Cesium Chloride Compatibility Testing Program—Final Report

G. H. Bryan

November 1989

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**Pacific Northwest Laboratory
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SUMMARY

The U.S. Department of Energy is considering the geologic disposal of the doubly encapsulated cesium chloride (CsCl) produced at the Waste Encapsulation and Storage Facility (WESF). Reliable estimates of long-term corrosion of the 316L stainless steel (SS) inner capsule material by the CsCl under repository storage conditions are needed to assess the hazards associated with geologic disposal of the fission product Cs. The Cesium Chloride Compatibility Program was carried out at PNL to obtain the short-term corrosion data required to accurately estimate long-term attack.

In the compatibility tests six standard WESF CsCl capsules were placed vertically in individual insulated containers and allowed to self-heat to a nominal maximum 316L SS/CsCl interface temperature of 450°C. The capsules were held at temperature for times ranging from 0.25 to 6 years. When a test was completed, the capsule was removed from the container and sectioned. Four samples were cut from the inner capsule at prescribed locations and subjected to metallographic examination. Corrosion of the 316L SS was determined from photomicrographs of the samples.

The corrosion data obtained showed that metal attack varied greatly between the test capsules. For example, the capsule tested for 6 years exhibited far less corrosion (up to 140 μm) than the capsule tested for 3 years (up to 460 μm).

The scatter in the corrosion data made it difficult to estimate long-term corrosion with any degree of accuracy. Evaluation of the data indicated, however, that the corrosion rate was linear for times up to 3 years. If one assumes a linear corrosion rate, as a worst case situation, a conservative estimate of long-term corrosion can be made. By using a linear-rate equation (and assuming a 316L SS/CsCl interface temperature of 450°C), the results obtained show that corrosion through the inner-capsule wall would occur in 15 to 21 years depending on the initial wall thickness (the nominal wall thickness of the inner capsule was changed from 0.095 in. to 0.136 in. during the WESF operations).

The long-term corrosion estimates are conservative for three reasons.

- The linear-rate equation was determined from selected data points that showed maximum corrosion.
- The metal/CsCl interface temperature would decrease with time as the capsule decay energy decreased.
- The concentration of impurities (which promote corrosion) in the CsCl would decrease with time as they are consumed and the corrosion rate will decrease accordingly.

Actual long-term corrosion in the WESF capsule would be less than the corrosion predicted by the linear-rate equation. From the data available, it is impossible to say how much less the corrosion would be.

Safety requirements for geologic disposal of the WESF CsCl capsules are not currently available. This makes it impossible to determine at the present time if the long-term corrosion predicted from the experimental data would preclude repository storage of the capsules at an initial interface temperature of 450°C.

If, when the repository safety requirements are available, it is found that the long-term corrosion predicted for a 450°C interface temperature is not acceptable, several options for capsule disposal are available, including the following:

- Additional compatibility studies at 450°C could be carried out to refine the corrosion data. This would provide a more reliable estimate of long-term corrosion and might make storage at a 450°C interface temperature acceptable.
- The initial metal/CsCl interface temperature in the repository could be reduced, which decreases the corrosion rate. Additional compatibility studies would be required in order to predict the long-term corrosion at the lower interface temperature.
- The existing WESF CsCl capsule could be provided with an overpack, which would permit repository storage at an initial interface temperature of 450°C.
- The WESF CsCl could be repackaged in a new capsule design, which would permit repository storage at an initial interface temperature of 450°C.

- Storage of the WESF CsCl capsules in the water pool could be continued until the heat output of the capsules drops to a low level. If the capsules were then placed in a repository, the interface temperature would be low enough that corrosion should not be a problem.

The additional compatibility studies required for options 1 and 2 would be extensive and would require at least 5 to 6 years to complete.

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CONTENTS

SUMMARY	iii
ACKNOWLEDGMENT	vii
1.0 INTRODUCTION	1.1
2.0 CONCLUSIONS AND RECOMMENDATIONS	2.1
3.0 OBJECTIVES	3.1
4.0 TESTING CRITERIA	4.1
5.0 RADIOACTIVE COMPATIBILITY TESTS	5.1
5.1 TEST PROCEDURES	5.1
5.1.1 Preparation of the Test Capsules	5.2
5.1.2 Thermal Aging of the Test Capsules	5.6
5.1.3 Sectioning and Examination of the Test Capsules	5.10
5.1.4 Metal Control Samples	5.15
5.2 TEST RESULTS	5.16
5.2.1 Zero-Time Capsules	5.16
5.2.2 Aging Times and Temperatures	5.16
5.2.3 Corrosion in the Thermally Aged Capsules	5.24
5.2.4 Microstructural Changes in the Metal Control Samples	5.35
5.2.5 Corrosion Mechanisms	5.35
5.3 ESTIMATES OF LONG-TERM CORROSION	5.41
6.0 REFERENCES	6.1
APPENDIX	A.1
A.1 WESF CsCl OPERATION	A.1
A.2 CHEMICAL COMPOSITION OF WESF-PRODUCED CsCl	A.5
A.3 PHYSICAL PROPERTIES OF WESF-PRODUCED CsCl	A.12

A.4	THERMODYNAMIC ANALYSIS OF THE 316L SS/WESF CsCl SYSTEM . . .	A.17
A.5	WESF CAPSULE HEAT-TRANSFER STUDIES	A.27
A.6	DESTRUCTIVE EXAMINATION OF WESF CsCl CAPSULES TAKEN FROM THE STORAGE POOL	A.33
A.7	EXTERNAL CORROSION OF THE WESF INNER CAPSULE	A.41
A.8	ORIGINAL PROGRAM PLAN FOR THE CESIUM CHLORIDE COMPATIBILITY TESTING PROGRAM	A.49
A.9	REFERENCES	A.65

FIGURES

1.1	Details of the WESF CsCl Capsule	1.1
5.1	Locations Where the Wall Thickness of the WESF Inner Capsules Was Measured	5.3
5.2	Sketch of a WESF Capsule in Its Insulated Container	5.7
5.3	The Insulated Containers in a Holding Rack in the Hot Cell	5.8
5.4	Locations Where the Outer-Capsule Surface Temperatures Were Measured	5.9
5.5	Sectioning of the Zero-Time Inner Capsules	5.11
5.6	Sectioning of the Thermally Aged Inner Capsules	5.12
5.7	Effect of Sample Alignment Error on Measuring the Residual Wall Thickness of a Mounted Sample by Photographic Methods	5.14
5.8	Photomicrographs of Samples Taken from the Zero-Time Capsules	5.17
5.9	Temperature Profiles for the Capsule Held at Temperature for 2,208 Hours	5.20
5.10	Temperature Profiles for the Capsule Held at Temperature for 8,784 Hours	5.21
5.11	Temperature Profiles for the Capsule Held at Temperature for 51,432 Hours	5.22
5.12	Metal Corrosion in the WESF CsCl Capsules Tested for 3 Years and 6 Years	5.27
5.13	Photomicrographs of Samples Taken from the Test Capsules at the Point of the Maximum Metal/CsCl Interface Temperature	5.28
5.14	Micrographs of the Ring #3 Samples Taken from the Test Capsules	5.29
5.15	Corrosion of the Ring #2 Samples as a Function of Exposure Time	5.30
5.16	Corrosion of the Ring #1 Samples as a Function of Exposure Time	5.31
5.17	Corrosion of the Ring #3 Samples as a Function of Exposure Time	5.32

5.18	Effect of Exposure Time on the Microstructure of the 316L SS Samples Taken from Ring #2	5.34
5.19	Microstructure of 316L SS Control Samples Aged for 51,432 Hours	5.36
5.20	Effects of Aging Time at 400°C on the Microstructure of 316L SS	5.37
5.21	Effects of Aging Time at 450°C on the Microstructure of 316L SS	5.38
5.22	Effects of Aging Time at 500°C on the Microstructure of 316L SS	5.39
5.23	Estimates of Long-Term Corrosion in the WESF CsCl Inner Capsule	5.43
A.1	Simplified Flowsheet for the Recovery and Purification of Fission Product Cs from PSN in B-Plant	A.2
A.2	Simplified Flow Diagram for the Preparation and Encapsulation of CsCl in WESF	A.3
A.3	Details of a WESF CsCl Capsule	A.5
A.4	The Effects of KCl Content on the Phase Transition Temperature of CsCl--Potassium Chloride Mixtures--Determined by Thermal Expansion Measurements	A.14
A.5	Thermal Expansion Scans for KCl-CsCl Mixtures	A.16
A.6	Standard Free Energy of Formation of Various Chlorides as a Function of Temperature	A.21
A.7	Side View of the Electrically Heated Dummy Capsule and Insulated Container	A.29
A.8	Top View of the Electrically Heated Dummy Capsule and Insulated Container	A.30
A.9	Typical Capsule Temperature Profiles Obtained Using the Electrically Heated Dummy Capsule	A.32
A.10	Photomicrographs of Samples Taken from the WESF CsCl Capsule that Had Been Held in the Storage Pool for 5 Years	A.35
A.11	Photomicrographs of Samples Taken from the WESF CsCl Capsule that Had Been Held in the Storage Pool for 8 Years	A.36

A.12	Micrographs of Samples Taken from the Storage Pool Cell CsCl Capsules Showing the Surfaces Exposed to the CsCl	A.38
A.13	Outer Surface of the Inner Capsule Showing Some of the Discolored and Possibly Pitted Areas	A.42
A.14	Outer Surface of a Pitted WESF CsCl Inner Capsule	A.43
A.15	Some of the Areas on the Outer Surface of the Inner Capsule that Were Subjected to Metallographic Examination	A.44
A.16	Typical Pitted Area--Outer Surface of the Inner Capsule from the 0.5-Year Test Capsule	A.45
A.17	Micrographs Showing Pitting Corrosion on the Outer Surface of Samples Taken from the Inner Storage Pool Capsules	A.48

TABLES

5.1	Wall Thickness Data for Three of the 316L SS Inner Capsules Used in Fabricating the Test Capsules	5.4
5.2	Pertinent Data on the Six WESF CsCl Capsules Used in the Thermal-Aging Tests	5.5
5.3	Estimates of Metal Attack in the Zero-Time Capsules	5.18
5.4	Test Parameters for the Six WESF CsCl Capsules Used in the Thermal Aging Tests	5.19
5.5	Temperature Data for Capsule C-1266, Tested for 2,208 Hours . .	5.23
5.6	Estimates of Metal Attack in the Thermally Aged WESF CsCl Capsules	5.25
A.1	Dimensional Tolerances for the 316L SS Tubing Used for the WESF CsCl Inner and Outer Capsules	A.6
A.2	Analysis of the Cs Feed Solution Entering WESF	A.7
A.3	Estimates of Impurity Levels in WESF-Produced CsCl	A.8
A.4	Calculated Impurity Content in Eight WESF CsCl Capsules	A.11
A.5	Composition of the Simulated WESF CsCl Mixture Used in the Physical Property Measurements	A.13
A.6	The Effect of Impurities on the Phase Transition Temperature and Melting Point of CsCl	A.17
A.7	Standard Free Energy of Formation Values for Selected Chlorides at Various Temperatures	A.20
A.8	Components of the 316L SS/CsCl System	A.23
A.9	Estimates of Metal Attack in Two Pool Capsules and Two Zero-Time Capsules	A.37
A.10	Estimates of Metal Attack in the 18 Storage Pool CsCl Capsules Examined	A.40

1.0 INTRODUCTION

At the Hanford site, fission product Cs containing 20 to 40% ^{137}Cs has been recovered from the high-level fuel reprocessing waste (HLW) and converted to cesium chloride (CsCl) for encapsulation and storage. Recovery of the Cs from the HLW and its subsequent purification was carried out in B-Plant. Conversion of the purified product to CsCl , encapsulation of the CsCl in 316L stainless steel (SS), and water storage of the CsCl capsules were conducted in the Waste Encapsulation and Storage Facility (WESF). Both facilities are operated for the U.S. Department of Energy (DOE) by the Westinghouse Hanford Company (WHC).^(a) Descriptions of the B-Plant and WESF Cs operations are given in the Appendix.

The CsCl was doubly encapsulated in 316L SS capsules. Details of the WESF CsCl capsule are shown in Figure 1.1. The CsCl was loaded into the inner capsule by melt-casting. The inner capsule has a nominal inside diameter of 2 in., an inner length of approximately 19 in., and can contain up to 3 kg of CsCl . The CsCl was prepared in small batches, sufficient to fill up to seven capsules. Each capsule contained up to ~80,000 Ci of ^{137}Cs at the time of loading depending on the age of the fission product Cs and the chemical purity of the CsCl .

The CsCl produced at WESF was not analyzed prior to encapsulation, but the product was known to contain substantial amounts of impurities (see Section A.2). The impurity content of the CsCl could have varied significantly from batch to batch. Therefore, the impurity content of capsules prepared from different batches of CsCl can vary over a wide range. The bulk of the impurities in the WESF CsCl should be present as chlorides. Some impurities may be present as oxides or oxychlorides, however, as a result of the hydrolysis of the less stable metal chlorides present when the CsCl solution is evaporated to dryness and the resulting solids melted for casting into the capsules. The CsCl in the sealed WESF capsule can contain small but significant amounts of water (see Section A.2).

(a) The facilities were operated by Rockwell Hanford Operations (RHO) when the program was started in FY 1982. WHC assumed operations in FY 1988.

FIGURE 1.1. Details of the WESF CsCl Capsule (Kenna and Schultz 1983)

Filling the capsules with molten CsCl was not completely uniform, and the internal void volume can vary substantially between capsules. Solidification of the molten CsCl and subsequent contraction of the solid CsCl on cooling could produce irregular contact between the 316L SS and the CsCl. The presence of impurities in the CsCl would affect the way in which the solid CsCl contracted on cooling and how it adhered to the capsule wall.

The DOE is considering the geologic disposal of the CsCl capsules. In order to evaluate the hazards associated with geologic disposal of the CsCl capsules, reliable estimates of long-term attack of the 316L SS by the CsCl under repository storage conditions are needed. The Cesium Chloride Compatibility Testing Program was started at the Pacific Northwest Laboratory (PNL)^(a) in FY 1982 to obtain the required compatibility data and was funded

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute.

through the DOE's Office of Assistant Secretary for Defense Programs (DP). The experimental phases of the program were completed in FY 1988. This report presents the results obtained and is the final report for the program.

2.0 CONCLUSIONS AND RECOMMENDATIONS

The results obtained in the compatibility tests with the WESF CsCl capsules that were held at a maximum metal/CsCl interface temperature of approximately 450°C for up to 6 years showed that the metal corrosion varied greatly from capsule to capsule. A specific cause for the variability in corrosion was not identified, but variations in the impurity content of the CsCl in the different capsules is the most reasonable explanation.

The variability in the short-term corrosion data makes it difficult to estimate long-term corrosion of the WESF capsule in a geologic repository with any degree of certainty. Analysis of the corrosion data for those capsules that exhibited the greatest attack indicated that the corrosion rate was linear for exposure times up to 3 years. As a worst-case scenario, using a linear-rate equation derived from the short-term corrosion data provides a conservative estimate of the long-term corrosion in the WESF CsCl capsule stored in a geologic repository at a 316L SS/CsCl interface temperature of 450°C. The results obtained with this equation show that (at the 90% level of certainty) corrosion through the inner-capsule walls would occur in 15 to 21 years, depending on the initial wall thickness. Actual corrosion in the capsule during long-term storage should be substantially less than that predicted by the linear-rate equation for a number of reasons; how much less cannot be determined from the existing data.

Safety requirements for the storage of the WESF CsCl capsules in a geologic repository are not currently available. Therefore, it is not possible at the present time to determine if the long-term corrosion predicted using the linear-rate equation would preclude storage of the CsCl capsules in a repository at an interface temperature of 450°C. Once the safety requirements have been established, however, it should be possible to determine if the estimated long-term corrosion is low enough to permit repository storage of the capsules at an initial interface temperature of 450°C.

If the analysis shows that the predicted corrosion is too great to permit capsule storage at an interface temperature of 450°C, several options for capsule disposal are available. These include the following:

- Additional compatibility studies at 450°C would refine the corrosion data and provide a more reliable estimate of long-term corrosion at 450°C. The revised estimate may show that the long-term corrosion is low enough to permit capsule storage at an interface temperature of 450°C.
- Decreasing the initial metal/CsCl interface temperature in the repository would thereby reduce the corrosion rate. Additional compatibility studies would be required at the new interface temperature to ensure that the corrosion rate is reduced to an acceptable level.
- The existing WESF CsCl capsule could be provided with an overpack that permits storage of the capsule in the repository at an initial interface temperature of 450°C.
- The CsCl could be reencapsulated in a new capsule design, which would permit repository storage at an interface temperature of 450°C.
- Storage of the WESF CsCl capsules in the water basin could be continued until the decay energy of the capsule decreases to a low level. If the capsules are then placed in a repository, the metal/CsCl interface temperature would be low and corrosion should not be a problem.

The additional compatibility work needed for the first two options would be extensive and require a number of years to complete. In addition, there are some questions as to whether reliable estimates of the long-term corrosion can be obtained because of variable composition of the CsCl in the WESF capsules. Therefore, before any additional compatibility work is started, serious consideration should be given to the other capsule disposal options available.

3.0 OBJECTIVES

The primary objective of the Cesium Chloride Compatibility Testing Program was to evaluate the compatibility of WESF-produced CsCl with 316L SS under the conditions that would be encountered in a geologic repository. The compatibility testing was to be done with full-size WESF CsCl capsules. Sufficient short-term (up to 6 year) compatibility data were to be obtained to permit estimates of the long-term attack of the 316L SS capsules by the CsCl under repository conditions.

