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Cesium Chloride Compatibility Testing Program: Annual Report for Fiscal Year 1986

G. H. Bryan

May 1987

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

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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CESIUM CHLORIDE COMPATIBILITY TESTING PROGRAM: ANNUAL REPORT FOR FISCAL YEAR 1986

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Richland, Washington 99352

SUMMARY

A program was started in FY 1982 to evaluate the compatibility of Waste Encapsulation and Storage Facility (WESF)-produced cesium chloride (CsCl) with 316L stainless steel (SS) under thermal conditions that may be encountered in a geologic repository. The program is funded through the Defense High-Level Waste Technology Program of the Department of Energy. The principal objective of the program is compatibility testing of six standard WESF capsules at a maximum metal/CsCl interface temperature of ~450°C. The capsules are placed vertically in insulated containers and allowed to self-heat to the test temperature, where they are maintained for intervals from 0.25 to 6 yr. After the required time has elapsed, each capsule is destructively examined to determine the extent of metal attack by the cesium chloride.

Test capsule No. C-1351 was removed from its insulated container after being held at temperature for 28,268 h (3.2 yr). The aged capsule was shipped to WESF for sectioning. Four ring sections from the inner capsule were returned to Pacific Northwest Laboratory (PNL), where metallographic samples were cut from each ring. Metallographic examination of the test samples was provided by the Westinghouse Hanford Company's Post-Irradiation Testing Laboratory.

The average maximum interface temperature for the 3.2-yr capsule was 445°C. Metal corrosion in the 3.2-yr capsule was extensive throughout the capsule, except in the upper portion of the capsule where the interface temperature was below 400°C. The maximum corrosion found was 460 μm (0.018 in.). Overall corrosion in the hotter portion of the 3.2-yr capsule increased linearly with time. There are indications that the attack mechanisms may be changing with time: intergranular attack was much more apparent in the tests of longer duration, while pitting and a general surface attack appeared to predominate in the shorter tests. In the portion of the capsule where the temperature was below 400°C, the attack was greatly reduced and did not appear to be much greater than that observed in the shorter tests.

The compatibility data obtained to date indicate that in the hotter portion of the capsule (where the metal/CsCl interface temperature is above 400°C)

the corrosion is proceeding at a linear rate. If metal corrosion at the higher temperatures proceeds at a linear rate for an extended period of time, it has serious implications with regard to the geologic disposal of the WESF CsCl capsules.

Estimates of long-term metal attack, assuming a linear corrosion rate, show that corrosion through the inner capsule wall would occur in 17 to 25 yr depending on the initial capsule wall thickness. The actual corrosion rates should be much lower than the estimated values, however, for two reasons.

- The metal/CsCl interface temperature will decrease substantially over long time periods as the ^{137}Cs decays.
- Corrosion of the 316L SS appears to be due primarily to impurities in the CsCl and the corrosion rate should decrease with time as the impurities are consumed.

Nevertheless, the corrosion may still be sufficient to raise serious questions regarding the long-term integrity of the capsule if the initial interface temperature is allowed to reach 450°C. Limiting the initial maximum interface temperature to 350°C should greatly reduce or eliminate the corrosion problem.

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1.0 INTRODUCTION

At Hanford, fission-product cesium containing 20% to 40% ^{137}Cs has been recovered from the high-level waste (HLW) and converted to cesium chloride (CsCl). Recovery of the Cs as a nitrate from the HLW and its subsequent purification takes place in B Plant. Conversion of the purified product to CsCl, encapsulation of the CsCl, and water storage of the CsCl capsules take place in the Waste Encapsulation and Storage Facility (WESF). Both facilities are operated for the Department of Energy (DOE) by Rockwell Hanford Operations (Rockwell).

The CsCl is doubly encapsulated in high-integrity Type 316L stainless steel (SS) capsules. The CsCl is loaded into the inner 316L SS capsules by melt casting. Each inner capsule, which has an inside diameter (ID) of 2 in. (50.8 mm) and an inner length of ~19 in. (483 mm), contains up to 3 kg of CsCl. The CsCl is prepared in small batches, sufficient to fill about seven capsules. The impurity content of the cesium can vary from batch to batch. Each filled capsule contains up to ~70,000 Ci of ^{137}Cs depending on the age of the fission-product Cs and the purity of the CsCl.

