility of mass transfer corrosion as well as corrosion by other processes.

* Fissium is the term applied to uranium-fission product alloys. The alloy employed in these tests contained 2.3 per cent (by weight) molybdenum, 1.9 per cent ruthenium, 0.3 per cent palladium, 0.2 per cent rhodium, 0.1 per cent zirconium, 0.01 per cent niobium, and the balance uranium.

IV. EXPERIMENTAL RESULTS

A. Static Corrosion Tests

1. Procedure

The usual procedure followed in the static tests consisted of containing the material to be tested along with the particular liquid metal in a capsule fabricated from material considered to be inert to attack by the corrosion system. Mild steel was selected as the capsule material for the molten cadmium alloy systems. Although very slightly attacked by molten zinc, tantalum was used as the capsule material for exposing coupons of other materials to zinc and zinc alloys. Spectrographic analyses showed no significant contamination of either zinc or zinc-46 weight per cent magnesium systems. In some instances the materials to be tested could be readily fabricated into capsules which then served both as corrosion specimen and container for the corrosion system. This was the case with several of the common materials, such as the steels.

However, the materials to be tested were usually cut from sheet stock in the form of coupons, $\frac{1}{2} \times 1 \times \frac{1}{8}$ -inch. Prior to containment in the capsules, the coupons were cleaned by one of several techniques depending upon the material. The iron-containing materials were cleaned successively in two acidic solutions: first, a 20 per cent sulfuric acid bath for 5 minutes to "break" any scale on the sample, and second, 20 per cent nitric acid for 5 minutes, which removed the broken scale. The nonferrous materials generally required only a degreasing operation with acetone, although in several instances the specimens were also sandblasted.

After the cleaning operation, the corrosion specimens along with 75 grams of cadmium or zinc alloy were loaded into cylindrical capsules, 1 inch OD x $2\frac{1}{4}$ inches high. The capsules were then purged with inert gas and sealed by welding caps on the capsules in an inert gas atmosphere.

The loaded capsules were placed in a resistance-heated furnace and held at test temperatures for 100 hours. The test temperatures were 750 C for the zinc alloy tests and 550 C to 700 C for the cadmium tests. After the 100-hour period, the capsules were removed and sectioned for examination.

The examination consisted principally of visual observation under the microscope. In many cases the liquid metal phase was also analyzed spectrographically. If a material exhibited any form of corrosion, it was disqualified from further consideration as a possible container for the liquid metal system at the test conditions.

2. Results of Tests in Cadmium Systems

In view of the reported inertness, described in the introduction, exhibited by ferrous metals and alloys toward molten cadmium, the ferrous metals were selected for testing in the molten cadmium alloy systems. Table 1 contains a summary of the results of 100-hour static corrosion tests on various ferrous materials and also on tantalum in molten cadmium alloy systems.

In pure cadmium at 550 C none of the nickel-free ferrous alloys or tantalum were corroded by the cadmium (Table 1, Tests 1 to 7, inclusive). Most of the specimens remained unwetted by the molten cadmium. The nickel-containing stainless steels represented by 304 and 310 stainless steel were intergranularly attacked (Tests 8 and 9). The attack was attributed to the leaching of nickel constituents from the grain boundaries. Figure 1 illustrates the corrosive leaching of nickel by molten cadmium from a 304 stainless steel specimen. In view of the large solubility of nickel in liquid cadmium, the leaching of nickel was not surprising. However, the attack was of the order of 1 mil and possibly would be tolerable for some applications. It should be borne in mind, however, that the resulting cadmium solution will be contaminated with nickel.

The same ferrous materials were tested in a molten alloy of 2 weight per cent uranium-cadmium (Tests 10-17, inclusive). With the exception of the nickel-containing steels, all of the materials tested were inert to the corrosion medium. Figure 2 shows the surface of a 410 stainless steel specimen after the 100-hour exposure to one of the molten alloys.

At 700 C, mild steel and 410 stainless steel appeared to be attacked by liquid cadmium (Tests 18 and 19). Specimens of these materials tested at 700 C were intergranularly corroded to an extent of approximately 0.5 mil. This would indicate that the applicability of ferrous alloys as containment vessels for cadmium solutions for long-time service would be limited to temperatures below 700 C.

Mild steel and 410 stainless steel were tested at 650 C in magnesium-cadmium alloys ranging in magnesium content from 2 weight per cent to 50 weight per cent (Tests 20-35, inclusive). Both were inert to attack by the alloys, even though in all cases the corrosive medium wet the surfaces of the corrosion specimens.

Several tests employing mild steel and 410 stainless steel as capsules were performed on 2, 4, 8, and 10 weight per cent zinc-0.2 weight per cent magnesium-cadmium alloys at 550 C (Tests 36-43, inclusive). No corrosion was observed upon mild steel or 410 stainless steel at 550 C by zinc-cadmium alloys containing 2, 4, or 8 weight per cent zinc.