Secondary objectives of the program, to obtain data needed to supplement the compatibility data, included the following:

- a chemical analysis of the WESF-produced CsCl to identify the types and amounts of impurities present
- a determination of the effects of impurities in the WESF CsCl on the melting point and solid-solid phase transition of CsCl
- a thermodynamic analysis of the WESF CsCl-316L SS system
- the destructive examination of 20 WESF CsCl capsules taken from the WESF storage pool to confirm that corrosion by the CsCl is not a threat to continued safe storage of the capsules in a water pool
- a study to determine the cause of pitting observed on the outer surface of some of the WESF CsCl inner capsules.

Work on the secondary objectives was completed in previous years and the details reported in program annual reports. For reference purposes the annual reports^(a) issued during the course of the study are listed in the reference section. In order to consolidate all of the data in a single source, the results of the secondary studies are summarized in the Appendix of this report.

(a) Note: No formal annual report was issued for FY 1987.

4.0 TESTING CRITERIA

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

- the 316L SS/CsCl interface temperature
- the types and amounts of impurities contained in the WESF-produced CsCl
- changes in the microstructure of the 316L SS due to thermal aging reactions (i.e., precipitation of carbide phases, etc.) at repository temperatures
- the degree of contact between the 316L SS and the CsCl.

The initial program plan proposed for the Cesium Chloride Compatibility Testing Program involved an extensive experimental program to investigate the variables that could affect 316L SS/CsCl compatibility at repository storage conditions (details of the initial program plan are presented in Section A.8). Sufficient experimental data should have been obtained from the proposed testing program to permit reliable estimates of long-term corrosion of the 316L SS by the CsCl under repository storage conditions.

Budget constraints required a major reduction in the scope of the program from that proposed in the original program plan, especially with regard to evaluating the effects of temperature and impurities on 316L SS/WESF CsCl compatibility. This reduction in scope greatly reduced the usefulness of the compatibility data subsequently obtained in predicting long-term capsule corrosion in a repository.

The limited testing program that was carried out was designed on the following basis:

- The maximum 316L SS/WESF CsCl interface temperature in the geologic repository would not exceed 450°C.
- The WESF CsCl capsules would be placed in the repository in a vertical orientation.

- The compatibility tests were to be carried out with standard production WESF capsules without regard to possible variations in the composition of the CsCl between capsules. Each of the capsules tested was to be prepared from a different batch of CsCl. Analysis of the CsCl was limited to a single sample taken from one test capsule prior to testing.

The last limitation can have a significant effect on the compatibility data obtained because theoretical considerations and previous work (Fullam 1972) indicate that certain impurities in the CsCl can have a significant effect on the metal attack. The data obtained from the tests provide a measure of the metal attack for a given set of WESF capsules, but do not provide a complete picture of how the metal attack may vary with changes in the CsCl composition.

5.0 RADIOACTIVE COMPATIBILITY TESTS

The radioactive compatibility tests were 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.

5.1 TEST PROCEDURES

In the radioactive compatibility tests, six standard WESF CsCl capsules were placed vertically in individual insulated containers and allowed to self-heat to a nominal maximum 316L SS/CsCl interface temperature of 450°C. The capsules were maintained at temperature for times up to 6 years. When the thermal cycle was completed, each test capsule, except for the capsule aged for ~3 years,^(a) was removed from the insulated container, cooled, and shipped to the Oak Ridge National Laboratory (ORNL) for sectioning and examination. At ORNL four small samples were cut from the inner capsule at well-defined locations and subjected to metallographic examination to determine the extent of metal attack by the CsCl. Some of the samples were also subjected to electron microprobe analysis in an attempt to identify the reaction mechanisms involved in the attack.

In addition to the thermal-aging tests, two WESF inner capsules were sectioned and examined after filling with CsCl. This provided a measure of the metal attack that occurred during the loading operation when the CsCl was molten. The two "zero-time" capsules serve as controls for determining the metal attack resulting from the thermal-aging tests.

Because of their extreme radioactivity, all work with the WESF CsCl capsules, including sectioning and examination of test samples,^(b) was carried out in heavily shielded facilities (hot cells).

-
- (a) The 3-year test capsule was shipped to WESF for sectioning. Examination of the capsule samples was provided by WHC.
 - (b) The test samples from the 3-year capsule were decontaminated and examined in shielded glove boxes.

5.1.1 Preparation of the Test Capsules

The CsCl capsules used in the radioactive compatibility tests were typical WESF-production capsules prepared in the normal manner and met all RHO and DOE quality control and quality assurance requirements. All metal capsule components were fabricated in the usual manner with one exception. In order to accurately measure attack of the 316L SS by the CsCl, it was necessary to know the initial wall thickness of the inner capsule at the points where the metal samples were taken for metallographic examination. The specification for the 316L SS tubing used in fabricating the inner capsules called for a nominal wall thickness of 0.136 ± 0.012 in. The specification also set the maximum acceptable eccentricity of the tubing at $\pm 10\%$ of the nominal wall thickness. Thus the actual wall thickness of the inner capsule could vary significantly from point to point. An ultrasonic procedure was used to measure the wall thickness of each of the eight capsules used in the tests at the 18 locations shown in Figure 5.1. With the procedure used, the wall thickness could be determined to 0.0001 in. The locations where the wall thickness was measured were marked on each inner capsule by means of location numbers and location lines etched on the outer surface of the capsule as shown in Figure 5.1.

Table 5.1 shows wall thickness data for three of the inner capsules. The data are typical of all eight inner capsules used in the test program. The data show that the wall thickness was fairly uniform over the length of a capsule along any given surface element, with thickness variations of ≤ 0.004 in. over the length of a capsule. The data also show, however, that the tubing used was not concentric, and wall thickness differences of up to 0.015 in. were observed at diametrically opposed locations on the capsule. Because of these variations, the initial wall thickness of each inner capsule is only known, with certainty, at those locations where the wall thickness was measured.

At WESF, the CsCl was loaded into the inner capsule by melt-casting. The melt-casting was a batch operation, and sufficient CsCl was melted in each batch to fill seven capsules. The temperature of the molten CsCl was

FIGURE 5.1. Locations Where the Wall Thickness of the WESF Inner Capsules Was Measured

TABLE 5.1. Wall Thickness Data for Three of the 316L SS Inner Capsules Used in Fabricating the Test Capsules

Inner Capsule No.	Location No. (a)	Wall Thickness, in.	Location No. (a)	Wall Thickness, in.
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	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	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 5.1 for the meaning of the location numbers.

approximately 750°C. Each of the capsules used in the testing program, including the two zero-time capsules, was prepared from a different batch of CsCl. Therefore, the chemical composition of the CsCl may have varied significantly from capsule to capsule.^(a) Table 5.2 gives the pertinent data for the six WESF CsCl capsules used in the thermal-aging tests.

The two zero-time inner capsules were filled with CsCl in the normal manner. After removal from the filling apparatus, the CsCl was removed from the capsule by water-leaching. Each empty capsule was rinsed, thoroughly dried, and then sealed by welding the end cap in place. The inner capsule was decontaminated, leak-checked, and sealed in an outer capsule in the normal manner. The two capsules were then shipped to ORNL for sectioning and metallographic examination. A single sample of CsCl was taken from one of the zero time capsules for chemical analysis, before the CsCl was removed by water leaching. The analytical results obtained are discussed in Section A.2.

TABLE 5.2. 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, Ci</u>	<u>Watts, t</u>
C-1266	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	19073-D	2.472	44,740	214
C-1451	19073-C	2.756	54,380	261
C-1486	19073-H	2.716	51,140	245

(a) As of 4-5-82.

(a) The CsCl product was not routinely analyzed for impurities (see subsection A.2). The ¹³⁷Cs content of each capsule was determined by calorimetry.

5.1.2 Thermal Aging of the Test Capsules

In the aging tests it was impossible to measure the actual 316L SS/CsCl interface temperature, but the surface temperature of the outer capsule was measured directly. Therefore, the inner-capsule/CsCl interface temperatures must be calculated from outer-capsule surface temperature measurements. In order to determine the relationship between the outer-capsule surface temperature and the inner-capsule/CsCl interface temperature, extensive heat transfer calculations and experimental studies were carried out using an electrically heated dummy WESF capsule filled with nonradioactive CsCl. The heat-transfer studies were described in detail in the FY 1982 annual report (Fullam 1982) and are summarized in the Appendix (Section A.5). The data from the heat-transfer studies were also used to design the insulated containers to assure that the test capsules reached the required maximum interface temperature of 450°C.

Figure 5.2 shows a sketch of a test capsule in the insulated container. The photograph presented in Figure 5.3 shows the insulated containers, containing the test capsules, in a holding rack in the hot cell. Each insulated container consisted of a metal canister lined with block insulation on the bottom and pipe insulation on the sides. Loose blanket insulation was placed on the top of the capsule in the canister. A 304L SS thermowell, running the length of the WESF capsule, was fastened to each capsule using three SS hose clamps. Figure 5.3 also shows one of the WESF capsules with the thermowell attached (third from right). Six calibrated chromel-alumel thermocouples, each having a different immersion depth, were used to measure the outer surface temperature of each WESF capsule. By rotating the six thermocouples between the thermowells on the six capsules, temperature profiles of the six capsules were obtained on a periodic basis. Figure 5.4 shows the locations where the outer-capsule surface temperatures were measured. As will be shown later, a substantial temperature gradient existed between the middle and ends of each capsule. Referring to Figure 5.4, thermocouple No. 4 was positioned to measure the maximum surface temperature. During the first several months of testing, the test temperatures were measured on a weekly basis, and at longer intervals during the latter stages of testing.

FIGURE 5.2. Sketch of a WESF Capsule in Its Insulated Container

Table 5.2 shows that the wattage of the six test capsules varied over a wide range (214 to 273 watts). In order to obtain the desired maximum interface temperature of 450°C , the thickness of insulation in each canister had to be varied accordingly. The problem was further complicated by the fact that there was considerable disagreement between various sources, when the

FIGURE 5.3. The Insulated Containers in a Holding Rack in the Hot Cell

program was started, on how much of the $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$ decay energy was absorbed within the WESF capsule. In designing the insulated containers it was assumed that 55 to 60% of the heat generated by the decay reactions would be released in the capsule. Subsequent results with the six test capsules

FIGURE 5.4. Locations Where the Outer-Capsule Surface Temperatures Were Measured

indicated that 57 to 62% of the energy was released in the capsules. As will be shown in the following section, the design of the six insulated containers was sufficient to maintain an initial maximum metal/CsCl interface temperature in each capsule of 451 to 458°C.

5.1.3 Sectioning and Examination of the Test Capsules

Five of the test capsules and the two zero-time capsules were shipped to ORNL for sectioning and examination (the other test capsule was sent to WESF for sectioning). At ORNL the outer capsules were opened and the inner capsules removed. The two zero-time inner capsules were sectioned as shown in Figure 5.5. Four ring sections were cut from each capsule at the locations shown, and a small sample was cut from each ring for subsequent examination. Each sample contained an area where the initial capsule wall thickness had been measured. The residual thickness of each sample was measured with a micrometer. The sample was then mounted lengthwise in mounting compound and ground to the midpoint. After polishing, 50X, 100X, and 500X photomicrographs were obtained of a) the surface area showing maximum attack by the CsCl, and b) the body of the sample. The sample was then etched and 50X, 100X, and 500X photomicrographs again obtained of the same areas. HCl-HNO₃ was the etchant used.

The thermally aged inner capsules were sectioned in a slightly different manner than the zero-time capsules (see Figure 5.6). This was necessary because the maximum 316L SS/CsCl interface temperature did not correspond to any of the four locations where the zero-time capsules were sectioned. Sectioning of the aged capsule was adjusted so that one ring section (ring #2 in Figure 5.6) was cut from the capsule at the point of maximum temperature (between locations #5 and #6 in Figure 5.6). The test sample was then cut from the ring at the location where the surface element passing through locations #5 and #6 passed through the ring section. Since the variation in wall thickness between adjacent measurement points on a surface element rarely exceeded 0.001 in., the initial wall thickness of ring #2 at the sample point was known with acceptable accuracy.

When the aged capsules were opened at ORNL, each capsule was longitudinally split into two sections and the CsCl was removed by physical means.

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 5.5. Sectioning of the Zero-Time Inner Capsules

During Thermal Aging Capsule is Positioned Vertical with Top as Shown

Four Ring Sections Cut From the Inner Capsule at the Locations Shown - Each Ring About 3/4 in. Wide

Area Where Wall Thickness was Measured

Ring Section #1

Sample About 1/2 in. 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.

Nos. 1-9 Indicate Areas Where Wall Thickness was Measured

FIGURE 5.6. Sectioning of the Thermally Aged Inner Capsules

The sections were not water-leached, unlike the sections from the zero-time capsules. Thus some CsCl (and reaction products) adhered to the surface of the test samples. This made it impossible to measure the residual wall thickness with a micrometer as was done with the samples from the zero-time capsules. Instruments such as the ultrasonic device used to measure the initial capsule wall thickness were not available in the ORNL hot cells. The problem could have been solved by water-leaching the samples to remove the CsCl and reaction products, but it was decided it was more important to retain the sample reaction zone for analysis.

A photographic technique was used to estimate the residual wall thickness of the mounted samples from the aged capsules sent to ORNL. Alignment problems in mounting the sample in plastic in the hot cell, however, affected the results obtained. If the sample was not mounted vertically (see Figure 5.7), the measured wall thickness would be greater than the actual wall thickness. A 15-degree error in alignment (from vertical), for example, would increase the apparent sample thickness by ~0.005 in. Because mounting alignment errors were unlikely to exceed 15 to 20 degrees, wall thickness measurements were used to determine if very extensive metal attack has occurred.

Metallographic examination of the samples from the aged capsules was carried out in the same way as the samples from the zero-time capsules.

The test capsule which had been thermally aged for 3 years was sent to WESF for sectioning. After the capsule was opened, the CsCl was removed by water-leaching. The four ring sections were cut from the capsule in the prescribed manner and returned to PNL where a metallographic sample was cut from each ring at the required location. The samples were then sent to WHC for metallographic examination in the Post-Irradiation Testing Laboratory. Metallographic examination of the samples at WHC was the same as for the samples examined at ORNL. The CsCl was removed from the capsule by water-leaching in order to reduce the residual radioactivity to an acceptable level. This resulted in the loss of the reaction layer on the metal surface but was necessary to permit the subsequent metallographic examination of the capsule samples at the WHC facility. The residual wall thickness of each

x = Actual Wall Thickness
 y = Measured Wall Thickness
 α° = Alignment Error From Vertical

FIGURE 5.7. Effect of Sample Alignment Error on Measuring the Residual Wall Thickness of a Mounted Sample by Photographic Methods

sample was measured using a micrometer. Removal by water leaching of the CsCl from the 3-year test capsule examined at WHC and the two zero-time capsules examined at ORNL should have had no effect on the corrosion results obtained. After the CsCl was removed, the capsules were water washed and thoroughly dried to prevent additional corrosion of the 316L SS by any residual solution during the period between CsCl removal and mounting of the metallographic samples for examination.

Corrosion of the 316L SS by the WESF CsCl was estimated from the residual wall thickness measurements and the metallographic examination of the capsule samples. The residual wall thickness measurements, determined by either micrometer measurements or the photographic technique described above, were used to show that extensive corrosion of a 316L SS sample had not occurred. If the residual wall thickness measurements showed no evidence of

extensive attack, the metal corrosion was estimated from photomicrographs of the as-polished and etched specimens. Micrographs obtained from the etched specimens were also used to determine if microstructural changes had occurred in the 316L SS as a result of the corrosion.

5.1.4 Metal Control Samples

In many 300 series stainless steels, carbide precipitates form at grain boundaries when the alloys are held within the sensitizing range (~400 to 900°C) for extended periods of time. The precipitate formation can reduce the corrosion resistance at the grain boundaries. The low C content of 316L SS is intended to reduce the precipitate problem, but does not eliminate it. When a WESF CsCl capsule is held at temperatures up to 450°C for extended periods of time, it is possible that precipitate formation at the grain boundaries could reduce the resistance to chemical attack by the CsCl. Conversely, the chemical attack by the CsCl could produce microstructural changes in the 316L SS. In order to differentiate between any microstructural changes resulting from chemical attack and those produced by thermal aging, control samples of 316L SS were aged in Ar at 400, 450, and 500°C for the same times as the test capsules. The aged samples were then subjected to metallographic examination to determine if microstructural changes had occurred.

The control samples were cut from a reject WESF 316L SS inner capsule.^(a) Each sample was sealed in an Ar-filled quartz envelope. The samples were heated in muffle furnaces whose temperatures were maintained within $\pm 2^\circ\text{C}$ of the control temperatures using solid-state proportioning controllers. Calibrated chromel-alumel thermocouples were used to monitor the furnace temperatures.

(a) The capsule was rejected because it did not meet dimensional tolerances but did meet all other WESF specifications.

5.2 TEST RESULTS

5.2.1 Zero-Time Capsules

Results obtained with the two zero-time capsules provide a measure of the metal attack that occurred during the capsule-filling operation. Photomicrographs of the samples taken from the capsules are shown in Figure 5.8. The residual wall thickness measurements obtained using a micrometer showed that extensive attack of the capsule had not occurred. Metal attack was estimated from the micrographs of the as-polished and etched samples and the results obtained are given in Table 5.3. The micrographs show that the filling operation resulted in only slight attack of the 316L SS ($\leq 25 \mu\text{m}$). The attack seemed to be slightly greater in the upper area of each capsule and appeared to involve general surface roughening with limited grain boundary attack at some locations.

