[redacted]
(CLASSIFICATION)

DOCUMENT NO.	
BNWL-CC-2111	BNWL-CC--2111
DATE: March 1969	DE90 013439

COPY NO. 13 —

PROJECT

BATTELLE-NORTHWEST
RICHLAND, WASHINGTON

TITLE

COMPATIBILITY STUDIES FOR THE WASTE PACKAGING PROGRAM
INTERIM REPORT

AUTHOR

H. T. Fullam

DISTRIBUTION

NAME	BUILDING	AREA	NAME	BUILDING	AREA
BATTELLE-NORTHWEST			ARHCO		
1. JM Atwood	324	300	14. GL Borsheim	271B	200-E
2. RE Burns	324	300	15. HH Hopkins, Jr.	2704-E	200-E
3-8 HT Fullam	325	300	16. RE Isaacson	2704-E	200-E
9. RL Moore	325	300	17. JR LaRiviere	271-T	200-W
10. LK Mudge	324	300	18. PW Smith	271-B	200-E
1. AM Platt	324	300	19. RE Tomlinson	2704-E	200-E
12. GL Richardson	324	300			
13 300 Area Files	3760	300			
Extra (10)					

DISCLAIMER

ROUTE TO	PAYROLL NO.	LOCATION	FILES ROUTE DATE

[redacted]
(CLASSIFICATION)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

(TO BE USED ON UNCLASSIFIED AND OFFICIAL USE ONLY DOCUMENTS)

54-1100-032 (1-68)

LEGIBILITY NOTICE

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

1

[redacted]

BNWL-CC-2111

COMPATIBILITY STUDIES FOR THE WASTE PACKAGING PROGRAM - INTERIM REPORT

by

H. T. Fullam

Applied Chemistry Section
Chemical Technology Department

NOTICE: PRELIMINARY REPORT

LEGAL NOTICE

PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

OPERATED BY

BATTELLE MEMORIAL INSTITUTE

for the

U.S. ATOMIC ENERGY COMMISSION Under Contract No. AT(45-1)-1830.

MASTER

54-1600-002 (4-65)

[redacted]

TABLE OF CONTENTS

[redacted]

BNWL-CC-2111

COMPATIBILITY STUDIES FOR THE WASTE PACKAGING PROGRAM - INTERIM REPORT

by

H. T. Fullam

Applied Chemistry Section

[redacted] BNWL-CC-2111

COMPATIBILITY STUDIES FOR THE WASTE PACKAGING PROGRAM - INTERIM REPORT

1. INTRODUCTION

The current waste management program at Hanford calls for the separation, preparation, packaging and long term storage of solid strontium and cesium compounds from high level wastes. A program is now underway by Battelle-Northwest to develop the technology required for a waste packaging plant. Cesium chloride and strontium fluoride have been selected as the prime candidates for packaging[1]. Cesium diuranate and strontium pyrophosphate have been selected as backup compounds for packaging in case either or both of the prime candidates should be rejected for any reason.

Previous work[2] has shown that 316L stainless steel and Hastelloy C are the best materials of containment for CsCl. However, no detailed studies of CsCl compatibility have been reported and long term data are needed. Some compatibility data on SrF_2 have been reported[2,3,4] and Hastelloy C, Hastelloy X and Haynes 25 appear to be the best materials. As in the case with CsCl however, no detailed studies have been made on SrF_2 compatibility. There are no reported data available on the compatibility of $Cs_2U_2O_7$ and $Sr_2P_2O_7$.

As a result of the lack of pertinent compatibility data, it is readily apparent that detailed studies are required on CsCl and SrF_2 compatibility and at least scouting studies must be made on the compatibility of the backup packaging compounds. This report summarizes the compatibility studies that are underway at PNL using non-radioactive compounds. Capsule fabrication procedures and tests schedules are outlined. Compatibility studies with radioactive compounds will start in the spring of 1969 and will be described in a subsequent report.