Table 1

RESULTS OF 100-HOUR STATIC CORROSION TESTS ON VARIOUS
MATERIALS IN LIQUID CADMIUM SYSTEMS

Test No.	Material	Form of Specimen	Composition of Liquid Cadmium System	Test Temp (C)	Results
1	1025 Carbon Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	100 w/o Cd	550	No corrosion
2	1040 Carbon Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	100 w/o Cd	550	No corrosion
3	1065 Carbon Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	100 w/o Cd	550	No corrosion
4	1095 Carbon Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	100 w/o Cd	550	No corrosion
5	410 Stainless Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	100 w/o Cd	550	No corrosion
6	Armco Iron	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	100 w/o Cd	550	No corrosion
7	Tantalum	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	100 w/o Cd	550	No corrosion
8	304 Stainless Steel	Capsule	100 w/o Cd	550	Corrosion in form of nickel leaching
9	310 Stainless Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	100 w/o Cd	550	Corrosion in form of nickel leaching
10	1025 Carbon Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	2 w/o U - 98 w/o Cd	550	No corrosion
11	1040 Carbon Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	2 w/o U - 98 w/o Cd	550	No corrosion
12	1065 Carbon Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	2 w/o U - 98 w/o Cd	550	No corrosion
13	1095 Carbon Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	2 w/o U - 98 w/o Cd	550	No corrosion
14	304 Stainless Steel	Capsule	2 w/o U - 98 w/o Cd	550	Corrosion in form of nickel leaching
15	310 Stainless Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	2 w/o U - 98 w/o Cd	550	Corrosion in form of nickel leaching
16	410 Stainless Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	2 w/o U - 98 w/o Cd	550	No corrosion
17	Armco Iron	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	2 w/o U - 98 w/o Cd	550	No corrosion
18	1040 Carbon Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	100 w/o Cd	700	Intergranular corrosion ~0.5 mil
19	410 Stainless Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	100 w/o Cd	700	Intergranular corrosion ~0.5 mil
20	1040 Carbon Steel	Capsule	2 w/o Mg-Cd	650	No corrosion
21	1040 Carbon Steel	Capsule	5 w/o Mg-Cd	650	No corrosion
22	1040 Carbon Steel	Capsule	10 w/o Mg-Cd	650	No corrosion
23	1040 Carbon Steel	Capsule	15 w/o Mg-Cd	650	No corrosion
24	1040 Carbon Steel	Capsule	20 w/o Mg-Cd	650	No corrosion
25	1040 Carbon Steel	Capsule	30 w/o Mg-Cd	650	No corrosion
26	1040 Carbon Steel	Capsule	40 w/o Mg-Cd	650	No corrosion
27	1040 Carbon Steel	Capsule	50 w/o Mg-Cd	650	No corrosion
28	410 Stainless Steel	Capsule	2 w/o Mg-Cd	650	No corrosion
29	410 Stainless Steel	Capsule	5 w/o Mg-Cd	650	No corrosion
30	410 Stainless Steel	Capsule	10 w/o Mg-Cd	650	No corrosion
31	410 Stainless Steel	Capsule	15 w/o Mg-Cd	650	No corrosion
32	410 Stainless Steel	Capsule	20 w/o Mg-Cd	650	No corrosion
33	410 Stainless Steel	Capsule	30 w/o Mg-Cd	650	No corrosion
34	410 Stainless Steel	Capsule	40 w/o Mg-Cd	650	No corrosion
35	410 Stainless Steel	Capsule	50 w/o Mg-Cd	650	No corrosion
36	1040 Carbon Steel	Capsule	2 w/o Zn-0.2 w/o Mg-Cd	550	No corrosion
37	1040 Carbon Steel	Capsule	4 w/o Zn-0.2 w/o Mg-Cd	550	No corrosion
38	1040 Carbon Steel	Capsule	8 w/o Zn-0.2 w/o Mg-Cd	550	No corrosion
39		Capsule	10 w/o Zn-0.2 w/o Mg-Cd	550	Slight intergranular corrosion ~0.5 mil
40	410 Stainless Steel	Capsule	2 w/o Zn-0.2 w/o Mg-Cd	550	No corrosion
41	410 Stainless Steel	Capsule	4 w/o Zn-0.2 w/o Mg-Cd	550	No corrosion
42	410 Stainless Steel	Capsule	8 w/o Zn-0.2 w/o Mg-Cd	550	No corrosion
43	410 Stainless Steel	Capsule	10 w/o Zn-0.2 w/o Mg-Cd	550	Slight intergranular corrosion ~0.5 mil
44	410 Stainless Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	10 w/o Zn-0.2 w/o Mg-Cd	700	Corrosion ~1 mil
45	1040 Carbon Steel	Coupon- $\frac{1}{2} \times 1 \times \frac{1}{8}$ in.	10 w/o Zn-0.2 w/o Mg-Cd	700	Corrosion ~1 mil
46	410 Stainless Steel	Capsule	2 w/o Fissium-Cd	650	0.2 mil layer on surface
47	1040 Carbon Steel	Capsule	2 w/o Fissium-Cd	650	0.2 mil layer on surface

Figure 1

Surface of 304 Stainless Steel Specimen Showing
Corrosion by Molten Cadmium in Static
Test for 100 Hours at 550 C

Photomicrograph 1

300X

Etchant: 2% HNO_3 -Ethyl Alcohol

Photomicrograph 2

750X

Etchant: 2% HNO_3 -Ethyl Alcohol

Figure 2

Type 410 Stainless Steel Specimen after 100-Hour
Exposure to 2 Per Cent Uranium-Cadmium Solution

Photomicrograph 3

250X

Electrolytic Etchant: 2% HCl-Ethyl Alcohol

The 10 weight per cent zinc-cadmium alloy caused slight intergranular corrosion of mild steel and 410 stainless steel to an extent of 0.5 mil. Additional tests were made on mild steel and 410 stainless steel in 10 weight per cent zinc-0.2 weight per cent magnesium-cadmium at 700 C (Tests 44 and 45). As expected, both steels were attacked more severely at this higher temperature, the average depth of corrosion being approximately 1 mil.

Two capsule tests with 2 weight per cent fissium-2 weight per cent magnesium-cadmium alloy in mild steel and 410 stainless steel were performed at 650 C (Tests 46 and 47). The only indication of interaction was the formation of a 0.2-mil layer on the surface of the specimens. This layer is indicative of possible reaction of the solute elements with steel or may have resulted from deposition of several fissium elements on the steel surface as a result of being present in amounts in excess of their solubility. This observation indicates that the stability of cadmium solutions at this temperature should be checked.

3. Results of Tests in Zinc Systems

Prior to the investigation of the zinc systems, a literature search was conducted in order to determine which materials could be used to contain molten zinc. The conclusions from this search emphasized the

lack of metallic materials inert to molten zinc. At that time the only metals that were reported to be fairly successful in containing molten zinc were tantalum, tungsten, and molybdenum. Other metallic materials were recommended by various research groups and corporations, but in all cases these materials had never been tested in molten zinc before. Therefore, the purpose of the zinc experiments was to test tantalum and other recommended materials in molten zinc and zinc alloys.