To evaluate the potential corrosion of the capsule during geologic disposal of the WESF CsCl capsules, reliable estimates of long-term attack of the capsule material by the CsCl at disposal temperatures are required. Available data on the compatibility of WESF-produced CsCl with 316L SS are not adequate for making the required evaluations. The Cesium Chloride Compatibility Testing Program was started at the Pacific Northwest Laboratory (PNL)[a] in FY 1982 to obtain the needed data. The program will take ~6 yr to complete. The work is funded by the long-term High-Level Defense Waste Technology Program of the DOE. This report summarizes the program activities for FY 1986.

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

2.0 OBJECTIVE

The primary objective of the Cesium Chloride Compatibility Testing Program is to evaluate the compatibility of WESF-produced CsCl with 316L SS capsule material at the temperatures that could be encountered in a geologic repository. Sufficient short-term (6 yr) compatibility data are to be obtained with WESF-produced CsCl to permit useful estimates of long-term attack on the 316L capsules at potential storage temperatures.

A secondary objective this fiscal year involved the destructive examination of 20 WESF CsCl capsules taken from the storage pool to confirm that corrosion by the CsCl is not a threat to continued safe storage of the capsules in a water basin and to provide an estimate of initial capsule conditions at the beginning of repository disposal.

3.0 TESTING CRITERIA

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

- 316L SS/CsCl interface temperature
- impurities 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.)
- degree of contact between the 316L SS and the CsCl.

Program scope does not permit a detailed testing program to evaluate all of the variables that can affect 316L SS/CsCl compatibility, especially with regard to impurity effects. The limited testing program now under way was designed on the following bases.

- Maximum temperatures in the geologic repository, based on estimates made by Rockwell and PNL personnel, will not exceed 450°C at the 316L SS/CsCl interface.
- The WESF CsCl capsules will be placed in the repository in a vertical orientation.
- The radioactive compatibility tests are to be carried out with standard production WESF CsCl capsules without regard to possible variations in the composition of the CsCl between capsules.

The limitations imposed by the last requirement can significantly influence the radioactive compatibility data obtained, since theoretical considerations indicate that certain impurities in the CsCl could have a significant effect on the capsule metal attack. Estimates of the impurity content of WESF CsCl, based on inductively coupled plasma (ICP) analysis results, and an elementary thermodynamic analysis of the 316L/WESF CsCl system have been reported (Fullam 1982). The data obtained in the radioactive tests now underway will provide a measure of the metal attack for a given set of WESF capsules, but will not provide a complete picture of how the attack may vary with changes in the CsCl composition.

The Cesium Chloride Compatibility Testing Program consists of seven tasks, as outlined below.

- Task 1--collection of radioactive compatibility data, lasting up to six years, using standard WESF CsCl capsules aged at elevated temperatures
- Task 2--heat transfer studies to define the relationship between the surface temperature of the inner and outer capsules of the WESF CsCl capsule
- Task 3--chemical analysis of the CsCl from a batch of WESF-produced CsCl (the CsCl product from WESF is not analyzed, although the Cs feed solution to WESF is analyzed)
- Task 4--thermodynamic analysis of the WESF CsCl/316L SS system
- Task 5--physical property measurements on CsCl-impurity mixtures
- Task 6--destructive examination of 20 WESF CsCl capsules taken from the WESF storage pool
- Task 7--study of the pitting observed on the outer surface of some WESF inner capsules.

The major emphasis was and continues to be on the first task. Tasks 2 and 5 have been completed and the results have been included in the FY 1982 annual report (Fullam 1982). Work on Task 6 has been completed; the results are contained in the FY 1985 annual report (Bryan 1986). Work on Task 7 has been completed and the results are discussed in the FY 1984 annual report (Bryan and Devine 1985).