2. COMPATIBILITY TEST REQUIREMENTS

The waste packaging concept calls for storage of packaged wastes for periods in excess of one hundred years. In these time periods, the strontium and cesium will have decayed several half-lives, the heat output of the package will have decreased several-fold and the decay products will have built up sufficiently to constitute a substantial fraction of the waste. For compatibility considerations, it is necessary to know how changes in the waste composition and temperature will affect the interaction with the containment material. Since it is impossible to run compatibility tests on all potential waste compositions and temperatures, it is necessary to select those conditions which it is felt will be most severe and run tests under those conditions. For cesium chloride, waste compositions corresponding to one-half and one half-lives were selected (assuming approximately 40% of the cesium is ^{137}Cs). A temperature of 400°C was selected (based on phase change considerations) as the maximum temperature a cesium chloride package would be likely to encounter. Current design considerations call for limiting the centerline temperature of the package to 400°C.

For strontium fluoride, waste compositions corresponding to zero, one-half and one half-lives were selected (assuming about 52% of the strontium is ^{90}Sr). A temperature of 400°C was selected as the normal temperature the SrF_2 package would likely encounter at the SrF_2-clad interface. (The centerline temperature will be held to 800°C or less in the fluoride package.)

Since it is impossible to obtain long term compatibility data (> 3 years) before plant operation is initiated, it is imperative to have some idea of what the long term effects might be before plant startup. The method selected to estimate this data is to run short term tests (up to three years) at temperatures above those which it is expected the compound-clad interface would normally encounter. Therefore, temperatures of 600°C for CsCl and 800°C for SrF_2 were selected as test temperatures in addition to the 400°C previously selected. 600°C was selected for cesium chloride since this is just below the melting point of the waste composition corresponding to one half-life. 800°C was selected for SrF_2 because this is just below the eutectic temperature of the expected fluoride product (see Section 3.1).

Cesium diuranate and strontium pyrophosphate compositions corresponding to zero and one-half half-lives for Cs and zero and one half-lives for Sr were selected for the scouting studies. Since the scouting studies are to be short term (3 months), a test temperature of 1000°C was selected to give a very stringent test of compatibility. Clad metals which show little attack after three months at 1000°C should show very little interaction at the temperatures which the packages would normally encounter.

When cesium chloride or strontium fluoride decay the exact decay products are not known. For example, in the decay of Sr-90 the final decay product is Zr-90 (the Y-90 concentration at any given time is negligible). However, if SrF_2 is the compound under consideration the exact form of the zirconium decay product is not known. Is zirconium difluoride the decay product, $SrF_2 \rightarrow (Y) \rightarrow ZrF_2$ (unlikely since the literature states ZrF_2 does not exist), or are the products zirconium tetrafluoride and zirconium metal? $2\ SrF_2 \rightarrow (Y) \rightarrow ZrF_4 + Zr$. The same question arises with CsCl. Is the reaction $CsCl \rightarrow BaCl$ (unlikely since Ba does not form a monovalent ion) or $2\ CsCl \rightarrow BaCl_2 + Ba$. The CsCl picture is even more complex in that if barium metal is one of the decay products, it could reduce the cesium chloride to give cesium metal, $2\ CsCl + Ba \rightarrow BaCl_2 + 2\ Cs$.

In making up the compositions to be used in the SrF_2 compatibility tests, it was assumed that ZrF_4 and Zr would be the decay products. For $Sr_2P_2O_7$ a similar assumption was made and ZrP_2O_7 and Zr were used in making up the compounds for testing.

With cesium, it was assumed that barium metal would be one of the decay products. However, finely divided barium metal was unavailable so only $BaCl_2$ and BaU_2O_7 were used in making up the waste compositions (see Section 4).

3. EXPERIMENTAL

3.1 Compound Preparation

Preparation and packaging of the waste compounds simulated as closely as possible the flowsheets and methods planned for the ARHCO waste packaging plant. Each procedure is described below.