Table 2 presents a summary of the results of 100-hour static corrosion tests on the various materials in liquid zinc systems at 750 C. Of all the metals tested in molten zinc, only tungsten, tantalum, and molybdenum were resistant to attack. Of these, tungsten was the only metal which remained completely inert to attack by molten zinc (see Figure 3). Unfortunately, at the present time tungsten leaves much to be desired from the standpoint of fabricability and, consequently, can be used in very few applications. For this reason a number of tungsten alloys, developed by Armour Research Foundation, which are considerably more ductile and malleable than pure tungsten were investigated. These alloys were made by powder metallurgy and were basically composed of tungsten with iron and nickel as minor constituents. All of these tungsten alloys were disintegrated in the zinc and to a lesser extent in 46 weight per cent magnesium-zinc. The mechanism of attack consisted of the leaching out of the nickel and iron, leaving behind a matrix of loosely bound tungsten globules (see Figure 3).

Tantalum also showed some promise in these initial experiments and, since it is more readily fabricated than tungsten, it was extensively tested in molten zinc and molten zinc alloys. The results of the investigations showed that tantalum interacted with pure zinc at 750 C. This attack occurred through the formation of what appears to be a solid intermetallic phase between the tantalum and zinc. The thickness of the interaction zone varied somewhat from specimen to specimen but was generally 1 mil or slightly greater. Figure 4 is representative of the type of intermetallic layers observed on the specimens. As the photomicrographs illustrate, the postulated intermetallic layer was adherent in some cases while in others it was beginning to break away, forming a solid suspension in solution.

The interaction zone between the tantalum and zinc phases was indicated to be an intermetallic compound layer by means of Vickers microhardness determinations. Photomicrograph 4 (Figure 5) shows a specimen in the as mechanically-polished phase and the microhardness indentations in the component materials at the interface. Four distinct areas are discernible. The darkest gray area is the tantalum phase. Adjacent to the tantalum is an entrapped zinc area; next, a border of intermetallic compound material and finally the zinc phase.

Table 2

RESULTS OF 100-HOUR STATIC CORROSION TESTS ON
VARIOUS MATERIALS IN LIQUID ZINC SYSTEMS

A. Tests in Molten Zinc at 750 C

Material ^a	Form of Specimen	Results
Tungsten	Coupon	No Corrosion
Tantalum	Coupons and Capsules	Mild corrosion through formation of inter-metallic layer
Molybdenum	Coupon	Mild corrosion through dissolution
Titanium	Coupon	Complete disintegration of specimen
Thermenol	Rod	Complete disintegration of specimen
Haynes No. 25 Alloy	Coupon	Complete disintegration of specimen
Haynes Multimet Alloy	Coupon	Complete disintegration of specimen
Haynes Stellite Alloy No. 6B	Coupon	Complete disintegration of specimen
Nitrided Steel	Coupon	Complete disintegration of specimen
Cyanided Steel	Coupon	Complete disintegration of specimen
Colmonoy 6 Spray Coated on Mild Carbon Steel	Coupon	Complete disintegration of specimen
Vitallium	Rod	Complete disintegration of specimen
Armour Research Foundation Tungsten Alloys Nos. 98, 97, 95, 90	Coupons	Complete disintegration of specimen

B. Tests in 46 Weight Per Cent Magnesium-Zinc at 750 C

Material ^a	Form of Specimen	Results
Tantalum	Coupons and Capsules	No Corrosion
Molybdenum	Coupon	Mild corrosion through dissolution
Titanium	Coupon	Severe corrosion
Thermenol	Rod	Severe corrosion
Haynes No. 25 Alloy	Coupon	Severe corrosion
Haynes Stellite Alloy No. 6B	Coupon	Severe corrosion
Haynes Multimet Alloy	Coupon	Severe corrosion
Nitrided Steel	Coupon	Severe corrosion
Cyanided Steel	Coupon	Severe corrosion
Colmonoy 6 Spray Coated on Mild Carbon Steel	Coupon	Severe corrosion
Vitallium	Rod	Severe corrosion
Armour Research Foundation Tungsten Alloys Nos. 98, 97, 95, and 90	Coupons	Severe corrosion

C. Tests of Tantalum in Zinc-Magnesium Systems at 750 C

Material	Composition of Liquid Metal	Results
Tantalum Capsule	5 w/o Mg-Zn	No corrosion
Tantalum Capsule	15 w/o Mg-Zn	No corrosion
Tantalum Capsule	20 w/o Mg-Zn	No corrosion
Tantalum Capsule	30 w/o Mg-Zn	No corrosion
Tantalum Capsule	46 w/o Mg-Zn	No corrosion

^aThe materials tested were subjected to test conditions for which they were not specifically designed, and the results of the tests do not constitute an endorsement or a criticism of any product tested.

Figure 3

Photomicrographs of Tungsten and Tungsten Alloy
Specimens after 100-Hour Static Exposure
to Molten Zinc at 750 C

Photomicrograph No. 5

300X

Zinc-Tungsten Interface

Etchant: 10% HF-H₂SO₄

Photomicrograph No. 6

750X

Tungsten Alloy 90

Etchant: 10% HF-H₂SO₄

Figure 4

Photomicrographs of Tantalum Specimens after
100-Hour Static Exposure to
Molten Zinc at 750 C

Photomicrograph No. 7

300X

Zinc-Tantalum Interface

Etchant: 10% HF-H₂SO₄

Photomicrograph No. 8

750X

Zinc-Tantalum Interface

Etchant: 10% HF-H₂SO₄

Figure 4 (Cont'd.)

Photomicrographs of Tantalum Specimens after
100-Hour Static Exposure to
Molten Zinc at 750 C

Photomicrograph No. 9

750X

Tantalum-Zinc Interface

Etchant: 10% HF-H₂SO₄

Photomicrograph No. 10

1500X

Tantalum-Zinc Interface

Etchant: 10% HF-H₂SO₄

Figure 4 (Cont'd.)