5.2.2 Aging Times and Temperatures

The compatibility tests with the six WESF CsCl capsules lasted up to about 6 years. Table 5.4 shows the duration of each test and the decay energy of each capsule at the start and end of the aging test.

The test criteria called for the capsules to be held at an initial maximum 316L SS/CsCl interface temperature of 450°C. Because of the differences in the decay energy of the six capsules, it was impossible to bring each of the capsules to exactly 450°C. Table 5.4 shows the initial maximum interface temperature that was attained with each capsule in its insulated container. In every case the maximum interface temperature occurred about 9 in. up from the bottom of the outer capsule. Although the initial maximum interface temperatures for the six capsules varied from 451°C to 458°C, they were sufficiently close to the control temperature to permit continued testing without modifying the insulated container. Table 5.4 also shows the average maximum interface temperature for the duration of each test.

When the WESF CsCl capsule self-heated in its insulated container, a temperature gradient existed over the length of the capsule with the maximum temperature occurring about 9 in. up from the bottom of the outer capsule.

Capsule No. 19073.F

Capsule No. 19459

FIGURE 5.8. Photomicrographs of Samples Taken from the Zero-Time Capsules

TABLE 5.3. Estimates of Metal Attack in the Zero-Time Capsules(a)

<u>Capsule No.</u>	<u>Depth of Metal Attack, μm (mils)</u>			
	<u>Ring No. 1</u> ^(b)	<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)
19073-F	18 (0.7)	18 (0.7)	25 (1.0)	18 (0.7)

(a) Attack estimated from photomicrographs.

(b) See Figure 5.3 for ring locations on capsule.

Because of the differences in decay energy between capsules and slight differences in the insulated containers the temperature profiles of the six capsules were similar but not identical. Figures 5.9 to 5.11 show the temperature profiles of three of the capsules. The temperature values shown in the figures are the average temperatures for the duration of the test. The locations where the four ring sections were removed from each inner capsule, after testing, for metallographic examination are also shown in the figures. Because of the differences in the temperature profiles and initial maximum interface temperature of the six test capsules, the average metal/CsCl interface temperature where a given ring section was removed varied over a substantial range between the six capsules.

One problem was encountered in measuring the outer-capsule surface temperatures. When a capsule was placed in its insulated container, thermal equilibrium was apparently reached in a relatively short period of time (~24 h). The outer-capsule surface temperatures were then monitored on a weekly basis for the first few months of testing. Although the capsule temperature at each measurement point remained constant for short periods of time, once thermal equilibrium had been reached, it soon became apparent that significant fluctuations in temperature occurred over extended periods of time (days to weeks). Table 5.5 shows the temperature data for the capsule that was held at temperature for 2208 h. The standard deviation (σ) associated with the average temperature values indicates the magnitude of the temperature fluctuations observed.

TABLE 5.4. Test Parameters for the Six WESF CsCl Capsules Used in the Thermal Aging Tests

Capsule No.	Test Duration, h (yr)	Watts (thermal)		Maximum 316L SS/CsCl Interface Temperature, °C	
		Start of Test	End of Test	Initial ^(a)	Average ^(b)
C-1266	2,208 (0.25)	220	219	455	455
C-1365	4,392 (0.50)	214	211	451	449
C-1451	8,784 (1.00)	261	255	458	458
C-1486	17,544 (2.00)	245	234	453	451
C-1351	28,268 (3.22)	252	234	453	445
C-1272	51,432 (5.87)	273	238	458	449

(a) See Section 5.2.2.

(b) Average temperature for the duration of the test.

FIGURE 5.9. Temperature Profiles for the Capsule Held at Temperature for 2,208 Hours

It is difficult to explain the rather large temperature fluctuations observed in the 2208-h test. No discernible decrease in temperature with time was observed because the test duration is very small compared with the half-life of ^{137}Cs (0.25 yr versus 30.2 yr). During the test the heat generation rate decreased only 0.6%. In addition, the slow decrease in

FIGURE 5.10. Temperature Profiles for the Capsule Held at Temperature for 8,784 Hours

capsule decay energy could not account for random fluctuations in temperature. Each time a thermocouple was placed in a capsule thermowell, sufficient time (20 to 30 min) was allowed for the thermocouple to come to a constant value before the temperature reading was recorded. This ensured that an accurate measure of the temperature was obtained (calibrated thermocouples and instruments were used for all of the temperature measurements).

FIGURE 5.11. Temperature Profiles for the Capsule Held at Temperature for 51,432 Hours

Fluctuations in the hot cell ambient-air temperature and air flow could have accounted for some of the temperature variations. The changes in cell temperature and air flow occur over long periods of time so it is unlikely that they could have caused all of the temperature fluctuations observed. At various times other gamma energy sources were present in the hot cell during

TABLE 5.5. Temperature Data for Capsule C-1266, Tested for 2,208 Hours

Thermocouple No. (a)	Number of Weekly Readings Taken	Average Surface Temperature, (b) °C	
		Outer Capsule	Inner Capsule (c)
TC-1	13	354 ± 5	382 ± 6
TC-2	13	382 ± 8	413 ± 8
TC-3	13	395 ± 7	436 ± 7
TC-4	13	408 ± 4	455 ± 4
TC-5	13	366 ± 3	415 ± 3
TC-6	13	349 ± 5	379 ± 5

(a) See Figure 5.4 for thermocouple locations.

(b) Average surface temperature for the duration of the test.

(c) Inner-capsule temperatures calculated from the measured outer-capsule temperatures.

the tests. These sources could have had a small effect on the capsule temperature over extended periods of time, but could not account for the fluctuations observed in weekly temperature readings.

It is impossible, therefore, to identify a single factor as the probable cause of the temperature variations observed in the test. It appears likely that the fluctuations are the result of several unrelated factors. Although the temperature variations complicated the analysis of the test data, they should have had little effect on the compatibility results obtained.

The temperature fluctuations observed in the 2208-h test were observed in all of the other tests. The temperature variations were observed throughout the duration of each test, and in the longer-duration tests (2 years and longer) the magnitude of the temperature variations appeared to increase slightly with time.

Because of the temperature fluctuations observed, a single temperature measurement was not a reliable measure of the capsule temperature at a given location. The initial maximum interface temperatures given in Table 5.4 are actually the average interface temperatures (calculated from 13 to 14 temperature measurements) for the first 2208 h of testing.

Evaluation of the temperature data for each test capsule showed, in the longer tests at least, a gradual decrease in the capsule temperature as the capsule decay energy decreased. The fluctuations in the measured capsule temperatures made it difficult to determine how much of the temperature change was due to the decrease in decay energy and how much was due to external factors. The capsule decay energy decreases exponentially with time. For the relatively short times used in the compatibility tests (compared to the 30.2 year half-life of ^{137}Cs), the decrease in the decay energy can be assumed to be linear with time. Therefore, linear-regression analysis was used to calculate the decrease in capsule surface temperature with time and the average surface temperature for each test period. The average maximum interface temperatures shown in Table 5.4 were determined using linear regression, as were the average capsule temperature profiles shown in Figures 5.9 to 5.11.

5.2.3 Corrosion in the Thermally Aged Capsules

Samples taken from the inner capsules were subjected to metallographic examination to determine the extent of the corrosion of the 316L SS by the CsCl. Residual wall thickness measurements, obtained from macrophotographs of the metal samples or micrometer measurements, showed that extensive corrosion of the 316L SS had not occurred in any of the test capsules. Therefore, the photomicrographs of the as-polished and etched test samples were used to estimate the metal corrosion. The results obtained with the six test capsules are presented in Table 5.6. The average metal/CsCl interface temperature for each sample is also given in the table. For the reasons discussed in the previous section, the average interface temperature at a given sample location varied over a substantial range from capsule to capsule.

Results obtained in the shorter tests (up to 3.2 years) indicated that corrosion of the 316L SS in the hotter parts of the capsules was proceeding at a relatively rapid rate. When the capsule from the 6-year test was examined, the metal corrosion was found to be far less than one would have predicted from the shorter tests. In addition, the type of corrosion

TABLE 5.6. Estimates of Metal Attack in the Thermally Aged WESF CsCl Capsules(a)

Capsule No.	Exposure, h	Ring No. 1(b)		Ring No. 2		Ring No. 3		Ring No. 4	
		Avg. Temp., °C	Attack, μm (mils)	Avg. Temp., °C	Attack, μm (mils)	Avg. Temp., °C	Attack, μm (mils)	Avg. Temp., °C	Attack, μm (mils)
C-1266	2,208	423	60 (2.4)	455	30 (1.2)	425	30 (1.2)	384	35 (1.4)
C-1365	4,392	430	110 (4.3)	449	80 (3.2)	400	85 (3.4)	350	50 (2.0)
C-1451	8,784	438	30 (1.2)	458	30 (1.2)	417	40 (1.6)	357	20 (0.8)
C-1486	17,544	431	200 (7.9)	451	260 (10)	428	160 (6.3)	386	40 (1.6)
C-1351	28,268	432	430 (17)	445	460 (18)	422	360 (14)	386	35 (1.4)
C-1272	51,432	436	60 (2.4)	449	30 (1.2)	422	140 (5.5)	380	40 (1.6)

(a) Attack estimated from photomicrographs; see discussion in text.

(b) See Figure 5.6 for ring locations on capsule.

(c) The average 316L SS/CsCl interface temperature for the duration of the test.

appeared to be different in the 6-year capsule from the corrosion found in the 2-year and 3-year capsules. Figure 5.12 shows photomicrographs of the four ring samples taken from capsules tested for 3 years and 6 years, respectively. Figures 5.13 and 5.14 show ring #2 and ring #3 samples taken from each of the six test capsules. Corrosion in the capsules tested for 2 years and 3 years appears to consist principally of grain boundary attack and subsurface void formation. In the other test capsules, the corrosion appears to involve a general surface dissolution with some pitting and grain boundary attack.

In Figure 5.15, corrosion found in the samples taken from ring #2 (maximum 316L SS/CsCl interface temperature) is plotted as a function of exposure time. Figures 5.16 and 5.17 show similar plots for the ring #1 and ring #3 samples. For each set of ring samples, the corrosion appeared to be proceeding at a linear rate for times up to 28,268 h (despite the fact that the average exposure temperature for samples taken from a given ring location varied by up to 28°C). Only the samples taken from the capsules tested for 8784 h (1 year) and 51,432 h (6 years) deviated from the linear corrosion rate. In every case, the samples from the two capsules exhibited far less corrosion than would be expected if the corrosion did proceed at a linear rate.

It is difficult to explain why the corrosion found in the capsules tested for 1 year and 6 years was so much less than one would have expected from the other test results. It is not uncommon in compatibility testing to observe significant variations in attack in similar tests, but the differences encountered in the current tests are much greater than the variations usually encountered. Possible explanations for the difference include the following:

- Corrosion of the SS is due primarily to certain impurities in the CsCl (see Appendix). Each test capsule was filled from a different batch of CsCl. As a result the impurities in the CsCl could have varied significantly from capsule to capsule. If a test capsule contained large amounts of the critical impurities, the corrosion of the 316L SS would have been much greater than that found in a test capsule which contained far less of the critical impurities.

Ring No. 1

Ring No. 2

Ring No. 3

Ring No. 4

51,432 h

FIGURE 5.12. Metal Corrosion in the WESF CsCl Capsules Tested for 3 Years and 6 Years

FIGURE 5.13. Photomicrographs of Samples Taken from the Test Capsules at the Point of the Maximum Metal/CsCl Interface Temperature (ring #2)

FIGURE 5.14. Micrographs of the Ring #3 Samples Taken from the Test Capsules

FIGURE 5.15. Corrosion of the Ring #2 Samples as a Function of Exposure Time

- The presence of certain impurities in the CsCl can result in the formation of low melting phases (see Appendix). The formation of a liquid phase in a test capsule could adversely affect capsule corrosion in two ways:
 - 1) The presence of a liquid phase could facilitate the diffusion of impurities from the bulk of the CsCl to the metal/CsCl interface. The amount of liquid phase present would depend on the temperature and impurity content of the CsCl, but even a very small amount of liquid phase could greatly increase the diffusion of impurities to the metal/CsCl interface.
 - 2) The presence of a liquid phase at the metal/CsCl interface could increase the corrosion rate because a liquid-solid reaction generally proceeds at a faster rate than a solid-solid reaction.

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FIGURE 5.16. Corrosion of the Ring #1 Samples as a Function of Exposure Time

- When pure molten CsCl is poured into a 316L SS capsule and allowed to solidify, the resulting solid mass of CsCl does not adhere to the capsule wall. Because of the contraction of the CsCl during solidification and cooling, the solid CsCl is easily removed as a single piece simply by inverting the capsule. When the CsCl contains impurities, however, the mixture adheres to the walls of the capsule as the molten CsCl solidifies and cools, making it impossible to remove the solid CsCl from the capsule in a single piece. As the CsCl mixture cools and contracts, void spaces are formed in the bulk of the CsCl and between the CsCl and the capsule wall. As a result it is possible that there are significant areas in the capsule where there is no direct contact between the capsule wall and the CsCl. Corrosion in those area where there is no contact with the CsCl should be much less than in those areas where contact does exist. The internal surface of the WESF inner capsule exposed to the CsCl (excluding end caps) is about 730 cm². Each metallographic sample taken from the inner capsule has an exposed surface area of ~2 cm². The total surface area of the four

FIGURE 5.17. Corrosion of the Ring #3 Samples as a Function of Exposure Time

samples taken from each capsule represented slightly more than 1% of the metal surface exposed to the CsCl. Therefore, the possibility exists that the samples taken from the 1-year and 6-year capsules were taken from areas where there was no direct contact with CsCl. More extensive examination of the two capsules may have shown metal corrosion similar to that found in the other test capsules.

By looking at Figure 5.12, it is obvious the sample taken from ring #3 of the capsule tested for 6 years exhibited much greater corrosion than the ring #1 and ring #2 samples from the capsule, even though its average exposure temperature was somewhat lower than those of the other two samples. This lends some credence to the possibility that metal/CsCl contact plays a part in the capsule corrosion.

Regardless of the reason(s) for the lower corrosion in the 1-year and 6-year capsules, safety considerations dictate that one accept the corrosion data for the other test capsules as the normal corrosion expected for WESF CsCl capsules held at an initial metal/CsCl interface temperature of ~450°C.

In all of the test capsules, corrosion of the samples taken from ring #4 was relatively slight. Overall, corrosion of the ring #4 samples was about twice as great as the corrosion found in the two zero-time capsules. There are two possible explanations for the reduced corrosion of the ring #4 samples:

- Ring #4 was taken from an area near the top of the inner capsule. The temperature was much lower at this point than the temperatures at the other locations where the rings were taken.
- The inner capsule is never completely filled to the top with solid CsCl. It is possible that the top of the CsCl in some or all of the test capsules was below the location where ring #4 was removed. If the top of the CsCl in a capsule was below the sample area, it is still possible that some CsCl may have adhered to the metal surface in the sample area as the Cl solidified and contracted after the capsule was filled. The CsCl adhering to the surface could cause some slight corrosion.

From the data available it is impossible to determine if there was contact between the 316L SS and the bulk of the CsCl in the ring #4 area of each capsule. Discussions with personnel involved in sectioning the inner capsules failed to resolve the problem. As a result, it is impossible to say with certainty that the reduced corrosion found in the ring #4 samples was due to the lower temperature or a lack of contact with the CsCl.

When the 316L SS inner capsule is held at temperatures above 400°C for extended periods of time, precipitates can form at the grain boundaries (see subsection 5.1.4). The precipitate formation can reduce the corrosion resistance of the alloy. The micrographs presented in Figure 5.18 show how the grain boundary precipitates increased with exposure time in the sample taken from ring #2 of each capsule. The ring #1 and ring #3 samples also exhibited grain boundary precipitates that increased with exposure time. Only the samples taken from ring #4, where the temperature was below 400°C, showed no indication of precipitate formation. Similar results were obtained

FIGURE 5.18. Effect of Exposure Time on the Microstructure of the 316L SS Samples Taken from Ring #2. Each number in parentheses is the average temperature for the duration of the test.

with the metal control samples (see subsection 5.2.4). The formation of precipitates in the grain boundaries could lead to increased grain boundary attacks and subsurface void formation similar to the corrosion found in the capsules tested for 2 and 3 years.

5.2.4 Microstructural Changes in the Metal Control Samples

The 316L SS control samples, prepared from the reject WESF inner capsule, were held in Ar at 400, 450, or 500°C for periods up to 51,432 h (5.9 years). The samples were then subjected to metallographic examination to determine if the thermal aging had produced microstructural changes which could affect the resistance to corrosion.

Figure 5.19 shows photomicrographs of the control samples which had been aged for 51,432 h. The micrographs show the marked increase in precipitate formation with increasing temperature. Figures 5.20 to 5.22 show the effects of aging time at a specific temperature on the grain boundary precipitation. The micrographs indicate that precipitate formation should not be a major problem at 400°C. At 500°C extensive grain boundary precipitation occurred, which would undoubtedly affect the corrosion resistance of the 316L SS. Some precipitate formation did occur at 450°C and appeared to be increasing with time. The extent of precipitate formation appeared to be sufficient to affect the corrosion resistance of the alloy, and is added incentive to decrease the maximum 316L SS/CsCl interface temperature in a repository below the planned 450°C. Limiting the maximum interface temperature to 400°C or less should eliminate the problem of precipitate formation.