Strontium fluoride was prepared from a synthetic feed whose analysis is shown in Table I. The feed composition was based on ARHCO estimates of what the strontium feed stream composition will be[5]. The synthetic feed was neutralized to pH 10 with sodium hydroxide and the resulting slurry centrifuged to remove the solids. A 10% excess of solid sodium fluoride was added to the supernate to precipitate the strontium as the fluoride. After digesting for one hour at 60-80°C, the solution was cooled and the fluoride filtered, washed and dried at 100°C. The dried fluoride was then calcined at 1000°C, cooled and ball-milled to a fine powder. A typical analysis of the fluoride product is given in Table II.

Cesium chloride was prepared from a synthetic feed whose composition is given in Table I. This feed composition was also based on ARHCO estimates of what the cesium waste stream composition will be[5]. The synthetic feed was prepared by dissolving the required amounts of reagent grade CsCl, NaCl, KCl and RbCl in water. The feed was evaporated to dryness and the resulting solid fired at 450°C. After cooling, the CsCl agglomerates were ball-milled to a fine powder. In the waste packaging plant cesium carbonate from the ion exchange purification will be converted to cesium chloride by the addition of hydrochloric acid.

Strontium pyrophosphate was prepared from the same feed used in preparing the SrF_2. After neutralizing to pH 10 and centrifuging, sodium hydrogen phosphate (Na_2HPO_4) was added to the supernate to precipitate the strontium. The slurry was digested for one hour at 60-80°C and then cooled. After filtering and washing, the cake was fired at 1100°C to form the pyrophosphate. After cooling the $Sr_2P_2O_7$ was ball-milled to fine powder.

TABLE I

Composition of Synthetic Feeds

STRONTIUM FEED*

Component	Concentration - Moles/Liter
Sr	0.4
Na	0.4
Fe	0.008
Mg	0.12
Al	0.008
Ca	0.04
HNO_3	0.5

*All components present as nitrate salts

CESIUM FEED**

Component	Concentration - Moles/Liter
Cs	0.58
Na	0.002
Rb	0.006
K	0.0058

**All components present as the chloride salt

TABLE II

Composition of Strontium Fluoride Product

Metal Ions Present

Component	Concentration - Wt. %
Sr	~ 96.6
Na	< 1.0
Fe	~ 0.01
Al	~ 0.2
Mg	~ 0.2
Ca	~ 2.0
Total	~100.0

Zirconium pyrophosphate was prepared by adding sodium hydrogen phosphate to a zirconium nitrate solution and digesting for fifteen minutes at 60-80°C. After cooling, filtering and washing, the cake was fired at 1100°C. The calcined product was then ball-milled to a powder.

Cesium diuranate was prepared by reacting a uranyl nitrate solution (containing a minimum of free acid) with cesium carbonate solution. The cesium diuranate precipitate was filtered, washed and calcined at 1100°C. After cooling the diuranate was ball-milled.

Barium diuranate was prepared by reacting barium hydroxide with uranyl nitrate in an aqueous solution. The diuranate precipitate was then filtered, washed and fired at 1100°C. It was ball-milled to a fine powder after cooling.

The other materials used in preparing the test capsules were obtained from commercial sources. The zirconium fluoride was obtained from AD Mackay, Inc. and was anhydrous powder 99% pure. The zirconium metal was also obtained from AD Mackay, Inc. as a 99% pure powder (minus 200 mesh). The metal powder was shipped moist (because of its incendiary character) and had to be vacuum dried prior to use.