Photomicrographs of Tantalum Specimens after
100-Hour Static Exposure to
Molten Zinc at 750 C

Photomicrograph No. 11

250X

Tantalum-Zinc Interface Showing Extensive
Intermetallic Compound Formation

Etchant: Cathodic

Photomicrograph No. 12

250X

Tantalum-Zinc Interface Showing
Adherent Intermetallic Layer

Etchant: 7 parts Perchloric Acid
5 parts Glacial Acetic Acid

Figure 5
Photomicrograph No. 4 Showing Vickers Microhardness
Indentations in Tantalum-Zinc Interface

Vickers Microhardness Values for Positions One to Four

Position	Tantalum	Entrapped Zinc Area	Intermetallic Compound Layer	Zinc
1	90.8	51.2	-	20.9
2	95.8	-	342	28.1
3	104	-	292	29.3
4	-	-	363	36.7

The Vickers microhardness readings in each area are shown in Figure 5. The very first microhardness indentation in the intermetallic compound layer was partly in the entrapped zinc area and was not included in the above readings. The fourth indentation in the zinc is partly in the intermetallic compound. This, no doubt, is responsible for its comparatively higher microhardness reading. The Vickers microhardness number found for the intermetallic layer is of the magnitude normally associated with intermetallic compounds.

Tantalum was also tested in magnesium-zinc alloys ranging in magnesium content from 5 weight per cent to 46 weight per cent magnesium (see Figure 6).

Figure 6

Photomicrographs of Tantalum after Exposure
to Magnesium-Zinc Alloys at 750 C

Photomicrograph No. 13

750X

Tantalum Specimen (Bottom) after Exposure
to 5 Weight Per Cent Magnesium-Zinc

Etchant: 10% HF-H₂SO₄

Photomicrograph No. 14

750X

Tantalum Specimen after Exposure to
30 Weight Per Cent Magnesium-Zinc

Etchant: 10% HF-H₂SO₄

Although one of the specimens seemed to be slightly attacked by 46 weight per cent magnesium-zinc, the rest of the specimens remained inert to the magnesium-zinc alloys. This would seem to indicate that the presence of magnesium inhibits the attack of zinc to a great extent.

Molybdenum was the only other metal which remained intact after exposure to molten zinc. Metallographic examination indicated that a slight corrosion had occurred. This observation was confirmed by the presence of molybdenum in the zinc phase to an extent dictated by its solubility, 0.02 weight per cent.

Titanium was severely corroded in both zinc and a 46 weight per cent magnesium-zinc alloy. The attack is shown by photomicrographs 15 and 16 (see Figure 7).

Steels and iron alloys were completely disintegrated by molten zinc at 750 C (see Figure 8). While the addition of magnesium inhibited the corrosion to some extent, it was still severe and these alloys appear to have little promise for containing molten zinc at elevated temperatures.

Several ceramic materials were tested by themselves and as refractory coatings on mild steel in molten zinc and molten 46 weight per cent magnesium-zinc. The results are given in Tables 3 and 4. With the exception of silicon nitride and Vycor, the ceramics as a rule were inert to both the zinc and the zinc-magnesium alloy. However, when the ceramics were used as coatings to protect mild steel they proved to be easily penetrated by molten zinc and in all cases but one by the magnesium-zinc alloy. Rokide "Z" (stabilized zirconia) was the only ceramic coating not penetrated by the 46 weight per cent magnesium-zinc.

B. Dynamic Corrosion Tests

As mentioned previously, materials which showed promise after testing in a static environment were subjected to dynamic testing in rotating capsules or in thermal or forced convection loops.

1. Rotating Capsule Tests

For the rotating capsule tests the materials to be studied were fabricated into capsules, 1-inch OD by $2\frac{1}{4}$ inches long. These were partially filled under an inert atmosphere with the liquid metal under consideration. The loaded capsules were subsequently placed into an apparatus that rotated the capsules end-over-end at the test temperature. This action caused the liquid metal to flow from one end of the capsule to the other at a rate depending upon the rpm of the apparatus.

Figure 7

Photomicrographs of Titanium after 100-Hour Exposure
to Zinc and Zinc-Magnesium Alloys at 750 C

Photomicrograph No. 15

120X

Zinc-Titanium Interface

Etchant: 2% HNO_3 -Ethyl Alcohol

Photomicrograph No. 16

300X

Titanium Specimen Shown on Right of Photo after
Exposure to Molten 46 Weight Per Cent
Magnesium-Zinc at 750 C

Etchant: 2% HNO_3 -Ethyl Alcohol

Figure 8

Photomicrographs of Various Iron Alloys after
100-Hour Exposure to Molten Zinc and
Zinc-Magnesium Alloys

Photomicrograph No. 12

750X

Haynes Multimet Alloy

Etchant: 2% HNO_3 -Ethyl Alcohol

Photomicrograph No. 18

300X

Disintegrated Specimen of Mild Steel
Spray-Coated with Colmonoy 6 Alloy
in Zinc

Etchant: None

Figure 8(Cont'd.)

Photomicrographs of Various Iron Alloys after
100-Hour Exposure to Molten Zinc and
Magnesium-Zinc Alloys

Photomicrograph No. 19

1500X

Thermenol Alloy Completely Disintegrated
by Molten Zinc

Etchant: None

Photomicrograph No. 20

300X

Zinc-Vitallium Interface

Etchant: 2% HNO_3 -Ethyl Alcohol

Figure 8 (Cont'd.)