5.2.5 Corrosion Mechanisms

Thermodynamic calculations indicate that pure CsCl should not react with 316L SS at the temperature regime proposed for the geologic repository (see Section A.4). The thermodynamic calculations do show, however, that certain impurities, which may be present in the WESF-produced CsCl, could react with the 316L SS at repository temperatures. Possible impurities in the CsCl that could react with the metal include the less stable chlorides, such as FeCl_2 , NiCl_2 , and CdCl_2 , and the less stable oxides such as Fe_3O_4 , NiO , and H_2O .

400°C

40 μ m

500X

450°C

500°C

FIGURE 5.19. Microstructure of 316L SS Control Samples Aged for 51,432 Hours

FIGURE 5.20. Effects of Aging Time at 400°C on the Microstructure of 316L SS

FIGURE 5.21. Effects of Aging Time at 450°C on the Microstructure of 316L SS

FIGURE 5.22. Effects of Aging Time at 500°C on the Microstructure of 316L SS

If impurities in the WESF CsCl are the principal cause of the metal corrosion, the extent of the metal attack should be limited by the amount of impurities available to react with the components of the 316L SS. As a result, the corrosion rate should be high initially and decrease with time as the impurities are consumed. Because the 316L SS/WESF CsCl system contains a large number of components, the corrosion of the SS probably involves a number of reactions. The rate-controlling step for each reaction is likely to be diffusion of the impurity reactant from the bulk of the CsCl to the metal/CsCl interface. The presence of impurities in the CsCl can result in the formation of low melting phases. If a liquid phase is present in the capsule, it can accelerate the diffusion of the impurities from the bulk of the CsCl to the interface and increase the corrosion rate.

When the 316L SS is held at temperatures above $\sim 400^{\circ}\text{C}$ for extended periods of time, particles of Cr-containing carbides precipitate at grain boundaries. Photomicrographs of samples taken from the six test capsules show how the grain boundary precipitates increased with exposure time (see Figure 5.19). The presence of the carbide precipitates reduces the resistance of the 316L SS to corrosion at the grain boundaries.

In an attempt to identify the corrosion reaction(s), samples from the capsule that was tested for 3 years were analyzed by scanning electron microscopy (SEM). It was necessary to partially decontaminate the samples so they could be analyzed. This resulted in the removal of the reaction product layer at the metal surface.

Micrographs of the 3-year test samples subjected to SEM are shown in Figure 5.12. The micrographs show that the metal attack in the capsule consisted principally of grain boundary corrosion and subsurface void formation. Unfortunately the results obtained from the SEM studies were not adequate for identifying specific reaction mechanisms. The best that could be accomplished was to identify some apparent trends. The results show the metal reaction zone was depleted of Mn indicating a leaching of Mn from the metal into the reaction layer. The Ni, Mo, and Si concentrations were also decreased slightly in the reaction zone indicating possible leaching. The subsurface voids contained particulates that were probably reaction products

or unreacted carbide precipitates. The particulates contained high concentrations of Cr, Mo, and Ni, but no Mn. The only reaction that can be identified with any degree of certainty is the leaching of Mn from the 316L SS in the reaction zone into the reaction layer.

5.3 ESTIMATES OF LONG-TERM CORROSION

The safe disposal of the WESF CsCl capsules in a geologic repository requires containment of the CsCl until the ^{137}Cs decays to an innocuous level. Corrosion of the capsule material by the CsCl at the temperature regime encountered in a repository could threaten the integrity of the capsule and the safe containment of the ^{137}Cs . By making some conservative assumptions, the short-term compatibility data obtained in this study can be used to estimate long-term corrosion of the 316L SS inner capsule by the CsCl under the proposed repository conditions.

Referring to Figure 5.15, the corrosion data for ring #2 samples as a function of time indicate that the corrosion rate is linear, if one ignores the data for the 1-year and 6-year tests. Similarly, the corrosion rates for the ring #1 and ring #3 samples appear to be linear if the data for the 1-year and 6-year tests are ignored (Figures 5.16 and 5.17). Conservative estimates of long-term capsule corrosion can be made using the corrosion data available if the corrosion rates are assumed to be linear.

If one assumes that the corrosion rate at a specific ring location is linear, the rate equation takes the form

$$y = k_1 t + k_2$$

where y = the corrosion in μm

t = the exposure time in years

k_1 = the rate constant

k_2 = a constant

Using linear-regression analysis and deleting the corrosion data for the capsules tested 1 year and 6 years, the rate equations for corrosion at the various sample locations were determined to be:

$$\text{Ring \#1: } y = 116t + 26$$

$$\text{Ring \#2: } y = 137t + 7$$

$$\text{Ring \#3: } y = 99t + 13$$

Long-term corrosion of the 316L SS by the WESF CsCl, as predicted by the three linear-rate equations, is shown in Figure 5.23. The estimate for ring #2 shows that (at the 90% level of certainty) corrosion through the inner-capsule wall would be achieved in 15 to 21 years depending on the capsule wall thickness,^(a) if the maximum 316L SS/CsCl interface temperature in the capsule is 450°C.

It must be re-emphasized that the use of the linear-rate equations to predict long-term corrosion represents a conservative approach for three reasons:

- The rate equations were determined from selected data points which showed the maximum corrosion.
- The capsule metal/CsCl interface temperature will decrease as the capsule decay energy decreases. The heat generation in the capsule would be cut in half every 30 years and the interface temperature decreased accordingly.
- Corrosion of the 316L SS appears to be due primarily to certain impurities in the CsCl. The critical impurities are consumed as the corrosion reactions proceed. Therefore, the corrosion rate should decrease with time as the concentration of reactants decreases.

Based on the above reasons, long-term corrosion in the WESF CsCl capsule, assuming an initial maximum 316L SS/CsCl interface temperature of 450°C, would be less than the corrosion predicted in Figure 5.23. From the data available, however, it is impossible to predict how much less the corrosion would be.

(a) During the WESF operation the nominal wall thickness specification for the 316L SS tubing used in fabricating the inner capsules was changed three times: from 0.095 ± 0.009 in. to 0.103 ± 0.001 in. to 0.136 ± 0.012 in. Most of the capsules were fabricated using the thickest tubing.

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FIGURE 5.23. Estimates of Long-Term Corrosion in the WESF CsCl Inner Capsule

The corrosion found in the short-term compatibility tests was sufficiently rapid to raise serious questions regarding the long-term integrity of the WESF CsCl inner capsule if the initial 316L SS/CsCl interface temperature is above 400°C. How serious the problem would be depends on the structural and containment requirements placed on the WESF capsule by the repository disposal criteria.

Safety requirements for disposal of the WESF CsCl capsules in a geologic repository are not currently available. Therefore, it is impossible at the present time to determine if the long-term corrosion predicted from the experimental data would preclude storage of the CsCl capsules in a repository at an initial metal/CsCl interface temperature of 450°C.

If repository safety requirements defined at some future date show that the long-term corrosion predicted for an interface temperature of 450°C is not acceptable, several options for capsule disposal are available.

1. Additional compatibility studies could be carried out to refine the corrosion data for a 450°C interface temperature. This would provide more reliable estimates of long-term corrosion to determine if the capsules could be stored at a 450°C interface temperature. An extensive experimental program, similar to the one described in Section A.8, would be required. The testing would be carried out at 450°C and at at least one lower temperature (i.e., 350°C).
2. The initial 316L SS/CsCl interface temperature for repository storage of the capsules could be reduced significantly below 450°C. The limited data available from various sources show that corrosion of the 316L SS by WESF CsCl is temperature dependent, as would be expected. For example,
 - Two WESF CsCl capsules were destructively examined after 5 years of service in the Sandia Irradiator for Dried Sewage Solids (SIDSS) (Sasmor et al. 1988). During the 5 years of service, the 316L SS/CsCl interface temperature was calculated to be between 140 and 200°C. Metallographic examination of the two capsules showed that corrosion in the capsules was very low. The maximum attack observed was only about 25 μm (0.001 in.), the same level of attack that was found to occur during the capsule filling operation (see Section 5.2.1). The authors concluded, therefore, that no incremental metal loss had occurred in the capsules during the 5 years of use in the SIDSS.

- In a separate study, a single WESF CsCl capsule was taken from the SIDSS after ~2.4 years of service and destructively examined (Kenna and Schultz 1983). The capsule temperature regime during service was not reported but should have been similar to that of the two capsules discussed previously. Metallographic examination of the capsule indicated that the corrosion was no greater than 75 μm (0.003 in.).
- Twenty WESF CsCl capsules taken from the water storage pool were destructively examined to measure the corrosion that had occurred during storage (see Section A.6). The storage time of the capsules examined varied from 0.4 to 8.9 years, and the metal/CsCl interface temperature during storage was estimated to be about 80°C. Although the corrosion observed varied significantly between capsules, at least half of the capsules examined, including some that had been stored for at least 8 years, exhibited no more attack than that which occurred during capsule loading (Section 5.2.1). There appeared to be no correlation between capsule corrosion and the storage time in the water pool.

Lowering the initial 316L SS/CsCl interface temperature of the capsules in the repository should, therefore, reduce the corrosion rate significantly. An extensive experimental program, similar to that required for option 1, would be required to evaluate 316L SS/WESF CsCl compatibility at the lower interface temperature. The compatibility tests would have to be carried out at at least two temperatures (i.e., 350°C and 250°C).

3. The existing WESF CsCl capsule could be provided with an overpack, which would permit capsule storage in the repository at an initial interface temperature of 450°C, even if the long-term corrosion is as high as predicted from the existing data.
4. The WESF CsCl could be repackaged in a new capsule design, which would permit repository storage at a 450°C interface temperature.
5. Storage of the existing WESF CsCl capsules in the water pool could be continued until the heat output of the capsules dropped to a low level. If the capsules were then placed in a repository, the metal/CsCl interface temperature would be low enough that corrosion should not be a problem.

Two problems would be encountered in any additional compatibility studies using the existing WESF CsCl capsules:

1. The original wall thickness of the existing inner capsules is not known with acceptable accuracy. This would make it very difficult to accurately measure capsule corrosion as a function of exposure temperature and time.

2. The chemical composition of the CsCl in the existing WESF capsules is not known. This would make it very difficult to correlate capsule corrosion with variations in the impurity content of the CsCl.

Therefore, the reliability of any compatibility data obtained using the existing WESF CsCl capsules may be questionable. There are two ways in which these problems could be overcome:

1. Existing capsules selected for testing could be opened. The CsCl from each capsule would be sampled for chemical analyses and then repackaged in a new inner capsule whose initial wall thickness had been accurately determined.
2. If the WESF CsCl operation is restarted to process future wastes, newly produced capsules could be used in the compatibility studies. The initial wall thickness of each inner capsule used in the test capsules could be accurately determined and the CsCl in each test capsule could be sampled for analyses prior to testing.

Unless the objections to using existing WESF capsules in future compatibility studies are overcome, it is doubtful if reliable estimates of long-term corrosion at 450°C (or lower temperatures) could be made from the corrosion data obtained in the tests.

6.0 REFERENCES

Bryan, G. H. 1984. Cesium Chloride Compatibility Testing Program Annual Report--Fiscal Year 1983. PNL-4847, Pacific Northwest Laboratory, Richland, Washington.

Bryan, G. H., and J. R. Devine. 1985. Cesium Chloride Compatibility Testing Program Annual Report--Fiscal Year 1984. PNL-5341, Pacific Northwest Laboratory, Richland, Washington.

Bryan, G. H. 1986. Cesium Chloride Compatibility Testing Program Annual Report--Fiscal Year 1985. PNL-5730, Pacific Northwest Laboratory, Richland, Washington.

Bryan, G. H. 1987. Cesium Chloride Compatibility Testing Program Annual Report for Fiscal Year 1986. PNL-6170, Pacific Northwest Laboratory, Richland, Washington.

Fullam, H. T. 1972. Compatibility of Cesium Chloride and Strontium Fluoride with Containment Materials. BNWL-1673, Pacific Northwest Laboratory, Richland, Washington.

Fullam, H. T. 1982. Cesium Chloride Compatibility Testing Program Annual Report--Fiscal Year 1982. PNL-4556, Pacific Northwest Laboratory, Richland, Washington.

Kenna, B. T., and F. J. Schultz. 1983. Characterization of an Aged WESF Capsule. SAND 83-0928, Sandia National Laboratories, Albuquerque, New Mexico and Livermore, California.

Sasmor, D. J., J. D. Pierce, G. L. Tingey, H. E. Kjarmo, J. Tills, and C. D. McKean. 1988. Characterization of Two WESF Capsules After Five Years Service. SAND 86-2808, Sandia National Laboratories, Albuquerque, New Mexico and Livermore, California.

Tingey, G. L., W. J. Gray, R. J. Shippell, and Y. B. Katayama. 1985. WESF Cesium Capsule Behavior at High Temperature or During Thermal Cycling. PNL-5517, Pacific Northwest Laboratory, Richland, Washington.

Tingey, G. L., E. J. Wheelwright, and J. M. Lytle. 1984. A Report of Safety Issues that Pertain to the Use of Cesium Chloride Capsules in an Irradiator. PNL-5170, Pacific Northwest Laboratory, Richland, Washington.

APPENDIX

APPENDIX

A.1 WESF CsCl OPERATION

At Hanford, fission product Cs has been recovered from the high-level fuel reprocessing waste, purified by ion exchange, converted to CsCl, doubly encased in stainless steel (SS) capsules, and stored in a water basin. Recovery of the Cs from the waste and subsequent purification was carried out in B-Plant. Conversion of the purified Cs to CsCl, encapsulation of the CsCl, and water storage of the CsCl capsules were carried out in the Waste Encapsulation and Storage Facility (WESF).

Several processes were used to recover the Cs from the waste depending on the waste source, while ion exchange was used to purify all the recovered Cs. Figure A.1 shows a simplified flow diagram for recovery of Cs from PUREX alkaline supernatant liquor (PSN) and its purification. The highly alkaline supernatant liquor (PSN) from the PUREX waste tanks was treated for solids removal and sent to B-Plant. In B-Plant the Cs was recovered from the clarified PSN by ion exchange using an organic ion-exchange resin. The resulting Cs solution was concentrated about 25-fold by evaporation. After clarification, the concentrated Cs was purified using two stages of ion exchange. An organic ion-exchange resin was used for the first stage of purification and an inorganic zeolite exchanger was used for the final purification. The purified Cs solution was then shipped to WESF.

The WESF specifications called for a molar ratio of Na + K + Rb to Cs in the purified Cs solution of ≤ 0.15 . Purified Cs solution that exceeded the specification was typically recycled for additional ion-exchange purification. The ^{137}Cs isotopic content of the purified Cs solution shipped to WESF varied from about 20% to 40% depending on the age of the waste processed.

A simplified flow diagram for the Cs operation in WESF is shown in Figure A.2. In the WESF operation the purified solution of cesium carbonate from B-Plant was reacted with hydrochloric acid. The CsCl solution was evaporated to dryness and the resulting CsCl solids were melted. Evaporation of the solution and melting of the CsCl was carried out in a tilt-pour melt-caster.

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FIGURE A.1. Simplified Flowsheet for the Recovery and Purification of Fission Product Cs from PSN in B-Plant

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FIGURE A.2. Simplified Flow Diagram for the Preparation and Encapsulation of CsCl in WESF

The molten CsCl was poured into an inner capsule of 316L SS. Each capsule, which had a nominal inner diameter of 2 in. and an inner length of 19 in., could hold up to approximately 3 kg of CsCl. Melting and casting of the CsCl was a batch operation, and a maximum of seven capsules could be filled from each batch of CsCl. After filling, each capsule was cooled and a sintered metal disk inserted in the top of the capsule. The capsule was then purged with He to saturate the pores of the disk. The top end cap was welded in place. The sealed capsule was subjected to a He leak-check having a sensitivity of $1 \times 10^{-8} \text{ cm}^3/\text{s}$, and a water bubble test to check for gross leaks. The capsule was decontaminated in an electropolisher.

The decontaminated inner capsule was sealed in an outer capsule of 316L SS by welding the top end cap in place. The quality of the outer-capsule weld was determined by an ultrasonic weld inspection.^(a) The thermal output of each sealed capsule was measured in a calorimeter. The curie content of each capsule was calculated from the calorimetry data. After calorimetry, the capsules were transferred to the water-filled storage pool.

Details of the CsCl capsule, giving the nominal capsule dimensions, are shown in Figure A.3 (Kenna and Schultz 1983). During the course of the CsCl operations at WESF, the wall thickness of both the inner and outer capsules was increased twice. Table A.1 shows the variations in capsule dimensions which resulted from the increased wall thickness. A majority of the CsCl capsules prepared at WESF were fabricated using the largest wall thickness for both the inner and outer capsules.

A total of 1,576 CsCl capsules were fabricated at WESF between September 1974 and October 1983. The capsules contained a total of approximately 77×10^6 Ci of ^{137}Cs at the time of loading. Individual capsules contained from approximately 2 to 80,000 Ci of ^{137}Cs with most of the capsules ranging between 40,000 and 60,000 Ci (at the time of filling).

(a) The bottom end caps of both the inner and outer capsules were welded in place prior to loading the capsule. Weld quality was determined by an ultrasonic weld inspection.