3.2 Fabrication of Test Couples

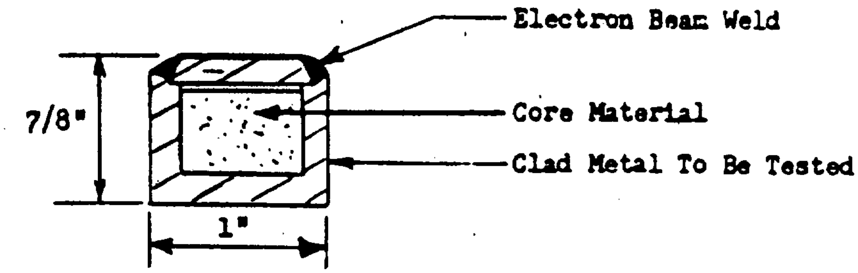
The capsules used in fabricating the test couples were machined from bar stock. The only exceptions to this being the capsules used in the scouting studies, which were made from 316L or 304L stainless steel pipe. Descriptions of the various metals used are given in Table III. All metal specimens used were cleaned in perchloroethylene and dried prior to use.

Figure 1 shows the dimensions of typical test couples. The individual couples (CsCl and SrF_2) were prepared in the following manner. The capsule was inserted into a hardened steel die block. A small amount of the compound to be loaded was placed in the capsule. The plunger was inserted and pressure applied with a hydraulic ram to

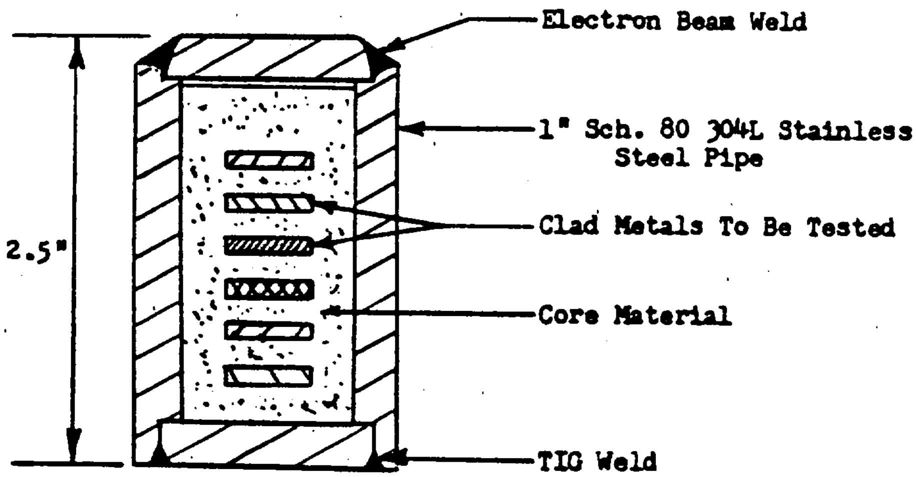
TABLE III

Specifications of Metals Used in Fabricating Capsules

Material	Vendor	Type	Condition
316L SS	Allen Fry Steel Co.	1" pipe	Seamless Sch 80
316L SS	Allen Fry Steel Co.	1" dia. Rod	Fully Annealed
304L SS	(BNW Shop)	1" pipe	Seamless Sch 80
Haynes 25	Union Carbide Corp	1" dia. Rod	Hot Rolled Bar
Hastelloy C	Union Carbide Corp	1" dia. Rod	Hot Rolled Bar
Hastelloy X	Union Carbide Corp	1" dia. Rod	Hot Rolled Bar



(a) Individual Test Couple



(b) Capsule For Scouting Studies

FIGURE 1

Typical Compatibility Capsules

give the desired compound density. The pressure was released, the plunger removed, additional compound placed in the capsule and the entire operation repeated. Step pressing was repeated as many times as was necessary to fill the capsule to the desired level. When the capsule was filled, the cap was pressed in place and the capsule was ejected from the die block. The entire operation was carried out in a small argon-filled glove box to prevent moisture pickup during the loading operation. The capsule was sealed by electron-beam welding the cap in place.

Cesium chloride test couples were filled approximately half full of chloride. The bulk density of the chloride in the capsule was held to 50-60% of theoretical. By filling the capsules only half full, volatilization of the $CsCl$ during the welding operation was not a problem. Figure 2 shows a $CsCl$ couple in various stages of fabrication.

Strontium fluoride test couples were completely filled with fluoride. Fluoride bulk density was held to 80-90% of theoretical.