Photographs of Various Iron Alloys after
100-Hour Exposure to Molten Zinc and
Magnesium-Zinc Alloys

Photomicrograph No. 21

300X

Haynes Multimet Alloy after Exposure to
46 Weight Per Cent Magnesium-Zinc

Etchant: 2% HNO_3 -Ethyl Alcohol

Photomicrograph No. 22

750X

Specimen of Colmonoy 6 Alloy Spray-Coated on
Mild Steel Base after Exposure to 46 Weight
Per Cent Magnesium-Zinc

Etchant: 2% HNO_3 -Ethyl Alcohol

Table 3

RESULTS OF 100-HOUR STATIC CORROSION TESTS ON CERAMIC
MATERIALS IN MOLTEN ZINC SYSTEMS AT 750 C

Ceramic Material	Composition of Liquid Metal System	Results
Alumina	Zn	No corrosion
Silicon Carbide	Zn	No corrosion
Silicon Nitride	Zn	No corrosion
Zirconia	Zn	No corrosion
Vycor	Zn	No corrosion
Graphite	Zn	No corrosion
Alumina	46 w/o Mg-Zn	No corrosion
Silicon Carbide	46 w/o Mg-Zn	No corrosion
Silicon Nitride	46 w/o Mg-Zn	Severe corrosion
Zirconia	46 w/o Mg-Zn	No corrosion
Vycor	46 w/o Mg-Zn	Severe corrosion
Graphite	46 w/o Mg-Zn	No corrosion

Table 4

RESULTS OF 100-HOUR STATIC CORROSION TESTS ON CERAMIC
COATINGS APPLIED TO MILD CARBON STEEL COUPONS
IN LIQUID ZINC SYSTEMS AT 750 C

Coatings Applied to Steel Coupon ^a	Composition of Liquid Metal System	Results
Rokide "A" (Aluminum Oxide)	Zn	Complete disintegration of specimen
Rokide "ZS" (Zirconium Silicate)	Zn	Complete disintegration of specimen
Rokide "Z" (Stabilized Zirconia)	Zn	Complete disintegration of specimen
Rokide "C" (Silicon Carbide)	Zn	Complete disintegration of specimen
CrB ₂	Zn	Complete disintegration of specimen
Rokide "A" (Aluminum Oxide)	46 w/o Mg-Zn	Severe corrosion
Rokide "ZS" (Zirconium Silicate)	46 w/o Mg-Zn	Severe corrosion
Rokide "Z" (Stabilized Zirconia)	46 w/o Mg-Zn	No corrosion
Rokide "C" (Silicon Carbide)	46 w/o Mg-Zn	Severe corrosion
CrB ₂	46 w/o Mg-Zn	Severe corrosion

^aThe coating materials tested were subjected to test conditions for which they were not specifically designed, and the results of the tests do not constitute an endorsement or a criticism of any product tested.

The apparatus itself was simple and consisted of a rectangular stainless steel box with compartments for the corrosion capsules. The box was supported on a shaft and was mounted in a resistance furnace. During the operation the box was rotated at approximately 20 rpm. The duration of the tests was 1000 hours.

Table 5 presents the results of the rotating capsule tests on 410 stainless steel and medium carbon steel in a number of cadmium systems at 550 C and 350 C. The only system that exhibited corrosiveness toward the steels was the 10 weight per cent zinc-0.2 weight per cent magnesium-cadmium. Even in this system, the extent of corrosion was limited to less than 1 mil.

Table 5

RESULTS OF 1000-HOUR DYNAMIC CORROSION TESTS
IN CADMIUM ALLOY

Material	Molten Metal	Temperature (C)	Results
Mild Steel	100 w/o Cd	550	No corrosion
Mild Steel	2 w/o U-Cd	550	No corrosion
Mild Steel	8 w/o Zn-0.2 w/o Mg-Cd	550	No corrosion
Mild Steel	5 w/o Mg-Cd	550	No corrosion
Mild Steel	2 w/o Zn-0.2 w/o Mg-Cd	350	No corrosion
Mild Steel	4 w/o Zn-0.2 w/o Mg-Cd	350	No corrosion
Mild Steel	6 w/o Zn-0.2 w/o Mg-Cd	350	No corrosion
Mild Steel	8 w/o Zn-0.2 w/o Mg-Cd	350	No corrosion
Mild Steel	10 w/o Zn-0.2 w/o Mg-Cd	350	Slight corrosion
410 SS	2 w/o Zn-0.2 w/o Mg-Cd	350	No corrosion
410 SS	4 w/o Zn-0.2 w/o Mg-Cd	350	No corrosion
410 SS	6 w/o Zn-0.2 w/o Mg-Cd	350	No corrosion
410 SS	8 w/o Zn-0.2 w/o Mg-Cd	350	No corrosion
410 SS	10 w/o Zn-0.2 w/o Mg-Cd	350	Slight corrosion

Figure 9 (Photomicrographs 23 and 24) illustrates the surfaces of medium carbon steel specimens after exposure to 2 weight per cent uranium-cadmium and 8 weight per cent zinc-0.2 weight per cent magnesium-cadmium at 550 C for 1000 hours. The photomicrographs show very little, if any, attack on the mild carbon steel specimens.

Figure 9

Surfaces of Mild Carbon Steel after 1000-Hour Exposure
to Cadmium Systems in Rotating Capsules

Photomicrograph 23

150X

Showing Surface of Mild Carbon Steel Specimen
after Exposure to 2 Weight Per Cent
Uranium-Cadmium at 550 C.
(Steel phase is the lower phase in photograph)

Etchant: 2% Nital

Photomicrograph 24

150X

Showing Surface of Mild Steel Specimen after Exposure to 8 Weight Per
Cent Zinc-0.2 Weight Per Cent Magnesium-Cadmium at 550 C
(Steel phase is lower phase in photograph)
Etchant: 2% Nital

2. Thermal Convection Loops

All of the present flowsheets for the reprocessing of EBR-II melt refining slags contemplate isothermal conditions in each of the individual operations. Therefore, the conditions for mass transfer of container metals by means of concentration differences caused by thermal gradients are virtually nonexistent in the present reprocessing schemes. Consequently, the container materials were mostly evaluated on the basis of corrosion tests conducted under isothermal conditions. However, two medium carbon steel thermal convection loops circulating 15 and 30 weight per cent magnesium-cadmium were built and operated in order to ascertain the extent of corrosion under adverse thermal conditions, i.e., under conditions which would produce corrosion by a mass transfer mechanism.

The design of the loops⁽¹⁰⁾ was similar to the type operated by Brookhaven National Laboratory. A high-temperature protective paint was applied to the exterior surfaces of the steel to prevent air oxidation.

