**Cesium Chloride
Compatibility Testing Program
Annual Report - Fiscal Year
1983**

G. H. Bryan

March 1984

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

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.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

CESIUM CHLORIDE COMPATIBILITY TESTING PROGRAM
ANNUAL REPORT - FISCAL YEAR 1983

G. H. Bryan

March 1984

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

ABSTRACT

A program was started in FY 1982 to evaluate the compatibility of WESF-produced CsCl with 316L stainless steel under the thermal conditions that would be encountered in a geologic repository. The program is funded through the long-term High-Level Defense Waste Program of the Department of Energy. The major part of the program involves compatibility testing of six standard WESF CsCl capsules at a maximum CsCl/metal interface temperature of 450°C. The capsules are allowed to self heat to the test temperature in insulated containers and then held at temperature for 2200 to 32,000 h. After thermal aging, the capsules are destructively examined to determine the extent of the metal attack by the CsCl. This report describes the test procedure and summarizes the results obtained during the second year of the program.

Metallographic examination was completed of the two zero-time capsules. The photomicrographs obtained of the metal samples indicate the maximum metal attack resulting from the capsule-filling operation was about 25 μm (0.001 in.).

Metallographic examination of the WESF CsCl capsules held at temperature for 2208 and 4392 h was completed. Both capsules exhibited substantial attack by the CsCl. Maximum attack observed in the 2208-hour capsule was estimated to be about 60 μm (0.0024 in.), while maximum attack in the 4392-h capsule was estimated at 110 μm (0.0043 in.). The data indicate the corrosion rate is linear with time for the first 4392 h.

Thermal aging of the 8394-h capsule was completed, and metallographic examination of the capsule is underway. Thermal aging of the three remaining test capsules is continuing.

When the 4392-h capsule was opened for metallographic examination, it was found that the outer surface of the inner capsule was discolored and pitted at several locations. Metallographic examination of the affected areas showed pits up to 300- μm (0.012-in.) deep in some areas. The maximum depth observed corresponded to about 9% of the initial capsule wall thickness. No similar pitting conditions observed on the outer surface of the 2208-h inner capsule; but was observed, although apparently to a lesser degree, on the outer surface of the 8784-h inner capsule.

ACKNOWLEDGMENTS

The author would like to thank H. T. Fullam for his assistance and guidance in the preparation of this document. Without his knowledge and willingness to help, completion would have been extremely difficult within the imposed time restraints.

CONTENTS

1.0	INTRODUCTION	1.1
2.0	OBJECTIVES	2.1
3.0	TESTING CRITERIA	3.1
4.0	RADIOACTIVE COMPATIBILITY TESTS	4.1
4.1	TESTING PROCEDURE	4.1
4.2	CAPSULE FABRICATION	4.1
4.3	ZERO-TIME CAPSULES	4.2
4.4	CAPSULE AGING	4.5
4.5	CAPSULE SECTIONING AND EXAMINATION	4.9
4.6	METAL CONTROL SPECIMENS	4.11
5.0	TEST RESULTS	5.1
5.1	ZERO-TIME CAPSULES	5.2
5.2	THERMAL AGING TESTS	5.5
5.3	METAL CONTROL SPECIMENS	5.17
5.4	EXTERNAL CAPSULE CORROSION	5.17
6.0	REFERENCES	6.1

FIGURES

1	Locations Where the Wall Thickness of the Inner WESF Capsule were Measured	4.3
2	Sketch of a WESF Capsule in its Insulated Container	4.6
3	Insulated Containers in a Holding Rack in the Hot Cell	4.7
4	Locations Where the Capsule Surface Temperatures are Measured	4.8
5	Sectioning of the Zero-Time Inner Capsules	4.10
6	Mounting of the Metal Samples Showing the Problem of Sample Alignment	5.2
7	Photomicrographs from Samples of Zero-Time Capsule 19459	5.3
8	Photomicrographs from Samples of Zero-Time Capsule 19073F	5.4
9	Average Temperature Profiles for the WESF Capsule held at Temperature for 2208 Hours	5.6
10	Average Temperature Profiles for the WESF Capsule held at Temperature for 4392 Hours	5.7
11	Average Temperature Profiles for the WESF Capsule Held at Temperature for 8784 Hours	5.8
12	Temperature Fluctuations Observed with the Capsule Held at Temperature for 2208 Hours	5.9
13	Temperature Fluctuations Observed with the Capsule Held at Temperature for 4392 Hours	5.10
14	Temperature Fluctuations Observed with the Capsule Held at Temperature for 8784 Hours	5.11
15	Photomicrographs of Samples Taken from the Capsule that was Thermally Aged for 2208 Hours - Showing the Metal/CsCl Interface	5.12
16	Photomicrographs of Samples Taken from the Capsule that was Thermally Aged for 4392 Hours - Showing the Metal/CsCl Interface	5.13
17	Maximum Metal Attack as a Function of Exposure Time - As Determined from Photomicrographs of Samples Taken from the Test Capsules	5.15
18	Metal Control Samples, 400°C	5.19
19	Metal Control Samples, 450°C	5.20
20	Metal Control Samples, 500°C	5.21

Figures (cont'd)