4.0 RADIOACTIVE COMPATIBILITY TESTS

The radioactive compatibility tests are designed to provide the short-term corrosion data needed to estimate long-term attack of 316L SS by WESF-produced CsCl at a maximum metal/CsCl interface temperature of 450°C. The data obtained from the tests should meet this requirement within the limitations outlined in the previous section. The testing procedures and initial test results are presented in detail in earlier reports (Fullam 1982; Bryan 1984; Bryan and Devine 1985; Bryan 1986) and are summarized below.

4.1 TESTING PROCEDURES

In the thermal aging tests, six standard WESF CsCl capsules are placed vertically in individual insulated containers and allowed to self-heat to a maximum metal/CsCl interface temperature of 450°C. The capsules are maintained at temperature for nominal times of 0.25, 0.5, 1, 2, 3, and 6 yr. The original schedule called for the last capsule to be thermally aged for 32,000 h but the time has been extended to 52,800 h (6 yr).

When thermal aging of a capsule is completed, it is removed from the insulated container, cooled, and sectioned. Four samples are cut at specific locations from the inner capsule for metallographic examination.

In addition to the thermal aging tests, two WESF inner capsules were sectioned and subjected to metallographic examination immediately after being filled with CsCl in the normal WESF manner. The data obtained provided a measure of the metal attack that occurred when the capsule was loaded with molten cesium chloride. The two "zero-time" capsules serve as controls for determining the metal attack resulting from capsule filling operations.

The CsCl capsules used in thermal aging tests are typical WESF production capsules. These capsules were fabricated and filled with CsCl in accordance with all pertinent Rockwell-WESF, DOE quality control (QC) and quality assurance (QA) requirements.

All capsule components used in the tests were fabricated in the usual manner with one additional step. To accurately determine the extent of metal corrosion by the CsCl, it is necessary to know the initial wall thickness of the inner capsules at the points at which the samples are taken for metallographic examination. Therefore, the wall thickness of each of the eight inner capsules used in the tests was measured at 18 locations, as shown in Figure 1, before the capsule was filled with CsCl. A number and location line were etched on the capsule outer surface to show where each measurement was taken. An ultrasonic technique was used to determine the wall thickness to within 0.0001 in. The results obtained show that the wall thickness of an inner capsule is fairly uniform over the length of a capsule along any given longitudinal surface element, with the thickness variations rarely exceeding 0.003 in. over the capsule length. The 316L SS tubing used for the capsules is not concentric, however, and differences in wall thickness of up to 0.015 in. were observed at diametrically opposite locations on a capsule. Because of the these variations, the initial wall thickness of an inner capsule is only accurately known at the exact location where a thickness measurement is made.

During testing, each capsule is held in the insulated container in a vertical position. Because of the configuration used, a substantial temperature gradient exists between the middle and end of each capsule. Calibrated chromel-alumel thermocouples are used to measure the temperature profile of the outer capsule. Temperature readings are taken periodically. The inner capsule/CsCl interface temperatures are calculated from the measured outer capsule temperature using the procedure described in the FY 1982 annual report (Fullam 1982). The insulated containers holding the capsules are designed to give maximum metal/CsCl interface temperatures of 450°C. Because the capsule temperature is dependent on decay of the radioactive cesium, the temperature will gradually decrease with time as the cesium decays.

When thermal aging of a test capsule is completed, it is removed from the insulated container and cooled, and the outer capsule is opened. The inner capsule is removed and sectioned for metallographic examination. Four ring sections are cut from each capsule at locations where the wall thickness is known (see Figure 2). A metallographic sample is then taken from each ring section at the point where the wall thickness was measured. Ring Section 2 (see Figure 2) is removed from the capsule at the point of maximum metal/CsCl