The conditions of operation may be summarized as follows:

Condition	Loop 1	Loop 2
Nominal composition:	30 weight per cent magnesium-cadmium	15 weight per cent magnesium-cadmium
Temp range:	575 to 675 C	630 to 725 C
Estimated flow rate:	0.02 to 0.04 ft/sec	0.02 to 0.04 ft/sec
Duration of test:	144 hours	1004 hours

It was intended that both loop tests operate for 1000 hours, but a Vycor sampling tube broke and remained in Loop 1, necessitating shutdown after 144 hours.

Both loops were sectioned and the sections examined with an optical microscope. It was readily apparent that mass transfer of iron had occurred in both loops. The cold leg of Loop 1 had a deposition layer of iron averaging about 2.5 mils. The surface of the hot region was pitted and devoid of grain structure, indicating attack by solid solution of iron. The total weight transfer of iron to the cold leg was estimated at 0.9 gram. This represents a maximum iron concentration difference between the cold and hot legs of 2.7 ppm.

The deposition layer of iron in the cold leg of Loop 2 had an average thickness of 6 mils. The total weight of iron transferred was calculated to be approximately 6.4 grams. The concentration difference between the hot and cold legs amounted to 2.8 ppm. Figure 10 illustrates the nature of the iron deposition layer and the corrosion areas in the thermal convection loops.

Figure 10

Appearance of Thermal Convection Loop No. 2

Photomicrograph 25

300X

Showing Deposition of Iron upon Cold Leg of Loop

Etchant: 2% HNO_3 -Ethyl Alcohol

Photomicrograph 26

750X

Showing Deposition Layer of Iron on Cold Leg

Etchant: 2% HNO_3 -Ethyl Alcohol

Figure 10 (Cont'd.)

Appearance of Thermal Convection Loop No. 2

Photomicrograph 27

300X

Showing Corrosion of Steel in Hot Leg
of Thermal Convection Loop

Etchant: 2% HNO_3 -Ethyl Alcohol

Photomicrograph 28

750X

Showing Corrosion in Hot Leg of Loop

Etchant: 2% HNO_3 -Ethyl Alcohol

Because solubility data for iron in magnesium-cadmium alloys are not available, the efficiency of iron mass transfer could not be determined. However, qualitative calculations and the considerations of the solubility of iron in pure magnesium and cadmium at the test temperatures seem to indicate efficiencies of mass transfer of less than 10 per cent. Thus, even relatively large thermal gradients could be tolerated in processing equipment without excessive corrosion.

3. Forced Convection Loops

Another severe test of the container materials consisted of circulating liquid metal systems to be encountered in the reprocessing schemes through loops fabricated from the container materials. Thus far in the program, two forced convection loop tests at 550 C employing medium carbon steel as the material of containment have been completed. Two weight per cent uranium-0.2 weight per cent magnesium-cadmium was circulated through one of these loops for slightly more than 1000 hours. Through the other medium carbon steel loop a cadmium alloy containing 0.89 weight per cent uranium, 2 weight per cent magnesium, and various fission product elements in trace amounts was circulated for 4800 hours.

The design utilized in the two medium carbon steel loops is shown in Figure 11. The loop consisted basically of three parts: a U-shaped test section fabricated from $\frac{1}{2}$ -inch OD steel tubing, a $2\frac{1}{2}$ -inch vertical steel reservoir, and an electromagnetic pump cell designed to operate with a General Electric AC electromagnetic pump. In addition, a one-inch OD sampling port was provided for the taking of periodic thief samples.

The pump selected for circulating the alloys was a General Electric AC Faraday Type electromagnetic pump (Model No. 9159849). This pump required the installation of a special pump cell in the circulating system, which is shown in Figure 12. The cell was also constructed from mild steel and was chromium plated on the exterior to protect it from air oxidation. The other parts of the loop were protected from oxidation by a corrosion-resistant coating of Markal SR10 paint.

Heating of the loops was accomplished by making the loops a one-turn secondary of a 10-kw power transformer. As a result, a 1428-ampere current at 7 volts was induced in the loop providing the resistance heating. Temperature control was obtained by varying the voltage input to the transformer.

Prior to installation of the loops an extensive cleaning procedure was followed. First, the loops were degreased with both a detergent and acetone. They were then pickled with dilute sulfuric acid and flushed with water.

Figure 11
Liquid Metal Forced Convection Loop

Figure 12
Electromagnetic Pump Cell

This was immediately followed by a flush with a one per cent caustic soda- $\frac{1}{2}$ per cent trisodium phosphate solution to remove any ferrous sulfate adhering to the surfaces. The loops were then flushed with acetone again and dried under inert gas atmosphere.

The flow rate of the circulating cadmium solutions were continuously measured by a modified General Electric electromagnetic flowmeter. Originally, the electromagnetic flowmeter was built and calibrated to operate in a nonmagnetic tantalum-lined Inconel system. Since the present loops were fabricated from a magnetic material the flowmeter had to be modified and recalibrated. The magnetic flux in the air gap of the flowmeter was 776 gauss. Calculations showed that this flux was below the saturation point of the carbon steel and therefore very little, if any, of the flux would penetrate the steel walls of the loop. However, by placing into the air gap of the flowmeter two tapered blocks of iron, it was possible to saturate the steel walls of the loop, thus allowing sufficient magnetic flux to pass through the molten cadmium. The actual value of the flux inside the steel tube of the flowmeter was measured by means of a gauss meter. This value of the flux was then used to calculate a plot of output emf from flowmeter versus flow rate from the following equation:

$$E = VBd \times 10^{-8} \left[\frac{2d/D}{1 + \left(\frac{d}{D}\right)^2 + \left(\frac{\rho_f}{\rho_w}\right) \left(1 - \left[\frac{d}{D}\right]^2\right)} \right]$$

where E = flowmeter emf

B = flux, gauss

d = inside diameter of loop

D = outside diameter of loop

ρ_f = resistivity of cadmium

ρ_w = resistivity of steel

V = velocity of cadmium.