21	Areas on the Outer Surface of the Inner Capsule (from the 4392 Hour Capsule) that were Sampled for Metallographic Examination	5.22
22	Additional Areas on the Outer Surface of the Inner Capsule that were Sampled for Metallographic Examination	5.23
23	Photomicrographs of Area A, Outer Surface of Inner Capsule	5.24
24	Photomicrographs of Area B, Outer Surface of Inner Capsule	5.25
25	Photomicrographs of Area C, Outer Surface of Inner Capsule	5.26
26	Photomicrographs of Area D, Outer Surface of Inner Capsule	5.27
27	Photomicrographs of Area E, Outer Surface of Inner Capsule	5.28
28	Photomicrographs of Area F-1, Outer Surface of Inner Capsule	5.29
29	Photomicrographs of Area F-2, Outer Surface of Inner Capsule	5.30
30	Photomicrographs of Area F-3, Outer Surface of Inner Capsule	5.31
31	Photomicrographs of Area G, Outer Surface of Inner Capsule	5.32

TABLES

1	Wall Thickness Data for Three of the 316L Stainless Steel Inner Capsules Used in Fabricating the Test Capsules	4.4
2	Pertinent Data on the Six WESF CsCl Capsules Used in the Thermal Aging Tests	4.5
3	Estimates of Metal Attack in the Zero-Time Capsules	5.5
4	Estimated Metal Attack in the Thermally Aged WESF CsCl Capsules	5.14
5	Wall Thickness Data for the WESF CsCl Test Capsules	5.16

1.0 INTRODUCTION

At Hanford, fission product cesium, containing 20-40% ^{137}Cs , is recovered from the high-level waste (HLW) and converted to cesium chloride (CsCl). The CsCl is doubly encapsulated in small high-integrity 316L stainless steel (SS) capsules. The CsCl capsules are then stored in water basins on the Hanford Reservation.

The CsCl is loaded into the inner 316L SS capsules by melt casting. Each capsule, which has an ID of two inches and an inner length of about 19 in., contains up to three kg of CsCl . The capsules contain up to about 70,000 Ci of ^{137}Cs , depending on the age and purity of the fission product CsCl .

Recovery of the Cs from the HLW and its subsequent purification take place in B-Plant. Conversion of the purified Cs to CsCl , encapsulation of the CsCl , and storage of the CsCl capsules take place in the Waste Encapsulation and Storage Facility (WESF). Both facilities are currently operated for the Department of Energy (DOE) by Rockwell Hanford Operations (Rockwell).

The Department of Energy is currently considering the geologic disposal of the CsCl capsules produced and stored at WESF. In order to evaluate the hazards associated with the geologic disposal of the WESF CsCl capsules, reliable estimates are required of long-term attack of the capsule material by the CsCl under repository conditions. Currently, available data on the compatibility of WESF-produced CsCl with 316L SS are not adequate for making the required estimates. The Cesium Chloride Compatibility Testing Program was started at the Pacific Northwest Laboratory in FY 1982 to obtain the needed compatibility data. The program will take ~5 years to complete. The work is funded by the long-term High-Level Defense Waste Program of the DOE. This report summarizes the program activities for Fiscal Year 1983.

2.0 OBJECTIVES

The primary objective of the Cesium Chloride Compatibility Testing Program is to evaluate the compatibility of WESF-produced CsCl with the 316L SS capsule material under the conditions that would be encountered in a geologic repository. Sufficient short-term compatibility data are to be obtained with the WESF-produced CsCl to permit useful estimates of long-term attack of the 316L SS by the CsCl under repository conditions.

Secondary objectives of the program are to:

- determine the effects of impurities in the WESF-produced CsCl on the attack of the SS and identify the reaction mechanisms involved
- determine the effects of the impurities in the WESF-produced CsCl on the melting point and solid-solid phase transition of CsCl.

3.0 TESTING CRITERIA

A number of variables can affect the compatibility of the WESF-produced CsCl with 316L SS in a geologic repository. The more important variables include:

- the reaction temperature (316L SS/CsCl interface temperature)
- impurities in the WESF-produced CsCl
- changes in the microstructure of the 316L stainless steel due to thermal aging reactions (i.e., precipitation of carbide phases, etc.)
- degree of contact between the 316L SS and the CsCl.

Program scope does not include a detailed testing program to evaluate all of the variables which affect 316L SS/WESF CsCl compatibility, especially with regard to impurity effects. The limited testing program now underway was designed on the following bases:

- the 316L SS/WESF CsCl interface temperatures in the geologic repository will not exceed 450°C
- the WESF CsCl capsules will be placed in the repository in a vertical orientation
- the radioactive compatibility tests are to be carried out with standard production WESF CsCl capsules without regard to possible variations in the composition of the CsCl between capsules.

The last limitation can have a significant effect on the overall validity of the radioactive compatibility data obtained, since theoretical considerations indicate that certain impurities in the CsCl could have a significant effect on the metal attack. The data obtained in the radioactive tests now underway will provide a measure of the metal attack for a given set of WESF capsules, but will not provide a complete picture of how the attack may vary with changes in the CsCl composition.

The CsCl compatibility testing program is divided into five tasks:

1. Radioactive compatibility data lasting up to 32,000 h using standard WESF CsCl capsules aged at elevated temperatures.
2. Heat transfer studies to define the relationship between the surface temperature of the inner and outer capsules of the WESF CsCl capsule.
3. Chemical analysis of the CsCl from a batch of WESF-produced CsCl (the CsCl product from WESF is not analyzed, although the Cs feed solution to WESF is analyzed).
4. A thermodynamic analysis of the WESF CsCl/316L SS system.
5. Physical property measurements on CsCl-impurity mixtures.