Couples used in the scouting studies were prepared as follows: the capsule was placed in the die block and a small amount of compound added. The plunger was inserted and the compound was pressed to the desired density. The plunger was removed and a piece of clad metal was placed on top of the compound layer. Additional compound was added and the plunger reinserted and a force applied. This sandwich construction was continued until the capsule was full (Figure 1-b). Up to seven different clad metal sections were evaluated in each capsule. Compound densities were held to 50-60% of theoretical. After the capsule was loaded, the cap was pressed in place and the capsule was ejected from the die block. The capsule was closed by electron-beam welding. As was the case with the individual capsules, the large capsules were loaded in an argon atmosphere. Figure 3 shows a typical capsule used in the scouting studies.

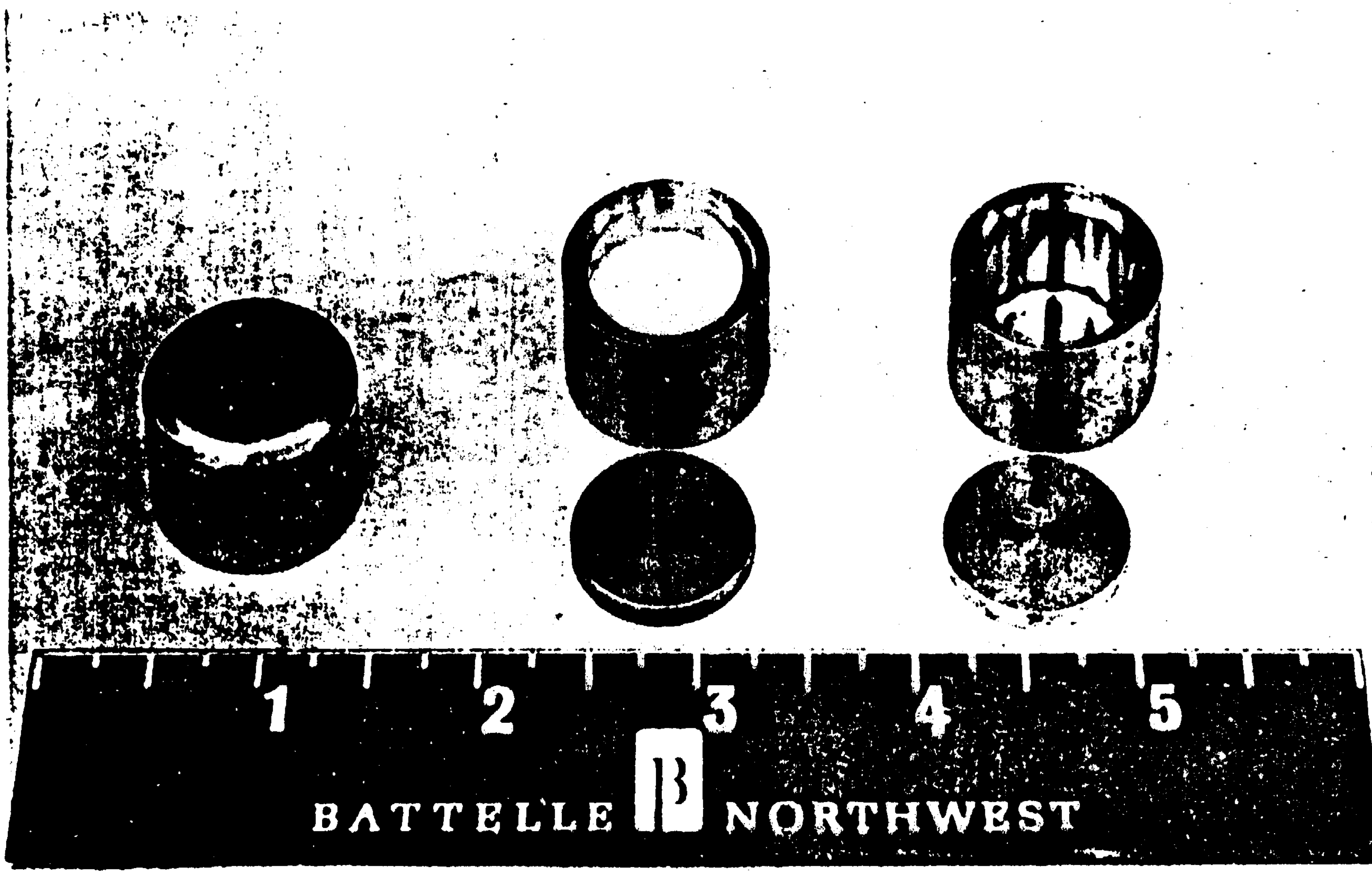


FIGURE 2 Cesium Chloride Capsule in Various Stages of Fabrication

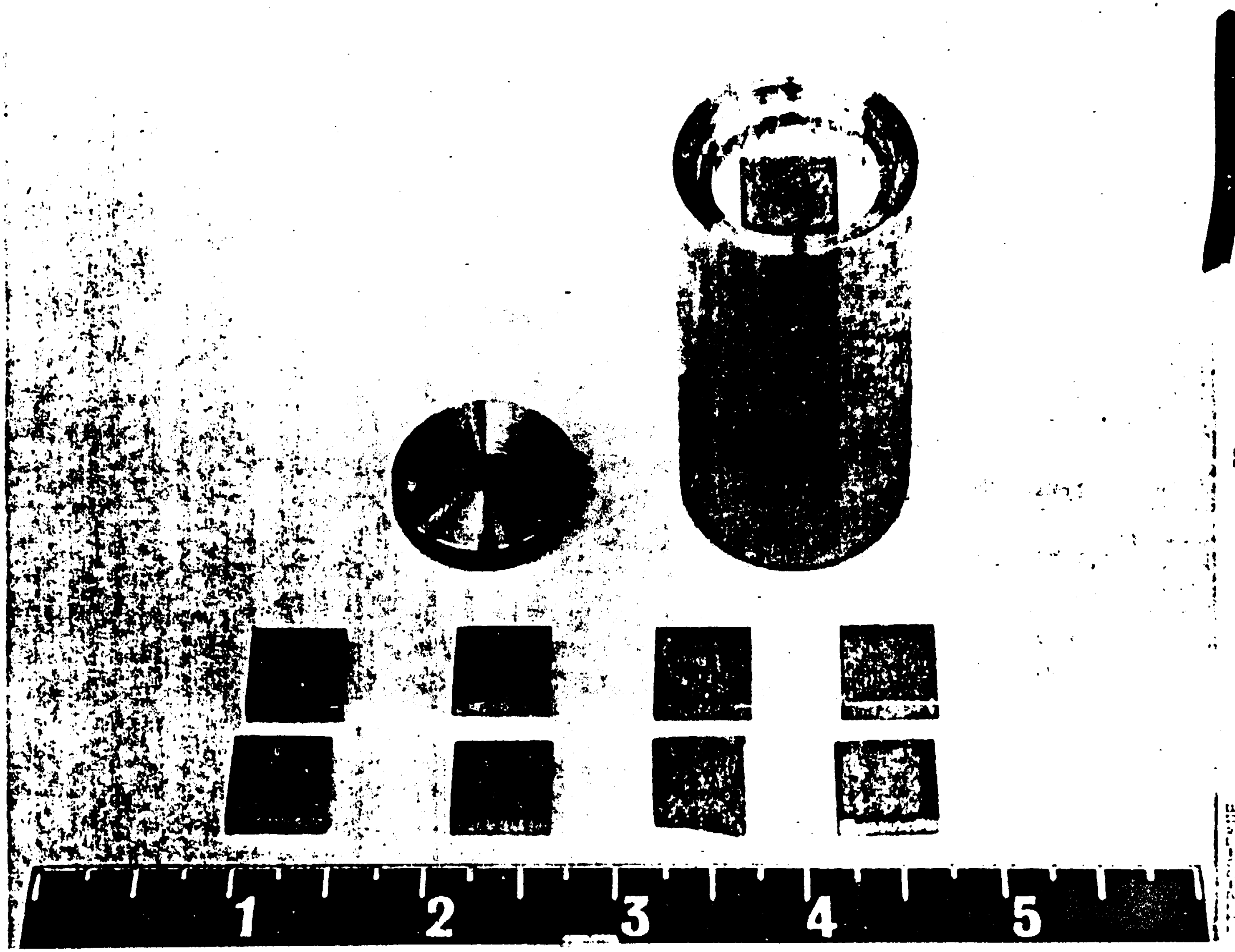


FIGURE 3 Typical Capsule Used in the [illegible]

3.3 Couple Testing and Evaluation

Testing of the various couples is being carried out in muffle furnaces. To prevent external oxidation of the capsules, the couples are sealed in glass, vycor or Inconel 600 protective envelopes. The envelope material used depends on the test temperature. Capsules being run at 400°C were sealed in Pyrex. Capsules being tested at 600 and 800°C were sealed in vycor and those being run at 1000°C were sealed in Inconel 600.