FIGURE A.3. Details of a WESF CsCl Capsule

A.2 CHEMICAL COMPOSITION OF WESF-PRODUCED CsCl

Based on thermodynamic considerations (see Section A.4), certain impurities are expected to have a detrimental effect on the compatibility of the WESF CsCl with the 316L SS capsule material. Impurities such as the chlorides of Fe and Cr should accelerate the metal attack even when present in the CsCl in low concentrations. Impurities present in the CsCl can arise from three sources:

- inadequate purification of the Cs feed solution,
- carry-over of the solid aluminosilicate ion exchangers used in purifying the Cs feed solution, and

TABLE A.1. Dimensional Tolerances for the 316L SS Tubing Used for the WESF CsCl Inner and Outer Capsules (Tingey, Wheelwright, and Lytle 1984)

<u>Inner Capsule, in.</u>	<u>Capsule Type</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Outer diameter	2.250 ± 0.005	2.250 ± 0.005	2.255 ± 0.010
Wall	0.095 ± 0.009	0.103 ± 0.009	0.136 ± 0.012
Length	19.725	19.725	19.725
Cap thickness	0.400	0.400	0.400
<u>Outer Capsule, in.</u>			
Inner diameter	2.407 ± 0.008	2.407 ± 0.008	2.385 ± 0.015
Wall	0.109 ± 0.009	0.119 ± 0.009	0.136 ± 0.012
Length	20.775	20.775	20.775
Cap thickness	0.400	0.400	0.400

- corrosion of the WESF equipment used to prepare the CsCl and fill the storage capsules.

Unfortunately, the CsCl produced at WESF was not routinely analyzed for impurities prior to encapsulation. The Cs feed solution entering WESF was analyzed on a periodic basis for a number of elements, but the data obtained were inadequate to permit reliable estimates of the impurities contained in the CsCl produced. Table A.2 shows typical results obtained from the analyses of several batches of Cs feed solution.

The WESF specification for the purified Cs feed solution required that the molar ratio of Na + K + Rb to Cs be ≤ 0.15 .^(a) If one assumes that the Na, K, and Rb are present in equimolar concentrations in the feed solution, the maximum concentrations of NaCl, KCl, and RbCl in the CsCl would be about 1.6 wt%, 2.0 wt%, and 3.3 wt%, respectively. If K was the only alkali metal impurity in the feed solution, the CsCl could contain up to about 6.2 wt% KCl. Referring to Table A.2, it can be seen that the analytical data indicate that the alkali metal impurity content of the feed solution is well below the specification limit.

(a) Does not include any Na contained in the solid ion-exchanger carry-over.

TABLE A.2. Analysis of the Cs Feed Solution Entering WESF(a)
(Tingey, Wheelwright, and Lytle 1984)

<u>Element</u>	<u>wt%</u>	<u>Element</u>	<u>wt%</u>	<u>Element</u>	<u>wt%</u>
Al	1.7	Fe	0.38	Pb	1.4
Ba	0.94	K	0.79	Rb	0.52
Ca	1.0	Mg	0.25	Si	7.0
Cr	0.27	Na	0.70	Sr	0.18
Cs	54.2	Ni	0.33		

(a) The carbonate solution containing the purified Cs was reacted with nitric acid, diluted, and analyzed by inductively coupled plasma atomic emission spectroscopy (ICP). The results shown are averages of several analyses normalized to the chloride form.

Several attempts have been made at different times to analyze the WESF-produced CsCl for impurities with varying degrees of success. The problem is complicated by the extreme radioactivity of the ^{137}Cs , which requires massive dilution of the analytical samples prior to examination. The results obtained from the various studies are sufficient, however, to show what impurities are likely to be present in the CsCl and their probable concentration ranges.

As part of the current Cesium Chloride Compatibility Testing Program, a single sample of CsCl, taken from the batch of molten CsCl used to fill one of the zero-time test capsules, was analyzed for impurities at Rockwell Hanford Operations (RHO). A small amount of the sample was dissolved in reagent grade nitric acid. A small aliquot of the resulting solution was diluted with ultrahigh-purity nitric acid, and samples of the diluted solution were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP). A "blank" solution prepared in a similar manner was also analyzed by ICP. The total Cs in the solution was determined chemically, and the ^{137}Cs content radiochemically. Estimates of the impurity content of the WESF CsCl based on the ICP results are given in column 1 of Table A.3. The ICP data

TABLE A.3. Estimates of Impurity Levels in WESF-Produced CsCl

Element	This Work, wt%(a)	Kenna and Schultz 1983, wt%(b)	Sasmor et al. 1988, wt% range(c)
Al	0.14	0.3	ND - 0.1
B	0.14	0.4	ND - 0.04
Ba	0.55(d)	ND	3.1 - 6.5
Ca	ND(e)	0.05	0.01 - 0.19
Cd	0.02	ND	--
Ce	ND	--	ND - 0.01
Co	0.10	0.02	--
Cr	1.4	0.1	0.02 - 0.5
Cu	ND	0.2	--
Fe	(f)	0.5	0.04 - 1.6
K	0.68	0.1	ND - 0.7
La	ND	ND	ND - 0.01
Mg	ND	ND	ND - 0.05
Mn	ND	0.05	ND - 0.09
Mo	ND	ND	ND - 0.26
Na	2.8	0.2	0.04 - 1.5
Ni	0.1	0.1	ND - 1.5
P	ND	0.1	--
Pb	0.14	ND	--
Pd	ND	0.02	--
Rb	ND	0.02	--
S	--	5	--
Si	0.21	5	ND - 0.2
Sr	0.02	0.001	ND - 0.005
Ti	0.07	ND	ND - 0.004
Zr	0.07	0.08	--

(a) Analyzed by ICP.

(b) CsCl solution analyzed by spark source mass spectrometer. Precision estimated as +100% - 50%.

(c) Range of values for 7 different samples.

(d) At time of analysis, will increase as the ^{137}Cs decays.

(e) Analyzed elements that were not detectable.

(f) Very high and nonreproducible--indicating probable contamination of CsCl solution.

showed the Fe content of the CsCl to be very high and nonreproducible, indicating probable contamination of the solution. The ^{137}Cs isotopic content of the CsCl was determined to be 25%.

Several years ago the Sandia National Laboratories (SNL) carried out the destructive examination of a WESF CsCl capsule that had been in use in the Sandia Irradiator for Dried Sewage Solids (SIDSS) Program (Kenna and Schultz 1983). The CsCl capsule had been prepared at WESF in September 1975 and stored in the WESF pool until August 1978 when it was shipped to SNL. The capsule was stored in the SNL water pool until placed in the SIDSS facility in May 1979. In August 1981 the capsule was removed from SIDSS and shipped to Oak Ridge National Laboratory (ORNL) for destructive examination. At ORNL the capsule was sectioned using a metal cutting saw. The CsCl taken from the sectioned capsule was analyzed for impurities using spark source mass spectrometry. The results obtained are shown in column 2 of Table A.3. Because the capsule was sectioned with a metal cutting saw, the possibility exists that the CsCl sample was contaminated with metal particles that could have affected the results obtained. The Cs content of the CsCl was approximately 53 wt% and the ^{137}Cs isotopic content was about 32% at the time of analysis.

In April 1984 two additional WESF CsCl capsules were removed from the SIDSS facility and subjected to destructive examination (Sasmor et al. 1988). The capsules had been fabricated in September 1975 and had been in SIDSS service for 5 years. Samples of CsCl from the sectioned capsules were analyzed for impurities using ICP. In addition, CsCl samples from five other WESF capsules, which had been opened to supply ^{137}Cs to fabricate waste glass for canister studies, were also analyzed for impurities using ICP.

Samples were prepared for analysis by dissolving the CsCl samples from the sectioned capsules in dilute nitric acid. A small fraction of each sample was insoluble in the acid solution. The insoluble fraction was determined to be a mixture of SS fines from the sectioning of the capsules, and aluminosilicate ion-exchanger particles. An aliquot from each soluble fraction was diluted ~1 to 1000 and then analyzed by ICP. Because of the dilution factor, the detection limit for most of the cation impurities was approximately 0.05 wt% (on CsCl bases). The results obtained are given in

column 3 of Table A.3. The values shown represent the range of concentrations observed for each element in the seven samples examined.

Analyses of the various CsCl samples examined were limited to the determination of cation impurities. Most of the impurities in the CsCl are expected to be present as chlorides. A small fraction of the impurities may be present as oxides or oxychlorides as a result of hydrolysis of the less stable metal chlorides when the CsCl solution is evaporated to dryness and the resulting solids melted for casting into the capsules. The CsCl after melting and solidification can also contain a significant amount of water. Analyses of nonradioactive CsCl samples prepared according to the WESF flowsheet, and having a cation composition similar to that shown in column 1 in Table A.3, had an oxygen content of approximately 0.5 wt% as determined by spark source mass spectrometer. It is estimated that at least half of the oxygen was present as water.

The possibility exists that some of the cation impurities in the CsCl may be present in metallic form. When the radioactive Cs decays to stable Ba there is a chemical imbalance with regard to Cl.

Barium monochloride is reported to exist but only at high temperatures; it should not be stable at temperatures encountered in the WESF capsule. If formed, the barium monochloride could disproportionate to BaCl_2 and elemental Ba.

Any elemental Ba so formed would be very reactive and could reduce less stable chlorides (and oxides if present) to elemental form.

Such reactions, if they occur, could have a beneficial effect on the compatibility of the WESF CsCl with the capsule because they reduce the amount of impurity chlorides available to react with the SS.

Cs isotopic analyses were performed on several batches of WESF CsCl feed solution prior to the evaporation, melting, and casting steps (Tingey, Wheelwright, and Lytle 1984). At WESF every CsCl capsule produced is subjected to calorimetry and its net weight of contained salt determined. Using this data, Tingey, Wheelwright, and Lytle studied eight different CsCl capsules, whose Cs isotopic composition was known, and estimated that the total impurity content of the capsules varied from 18 wt% to 31 wt% (see Table A.4). These calculations indicate the possibility of a much higher impurity content in the WESF CsCl than the data in Table A.2 show, but provide no information on the types of impurities present.

Referring to Table A.3 it can be seen that the concentrations of most impurities varied over a considerable range in the CsCl samples analyzed. This is not surprising considering the variable composition of the Cs feed solution to WESF, potential carryover of ion exchanger, and corrosion of

TABLE A.4. Calculated Impurity Content in Eight WESF CsCl Capsules (Tingey, Wheelwright, and Lytle 1984)

CsCl Batch No.	Capsule No.	<u>Batch Isotopic Content</u>			Capsule Calorimetry, w	Capsule Contents, g	Calculated Impurity Contents, wt%
		¹³³ Cs, wt%	¹³⁵ Cs, wt%	¹³⁷ Cs, wt%			
83-1	C1511	53.2	13.67	33.13	230.9	2639	21
83-1	C1512	53.2	13.67	33.13	219.1	2651	25
82-6	C1411	53.37	13.82	32.79	138.5	1650	23
82-6	C1414	53.37	13.82	32.79	224.0	2686	24
81-57	C1216	52.45	14.15	33.40	229.3	2983	31
81-57	C1226	52.45	14.15	33.40	235.4	2980	29
79-9	C540	53.63	12.68	33.69	235.0	2558	18
79-9	C530	53.63	12.68	33.69	260.7	2948	21

WESF process equipment. Possible contamination of some CsCl samples with metal particles from the sectioned capsules could also account for some of the variations observed.

Impurities in the CsCl can have a marked effect on the compatibility of the CsCl with the 316L SS WESF capsule. Because the analytical data indicate that the critical impurities can vary over a wide range from capsule to capsule, corrosion of the WESF CsCl capsules by the CsCl for a given set of storage conditions could vary widely depending on the impurity content of each capsule.

A.3 PHYSICAL PROPERTIES OF WESF-PRODUCED CsCl (Fullam 1982)

When heated, pure CsCl undergoes a phase transition from a low-temperature body-centered cubic structure to a high-temperature face-centered cubic (NaCl) structure at approximately 475°C. The volumetric expansion due to the phase transition is 16 to 17%. Pure CsCl melts at 645°C.

Thermal expansion of pure CsCl up to the solid-solid phase transition is almost linear with temperature. Between 25°C and 300°C, the average value for the linear thermal expansion coefficient (α) is $55.5 \times 10^{-6}/^{\circ}\text{C}$ (Fullam 1971). The corresponding volumetric thermal expansion coefficient (α_v) is $1.70 \times 10^{-4}/^{\circ}\text{C}$. For the high-temperature CsCl structure, the average value for α between 500°C and 540°C is $42.5 \times 10^{-6}/^{\circ}\text{C}$, and the corresponding value for α_v is $1.28 \times 10^{-4}/^{\circ}\text{C}$.

The addition of metal chloride impurities to the CsCl results in the formation of low melting phases and may affect the solid-solid phase transition. Previous work has shown that the addition of KCl to the CsCl can reduce the temperature at which a solid-solid phase transition begins to as low as 315°C (Fullam 1971). The rate at which the phase transition occurs on heating is also decreased. More important, however, is the fact that the rate of the phase transition on cooling is decreased markedly so that with cooling rates of 0.5°C/min or greater very little reversion occurs on cooling a CsCl-KCl sample. It is necessary to anneal the sample at 250 to 300°C for 4 h or longer to ensure complete reversion to the low-temperature form. X-ray diffraction data obtained at room temperature with unannealed samples

containing 1 to 5 wt% KCl, which had been rapidly cooled, showed a mixture of the low-temperature and high-temperature structures were present.

As part of this program, additional work was carried out to:

- confirm the effects of KCl additions on the CsCl solid-solid phase transition, and
- determine the effects of other chloride impurities, which may be present in WESF-produced CsCl, on the CsCl phase transition and melting point.

Thermal expansion measurements and differential scanning calorimetry (DSC) measurements were made using a DuPont Model 990 thermal analyzer with the Model 943 thermomechanical analyzer and DSC cell. The nonradioactive salt mixtures used in the study were prepared by melting mixtures of anhydrous chlorides in quartz vials and annealing the resolidified mixtures at 250°C overnight. The melting and annealing steps were carried out in an inert atmosphere. The samples were stored in glass jars in a desiccator. In addition to the binary chlorides systems, a simulated WESF CsCl mixture, whose composition is given in Table A.5, was also studied. The CsCl used in the study had a purity of >99.995% and other chlorides were reagent grade.

Thermal expansion studies with the CsCl-KCl system confirm the results previously reported. The data show that the addition of as little as 3 wt% KCl to CsCl lowers the temperature at which a solid-solid phase transition begins below 350°C (see Figure A.4). The addition of the KCl to the CsCl also severely retarded the reversion to the low-temperature structure when

TABLE A.5. Composition of the Simulated WESF CsCl Mixture Used in the Physical Property Measurements

<u>Component</u>	<u>wt%</u>	<u>Component</u>	<u>wt%</u>
CsCl	90.0	FeCl ₃	0.2
NaCl	4.5	CrCl ₃	0.2
KCl	3.0	NiCl ₂	0.2
RbCl	0.5	MnCl ₂	0.2
BaCl ₂	0.5	PbCl ₂	0.2
CaCl ₂	0.5

FIGURE A.4. The Effects of KCl Content on the Phase Transition Temperature of CsCl--Potassium Chloride Mixtures--Determined by Thermal Expansion Measurements

the system was cooled. The simulated WESF CsCl mixture, which contained 3 wt% KCl, exhibited a solid-solid phase transition which started at about 343°C. This compares with a phase transition temperature of about 344°C for a CsCl-3.1 wt% KCl mixture. Figure A.5 shows some of the actual thermal expansion scans obtained with pure CsCl and CsCl-KCl mixtures.

A number of CsCl-impurity chloride systems were investigated. The results obtained are shown in Table A.6. None of the individual impurity chlorides studied, except KCl, had a major effect on the solid-solid phase transition temperature, but all formed low melting phases with the CsCl. No phase transition was detected with the CsCl-FeCl₃ system because the minimum melting point was about 270°C. The simulated WESF CsCl mixture exhibited a minimum melting point of about 452°C.

The CsCl-Cs₂O and CsCl-CsOH systems were also studied briefly. The addition of Cs₂O or CsOH to CsCl appeared to increase the phase transition temperature to about 494°C. The effect of Cs₂O and CsOH additions on the melting point of CsCl was not completely determined, but preliminary data gave no indication of the formation of a low melting phase.

The presence of a liquid phase in the WESF CsCl capsule during geologic storage could adversely affect capsule corrosion in the following ways.

- The presence of a liquid phase at the metal/CsCl interface could increase the corrosion rate because a liquid-solid reaction generally proceeds at a faster rate than a solid-solid reaction.
- The presence of a liquid phase could facilitate diffusion of impurities from the bulk of the CsCl to the metal/CsCl interface.

The amount of liquid phase present would depend on the impurity content of the CsCl and the temperature. Since a temperature gradient would exist over the length of the stored capsule, the amount of liquid phase could vary in different sections of the capsule. In general, the amount of liquid phase in the capsule should be low even where the interface temperature is a maximum (450°C), but even a small amount of liquid phase could facilitate diffusion of impurities to the metal/CsCl interface.