The major emphasis throughout the duration of the program is on the first task. Tasks 2-5 were completed during FY 1982 (Fullam 1982b).

4.0 RADIOACTIVE COMPATIBILITY TESTS

The radioactive compatibility tests are designed to provide the short-term data needed to estimate long-term attack of 316L SS by WESF-produced CsCl at a maximum metal/CsCl interface temperature of 450°C. The data obtained from the tests should meet this requirement, within the limitations described in the previous section.

4.1 TESTING PROCEDURE

In the radioactive compatibility tests, six standard WESF CsCl capsules are placed vertically in individual insulated containers and allowed to self heat to a maximum metal/CsCl interface temperature of 450°C. The capsules are maintained at temperature for times of 2000, 4000, 8000, 16,000, 24,000, or 32,000 h. When thermal aging of a capsule is completed, it is removed from the insulated container, cooled, and shipped to the Oak Ridge National Laboratory (ORNL) for sectioning and examination. At ORNL, small samples are taken from the inner capsule at various locations and subjected to metallographic examination to determine the extent of metal attack by the CsCl. Some of the samples will also be subjected to electron microprobe analysis in an attempt to identify the reaction mechanisms involved in the metal attack.

In addition to the aging tests, two WESF inner capsules were sectioned and examined immediately after filling with CsCl. This provides a measure of the metal attack that occurs during the loading operation when the CsCl is molten. These two "zero time" capsules will serve as the controls for determining the metal attack resulting from the thermal aging tests.

Because of their high ^{137}Cs content, all work with the WESF CsCl capsules, including sectioning and examination of test samples, is carried out in heavily shielded facilities (hot cells).

4.2 CAPSULE FABRICATION

The CsCl capsules used in the radioactive compatibility tests are typical WESF-production capsules prepared in the normal manner and meeting all Rockwell and DOE QC and QA requirements. All capsule components were fabricated in the usual manner with one exception. In order to accurately determine

metal attack by the CsCl, it is necessary to know the initial wall thickness of the inner capsules at the points where the samples are taken for metallographic examination. Therefore, the wall thickness of each of the eight inner capsules used in the tests was measured at the 18 locations shown in Figure 1 before the capsule was filled with CsCl. An ultrasonic procedure was used to determine the wall thickness.

Table 1 shows wall thickness data for three of the inner capsules, which is typical of all eight capsules. The data show that the wall thickness is fairly uniform over the length of a capsule along any given surface element, with thickness variations rarely exceeding 0.003 in. The data also show, however, that the tubing used in fabricating the inner capsules is not concentric, and substantial differences in wall thickness (up to 0.015 in.) were observed at diametrically opposite locations on the capsule. Because of these variations, the initial wall thickness of the inner test capsule is only known, with any degree of certainty, at those locations where the wall thickness measurements were made. The measurement locations are clearly shown on the test capsules by means of location numbers and location lines etched on the surface of the capsule (see Figure 1).

Loading of the molten CsCl into the inner capsules at WESF is a batch operation. Sufficient CsCl is melted in each batch to fill seven capsules. Each of the test capsules, including the two zero-time capsules, was loaded from a different batch of CsCl. Therefore, the chemical composition and cesium isotopic composition of the CsCl in the different test capsules can vary significantly. Table 2 gives the pertinent data on the six capsules used in the thermal aging tests. From the data, one can calculate an approximate ^{137}Cs isotopic concentration for each capsule, but the amount and types of impurities present in each capsule are unknown.

4.3 ZERO-TIME CAPSULES

The two "zero-time" inner capsules were filled with CsCl in the normal manner. After removal from the loading apparatus, the CsCl was removed from the two capsules by water leaching. Each empty capsule was rinsed, thoroughly dried, and then sealed by welding the end cap in place. The sealed inner capsules were decontaminated, leak-checked, and sealed in outer capsules in

FIGURE 1. Locations Where the Wall Thickness of the Inner WESF Capsules were Measured

TABLE 1. Wall Thickness Data for Three of the 316L Stainless Steel Inner Capsules Used in Fabricating the Test Capsules

<u>Inner Capsule No.</u>	<u>Location No. (a)</u>	<u>Wall Thickness, in.</u>	<u>Location No. (a)</u>	<u>Wall Thickness, in.</u>
19073-A	1	0.1342	10	0.1401
	2	0.1332	11	0.1387
	3	0.1341	12	0.1393
	4	0.1326	13	0.1392
	5	0.1345	14	0.1382
	6	0.1341	15	0.1387
	7	0.1345	16	0.1383
	8	0.1341	17	0.1364
	9	0.1341	18	0.1365
19073-C (8800 h)	1	0.1346	10	0.1431
	2	0.1320	11	0.1425
	3	0.1330	12	0.1417
	4	0.1342	13	0.1431
	5	0.1315	14	0.1414
	6	0.1310	15	0.1419
	7	0.1315	16	0.1399
	8	0.1319	17	0.1411
	9	0.1307	18	0.1422
19073-G (2200 h)	1	0.1455	10	0.1317
	2	0.1441	11	0.1306
	3	0.1458	12	0.1318
	4	0.1455	13	0.1326
	5	0.1444	14	0.1306
	6	0.1456	15	0.1303
	7	0.1435	16	0.1315
	8	0.1454	17	0.1321
	9	0.1445	18	0.1302

(a) See Figure 1 for the meaning of the location numbers.