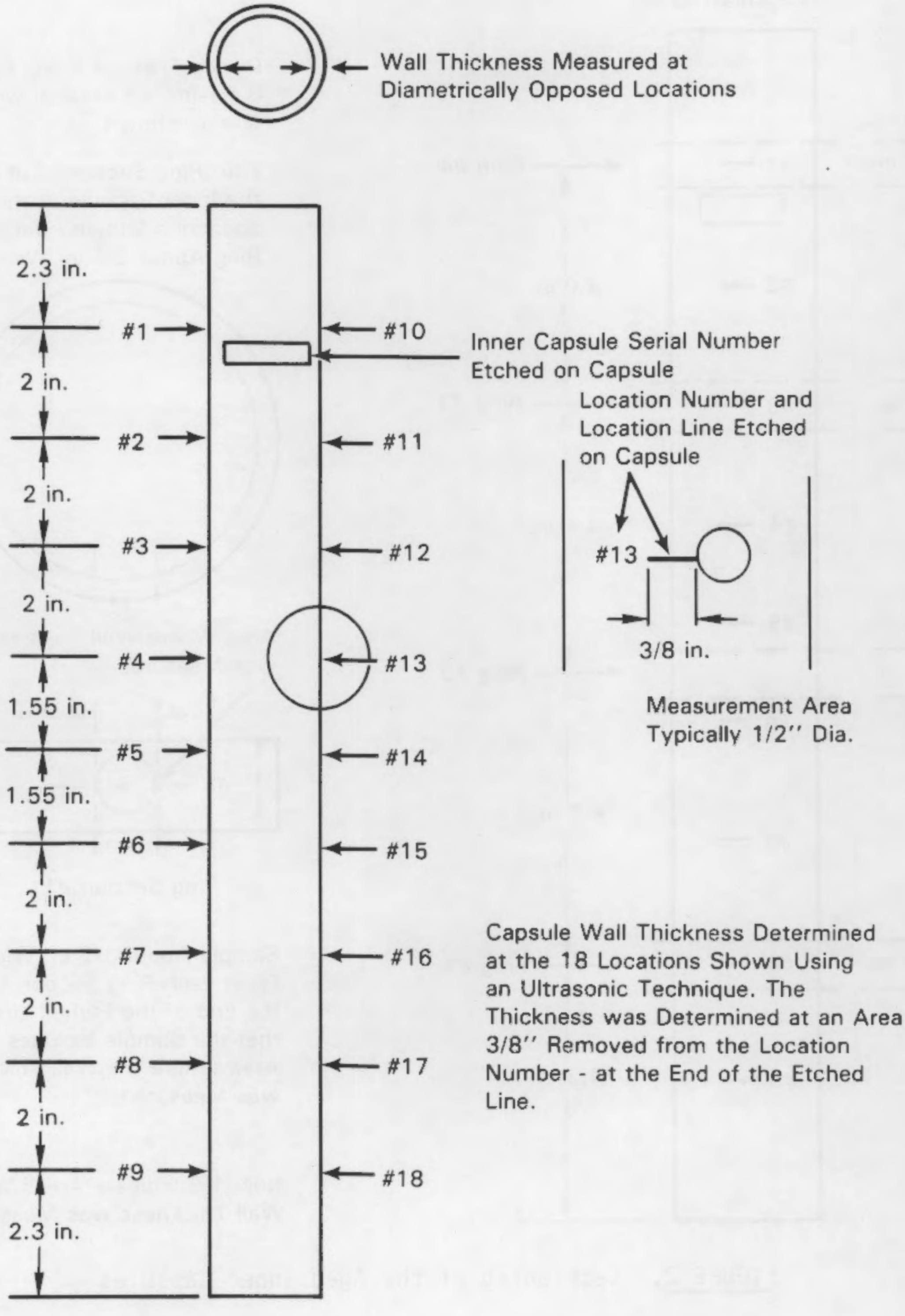


FIGURE 1. Locations at Which the Wall Thickness of the Inner WESF Capsules Was Measured