The obtained plot was checked at the operating flow rates by the following method: A radiograph employing a 2-curie iridium-192 source was taken of the location where the $\frac{1}{2}$ -inch OD test section exited into the reservoir. A profile of the molten metal stream emptying into the reservoir was clearly discernible on the radiograph (Figure 13). By measuring the vertical and horizontal travel of the stream ejecting from the $\frac{1}{2}$ -inch steel loop, the flow rate could be calculated. Very good agreement between the flowmeter readings and the radiograph calculations was obtained.

Figure 13
Typical Radiograph Used to Calculate Flowrate

A typical reading on the flowmeter indicated a flow rate of 0.82 gal/min (2.45 ft/sec) while the calculated value from the radiograph was 0.85 gal/min (2.54 ft/sec). The conditions pertinent to the two forced-convection loops are summarized in Table 6.

Loop No. 1 operated without incident for 1021 hours, at which time it was shut down because the scheduled operating time of 1000 hours had elapsed. The loop was then dismantled, sectioned, polished, and etched with 2 per cent nitric acid-ethyl alcohol for metallographic examination.

Radiographs taken periodically of the loop during operation did not show any signs of major corrosion. This was substantiated in most part by metallographic examination. Only in three locations were there indications of slight interaction with the medium carbon steel.

Table 6

CONDITIONS PERTINENT TO THE FORCED-CONVECTION
CADMIUM LOOP

	Loop No. 1	Loop No. 2
Container material	medium carbon steel	medium carbon steel
Total loading of circulant	13.169 kg	13.246 kg
Nominal composition of circulant	2 w/o U, 0.2 w/o Mg, 97.8 w/o Cd	0.85 w/o U, 2 w/o Mg, 0.007 w/o Sr, 0.004 w/o Y, 0.02 w/o Zr, 0.001 w/o Nb, 0.002 w/o Mo, 0.002 w/o Ru, 0.003 w/o Rh, 0.002 w/o Pd, 0.002 w/o Te, 0.009 w/o Ba, 0.065 w/o Rare Earths, 96.9 w/o Cd
Average loop temp	550 C	550 C
Maximum loop temp gradient	25 C	25 C
Average flow rate	0.8 gal/min (2.5 ft/sec)	0.8 gal/min (2.5 ft/sec)
Heating Transformer output	2.4 kw	1.4 kw
Power to electromagnetic pump	0.52 kw	0.52 kw
Pump differential pressure	5 psi	5 psi
Duration of test	1021 hours	4800 hours

These locations were: the bottom of the reservoir, the electromagnetic pump cell throat, and the loop exit to the reservoir. The interaction at these points consisted of a double reaction layer on the steel wall accompanied by the presence of various intermetallic compound particles in the near vicinity of the layer. Photomicrographs 29 and 30 (see Figure 14) are typical photomicrographs of these interaction zones. Photomicrographs 31 and 32 (see Figure 14) show the surface of a portion of the $\frac{1}{2}$ -inch OD loop section. No evidence of corrosion is discernible.

Figure 14

Appearance of Cadmium Circulating Loop No. 1
after 1021 Hours of Operation

Photomicrograph 29

750X

Showing Intermetallic Phase Adjacent to Pump Cell
Surface (Steel Phase on Right)

Etchant: 2% HNO_3 -Ethyl Alcohol

Photomicrograph 30

750X

Showing Intermetallic Buildup at Point of Loop Exit
to Reservoir (Steel Phase on Left)

Etchant: 2% HNO_3 -Ethyl Alcohol

Figure 14 (Cont'd.)

Appearance of Cadmium Circulating Loop No. 1
after 1021 Hours of Operation

Photomicrograph 31

300X

Showing Surface of $\frac{1}{2}$ inch OD Medium Carbon
Steel Loop Test Section

Etchant: 2% HNO_3 -Ethyl Alcohol

Photomicrograph 32

750X

Showing Surface of $\frac{1}{2}$ inch OD Medium Carbon
Steel Loop Test Section

Etchant: 2% HNO_3 -Ethyl Alcohol

X-ray examination of the pump cell section qualitatively established the presence of an iron-uranium intermetallic. The same examination also identified uranium as the major constituent and iron as the minor constituent in the corrosion phase near the steel surface.

One possible explanation of the localized interactions is indicated by an examination of the chemical analyses of periodic thief samples which are tabulated in Table 7. Initially, enough uranium in the form of rods was charged into the loop to make an alloy of 2 nominal weight per cent composition. However, the chemical analyses show that the composition of the uranium remained nearly constant at a value of around 1.5 weight per cent.

Table 7

PERIODIC URANIUM AND IRON CONCENTRATIONS IN
CADMIUM ALLOY CIRCULATED FOR 1000 HOURS
IN MILD STEEL CORROSION LOOP

Alloy Composition : Cadmium-0.2 w/o Magnesium-U
as shown

Temperature of Circulation: 550 C

Sample No.	Elapsed Time of Circulation (hr)	Temp (C)	Concentration	
			Uranium (wt per cent)	Iron (ppm)
1	113	480	1.47	-
2	209	548	1.58	-
3	283	552	1.55	-
4	621	555	1.42	5.6
5	669	542	1.47	4.3
6	717	560	1.45	4.1
7	837	555	1.47	3.8

This would seem to indicate that not all of the uranium charged remained in solution and that some of it precipitated at cold spots in the loop as alpha uranium or cadmium-uranium intermetallic. The highly localized interactions are believed attributable to the presence of precipitated uranium or cadmium-uranium intermetallic in contact with the steel walls at cold regions. All three of the locations where attack occurred are points of high heat loss and consequently cold spots. The pump cell which had the thickest interaction layer was the coldest point in the loop because of massive bus bars which conducted a large amount of heat away.

Loop No. 2 operated without incident for 4800 hours, at which time a power failure necessitated shutdown of the loop before the scheduled operating time of 5000 hours had elapsed. As with the first loop, it was then prepared for metallographic examination.