TABLE 2. Pertinent Data on the Six WESF CsCl Capsules
Used in the Thermal Aging Tests^(a)

<u>Outer Capsule No.</u>	<u>Inner Capsule No.</u>	<u>CsCl, kg</u>	<u>¹³⁷Cs, Curies</u>	<u>Watts, t</u>
C-1266 (2200 h)	19073-G	2.388	45,870	220
C-1272	19073-B	2.701	56,930	273
C-1351	19073-E	2.597	52,520	252
C-1365 (4400 h)	19073-D	2.472	44,740	214
C-1451 (8800 h)	19073-C	2.756	54,380	261
C-1486	19073-H	2.716	51,140	245

(a) As of 4-5-82.

the normal manner. The two capsules were then shipped to ORNL for sectioning and metallographic examination. The procedure used in sectioning the capsules is described in Section 4.5.

4.4 CAPSULE AGING

The six WESF CsCl capsules to be thermally aged were placed in insulated containers and allowed to self heat to a maximum metal/CsCl interface temperature of 450°C. Figure 2 shows a sketch of a test capsule in its insulated container. Figure 3 shows a photograph of the insulated containers, containing the CsCl capsules, in a holding rack in the hot cell.

The insulated container consists of a metal canister lined with block insulation on the bottom and pipe insulation on the sides. Loose blanket insulation is placed on top of the capsule in the canister. A SS thermowell, running the length of the WESF capsule, is fastened to each capsule using SS hose clamps. The photograph in Figure 3 shows one of the WESF capsules with the thermowell attached.

Six calibrated movable chromel-alumel thermocouples, each having a different immersion depth, are used to measure the surface temperature of each WESF capsule. Figure 4 shows the locations at which the capsule surface temperature is measured. By rotating the six thermocouples between the thermowells on the six capsules, temperature profiles of each capsule are obtained on a periodic basis. As will be shown later, substantial temperature gradients

FIGURE 2. Sketch of a WESF Capsule in its Insulated Container

FIGURE 3. The Insulated Containers in a Holding Rack in the Hot Cell

FIGURE 4. Locations where the Capsule Surface Temperatures are Measured

exist between the middle and ends of each capsule. The temperature readings are normally taken on a weekly basis.

The temperature readings obtained provide a measure of the surface temperature of the outer capsule. It was impossible to measure directly the inner capsule/CsCl interface temperature. Therefore, the inner capsule/CsCl interface temperature must be calculated from the outer capsule surface temperature. In order to determine the relationship between the outer capsule surface temperature and the inner capsule/CsCl interface temperature, extensive heat transfer studies were carried out with an electrically heated dummy WESF capsule. Data from the heat transfer studies were also used to design the insulated containers to assure the test capsules reached the required aging temperature.

4.5 CAPSULE SECTIONING AND EXAMINATION

The test capsules are shipped to ORNL for sectioning and examination. In the case of the thermally-aged capsules, the capsules are shipped to ORNL without removing the contained CsCl. At ORNL, the outer capsules are opened and the inner capsules removed. The two zero-time inner capsules were sectioned as shown in Figure 5. Four ring sections were cut from each inner capsule, as shown, and then a small sample was cut from each ring for subsequent examination. Each sample contained an area where the capsule wall thickness had been measured. Each sample was mounted lengthwise, ground to the midpoint, polished, and photomicrographs of the reaction zone obtained. After etching, additional micrographs of the sample were obtained.

The thermally-aged inner capsules were sectioned in slightly different locations than the zero-time capsules. This is necessary because of the temperature gradients that exist over the length of the test capsules during aging. The maximum interface temperature does not correspond to any of the four locations where test samples were taken from the zero-time capsules. Sectioning of the aged capsules was adjusted so that a sample is obtained at the surface element passing through the measurement areas and the point of maximum temperature. This occurs at a point about nine inches up from the bottom of the outer capsule, or between measurement points 5 and 6 on the inner capsule. Since the initial wall thickness along a surface element of a

FOUR RING SECTIONS CUT FROM
THE INNER CAPSULE AT THE
LOCATIONS SHOWN - EACH
RING ABOUT 3/4" WIDE

SAMPLE ABOUT 1/2" WIDE CUT
FROM EACH RING SECTION - AT
THE END OF THE ETCHED LINE SO
THAT THE SAMPLE INCLUDES THE
AREA WHERE THE WALL THICKNESS
WAS MEASURED

FIGURE 5. Sectioning of the Zero-Time Inner Capsules

capsule does not vary by more than 0.001-0.003 inches, the initial wall thickness at the point where the sample is taken will be known with sufficient accuracy. The other three samples were taken at the same locations as those from the zero-time capsules.