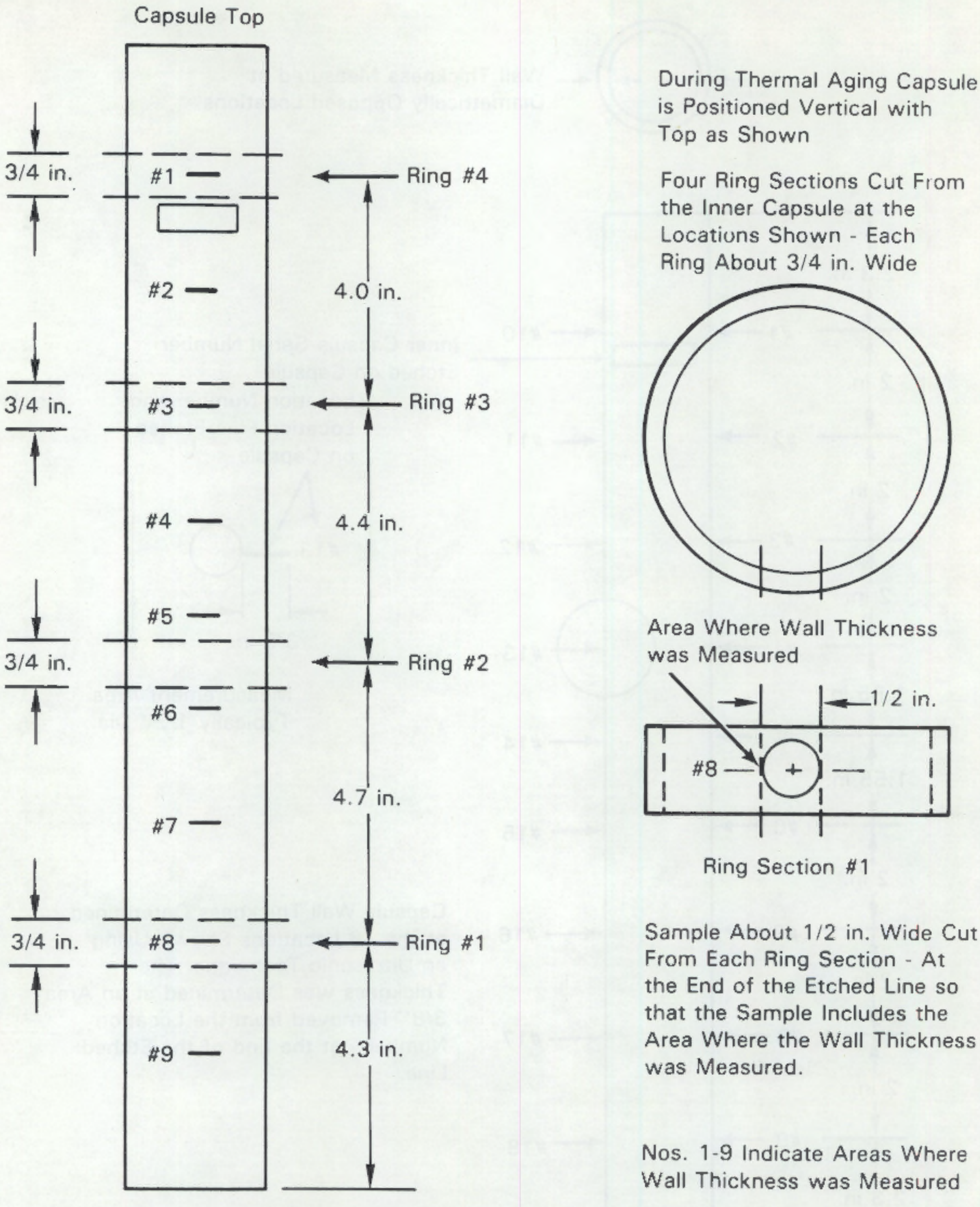


FIGURE 2. Sectioning of the Aged Inner Capsules

interface temperature. With each test capsule this point occurs somewhere between thickness measurement points 5 and 6. Since the variation in wall thickness rarely exceeds 0.001 in. between adjacent measurement points on a surface element, the initial wall thickness of Ring 2 at the sample point is known with acceptable accuracy.

Loading the molten CsCl into the inner capsules at WESF is a batch operation. Sufficient CsCl can be melted in each batch to fill seven capsules. Each of the test capsules, including the two "zero-time" capsules, was filled from a different batch of CsCl. Therefore, the chemical composition and the cesium isotopic composition of the CsCl can vary significantly among the different test capsules. Table 1 gives the pertinent data on the six capsules used in the thermal aging tests. From the data available, one can calculate an approximate ^{137}Cs isotopic concentration for each capsule, but the amount and types of impurities present in each capsule are unknown.