At the conclusion of the tests, compound-clad interaction will be evaluated in the following way. The couple will be sectioned on an abrasive saw. A section of the couple will be examined by metallographic techniques. Photomicrographs will be obtained of the compound-clad interface. The interface will also be studied by electron microprobe analysis. If gross reactions have occurred, x-ray diffraction will be utilized to determine the compounds present. Based on the analytical data, the rate of compound-clad interaction will be determined as a function of time at temperature.

4. TESTING CONDITIONS AND SCHEDULES

The cesium chloride tests are being run at two different core compositions, in two different metals, at two different temperatures and for five different time periods; a total of forty different sets of conditions. Since duplicate couples are run for each set of conditions, a total of eighty couples are required. Table IV summarizes the test conditions and timing schedule for the CsCl tests.

Strontium fluoride tests are being run at three different core compositions, in three different metals, at two different temperatures and for five different time periods. However, the tests with pure SrF_2 are being run for only three time periods, so that the total number of different test conditions is only 78. Since duplicate samples are being run for each set of conditions, a total of 156 couples are being tested. Table V summarizes the timing schedule and test conditions for the SrF_2 tests.

Scouting studies are being run on three compounds; $Sr_2P_2O_7$, $Cs_2U_2O_7$ and SrF_2. The strontium pyrophosphate studies are being run in 304L stainless steel capsules. A total of seven different metals are evaluated in each capsule. The test conditions are summarized in Table VI. Duplicate couples are being run for each set of conditions, a total of four capsules.