4.6 METAL CONTROL SPECIMENS

When 316L SS is held in contact with WESF-produced CsCl at temperatures up to 450°C for extended periods of time, it is possible that chemical attack by the CsCl could produce changes in the microstructure of the metal. The thermal aging of the 316L SS may also produce changes in its microstructure. To help differentiate between microstructural changes produced by thermal aging and those resulting from chemical attack, control samples of 316L SS are being aged in argon at 400°C, 450°C, and 500°C for varying times up to 32,000 h. The aged samples are subjected to metallographic examination. The photomicrographs obtained will show what microstructural changes result from the thermal aging.

The control samples were cut from a rejected WESF SS inner capsule. Each sample was sealed in an argon-filled quartz envelope. The samples are heated in muffle furnaces whose temperatures are maintained within $\pm 2^\circ\text{C}$ of the control temperatures using solid state proportioning controllers. The samples are maintained at temperature for 2000, 4000, 8000, 16,000, 24,000, or 32,000 h (the same times as the radioactive test capsules).

5.0 TEST RESULTS

Thermal aging of the three-month (2208-h) capsule was completed in FY 1982. Thermal aging of the six-month (4392-h) and one-year (8784-h) capsules was completed during FY 1983. Destructive examination of the zero time, three month and six month capsules was also completed during the year. Destructive examination of the one year capsule was to be completed in FY 1983, but not in time to include the test results in this report.

In examining the test capsules to determine the extent of metal attack by the WESF CsCl, it was impossible to obtain a precise measure of the corrosion. Although the wall thickness of the inner capsule was accurately measured at 18 locations before testing, it was not possible to obtain similar measurements after testing. Adhesion of CsCl to the capsule surface makes it difficult to measure the wall thickness accurately using a micrometer or similar instrument. The CsCl could not be leached from the metal surface without destroying any reaction layer present. Determining the wall thickness of mounted specimens was equally difficult because of alignment problems. For example, when the metal sample is mounted in plastic in the hot cell for metallographic examination, the sample alignment could be as much as 15° to 20° from a vertical plane (see Figure 6). For a capsule having an initial wall thickness of 0.140 in. at a given location, this error in mounting alignment could result in an error of up to about 0.010 in. in the measured wall thickness. This error would tend to reduce the estimate of metal corrosion since it exaggerates the residual wall thickness of the test samples.

The metal corrosion can be estimated from photomicrographs of the test specimens, assuming the specimens have not suffered extensive uniform corrosion of the surface. Metal attack determined from the photomicrographs represent the minimum attack at a given location, since it is impossible to tell the initial location of the metal surface from the micrographs if there has been significant uniform corrosion. Efforts are still underway to accurately determine the residual wall thickness of the various test specimens. The corrosion data presented in subsequent sections were estimated from photomicrographs. Therefore, the data given represent a minimum measure of the attack; the actual attack could be significantly greater than the values shown. Hopefully, the discrepancies can be resolved when better measurements on the residual sample wall thickness are obtained.

FIGURE 6. Mounting of the Metal Samples Showing the Problem of Sample Alignment

Thermal aging of the three remaining WESF CsCl capsules is continuing. The next capsule will be taken off test in April 1984 after two years at temperature.

5.1 ZERO-TIME CAPSULES

Samples taken from the two zero-time capsules were subjected to metallographic examination. Table 3 provides estimates of the metal attack observed as determined from the photomicrographs obtained of each sample (within the limits described in the previous section). The photomicrographs of the various samples are shown in Figures 7 and 8. Etching of the samples was accomplished using an $\text{HNO}_3\text{-HCl}$ mixture.

Ring 4 Location 1

Ring 3 Location 3

Ring 2 Location 6

200 μ m

Ring 1 Location 8

100X

FIGURE 7. Photomicrographs from Samples of Zero Time Capsule 19459

Ring 4 Location 1

Ring 3 Location 3

Ring 2 Location 6

Ring 1 Location 8

200 μ m

100X

FIGURE 8. Photomicrographs from Samples of Zero Time Capsule 19073-F

The photomicrographs indicate that filling the capsules with molten CsCl produces relatively little attack of the 316L SS (<0.001 in.). The attack seems to be somewhat greater in the upper part of the capsules. The attack appears to involve general surface dissolution with some limited grain boundary attack at some locations.

TABLE 3. Estimates of Metal Attack in the Zero-Time Capsules

<u>Capsule No.</u>	<u>Depth of Attack,^(a) μm (mils)</u>			
	<u>Ring No. 1^(b)</u>	<u>Ring No. 2</u>	<u>Ring No. 3</u>	<u>Ring No. 4</u>
19459	10 (0.4)	8 (0.3)	25 (1.0)	25 (1.0)
19073F	18 (0.7)	18 (0.7)	25 (1.0)	18 (0.7)

(a) Minimum attack estimated from photomicrographs - see discussion in text on page 5.1.

(b) See Figure 4 for ring locations on capsule.

5.2 THERMAL AGING TESTS

Figures 9, 10, and 11 show the average surface temperature profiles for the WESF CsCl capsules aged for 2208, 4392, and 8784 h, respectively. The average maximum metal/CsCl interface temperature was 455°C for the 2208-h capsule, 449°C for the 4392-h capsule, and 460°C for the 8784-h capsule. The maximum interface temperature occurred about nine inches up from the bottom of the outer capsule in each case.

Figures 12, 13, and 14 show the inner capsule surface temperature at various locations as a function of time for each of the three aged capsules. All three capsules exhibit substantial fluctuations in temperature as a function of time at each location.