PART NO. 990088

RUN NO. DATE <u>6-12-82</u> OPERATOR <u>HTF</u> SAMPLE ATM <u>Air</u> @ <u>1 atm.</u> FLOW RATE <u>0</u>	T-AXIS SCALE, °C/in <u>50</u> PROG RATE, °C/min <u>20</u> HEAT ☒ COOL ☐ ISO ☐ SHIFT, in <u>0</u>	DTA-DSC SCALE, °C/in (mcal/sec)/in WEIGHT, mg REFERENCE	TGA SCALE, mg/in SUPPRESSION, mg WEIGHT, mg TIME CONST., sec dY, (mg/min)/in	TMA SCALE, mils/in <u>2</u> MODE <u>Expansion</u> SAMPLE SIZE <u>0.146"</u> LOAD, g <u>5</u> dY, (10X), (mils/min)/in <u>2</u>	
--	---	--	--	--	--

- A. Pure CsCl (>99.995%)
 B. CsCl + 0.1 wgt% KCl
 C. CsCl + 1.8 wgt% KCl
 D. CsCl + 3.3 wgt% KCl
 E. CsCl + 5.1 wgt% KCl
 F. CsCl + 11.6 wgt% KCl
 G. CsCl Mixture (see Table 7)

FIGURE A.5. Thermal Expansion Scans for KCl-CsCl Mixtures

TABLE A.6. The Effect of Impurities on the Phase Transition Temperature and Melting Point of CsCl

System ^(a)	Start of the Phase Transition, C°	Minimum Melting Point, C°
CsCl	475	645
CsCl + 5% KCl	330	605
CsCl + 5% NaCl	470	493
CsCl + 5% KCl + 5% NaCl	332	478
CsCl + 5% BaCl ₂	475	557
CsCl + 5% CaCl ₂	468	610
CsCl + 3% FeCl ₃	(b)	270
CsCl + 3% CrCl ₃	475	622
CsCl + 3% PbCl ₂	472	480
CsCl + 3% MnCl ₂	477	489
CsCl + 3% NiCl ₂	479	520
CsCl + 3% Cs ₂ O	494	--
CsCl Mixture ^(c)	343	452

(a) Composition in wt%.

(b) Melting began before the phase transition was detected.

(c) See Table A.5 for composition.

A.4 THERMODYNAMIC ANALYSIS OF THE 316L SS/WESF CsCl SYSTEM (Fullam 1982)

Potential reactions between CsCl and a containment material at elevated temperatures can be predicted from thermodynamic considerations. Calculation of the Gibbs free energy of reaction (ΔG_R) can provide an estimate of the potential for a given reaction to occur, but provides no insight on reaction kinetics. For a thermodynamic analysis of any system to be of real value, however, every possible reaction must be considered. Carrying out a rigorous thermodynamic analysis can be relatively easy for simple systems, but may be very difficult or impossible for complex systems.

For the general reaction

the free-energy change ΔG_R is given by the equation

$$\Delta G_R = \Delta G_R^\circ + RT \ln J_a$$

$$\text{where } J_a = \frac{a_{(X)}^x \cdot a_{(Y)}^y}{a_{(B)}^b \cdot a_{(C)}^c} \quad \text{Equation (A.1)}$$

ΔG_R° = standard free-energy change of the reaction

$a()$ = activity of a given component

T = absolute temperature, K

R = gas constant.

The standard free-energy change (ΔG_R°) is given by the equation

$$\Delta G_R^\circ = x\Delta G_{f(X)}^\circ + y\Delta G_{f(Y)}^\circ - b\Delta G_{f(B)}^\circ - c\Delta G_{f(C)}^\circ \quad \text{Equation (A.2)}$$

where $\Delta G_{f()}^\circ$ = the standard free energy of formation of a given component.

If the value of ΔG_R for Reaction (A.1) for a given set of conditions is negative, the reaction can proceed spontaneously. If the value of ΔG_R is positive, the reaction cannot take place, although it may do so if the system conditions are altered. This can be done by 1) changing the temperature or 2) changing the activities of the system components so as to decrease the value of J_a .

For a simple system containing pure CsCl and a pure metal, such as Fe, the reaction of interest is

For Reaction (A.2), the free-energy change (ΔG_R) is given by the equation

$$\Delta G_R = \Delta G_R^\circ + RT \ln \frac{a_{(Cs)}^2 \cdot a_{(FeCl_2)}}{a_{(CsCl)}^2 \cdot a_{(Fe)}} \quad \text{Equation (A.3)}$$

The standard free-energy change (ΔG_R°) is given by

$$\Delta G_R^\circ = \Delta G_f^\circ(FeCl_2) - 2 \Delta G_f^\circ(CsCl) \quad \text{Equation (A.4)}$$

If the reactants and products are all in their standard states at unit activity, then

$$\Delta G_R = \Delta G_R^\circ = \Delta G_f^\circ(FeCl_2) - 2 \Delta G_f^\circ(CsCl) \quad \text{Equation (A.5)}$$

Table A.7 gives standard free energy of formation data for a number of chlorides at different temperatures. Figure A.6 shows some of the standard free-energy data in graphic form. Using the data from Table A.7, the standard free-energy change for Reaction (A.2) as a function of temperature is as follows:

<u>Temp., K</u>	<u>ΔG_R°, kcal/mol.</u>
298	+ 126
723	+ 118
1000	+ 112

Since ΔG_R° for Reaction (A.2) is positive, Fe will not react with CsCl over the temperature range of interest when the components are in their standard states.

TABLE A.7. Standard Free Energy of Formation Values for Selected Chlorides at Various Temperatures^(a)

<u>Compound</u>	<u>-ΔG_f[°], kcal/g-atom of Cl</u>		
	<u>298K</u>	<u>500K</u>	<u>1000K</u>
AlCl ₃	50	46	43
BaCl ₂	97	93	84
CCl ₄	4	2	-2
CaCl ₂	90	87	78
CdCl ₂	42	38	25
CrCl ₂	42	39	33
CrCl ₃	38	35	25
CsCl	99	94	82
FeCl ₂	36	33	26
FeCl ₃	27	23	21
HCl	23	23	24
KCl	98	93	82
MgCl ₂	71	67	58
MnCl ₂	53	50	43
MoCl ₅	20	17	13
NaCl	92	87	76
NiCl ₂	31	28	20
PCl ₃	21	20	19
PbCl ₂	38	34	26
RbCl	96	92	80
S ₂ Cl ₂	6	--	--
SiCl ₄	37	35	32
SrCl ₂	93	90	82

(a) Glassner 1957, Kellogg 1950, Kubaschewski and Alcock 1979, Lindsay 1979, Rosenqvist 1970, Smithells 1976, Villa 1950.

FIGURE A.6. Standard Free Energy of Formation of Various Chlorides as a Function of Temperature

In order for Reaction (A.2) to proceed spontaneously, ΔG_R must be negative. Therefore, the value of the activity term $RT \ln J_a$ must be less than ΔG_R° . At 450°C (723K),

$$\Delta G_R = +118 + RT \ln J_a \quad \text{Equation (A.6)}$$

For ΔG_R to be negative,

$$RT \ln \frac{a_{(Cs)}^2 \cdot a_{(FeCl_2)}}{a_{(CsCl)}^2 \cdot a_{(Fe)}} < -118 \quad \text{Equation (A.7)}$$

Taking the activities of CsCl and Fe as unity,

$$\begin{aligned} RT \ln a_{(Cs)}^2 \cdot a_{(FeCl_2)} &< -118 \\ \ln a_{(Cs)}^2 \cdot a_{(FeCl_2)} &< -82 \end{aligned} \quad \text{Equation (A.8)}$$

If one further assumes that the activity of Cs is unity,

$$\begin{aligned} \ln a_{(FeCl_2)} &< -82 \\ a_{(FeCl_2)} &< 2.1 \times 10^{-36} \end{aligned} \quad \text{Equation (A.9)}$$

If the $FeCl_2$ forms a solid solution with the CsCl, the activity of the $FeCl_2$ is approximately equal to its mole fraction in the solid solution. Therefore, the mole fraction of $FeCl_2$ in the solid solution must be less than 2.1×10^{-36} for Reaction (A.2) to proceed spontaneously at 450°C.

From a thermodynamic standpoint, the 316L SS CsCl system is an extremely complex one because of the many components it contains. Table A.8 gives the nominal composition of the 316L SS and also shows the cation

TABLE A.8. Components of the 316L SS/CsCl System

316L SS - Nominal Composition

<u>Component</u>	<u>wt%</u>
C	0.03 max.
Cr	17.0-19.0
Fe	Remainder
Mn	2.00 max.
Mo	2.0-3.0
Ni	10.0-14.0
P	0.045 max.
S	0.03 max.
Si	1.0 max.

WESF CsCl - Probable Impurities

<u>Component</u>	<u>Probable Conc. Range, wt%</u>
Al	0-0.3
Ba	(a)
Ca	0-0.2
Cr	0-1.5
Fe	0-2.0
K	0-3.0
Mg	0-0.2
Mn	0-0.2
Na	0-3.0
Ni	0-1.5
Pb	0-0.2
Rb	0-0.2
Si	0-0.5
Sr	0-0.2

(a) Increases as the ^{137}Cs decays.

impurities that may be present in the WESF CsCl. The cation impurities in the CsCl are probably present primarily as metal chlorides, but small quantities of metal oxides may also be present (see Section A.2). The CsCl may also contain small amounts of free water. The system is further complicated by the fact that the components may not be present in their standard states. The components of the SS, for example, may be present as solid solutions, intermetallic compounds, or carbides. The components of the CsCl may be present as solid solutions, complex chlorides, complex oxides, oxychlorides, or hydrates.

A rigorous thermodynamic analysis of the system is extremely difficult, if not impossible, because the system cannot be adequately defined. By making a number of simplifying assumptions, however, an elementary thermodynamic analysis of the system can be made which can help to identify potentially troublesome reactions. These assumptions are

- components of the SS are present in their standard states at unit activity
- cation impurities in the CsCl are present as simple chlorides or oxides at unit activity, and
- each reaction product is at unit activity.

Using these assumptions, one can estimate the potential for a reaction to occur between a component of the CsCl and a constituent of the 316L SS by calculating the standard free energy of reaction, as was done for Reaction (A.2) above.

From Table A.7 it can be seen that CsCl is very stable and it should not react with any of the components of the SS up to at least 1000K, when the components are in their standard states. Other reactions may be possible, however, involving cation impurities and components of the SS. Assuming all reactants and products are in their standard states at unit activity, a metal can react with any chloride which has a standard free energy of formation more positive than that of its own chloride. This means that in Figure A.6 a metal could react with any chloride that appears above its chloride on the diagram. For example, consider the reaction of ferrous chloride in the CsCl with Mn in the SS at 298K.

Reaction (A.3)

$$\Delta G_R^\circ = \Delta G_f^\circ(\text{MnCl}_2) - \Delta G_f^\circ(\text{FeCl}_2)$$

$$\Delta G_{R_{298K}}^\circ = -106 - (-72) = -34 \text{ kcal}$$

Since ΔG_R° at 298K is negative, Reaction (A.3) could proceed spontaneously. Other reactions could occur between the more reactive metal components of the SS (i.e., Cr, Mn) and the less stable chloride impurities in the CsCl (i.e., CdCl_2 , NiCl_2 , FeCl_2).

Barium forms a very stable chloride. If Ba metal is present in the CsCl as a result of the decay of the ^{137}Cs (see Section A.2), it could reduce most of the metal chloride impurities in the CsCl to elemental form. This could have a beneficial effect on the compatibility of the WESF CsCl with the 316L SS in two ways:

- The impurity chlorides would no longer be available to react with components of the SS.
- The impurity chlorides would not be available to react with the CsCl to form low melting phases.

The barium chloride, being very stable, would not react directly with any of the components of the SS.

In the actual WESF system, the system components would not all be in their standard states at unit activity. Consider again Reaction (A.3); the free energy of the reaction is given by the equation

$$\Delta G_R = \Delta G_R^\circ + RT \ln \frac{a(\text{MnCl}_2) \cdot a(\text{Fe})}{a(\text{FeCl}_2) \cdot a(\text{Mn})} \quad \text{Equation (A.10)}$$

The Mn in the SS would not be present in its standard state. It would likely be present in solid solution or as an intermetallic compound. If one assumes the Mn is in a solid solution, its activity can be calculated from its partial molar free energy of solution (mixing) by the equation

$$\Delta \tilde{G}_{\text{Mn}} = RT \ln a_{\text{(Mn)}} \quad \text{Equation (A.11)}$$

The partial molar free energy of solution ($\Delta \tilde{G}$) can be estimated for components of solid metallic solutions by established thermodynamic methods. For Mn in 316L SS, the estimated partial molar free energy of solution at 298K is estimated to be -2 kcal/mol. With the remaining reactant and products in their standard states, ΔG_R at 298K is

$$\begin{aligned} \Delta G_R &= \Delta G_R^\circ + RT \ln \frac{1}{a_{\text{(Mn)}}} && \text{Equation (A.12)} \\ &= \Delta G_R^\circ - RT \ln a_{\text{(Mn)}} \\ &= -106 - (-72) - (-2) \\ &= -32 \text{ kcal} \end{aligned}$$

Thus, the net effect of the Mn being present in the SS in a solid solution is to make Reaction (A.3), as written, slightly less favorable, although the reaction would still proceed spontaneously. Similarly, if the ferrous chloride were present in the CsCl as a component of a solid solution, Reaction (A.3) would be slightly less favorable by the partial molar free energy of solution of the FeCl_2 . Therefore, it is apparent that factors that reduce the activities of the reactants make ΔG_R more positive and reduce the driving force for the reaction, as written, to proceed. Similarly, reducing the activities of the products makes ΔG_R more negative and increases the potential for the reaction to proceed spontaneously.

A thermodynamic analysis of potential reaction between oxide impurities in the WESF CsCl and the SS can be carried out in a similar manner. The analyses show that less stable oxides present in the CsCl (i.e., Fe_3O_4 , NiO , H_2O) could react with the more reactive component of the SS (i.e., Mn, Cr).

It must be re-emphasized that the thermodynamic analysis of the WESF CsCl capsule system provides no insight into reaction kinetics. Even though thermodynamics indicate a reaction can proceed spontaneously, the reaction may or may not proceed at a measurable rate under the conditions encountered in the capsule. The reaction rates can only be determined experimentally.

A.5 WESF CAPSULE HEAT-TRANSFER STUDIES (Fullam 1982)

In the radioactive compatibility tests with WESF CsCl capsules, it was impossible to measure the 316L SS/CsCl interface temperature directly. It was possible, however, to measure the outer-capsule surface temperature. The 316L SS/CsCl interface temperatures were then calculated from outer-capsule surface temperature data. The relationship (ΔT) between the outer-capsule surface temperature and the metal/CsCl interface temperature was determined through heat-transfer calculations and extensive experimental studies using an electrically heated dummy WESF capsule. The data from the heat-transfer studies were also used in designing the insulated containers to ensure the test capsules reached the required aging temperature.

The heat-transfer studies were complicated by the fact that the tests with the electrically heated dummy capsule did not completely reproduce the situation which exists in the WESF capsule. In the actual WESF capsule, ~60% of the ^{137}Cs decay energy is absorbed in the capsule. Of the energy absorbed within the capsule, ~70% is absorbed in the CsCl and the remaining energy is absorbed in the inner and outer capsules in approximately equal amounts. In the electrically heated dummy capsule, all of the energy was generated within the CsCl. Heat-transfer calculations indicate that the ΔT between the inner

and outer capsules is reduced slightly (~5%) if one assumes the energy is distributed between the capsules and the CsCl compared to the case where the energy is absorbed only in the CsCl.

The electrically heated dummy capsule was fabricated from standard WESF inner and outer capsules. The capsule was mounted vertically in an insulated container for the heat-transfer tests. The container was lined with 3 in. of block insulation on the bottom and pipe insulation on the side. The capsule top was covered with loose blanket insulation. By varying the diameter of the canister, the thickness of the pipe insulation could be varied from 0.9 to 3.0 inches. Figures A.7 and A.8 show side and top views of the dummy capsule and its insulated container.

The capsule was heated with a 500-W cartridge heater that was 0.5 in. in diameter by 15 in. long. The heater was placed in the CsCl in the center of the inner capsule. Electrical leads from the heater passed through small holes drilled in the top of the inner and outer capsules. Power to the heater was controlled with a variable transformer. Heater voltage and current were measured with a digital voltmeter and ammeter, respectively.

A small slot was machined the entire length of the outer surface of the inner capsule to serve as a thermowell. The slot was covered with a thin strip of 316L SS welded to the capsule surface. A movable thermocouple inserted in the slot served to measure the inner-capsule temperature along its length.^(a) Small holes in the end caps of the capsules provided free movement of the thermocouple.

Four thermowells, fabricated from SS tubing, were welded lengthwise on the outer-capsule surface 90 degrees apart. A fifth SS thermowell was fastened to the outer capsule using three SS hose clamps. Five movable thermocouples placed in the thermowells were used to measure the outer-capsule surface temperature at various locations along the capsule length. A loose thermocouple was also placed in the space between the outer capsule and the

(a) The capsule temperature measured was assumed to be the same as the 316L SS/CsCl interface temperature.

FIGURE A.7. Side View of the Electrically Heated Dummy Capsule and Insulated Container

FIGURE A.8. Top View of the Electrically Heated Dummy Capsule and Insulated Container

pipe insulation around the capsule. Outputs of the thermocouples were monitored with a multipoint digital thermometer. All the thermocouples and measuring instruments were calibrated prior to use.

In carrying out a test, a constant voltage was applied to the heater and the system was allowed to come to thermal equilibrium. When equilibrium was reached, the inner- and outer-capsule temperatures were measured. By moving the thermocouples up and down the length of the capsules (allowing the thermocouples to stabilize after each movement), temperature profiles for the inner and outer capsules were obtained as a function of power input to the

heater and insulation thickness. In the tests, the power input was varied from 80 to 221 W and the insulation thickness from 0.9 to 3.0 inches. Tests were also carried out with a bare outer capsule.