Because the test temperature of each capsule is attained by self-heating, it was impossible to attain identical temperature profiles for all six test capsules. The insulated container holding each capsule was designed to provide an initial maximum 316L SS/CsCl interface temperature of 450°C. In the five aging tests completed to date (up to 3.2 yr), the average maximum interface temperature for each test period varied from 460°C to 445°C. Similar temperature variations were observed at the other locations where the capsules were

TABLE 1. Pertinent Data on the Six WESF CsCl Capsules Used in the Thermal Aging Tests[a]

Outer Capsule No.[b]	Inner Capsule No.	CsCl, kg	^{137}Cs, Ci	Watts, t
C-1266 (2208 h)	19073-G	2.388	45,870	220
C-1272	19073-B	2.701	56,930	273
C-1351 (28,268 h)	19073-E	2.597	52,520	252
C-1365 (4,392 h)	19073-D	2.472	44,740	214
C-1451 (8,784 h)	19073-C	2.756	54,380	261
C-1486 (17,544 h)	19073-H	2.716	51,140	245

(a) As of April 5, 1982.
(b) Numbers in parentheses designate aging time.

sampled. The variations in the average test temperatures reflect the effects of the 1) initial radioactive cesium content of a capsule, 2) minor variations in the insulation between containers, 3) periodic capsule temperature fluctuations due to changing conditions in the hot cell holding the capsule containers, and 4) decay of the radioactive cesium on the temperature profile of each capsule.

In examining the test capsules to determine the extent of metal attack by the WESF CsCl, it was not possible to obtain a precise measurement of the corrosion. Adhesion of CsCl to the metal surface makes it impossible to accurately measure the residual wall thickness using a micrometer or similar device. Instruments such as the ultrasonic device used to measure the initial capsule wall thickness were not available in a shielded facility (hot cell) to measure the residual metal thickness of the highly radioactive samples from the test capsules.

Photographic techniques can be used to estimate the residual metal thickness of the samples mounted in plastic for metallographic examination. Alignment problems in mounting the sample in plastic in the hot cell, however, can affect the results obtained. If the sample is not mounted vertically (see Figure 3) the measured wall thickness will be greater than the actual wall thickness. A 15° error in alignment (from vertical), for example, would increase the apparent metal thickness by about 0.005 in. for the mounted test samples.

Because the mounting alignment error is unlikely to exceed 15° to 20°, even in a hot cell, wall thickness measurements on the mounted samples can be used to determine whether extensive attack of the exposed metal surface has occurred. If these measurements indicate no such attack, then the photomicrographs can be used to estimate the corrosion with reasonable precision.

Metal corrosion can be estimated from photomicrographs of the exposed surface of the test samples, assuming that the specimens have not suffered extensive attack. Metal attack estimated from the micrographs represents a minimum measure of the corrosion, however, because it is not possible to determine the initial surface location in the micrographs if there has been extensive dissolution of the metal surface.