Metal samples from the three aged capsules were subjected to metallographic examination. Estimates of metal attack in the 2208- and 4392-h capsules, based on the photomicrographs obtained, are presented in Table 4. The limitations on the accuracy of the corrosion estimates discussed in the previous sections also apply to the results for the two thermally-aged capsules completed in time to include the results with this report. Photomicrographs of the samples from the 2208- and 4392-h capsules are shown in Figures 15 and 16.

FIGURE 9. Average Temperature Profiles for the WESF Capsule Held at Temperature for 2208 Hours

FIGURE 10. Average Temperature Profiles for the WESF Capsule Held at Temperature for 4392 Hours

FIGURE 11. Average Temperature Profiles for the WESF Capsule Held at Temperature for 8784 Hours

FIGURE 12. Temperature Fluctuations Observed with the Capsule Held at Temperature for 2208 Hours

FIGURE 13. Temperature Fluctuations Observed with the Capsule Held at Temperature for 4392 Hours

FIGURE 14. Temperature Fluctuations Observed with the Capsule Held at Temperature for 8784 Hours

Ring 4 Location 1

Ring 3 Location 3

Ring 2 Location 5

Ring 1 Location 8

200 μ m

100X

FIGURE 15. Photomicrographs of Samples Taken from the Capsule that was Thermally Aged for 2288 Hours - Showing the Metal/CsCl Interface

Ring 4 Location 1

Ring 3 Location 3

Ring 2 Location 5

Ring 1 Location 8

200 μ m

100X

FIGURE 16. Photomicrographs of Samples Taken from the Capsule that was Thermally aged for 4392 Hours - Showing the Metal/CsCl Interface

Selected samples from the three thermally-aged samples are being subjected to electron microprobe analyses. The work will be completed next fiscal year. The results obtained will be used to help interpret the corrosion data and to try to identify corrosion mechanisms.

The results presented in Table 4 indicate that the maximum metal attack occurs near the bottom of each capsule and not at the point of maximum temperature. Metal attack was much greater in the 4392-h capsule than in the 2208-h capsule. In addition, two of the samples from the 4392-h capsule exhibited extensive intergranular attack that was not observed with the 2208-h capsule. Metal attack in the 2208-h capsule appeared to involve general surface dissolution with some pitting.

Metal attack in the thermally-aged capsules was much greater than that observed in the initial compatibility studies for the WESF program.⁽²⁾ In the original studies, the maximum corrosion observed when 316L SS was exposed to radioactive CsCl at 400°C for up to 8760 h was 0.001 in. (25 μ m). This compared with a maximum attack of about 0.004 in. (110 μ m) after 4392 h in the current study. The increased attack observed in the current study is probably due to an increase in impurity levels in the CsCl. Additional work will be required, however, to confirm this assumption.

If one plots the maximum attack observed in the test capsules as a function of exposure time, the corrosion rate appears to be linear with time (see Figure 17). Additional test points are needed, however, to determine the form of the corrosion rate equation. If the results from the remaining capsules under test show that the corrosion rate continues to exhibit a linear relationship with time, it raises serious questions as to the long-term containment of WESF CsCl at the elevated temperatures tested.

TABLE 4. Estimated Metal Attack^(a) in the Thermally-Aged WESF CsCl Capsules

Exposure, hours	Ring No. 1 ^(b)		Ring No. 2		Ring No. 3		Ring No. 4	
	Average Temp, °C	Attack μ m, mils	Average Temp, °C	Attack μ m, mils	Average Temp, °C	Attack μ m, mils	Average Temp, °C	Attack μ m, mils
2208	415	60(2.4)	455	30(1.2)	420	30(1.2)	354	35(1.4)
4392	430	110(4.3)	449	80(3.2)	400	85(3.4)	350	50(2.0)
8784	432	(c)	460	(c)	415	(c)	356	(c)

(a) Minimum attack estimated from photomicrographs--see discussion in text on p. 30.

(b) See text and Figure 5 for ring locations in capsules.

(c) Results will be presented at a later date.

FIGURE 17. Maximum Metal Attack as a Function of Exposure Time - As Determined from Photomicrographs of Samples Taken from the Test Capsules

As discussed earlier, the corrosion data presented in Tables 3 and 4 were estimated from sample photomicrographs. These estimates represent the minimum level of attack that has occurred in each capsule. The attack could be significantly greater than the values given in Tables 3 and 4 if the samples have suffered any degree of general surface dissolution which would not be evident from the micrographs. Some initial attempts were made to determine the residual wall thickness of the mounted samples from which the photomicrographs were obtained. Table 5 lists the initial and residual wall thickness for each of the test specimens examined from one of the two zero-time capsules and the two thermally-aged capsules. In almost every case, the measured residual wall thickness of a sample was equal to or greater than the initial wall thickness. These discrepancies reflect the problems involved in accurately determining the residual wall thickness of a given mounted sample. The results do indicate, however, that the maximum metal corrosion in the test capsule cannot exceed the values given in the test capsule cannot exceed the values given in Tables 3 and 4 by more than about 0.010 in. (254 μm). Additional work is underway at ORNL to obtain more accurate measurements of the residual wall thicknesses of the test samples. This, in turn, will permit more reliable estimates of the metal attack.