At no point in the loop did the metallographic examination disclose any corrosion. Figure 15 (photomicrographs 33 and 34) illustrate the lack of corrosion at several locations in Loop No. 2. The uranium concentration as indicated in Table 8 was maintained at 0.85 weight per cent during 4300 hours of operation.

Figure 15

Appearance of Sections of Cadmium Circulating Loop No. 2

Photomicrograph 33

120X

Etchant: 2% HNO_3 -Ethyl Alcohol

Photomicrograph 34

750X

Etchant: 2% HNO_3 -Ethyl Alcohol

Table 8

PERIODIC URANIUM CONCENTRATIONS^a IN CADMIUM-
FISSIUM ALLOY CIRCULATED FOR 4800 HOURS
IN MILD STEEL CONVECTION LOOP

Temperature of circulation: 550 C

Sample No.	Elapsed Time of Circulation (hr)	Concentration Uranium (wt per cent)
1	0	0.97
2	427	0.85
3	651	0.86
4	815	0.88
5	1012	0.88
6	1325	0.85
7	1709	0.87
8	1875	0.84
9	2075	0.83
10	2213	0.87
11	2380	0.85
12	2548	0.84
13	2741	0.85
14	2885	0.84
15	3077	0.87
16	3269	0.85
17	4181	0.85

^aAs obtained from filtered thief samples.

However, this concentration was 0.12 weight per cent below the calculated nominal composition of 0.97 weight per cent uranium. The difference between nominal concentration and actual concentration was probably caused by oxygen contamination during startup. This was borne out by the presence of a slag in the reservoir, which was found to have a uranium concentration of 2 per cent. Moreover, unfiltered samples taken during the first 500 hours analyzed higher than filtered samples taken during the same time, indicating that suspended uranium oxide was being circulated in the loop.

Since cold spots were avoided in the second loop by improved insulation, the conclusion is reinforced that interactions with uranium in Loop No. 1 were caused by precipitation of uranium at cold spots.

From an overall evaluation of the two loops it seems likely that mild steel will be a satisfactory material of containment for the cadmium-uranium and cadmium-fissium systems at temperatures up to 550 C.

V. CONCLUSIONS

The observations presented in this report are the results of preliminary work to find suitable containment materials for molten cadmium and molten zinc systems. These studies have shown that molten cadmium alloys may be satisfactorily contained in mild steel or nickel-free ferrous alloys (such as chromium-iron alloys) under static and dynamic conditions up to at least 550C, and probably somewhat higher. At 700C, however, there is intergranular attack of the steel by molten cadmium. Since nickel is soluble in cadmium and is slowly leached from alloys which contain it, use of nickel-containing alloys should be avoided.

Factors other than corrosion should also be considered in the selection of a container alloy. Some of these factors are the strength at the temperatures and pressures involved, ease of fabrication, and the stability of process solutions in the particular material. These were not evaluated in the present work, although the uranium-cadmium solutions appeared stable under long-term circulation (4800 hours) at 550C in a mild steel loop.

Tungsten was found to be very inert to zinc. However, problems of fabrication must be overcome before its use will be practical. Both tantalum and molybdenum were attacked slightly in 100 hours at 750C, tantalum by formation of an intermetallic compound, molybdenum by solution to the extent of its very low solubility (0.02 per cent). Both are acceptable for short-term experimental work. However, the practicality of use in plant equipment must be evaluated in the light of expected exposure, equipment costs, and ease of replacement of particular items.

There are indications that impurities in tantalum may contribute to the corrosion by molten zinc. Reduced corrosion was evident in those tests which employed magnesium as an alloying constituent in molten zinc. This suggests that oxygen contamination might be a cause of corrosion. Therefore, tantalum of better quality and care in welding for fabrication of components may result in better tantalum performance.

The inertness of tungsten may possibly be utilized through use of tungsten alloys which may be more readily fabricated than tungsten, or through tungsten coatings which may be deposited from the vapor, or by various high-temperature spraying techniques. It is recommended that these procedures be further explored.

Although emphasis in this work has been on metallic containment, in the future it is recommended that more consideration be given to graphite and graphite coatings for the containment of molten zinc. Pyrolytic graphite is one form which shows promise as a coating material.

In general, the corrosion-testing procedure was considered to be satisfactory. However, in the future more emphasis should be placed on dynamic tests. The use of static testing methods is useful for the screening of numerous materials, but it is felt that dynamic testing gives more valuable corrosion information.

ACKNOWLEDGEMENTS

The authors are indebted to the following members of the Chemical Engineering Division, Argonne National Laboratory: James C. Hesson for supervision of the corrosion program during the military leave of absence of John DeKany; and John Pavlik for his assistance in the operation of equipment and preparation of samples for metallography.

The authors are also indebted to Joseph C. Florek of the Metallurgy Division, Argonne National Laboratory for his microhardness testing of several of the metallographic samples.

REFERENCES

1. M. Hansen, Constitution of Binary Alloy Systems, McGraw-Hill Book Co., Inc., New York (1958).
2. W. Oelsen, Z. Anorg. Allgem. Chem. 186, 257 (1930).
3. N. Ageew and M. Zamotorin, Ann. Institute Polytech. Leningrad, 31, 15-28 (1928).
4. H. Schottky, K. Schichtel, and R. Stolle, Iron Steel Ind., 4, 332-3 (1931).
5. G. DeLattre, Rev. Met., 25, 630-6 (1928).
6. L. J. G. Van Ewijk, J. Inst. Metals, 56, 241-8 (1935).
7. V. W. Eldred, Interactions between Solid and Liquid Metals and Alloys, AERE X/R-1806.
8. Von Werner Köster and H. Schmid, Zeit. Metallkunde, 46, 462-3 (1955).
9. W. Hodge, R. M. Evans, and A. Hoskins, J. Metals, 7, 824 (1955).
10. J. E. Atherton, D. H. Gurinsky, O. F. Kammerer, C. J. Klamut, M. Silberberg, B. Turovlin, and J. R. Weeks, Studies in the U-Bi Fuel System, Chem. Eng. Progress Symposium Nuclear Eng., Part II, Ser. No. 12 (1954).