The cesium diuranate scouting studies are being run in 304L stainless steel capsules. Seven different clad metals are being evaluated in each capsule. $Cs_2U_2O_7$ test conditions and time schedules are summarized in Table VII. Duplicate couples are run for each set of conditions (4 capsules total).

Although detailed compatibility studies are being run on SrF_2 with Haynes 25, Hastelloy C and Hastelloy X, there is some question as to whether any of these metals will be an entirely satisfactory containment material. For this reason, it was decided to run a series of short term scouting studies with SrF_2 and a variety of clad metals. The tests are being run in 316L stainless steel capsules. Since a maximum of seven metals can be tested in one capsule and since twelve metals are to be tested, two capsules are required for each set of conditions. Table VIII summarizes the test conditions and schedules. Again duplicate couples are being run so that a total of eight capsules are being tested.

TABLE IV

Test Conditions for Cesium Chloride Couples

Clad Metals Tested	- 316L stainless steel - Hastelloy C
Core Composition*	- 89 mol. % CsCl + 11 mol. % $BaCl_2$ - 80 mol. % CsCl + 20 mol. % $BaCl_2$
Test Temperatures	- 400°C - 600°C

Test Time Periods	Test Started	Test Completed
3 months	10/68	1/69
6 months	10/68	4/69
12 months	10/68	10/69
24 months	10/68	10/70
36 months	10/68	10/71

*Approximately 40% of cesium in feed 137 assumed to be ^{90}Cs.