Figure A.9 shows typical results obtained at a power input of 141 W using a 1.5-in. thickness of pipe insulation. Similarly shaped curves were obtained with other power inputs and thicknesses of insulation. The results obtained showed that a large temperature gradient existed between the middle and ends of the capsules. The maximum temperature of both the inner and outer capsules occurred about 9 in. up from the bottom of the outer capsule, regardless of the power input to the heater and the side insulation thickness.

At each elevation the four thermocouples in the thermowells welded to the outer capsule agreed with each other within 5°C. This was true even if the inner capsule was touching the outer capsule along one side. At a given location, the thermocouple in the thermowell clamped to the outer capsule read 7 to 14°C lower than the average of the four thermocouples in the welded thermowells, depending on the power input and insulation thickness. The loose thermocouple positioned between the outer capsule and the insulation gave the same reading, within $\pm 1^\circ\text{C}$, as the thermocouple in the clamped thermowell at the same elevation.

Sufficient heat-transfer tests were run to determine the ΔT between the inner and outer capsules as a function of elevation, power input, and insulation thickness. Comparison of the experimental data with heat-transfer calculations (based on energy distribution between the CsCl, inner capsule, and outer capsule) showed that the experimental data provided an acceptable measure of the ΔT that would be encountered in the actual WESF capsules during the thermal aging tests. The experimental data were used, therefore, in designing the insulated containers which held the WESF capsules during the test. Because the decay energy of the six CsCl capsules varied from 214 to 273 W at the start of the tests, the thickness of insulation in each insulated container had to be varied accordingly to give the desired maximum interface temperature of 450°C.

FIGURE A.9. Typical Capsule Temperature Profiles Obtained Using the Electrically Heated Dummy Capsule

A.6 DESTRUCTIVE EXAMINATION OF WESF CsCl CAPSULES TAKEN FROM THE STORAGE POOL (Bryan and Divine 1985, Bryan 1986)

The WESF CsCl capsules are stored in a water pool at WESF. Current planning calls for continued storage of the capsules in the WESF pool until the final disposal option is selected. Potential utilization of the WESF CsCl capsule as a radiation source could influence the number of capsules contained in the pool at any one time, but some capsules would always be present.

Compatibility data were needed to confirm that corrosion by the CsCl was not a threat to the continued safe storage of the WESF capsules in the water pool. Attack of the 316L SS by the CsCl in the pool capsules can be divided into two phases:

- The corrosion that occurs during the loading operation when the 316L SS is in contact with molten or hot solid CsCl.
- The corrosion that occurs during storage in the water pool when the metal/CsCl interface temperature is relatively low.

It is necessary to know the extent of corrosion resulting from the loading operation in order to estimate the effect of long-term pool storage on the corrosion.

Examination of the two "zero-time" capsules provided a measure of the corrosion that occurred during the loading operation (see Sections 5.1 and 5.2.1). A total of 20 WESF capsules from the storage pool were subjected to destructive examination to determine the metal corrosion resulting from storage. The capsules had been stored in the water pool for periods ranging from 0.4 to 8.9 years. The work was carried out in two stages. In the first stage, two capsules, which had been stored in the pool for 5 years and 8 years, were shipped to ORNL for sectioning and examination. The sectioning and metallographic examination of the capsules was carried out using the same procedure used with the zero-time capsules (see subsection 5.1.3). Corrosion

in the capsules was estimated from the photomicrographs obtained (Figures A.10 and A.11) and the results are given in Table A.9.^(a) Corrosion data for the two zero-time capsules are included in Table A.9 for comparison purposes. From the results given in Table A.9, it appears that most of the attack observed in the two stored capsules occurred during the loading operation.

In the second stage of the work, 18 additional pool capsules were subjected to destructive examination. The capsules were sectioned at WESF. Any loose CsCl was dumped from each opened inner capsule and any residual CsCl was removed by water washing. A ring about 1-1/2 in. wide was cut from the inner capsule near the midpoint. The rings from the 18 capsules were shipped to PNL where a metallographic sample was cut from each ring using a diamond saw. The water washing had reduced the residual radioactivity on the rings to a level where they could be handled in an open-faced hood at PNL. The ring samples were sent to WHC for metallographic examination.

Attack of the 316L SS by the chloride in the 18 capsules was estimated from the photomicrographs obtained from the metallographic samples. Residual wall thickness measurements could not be used to estimate the attack because the initial wall thickness data were not available.

Micrographs from several capsules, showing the different levels and types of attack found, are shown in Figure A.12. The corrosion appears to involve a general surface attack and pitting. There was little indication of grain boundary attack. Overall, the general surface attack was significantly reduced in those samples which exhibited the greatest pitting. The nature of the pitting appears similar to the pitting observed with Series 300 stainless steels exposed to aqueous halide solutions.

Estimates of the corrosion found in the 18 capsules are given in Table A.10. Even though the metal attack varied widely between the 18 capsules examined, the overall attack was quite low. There appeared to be little correlation between storage time in the pool and the extent of metal

(a) Residual wall thickness measurements could not be used to measure the corrosion because the initial wall thicknesses were not known.

Ring 4 Location 1

Ring 3 Location 3

Ring 2 Location 5

200 μm

Ring 1 Location 8

100X

FIGURE A.10. Photomicrographs of Samples Taken from the WESF CsCl Capsule that Had Been Held in the Storage Pool for 5 Years

Ring 4 Location 1

Ring 3 Location 3

Ring 2 Location 5

200 μ m

Ring 1 Location 8

100X

FIGURE A.11. Photomicrographs of Samples Taken from the WESF CsCl Capsule that Had Been Held in the Storage Pool for 8 Years

TABLE A.9. Estimates of Metal Attack in Two Pool Capsules and Two Zero-Time Capsules

Capsule No.	Storage Time, yr	Depth of Metal Attack, ^(a) μm (mils)			
		Ring #1 ^(b)	Ring #2	Ring #3	Ring #4
19459	0	10 (0.4)	8 (0.3)	25 (1.0)	25 (1.0)
19073	0	18 (0.7)	18 (0.7)	25 (1.0)	18 (0.7)
C-312	5	16 (0.6)	25 (1.0)	20 (0.8)	18 (0.7)
C-67	8	12 (0.5)	16 (0.6)	14 (0.6)	18 (0.7)

(a) Estimated from photomicrographs.

(b) See Figure 5.5 for locations where the rings were cut from the capsules.

corrosion. At least half of the capsules examined, some with storage times greater than 8 years, exhibited no more attack than the two zero-time capsules.

It is difficult to explain the differences in the extent and types of attack observed in the storage pool capsules. Two factors should be considered, however, in evaluating the data.

- In compatibility testing, it is not uncommon to observe wide variations in the level of attack in replicate tests.
- Only one sample, having an area of about 1.6 cm², was taken from most of the storage capsules, and only four samples from each of two storage capsules and the zero-time capsules. Therefore, the metal surface from each capsule that was examined represented only a small fraction of the surface that was exposed to the CsCl. A more extensive examination of the storage capsules may have provided more consistent results.

Impurities in the CsCl are expected to have a major effect on the metal corrosion. Most of the storage pool capsules examined were filled from different batches of CsCl, and may have contained different types and amounts of impurities. This could help account for the scatter observed in the corrosion data. The 20 pool capsules examined, however, included four pairs of capsules, each pair of which was filled from the same batch of CsCl. The impurity content of each pair of capsules should be very similar, and their

Capsule No. C-1787
Storage Time - 0.4 yr

Capsule No. C-920
Storage Time - 3.6 yr

Capsule No. 368
Storage Time - 4.6 yr

Capsule No. C-282
Storage Time 6.6 yr

200 μ m 100X

FIGURE A.12. Micrographs of Samples Taken from the Storage Pool Cell CsCl Capsules Showing the Surfaces Exposed to the CsCl

FIGURE A.12. (contd)

TABLE A.10. Estimates of Metal Attack in the 18 Storage Pool CsCl Capsules Examined

Capsule No.	Capsule Thermal Power, (a) W	Capsule ^{137}Cs Content, (a) kCi	Capsule Storage Period, (b) yr	Depth of Metal Attack, (c) μm (mils)
C-17	282	58.0	8.9	50 (2.0)
C-88 } (d)	214	43.9	8.7	50 (2.0)
C-97 }	215	44.1	8.7	30 (1.2)
C-64	266	55.4	8.5	10 (0.4)
C-130 } (d)	358	74.5	8.2	80 (3.2)
C-134 }	359	74.8	8.2	25 (1.0)
C-206	250	52.1	7.5	15 (0.6)
C-253	259	53.9	7.0	20 (0.8)
C-281 } (d)	288	59.9	6.8	30 (1.2)
C-282 }	247	51.4	6.8	25 (1.0)
C-413	267	55.7	5.3	40 (1.6)
C-366 } (d)	233	48.7	4.6	25 (1.0)
C-368 }	234	48.7	4.6	100 (3.9)
C-603	270	56.2	4.1	15 (0.6)
C-809	240	49.1	3.6	25 (1.0)
C-920	240	50.0	3.6	5 (0.2)
C-1777	210	43.7	0.5	25 (1.0)
C1787	175	36.4	0.4	30 (1.2)

(a) At the time of capsule filling.

(b) Approximate storage period (within 0.1 yr) from the time the capsule was filled until it was sectioned for examination.

(c) Metal attack was estimated from photomicrographs of the metallographic specimens cut from the midpoint of each inner capsule.

(d) Bracket indicates that the pair of capsules were filled from a given batch of molten CsCl.

storage times prior to examination were the same. Therefore, theoretically the corrosion in each pair of capsules should be similar. This was found to be the case for two pairs of capsules. Each of the other pairs of capsules, however, showed widely different levels of attack. In each case one capsule of the pair exhibited pitting that was 3 to 4 times deeper than the pitting found in the other capsule. There is no reasonable explanation for such differences unless it reflects a failure to thoroughly examine each capsule.

From the above discussion it is obvious that there is insufficient data to provide a detailed explanation of metal corrosion in the storage pool capsules by the CsCl. The data do indicate, however, that corrosion in the stored capsules is quite low ($\leq 100 \mu\text{m}$), and much of the attack probably occurred during the loading operation. There appears to be little correlation between the metal attack and pool storage time. Overall, the metal corrosion observed in the 20 CsCl capsules examined does not appear to seriously affect capsule integrity, and should not prohibit long-term safe storage of the capsules in a water pool. As a precautionary measure, however, it would be advisable to destructively examine additional capsules on a periodic basis if long-term water storage of the capsules is planned. Each capsule examined should be sampled and analyzed at several locations.

A.7 EXTERNAL CORROSION OF THE WESF INNER CAPSULE (Bryan and Divine 1985)

When the test capsule, which had been thermally aged for 0.5 year, was opened at ORNL, the outer surface of the inner capsule was found to be discolored and possibly pitted at a number of locations (see Figure A.13). Although the other test capsules did not exhibit similar markings, discussions with RHO personnel revealed that some of the CsCl capsules, which had been opened at WESF, did exhibit such markings. Figure A.14 shows one of the inner capsules.

Work was carried out at ORNL to examine the outer surface of the 0.5-year inner capsule at seven locations that were discolored. Figure A.15 shows some of the areas examined. Photomicrographs were obtained of the affected areas. The micrographs indicated that extensive pitting had occurred at most of the locations. Figure A.16 shows typical examples of

FIGURE A.13. Outer Surface of the Inner Capsule (from the 0.5-year test capsule) Showing Some of the Discolored and Possibly Pitted Areas

the pitting observed. The maximum attack found was about $300\ \mu\text{m}$ (0.012 in.), which corresponds to about 9% of the initial capsule wall thickness.

Evaluation of the pitting problem by PNL and RHO personnel suggested that the pitting was probably caused by the electropolishing operation, which is used to decontaminate the filled inner capsule after it was welded shut. To confirm this, a study was carried out at PNL to

- determine if the pitting problem was associated with the electropolishing operation,
- identify the probable cause, and
- identify acceptable solutions to the problem.

FIGURE A.14. Outer Surface of a Pitted WESF CsCl Inner Capsule (~2.5X)

FIGURE A.15. Some of the Areas on the Outer Surface of the Inner Capsule (from the 0.5-year test capsule) that Were Subjected to Metallographic Examination

FIGURE A.16. Typical Pitted Area--Outer Surface of the Inner Capsule from the 0.5-Year Test Capsule

Because the electropolishing operation was also used to decontaminate $^{90}\text{SrF}_2$ inner capsules, which were also prepared at WESF, Hastelloy C-276 (the inner-capsule material for the $^{90}\text{SrF}_2$) was studied as well as 316L SS.

Electropolishing procedures were developed in the mid-1970s for use in decontaminating radioactively contaminated surfaces (Arrowsmith et al. 1977, Allen et al. 1978). Much of the work was devoted to the removal of Pu from SS. There was also a concerted effort to design a system to decontaminate the WESF $^{90}\text{SrF}_2$ capsules. The electropolishing system for the 316L SS WESF CsCl capsules was designed using the information developed from both studies.

The WESF electropolishing system for the CsCl capsules consisted of a vessel with the necessary electrodes. The vessel was an ~50-L SS tank equipped with cooling coils. It contained a concentric cylindrical cathode and a rack to hold the inner capsule, which served as the anode. The electrolyte was nominally 75% phosphoric acid and the recommended operating

temperature was 50°C. In actual plant operation, the cooling coils were not used. During electropolisher operation, heating of the electrolyte was not a problem and the temperature was controlled without using the cooling coils. Chloride contamination of the bath was possible even though the capsule was thoroughly water-washed before electropolishing.

The following were objectives of the PNL study of WESF capsule pitting:

- Identify the cause of the pits, consider the relationship of the pits with electrical contact, and evaluate the effect of electropolishing variables on the pitting processes.
- Consider the effects of pits on the mechanical properties of the capsule.

All tests were carried out on a laboratory scale using nominal 1-in. 316L SS pipe and reject 316L SS inner capsules. The test rack consisted of a tantalum frame with either four point contacts or plate contacts to simulate the WESF rack design. Both racks were readily modified to reduce the number of contacts, and, thereby, increase the current passing through a given contact. Studies were carried out to evaluate the effects of the various process operating parameters on the pitting. Details of the experimental work and the results obtained are presented by Bryan and Devine (1985). The conclusions reached in the study are summarized below.

- The experimental study showed that the discoloration and pitting observed on the outer surface of some inner capsules did result from the electropolishing operation.
- The pitting was caused by a nonuniform current distribution at the rack/capsule contact, which formed localized hot spots. The high temperature produced an increase in the acid concentration through boiling. The concentrated boiling phosphoric acid caused a high rate of localized corrosion, which formed the crevice.
- An attempt to penetrate the capsule wall by electropolishing failed after 30 min with the loss of electrical contact. The maximum wall penetration observed was $\sim 1000 \mu\text{m}$ (0.040 in.), out of a total wall thickness of ~ 0.136 in.
- Tensile tests with pitted specimens showed that pitting was only harmful to the extent that it reduced the cross sectional area of the material. Fracture morphology examinations showed that pitting had little effect on the fracture mode. Examination of the fracture surface near the base of the pits revealed no evidence of

brittle failure. The strength and ductility of the pitted specimens were sufficient to ensure the integrity of the WESF CsCl capsule during storage.

- No justification was found, as a result of the study, to require examination and repackaging of the existing CsCl capsules. A modification of electropolisher rack design was recommended for future work, however, to eliminate the pitting problem.

Pitting attack in Hastelloy C-276 was similar to that observed with the 316L SS capsule material, although the corrosion depth was less with the Hastelloy C-276. The data obtained indicate the same pitting mechanism applies to both metals.

As discussed in Section A.6, 18 CsCl capsules were taken from the storage pool for destructive examination. One sample was cut from near the midpoint of each inner capsule, which was a substantial distance from any point of support rack/capsule contact during electropolishing. Each sample was examined for external corrosion as well as internal corrosion. Of the 18 samples examined, only four exhibited significant corrosion on the outer surface. In each case the attack consisted of isolated pitting to depths up to 60 μm (2.5 mils). Micrographs of the four samples are shown in Figure A.17. (The dark spherical blobs shown in the micrographs are etch marks and not part of the metal microstructure.) The nature of the pitting is quite different from that observed on the aged (0.5 year) capsule or the pitting produced in the electropolishing studies. Considering the differences in pit morphology and pit locations, it is unlikely that the pitting observed with the 18 storage capsules can be attributed to the electropolishing operation. No cause of the pitting has been determined.

Each sample examined from the eighteen storage capsules represents only a small fraction of the capsule surface. A more thorough examination of the capsules may have shown the external corrosion was more widespread than the available data indicate. Even so, it appears very unlikely that the external corrosion is sufficient to represent a threat to capsule integrity.

40 μ m

500X

Capsule No. C-17
Storage Time - 8.9 yr

Capsule No. C-64
Storage Time - 8.5 yr

Capsule No. C-282
Storage Time - 6.8 yr

Capsule No. C-940
Storage Time - 3.6 yr

FIGURE A.17. Micrographs Showing Pitting Corrosion on the Outer Surface of Samples Taken from the Inner Storage Pool Capsules

A.8 ORIGINAL PROGRAM PLAN FOR THE CESIUM CHLORIDE COMPATIBILITY TESTING PROGRAM

The original program plan for the Cesium Chloride Compatibility Testing Program involved an extensive investigation of the important variables that affect 316L SS/CsCl compatibility. The plan was prepared on the assumptions that: 1) technical considerations were the controlling factor, and 2) funding availability was not to influence the initial scope of the program plan. The original program plan is provided.