TABLE 5. Wall Thickness Data for the WESF CsCl Test Capsules

Capsule No.	Exposure, h	Location Ring No.	Wall Thickness, in. (μm)		Wall Thickness Difference, in. (μm)
			Initial	Residual ^(a)	
19073F	Zero	1	0.139(3530)	0.144(3660)	+0.005(+130)
		2	0.137(3480)	0.140(3560)	+0.003(+80)
		3	0.139(3530)	0.149(3780)	+0.010(+250)
		4	0.139(3530)	0.138(3510)	-0.001(-25)
19073G	2208	1	0.145(3680)	0.150(3810)	+0.005(+130)
		2	0.144(3660)	0.152(3860)	+0.008(+200)
		3	0.146(3710)	0.153(3890)	+0.007(+180)
		4	0.146(3710)	0.146(2710)	0(0)
19073D	4392	1	0.138(3510)	0.140(3560)	+0.002(+50)
		2	0.137(3480)	0.138(3510)	+0.001(+25)
		3	0.138(3510)	0.138(3510)	0(0)
		4	0.139(3530)	0.148(3760)	+0.009(+230)

(a) Residual wall thickness determined from mounted samples.

(b) Difference = residual wall thickness - initial wall thickness

5.3 METAL CONTROL SPECIMENS

The 316L SS control samples held at 400°C, 450°C, or 500°C for 2200, 4400, and 8800 h were subjected to metallographic examination. The photomicrographs obtained are shown in Figures 18 through 20. Examination of the photomicrographs indicate that aging of the alloy at 400°C and 450°C for up to 800 h has little effect on the microstructure of the 316L SS. This agrees with the results obtained with the thermally-aged WESF CsCl capsules. Aging of the alloy at 500°C for up to one year produced some grain boundary precipitation. There may also be some increase in the Figure 18 intragranular precipitates in the samples aged at 450°C and 500°C. The formation of grain boundary precipitates could influence attack of the metal by the CsCl if the interface temperature exceeds 450°C for any extended period of time.

5.4 EXTERNAL CAPSULE CORROSION

When the 4392-h capsule was opened for metallographic examination, it was found that the outer surface of the inner capsule was discolored and possibly pitted in several locations. Similar damage was not observed with the two zero-time and 2208-h capsules. Additional work was authorized at ORNL to examine the affected areas to determine the extent of the possible damage and identify the probable cause(s). A total of seven areas on the outer surface were examined; these areas are shown in Figures 21 and 22.

Photomicrographs of the affected areas are shown in Figures 23 through 31. The micrographs indicate extensive pitting has occurred at most of the affected areas. The micrographs also indicate the formation of a second phase in most of the affected areas. The maximum attack observed was about 300 μm or 0.012 in. (see Figure 26). This corresponds to about 9% of the initial capsule wall thickness.

Without additional data, it is impossible to determine the composition(s) of the second phases that formed in the affected zones. It is possible that they could be an oxide phase(s) or a modification of the basic 316L SS microstructure. Electron microprobe and/or SEM analysis of the affected areas will be carried out in FY 1984 to help identify the second phases and probable cause(s) of the attack.

At the present time, it is impossible to identify the cause of the attack. Current speculation is that the attack results from arcing, which occurs during the electropolishing operation. The electropolishing step is used to decontaminate the outer surface of the inner capsule after the capsule is filled with CsCl and welded closed, but before it is inserted in the outer capsule. Experimental tests are planned for a separate program to determine if the electropolishing operation is responsible for the attack observed.

When the 8784-h capsule was opened at ORNL, it was found that the outer surface of the inner capsule was also discolored and/or possibly pitted at several locations. The affected areas did not appear to be as extensive as with the 4392-h capsule. Samples from the affected areas may be subjected to metallographic examination after further evaluation.

2200 hr (500X)

4400 hr (500X)

8800 hr (500X)

Figure 18. Metal Control Sample, 400°C.

2200 hr (500X)

4400 hr (500X)

8800 hr (500X)

Figure 19. Metal Control Sample, 450°C

2200 hr (500X)

4400 hr (500X)

8800 hr (500X)

Figure 20. Metal Control Sample, 500°C.

FIGURE 21. Areas on the Outer Surface of the Inner Capsule (from the 4392 Hour Capsule) that were Sampled for Metallographic Examination

FIGURE 22. Additional Areas on the Outer Surface of the Inner Capsule that were Sampled for Metallographic Examination

50X

100X

500X

Figure 23. Photomicrographs of Area A, Outer Surface of Inner Capsule.

50X

100X

500X

8306099-18

Figure 24. Photomicrographs of Area B, Outer Surface of Inner Capsule.

50X

100X

500X

8306099-19

Figure 25. Photomicrographs of Area C, Outer Surface of Inner Capsule.

50X

100X

500X

8306099-20

Figure 26. Photomicrographs of Area D, Outer Surface of Inner Capsule.

50X

100X

500X

8306099-21

Figure 27. Photomicrographs of Area E, Outer Surface of Inner Capsule.

50x

500x

100x

8306099-22

Figure 28. Photomicrographs of Area F-1, Outer Surface of Inner Capsule.

50X

100X

500X

8306099-23

Figure 29. Photomicrographs of Area F-2, Outer Surface of Inner Capsule.

50X

100X

500X

8306099-24

Figure 30. Photomicrographs of Area F-3, Outer Surface of Inner Capsule.