TABLE V

Test Conditions for Strontium Fluoride Couples

Clad Metals Tested	- Hastelloy C - Hastelloy X - Haynes 25
Core Composition*	- 100% SrF_2 - 88 mol. % SrF_2 + 6 mol. % Zr + 6 mol. % ZrF_4 - 74 mol. % SrF_2 + 13 mol. % Zr + 13 mol. % ZrF_4
Test Temperatures	- 400°C - 800°C

Test Time Periods	Test Started	Test Completed
3 months	10/68	1/69
6 months	10/68	4/69
12 months	10/68	10/69
24 months	10/68	10/70
36 months	10/68	10/71

*Approximately 52% of strontium in feed assumed to be ^{90}Sr.

TABLE VI

Scouting Studies for Strontium Pyrophosphate

Clad Metals Tested	- Inconel 600 - Haynes 25 - Hastelloy C - Hastelloy X - Udimet 700 - Waspelloy - 304L Stainless Steel - 316L Stainless Steel
Core Composition*	- 100 mol. % $Sr_2P_2O_7$ - 74 mol. % $Sr_2P_2O_7$ + 13 mol. % Zr + 13 mol. % ZrP_2O_7
Test Temperature	- 1000°C
Test Time Period	- 3 months
Tests Started	- 11/68
Tests Completed	- 2/69

*Approximately 52% of strontium in feed is assumed to be ^{90}Sr.

TABLE VII

Scouting Studies for Cesium Diuranate

Clad Metals Tested	- Inconel 600 - Haynes 25 - Hastelloy C - Hastelloy X - Udimet 700 - Zircaloy - 304L Stainless Steel - 316L Stainless Steel
Core Composition*	- 100% $Cs_2U_2O_7$ - 89 mol. % $Cs_2U_2O_7$ + 11 mol. % BaU_2O_7
Test Temperature	- 1000°C
Test Time Period	- 3 months
Tests Started	- 11/68
Tests Completed	- 2/69

*Approximately 40% of cesium in feed is assumed to be ^{137}Cs.

TABLE VIII

Scouting Studies for Strontium Fluoride

Clad Metals Tested	- Inconel 600 - Haynes 25 - Hastelloy C - Hastelloy X - Hastelloy F - Udimet 700 - Rene 41 - Waspelloy - Incoloy 804 - Multimet - TZM - 304L Stainless Steel - 316L Stainless steel
Core Composition*	- 100% SrF_2 - 88 mol. % SrF_2 + 6 mol. % ZrF_4 + 6 mol. % Zr
Test Temperature	- 800°C
Test Time Period	- 3 months
Tests Started	- 10/68
Tests Completed	- 1/69

*Approximately 52% of the strontium in the feed is assumed to be ^{90}Sr.

REFERENCES

1. T. S. Soine and H. T. Fullam, "An Evaluation of Strontium and Cesium Compounds for Waste Packaging", BNWL-CC-1695, Pacific Northwest Laboratory, Richland, Washington, June 1968.

2. S. J. Rimshaw and E. E. Ketchen, "Compatibility Data Sheets for Ce-144, Cs-137, Curium and Sr-90", ORNL-4189, Union Carbide Corporation, ORNL, Oak Ridge, Tennessee, November 1967 (Confidential).

3. W. A. Vogele, "Strontium-90 Fuel Program Monthly Progress Report", MND-2848-47, Martin Marietta Corporation, Baltimore, Maryland, May 1966, (Confidential).

4. F. J. Maraglia, 'Compatibility of Strontium Space Fuel Forms", MND-3062-27, Martin Marietta Corporation, Baltimore, Maryland, June 1966 (Confidential).

5. G. L. Borsheim, Personal communication, ARHCO, Richland, Washington, July, 1968.

END

DATE FILMED

07 / 24 / 90