ESTIMATED PROGRAM COST

The estimated cost of the proposed program as outlined above was \$2,700,000 (in FY 1981 dollars). Approximately 60% of the estimated cost was to carry out the radioactive compatibility tests (Task 5).

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August 19, 1981

Mr. M. W. Gibson
Systems Engineering Department
Rockwell Hanford Operations
Richland, WA 99352

Subject: WESF CsCl Compatibility Program

Dear Mr. Gibson:

Enclosed is a preliminary program plan for evaluating the compatibility of WESF-produced CsCl with 316L stainless steel under the conditions which would exist in a geologic repository. The program, as defined, would take 5-6 years to complete at a cost of approximately \$2,700,000 in FY 1981 dollars. The plan was prepared on the assumption that: (a) technical considerations were the controlling factor, (b) funding availability was not to influence the initial scope of the program plan, and (c) facility availability for carrying out the tests was not to be considered.

Very truly yours,

A handwritten signature in cursive script, appearing to read "H. T. Fullam".

H. T. Fullam
Staff Engineer
Nuclear Fuel Cycle Chemistry Section
Chemical Technology Department

HTF:lm

Enclosure

WESF CESIUM CHLORIDE COMPATIBILITY PROGRAM
PRELIMINARY PROGRAM PLAN

H. T. FULLAM

PROGRAM OBJECTIVES

The primary objective of the CsCl compatibility program is to evaluate the short-term compatibility of WESF produced CsCl with 316L stainless steel under the conditions that would exist in a geologic repository.

Secondary objectives of the program would include: (1) reliable estimates of the long-term compatibility of WESF CsCl and 316L SS in a geologic repository by extrapolating the short-term experimental compatibility data, and (2) identifying the general reaction mechanisms involved in the corrosion of 316L SS by the CsCl under repository conditions.

BASES AND ASSUMPTIONS

The program plan outlined in subsequent pages was developed on the following bases and assumptions:

- The plan was to provide an optimum program for meeting the stated objectives,
- Technical considerations were the overriding factors in preparing the plan,
- Availability of facilities was not considered in preparing the plan,
- Program costs were not considered in preparing the plan,
- The program can be scaled down from the one described, depending on funding availability, but the ability to meet program objectives will be reduced accordingly. Any reduction in program scope should be directed initially at efforts to determine corrosion mechanisms.

INFORMATION NEEDS

Before a detailed program plan can be prepared certain information is needed with regard to any requirements placed on the WESF CsCl storage capsule and the conditions which would exist in the repository.

- Repository Conditions

The maximum CsCl/316 SS interface temperature in the repository must be defined. However, specifying the interface temperature cannot be done independent of compatibility and CsCl physical property considerations. The repository designer cannot unilaterally specify repository temperatures unless the temperatures are so low that corrosion of the 316L SS is guaranteed not to be a problem. Unfortunately, compatibility data with WESF produced CsCl are not presently available and such a guarantee cannot be made. Selection of test temperatures to be used in any compatibility program must take into account both repository requirements and compatibility and CsCl physical property considerations.

- Capsule Requirements

If the WESF CsCl storage capsule must meet certain structural strength requirements prior to disposal, this could affect the scope of the compatibility program. Consideration would have to be given to evaluating the effect of corrosion on the structural strength and integrity of the WESF inner capsule.

The preliminary program plan for the CsCl compatibility program, as outlined in the following sections, does not specify test parameters in absolute terms. Some variations in parameters can be tolerated depending on funding levels available. There are, however, two variables where minimum levels of testing are necessary.

- The compatibility tests with both radioactive and nonradioactive CsCl must last at least 25,000 hours and preferably longer. A maximum exposure time of 32,000 h is recommended. This means that the CsCl compatibility program would last at least 4-5 years. The long exposure times are required to obtain a meaningful measure of the corrosion rate of 316L SS.
- The compatibility tests must be carried out at at least two control temperatures. One temperature would be the maximum temperature that the CsCl/316L SS interface could realistically be expected to encounter in a geologic repository. The second test temperature would be significantly lower. Typical of the test temperatures that might be considered would be 200° and 350°C.

Other test parameters will be defined in detail when the program plan is finalized, and preliminary data from the repository people are available.

PROGRAM TASKS

The proposed CsCl compatibility program is divided into six major tasks:

1. Analysis of the WESF CsCl product
2. WESF CsCl physical property studies
3. Thermodynamic analysis of CsCl/316L SS compatibility
4. Nonradioactive compatibility tests
5. Radioactive compatibility tests
6. Data assessment.

The first three tasks would be completed during the first year of the program. Tasks 4 and 5 would be carried out concurrently; they would start in the first year of the program, and would be completed in the fifth year of the program. The last task would continue throughout the program and would be completed in the sixth year.

Although final program details remain to be defined, the program, as outlined will require six years to complete from the time work is started. Preliminary estimates of the costs associated with each task and yearly funding levels required (in FY 1981 dollars) are given below:

TASK COSTS (FY 1981 Dollars)

1. CsCl Analysis	\$ 60,000
2. CsCl Physical property studies	40,000
3. Thermodynamic Analysis	30,000
4. Nonradioactive Compatibility Test	550,000
5. Radioactive Compatibility Tests	1,638,000
6. Data Assessment	375,000
Total	<u>\$2,693,000</u>

YEARLY FUNDING REQUIRED (FY 1981 dollars)

1st year	\$1,050,000
2nd year	650,000
3rd year	400,000
4th year	100,000
5th year	380,000
6th year	113,000
	<u>\$2,693,000</u>

An estimated time schedule for the program is shown in Table I.

TABLE 1 - Estimated Time Schedule for the Proposed Cesium Chloride Compatibility Program

Task Activities	Time - Calendar Years					
	1st	2nd	3rd	4th	5th	6th
1. CsCl Product Analysis	XXXXXXX					
2. CsCl Property Measurements	XXXXXXXXX					
3. Thermodynamic Analysis	XXXXXXXXX					
4. Nonrad. Compatibility Tests						
Capsule Fabrication	XXXXXX					
2,000 H Tests	XXX					
Analysis 2,000 H Tests	XXXX					
4,000 H Tests	XXXXXX					
Analysis 4,000 H Tests	XXXX					
8,000 H Tests	XXXXXXXXXXXX					
Analysis 8,000 H Tests	XXXX					
16,000 H Tests	XXXXXXXXXXXX					
Analysis 16,000 H Tests	XXXX					
32,000 H Tests	XXXXXXXXXXXX					
Analysis 32,000 H Tests	XXXX					
5. Radioactive Compatibility Tests						
Capsule Fabrication	XXXXXX					
Zero Time Tests	X					
Analysis Zero Time Tests	XXXXXXXXX					
2,000 H Tests	XXX					
Analysis 2,000 H Tests	XXXXXXX					
4,000 H Tests	XXXXXX					
Analysis 4,000 H Tests	XXXXXX					
8,000 H Tests	XXXXXXXXXXXX					
Analysis 8,000 H Tests	XXXXXX					
16,000 H Tests	XXXXXXXXXXXX					
Analysis 16,000 H Tests	XXXX					
32,000 H Tests	XXXXXXXXXXXX					
Analysis 32,000 H Tests	XXXX					
6. Data Assessment	XXXXXXXXXXXX					

Task 1 - Analysis of the WESF CsCl Product

It is absolutely essential to the compatibility program that the composition of the CsCl product be reliably known. This includes not only a knowledge of the types of impurities present, but also the range of impurity concentrations from batch to batch. The effect of recycle and rework material on product composition must also be defined.

Activities required would include:

- Assembling and evaluating analytical data obtained on the CsCl produced to date.
- Analysis of a number of batches of feed solution,
- Analysis of the CsCl products from the same batches of feed solution,
- Analysis of the CsCl product in each batch of CsCl capsules used for the radioactive compatibility tests, and
- Analysis of several batches of CsCl which contains rework and recycle material.

Each CsCl sample should be analyzed for Cs, Na, K, Rb, Fe, Cr, Ni, Mn, H₂O, O⁻², OH⁻, if at all possible.

Estimated cost \$60,000

Task 2 - CsCl Physical Property Measurements

The physical properties of the WESF CsCl product must be determined, especially with regard to the effect of impurities on the melting point and the phase transition temperature. The vapor pressure of impurities as a function of temperature should also be investigated. The physical property

measurements can be made using nonradioactive materials once the composition of the WESF CsCl product is reasonably well-defined.

It is important to know the physical properties of the CsCl product because this can affect the compatibility of the CsCl with 316L SS in several ways. The presence of a liquid phase could increase corrosion rates and increase diffusion of impurities to the interface. The temperature at which the solid phase transition occurs, and possible hysteresis effects, can affect the contact between the CsCl and the 316L SS. Volatilization of impurities could affect corrosion in the capsule closure area (weld metal, crevice corrosion, etc.).

Estimated cost	\$40,000
----------------	----------

Task 3 - Thermodynamic Analysis of CsCl/316L SS Compatibility

A thermodynamic analysis of the WESF CsCl/316L SS system should be carried out to identify potentially troublesome reactions. Analytical data on the CsCl product is necessary in order to carry out the analysis. A rigorous analysis of the system is not practical because of the many system components and a lack of needed chemical and thermodynamic data. By making a number of simplifying assumptions, a useful analysis can be made. Such an analysis would help to identify potential problem areas and to interpret the results obtained in the compatibility tests.

Estimated cost	\$30,000
----------------	----------

Task 4 - Nonradioactive Compatibility Tests

A large number of compatibility tests should be carried out with nonradioactive CsCl to investigate the effects of specific variables on CsCl/316L SS compatibility. Such tests can be carried out at a much lower cost than radioactive tests, and while they do not completely reproduce the WESF CsCl/316L SS system, they can produce very valuable data when carried out in the proper manner.

Parameters to be evaluated^(a)

- Temperature (2)
 - 200°C
 - 350°C
- Times (5)
 - 2000 h
 - 4000 h
 - 8000 h
 - 16000 h
 - 32000 h
- CsCl Compositions (5)
 - (Cs, Na, K) Cl
 - " + FeCl₃
 - " + CrCl₃
 - " + CsOH
 - " + H₂O
- S/V Ratio
 - 1.0 cm⁻¹
 - 2.5 cm⁻¹
 - 4.0 cm⁻¹
- Replication
 - Duplicate capsules

Total Capsules Required = 2x5x5x3x2=300

Analysis of Test Capsules

1. Analysis of CsCl
2. Metallographic Examination of 316L SS
3. SEM & EM of 316L SS

(a) Values given for various parameters are for illustration only, will be finalized as the program plan is developed.

Cost of Nonradioactive Tests (FY1981 Dollars)
(Cost Figures Include Supervision)

1. Equipment and Installation	\$ 30,000
2. Capsule Preparation	65,000
3. Capsule Testing	30,000
4. Capsule Sectioning	15,000
5. Capsule Examination-CsCl Analysis	30,000
-Metallography	190,000
-SEM & EM	150,000
6. Data Assessment	<u>40,000</u>
Total	\$550,000

Task 5 - Radioactive Compatibility Tests

The radioactive compatibility tests with standard WESF CsCl capsules will provide the bulk of the data needed to meet the program objectives. Sufficient tests must be conducted to accurately determine the corrosion rate of 316L stainless steel as a function of temperature, exposure time, and CsCl composition. If the composition of the WESF CsCl product is not fairly uniform from batch to batch, the number of tests required may be substantially greater than the number assumed below.

Parameters to be Evaluated

1. Control Temperatures (2)	- Nominal 350°C
- Nominal 200°C
2. Times (6)	- Zero exposure
- 2000 Hr
- 4000 Hr
- 8000 Hr
- 16000 Hr
- 32000 Hr

3. CsCl Composition (1)^(a)

- 3 Batches CsCl
(6 capsules/batch +
analytical sample)

4. Replication

- Duplicates at 350°C
- Single at 200°C

Total Capsules Required $2 \times 6 + 1 \times 6 = 18$

Analysis of Test Capsule

1. Analysis of CsCl
2. Metallographic examination of 316L SS
3. SEM & EM of 316L stainless steel

Cost of Radioactive Tests (FY 1981 Dollars)

<u>Activity</u>	<u>\$/Capsule</u>
1. Capsule	\$ 1,000
2. Capsule load, weld, decon, leak test	7,000
3. Analyze CsCl batch (1/6 of cost)	1,000
4. Prepare capsule for testing + equipment	12,000
5. Capsule testing (average)	10,000
6. Section capsule	6,000
7. Ship capsule specimens to ORNL	6,000
8. Metallography (8 samples/capsule)	16,000
9. Microprobe (4 samples/capsule)	12,000
10. Engineering-Supervision	<u>20,000</u>
Total	\$ 91,000

Capsules Required 18

Total Cost = $\$91,000 \times 18 = \$1,638,000$

(a) Assumes CsCl composition is fairly uniform with regard to critical impurities, i.e., Fe, Cr, OH⁻, O²⁻, H₂O, etc.)

Preferred Capsule Testing Configuration

1. Test inner capsule only to ensure accurate values for interface temperature
2. Test capsule mounted in vertical position to simulate repository geometry
3. Capsule to have at least 6 and preferably 8 thermocouples welded to outer surface
4. Capsule allowed to self-heat to test temperature, if possible

Sketch below shows possible test configuration for self-heating capsule. Electrically heated dummy capsule used to estimate insulation required to give desired control temperature.

FIGURE 2 Sketch of Test Configuration for Compatibility Testing of the WESF CsCl Capsule - Inner Capsule Only

8 Thermocouples (or thermocouples in thermowells) welded to capsule surface at various locations to monitor capsule surface temperature

Typical temperature along the length of the WESF cesium chloride capsule

With the capsule mounted vertically in an insulated container and allowed to self-heat, a temperature gradient would exist along the length of the capsule. The maximum surface temperature would depend on the amount of insulation used.

Capsule Sectioning

Section capsule as shown. Cut rings ~1" wide at locations shown

The capsule should be sectioned in at least four locations and preferably in eight sections. One section should be through the upper endcap of the capsule and show the weld zone

Task 6 - Data Assessment

Evaluate data, as available, interpret results, and make necessary estimates of long-term attack. Prepare all topical and final reports.

Estimated cost \$375,000.

A.9 REFERENCES

Allen, R. P., H. W. Arrowsmith, L. A. Charlott, and J. L. Hooper. 1978. Electropolishing as a Decontamination Process: Progress and Applications. PNL-SA-6858, Pacific Northwest Laboratory, Richland, Washington.

Arrowsmith, H. W., W. C. Budke, R. P. Allen, and D. W. Jeppson. 1977. Electrochemical Decontamination of Strontium Fluoride Storage Capsules. BNWL-2125, Battelle, Pacific Northwest Laboratories, Richland, Washington.

Bryan, G. H. 1986. Cesium Chloride Compatability Testing Program Annual Report--Fiscal Year 1985. PNL-5730, Pacific Northwest Laboratory, Richland, Washington.

Bryan, G. H., and J. R. Divine. 1985. Cesium Chloride Compatibility Testing Program Annual Report--Fiscal Year 1984. PNL-5341, Pacific Northwest Laboratory, Richland, Washington.

Fullam, H. T. 1971. Physical Property Measurements on Cesium Chloride and Cesium Chloride-Alkali Metal Chloride Systems. BNWL-B-74, Battelle, Pacific Northwest Laboratories, Richland, Washington.

Fullam, H. T. 1982. Cesium Chloride Compatability Testing Program Annual Report--Fiscal Year 1982. PNL-4556, Pacific Northwest Laboratory, Richland, Washington.

Glassner, A. 1957. The Thermodynamic Properties of the Oxides, Fluorides, and Chlorides to 2500K, ANL-5750, Argonne National Laboratory, Argonne, Illinois.

Kellogg, H. H. 1950. "Thermodynamic Relations in Chlorine Metallurgy," J. Metals 188:862-872.

Kenna, B. T., and F. J. Schultz. 1983. Characterization of an Aged WESF Capsule. SAND83-0928, Sandia National Laboratories, Albuquerque, New Mexico and Livermore, California.

Kubaschewski, O., and C. B. Alcock. 1979. Metallurgical Thermochemistry. Pergamon Press, New York.

Lindsay, W. W. 1979. Chemical Equilibria in Soils. John Wiley and Sons, New York.

Rosenqvist, T. 1970. Thermochemical Data for Metallurgists. University of Trondheim, Tapir Forlag, Norway.

Sasmor, D. J., J. D. Pierce, G. L. Tingey, H. E. Kjarmo, J. Tills, and D. C. McKeon. 1988. Characterization of Two WESF Capsules After Five Years Service. SAND86-2808, Sandia National Laboratories, Albuquerque, New Mexico and Livermore, California.

Smithells, C. J., ed. 1976. Metals Reference Book. Butterworths, Boston, Massachusetts.

Tingey, G. L., E. J. Wheelwright, and J. M. Lytle. 1984. A Review of Safety Issues that Pertain to the Use of WESF Cesium Chloride Capsules in an Irradiator. PNL-5170, Pacific Northwest Laboratory, Richland, Washington.

Villa, H. 1950. "Thermodynamical Data for Some Important Metallurgical Materials," J. Soc. Chem. Ind. Suppl. 1:S9-S17.

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