50X

100X

500X

8306099-25

Figure 31. Photomicrographs of Area G, Outer Surface of Inner Capsule.

6.0 REFERENCES

1. Fullam, H. T. 1982. Compatibility of Cesium Chloride and Strontium Fluoride with Containment Materials. BNWL-1673, Pacific Northwest Laboratory, Richland, Washington.
2. Fullam, H. T. 1982. Cesium Chloride Compatibility Testing Program Annual Report - Fiscal Year 1982. PNL-4556, Pacific Northwest Laboratory, Richland, Washington.

DISTRIBUTION

<u>No. of Copies</u>		<u>No. of Copies</u>	
<u>OFFSITE</u>			
27	DOE Technical Information Center		J. W. Bennett Geologic Repository Division DOE Nuclear Waste Policy Act Project Office S-10, Forrestal Washington, DC 20585
2	Nuclear Regulatory Commission 7915 Eastern Avenue Silver Springs, MD 20910 ATTN: R. E. Cunningham J. Roberts		
	R. D. Smith Division of Waste Management Nuclear Regulatory Commission Washington, DC 20555	3	Geologic Repository Division DOE Nuclear Waste Policy Act Project Office GTN Washington, DC 20545 ATTN: C. R. Cooley, S-10/NE-22 C. H. George, S-10/NE-22 R. Stein
	Materials Section Leader High-Level Waste Licensing Branch Nuclear Regulatory Commission Washington, DC 20555		J. O. Neff DOE National Waste Program Office 505 King Avenue Columbus, OH 43201
	W. F. Holcomb Environmental Protection Agency Office of Radiation Programs Washington, DC 20460	3	Oak Ridge National Laboratory P.O. Box Y Oak Ridge, TN 37830 ATTN: L. J. Mezga T. H. Row R. S. Crouse
2	DOE Terminal Waste Disposal and Remedial Action GTN Washington, DC 20545 ATTN: F. E. Coffman, NE-20 D. J. McGoff, NE-23		DOE Savannah River Operations Office P.O. Box A Aiken, SC 29801 ATTN: T. B. Hindman
4	DOE Office of Defense Waste and Byproducts Management GTN Washington, DC 20545 ATTN: J. E. Dieckhoner J. J. Jicha G. K. Oertel W. C. Remini	5	W. McMullen DOE Albuquerque Operations Office P.O. Box 5400 Albuquerque, NM 87185

No. of
Copies

- 3 Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
ATTN: J. H. Kittel
M. J. Steindler
L. E. Trevorrow
- Battelle Memorial Institute
Office of Nuclear Waste
Isolation
505 King Avenue
Columbus, OH 43201
ATTN: N. E. Carter
- Beverly Rawles
Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201
- K. V. Gilbert
Rockwell International
Rocky Flats Plant
P.O. Box 464
Golden, CO 80401
- 2 E. I. du Pont de Nemours Company
Savannah River Laboratory
Aiken, SC 29808
ATTN: J. L. Crandall
W. McDonnell
- R. Williams
Electric Power Research
Institute
3412 Hillview Avenue
P.O. Box 10412
Palo Alto, CA 94304
- R. K. Brown
Westinghouse Electric
Corporation
Advanced Energy Systems Div.
WIPP Library
P.O. Box 40039
Albuquerque, NM 87196
- J. L. Knabenschuh
Nuclear Fuels Services, Inc.
P.O. Box 191
West Valley, NY 14171

No. of
Copies

Bechtel National, Inc.
Box 3965
San Francisco, CA 94119
ATTN: J. L. Jardine

J. L. Larocca, Chairman
Energy Research and Development
Authority
Empire State Plaza
Albany, NY 12223

R. G. Post
College of Engineering
University of Arizona
Tucson, AZ 85721

S. Ahlstrom
CH2M Hill
6121 Indian School Road
Albuquerque, NM 87110

ONSITE

- 6 DOE Richland Operations Office
- O. J. Elgert
R. D. Izatt
N. Karagianes
H. E. Ransom
J. J. Schreiber
J. W. White
- 9 Rockwell Hanford Operations
- K. A. Gasper
M. W. Gibson
H. E. McGuire
J. W. Patterson
I. E. Reep
J. H. Roecker
P. F. Shaw
D. D. Wodrich
File Copy
- UNC United Nuclear Industries
- T. E. Dabrowski
- Westinghouse Hanford Company
- A. G. Blasewitz

No. of
Copies

No. of
Copies

43 Pacific Northwest Laboratory

W. F. Bonner
G. H. Bryan (10)
L. L. Burger/R. D. Scheele/
L. A. Bray
T. D. Chikalla
R. L. Dillon
J. R. Divine
J. H. Jarrett
D. E. Knowlton
J. M. Latkovich
R. C. Liikala
R. P. Marshall/W. R. Wiley/
D. B. Cearlock
J. L. McElroy
J. E. Mendel/M. D. Merz

J. E. Minor
K. S. Murthy/R. F. McCallum
I. C. Nelson/J. G. Stephan
A. M. Platt
E. J. Wheelwright
G. L. Tingey
R. P. Turcotte/G. L. McVay
H. H. Van Tuyl
R. E. Westerman
L. D. Williams
Technical Information (5)
Publishing Coordination (2)