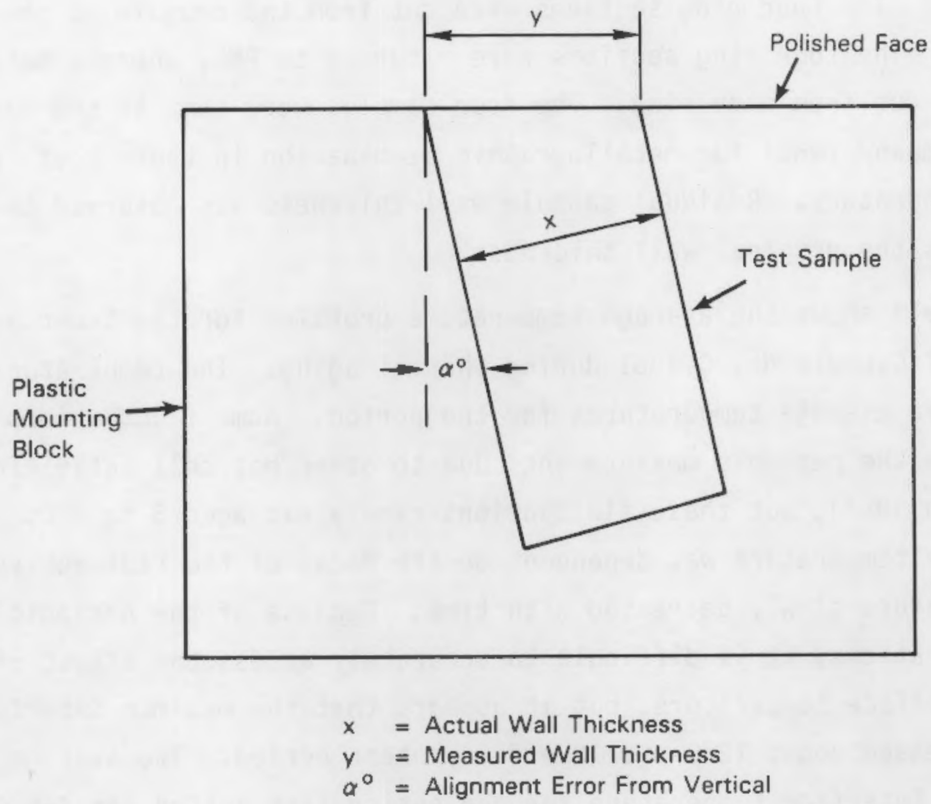


FIGURE 3. Effect of Sample Alignment Error on Measuring the Residual Wall Thickness of Mounted Samples Photographically

4.2 TEST RESULTS

Thermal aging and examination of the first five test capsules (up to 3.2 yr exposure) has been completed. Results obtained with the first four capsules (up to 2 yr exposure) were presented in previous reports (Bryan 1984; Bryan and Devine 1985). Results obtained with the 3.2-yr capsule are presented in this report.

4.2.1 Thermally Aged Capsules

Capsule No. C-1351 was removed from the insulated container after being held at the test temperature for 28,268 h (3.23 yr). The capsule was shipped to WESF for sectioning. The CsCl was removed from the inner capsule by water washing.[a] The four ring sections were cut from the capsule at the prescribed locations. The four ring sections were returned to PNL, where a metallographic sample was cut from each ring. The four samples were sent to the Westinghouse Hanford Company (WHC) for metallographic examination in their Post-Irradiation Testing Laboratory. Residual capsule wall thickness was observed to be about the same as the original wall thickness.

Figure 4 shows the average temperature profiles for the inner and outer capsules of Capsule No. C-1351 during thermal aging. The temperatures shown in Figure 4 are average temperatures for the period. Some fluctuations were observed in the periodic measurements due to other hot cell activities (Fullam 1982; Bryan 1984), but these fluctuations rarely exceeded 5 to 6°C. Because the capsule temperature was dependent on the decay of the radioactive cesium, the temperature slowly decreased with time. Because of the periodic temperature fluctuations, it is difficult to accurately access the effect of the decay on the interface temperature, but it appears that the maximum interface temperature decreased about 12°C over the 3.2-yr test period. The average maximum metal/CsCl interface temperature for the entire test period was 445°C.

Residual wall thickness measurements, obtained photographically, on the four mounted metallographic samples showed that the apparent residual wall thickness of each sample was somewhat greater than the initial wall thickness, as shown below.

Dimension	Ring Sample No. 1	Ring Sample No. 2	Ring Sample No. 3	Ring Sample No. 4
Initial Wall Thickness, in.	0.135	0.131	0.135	0.135
Final Wall Thickness, in.	0.141	0.136	0.140	0.136
Difference, in.	+0.006	+0.005	+0.005	+0.001

(a) The capsules tested for 2 yr or less were shipped to the Oak Ridge National Laboratory (ORNL) for sectioning and metallographic examination of the metal samples. After an inner capsule was sectioned, the contained CsCl was physically removed from the section. Neither the inner capsules nor metal samples were water washed before metallographic examination of the samples.

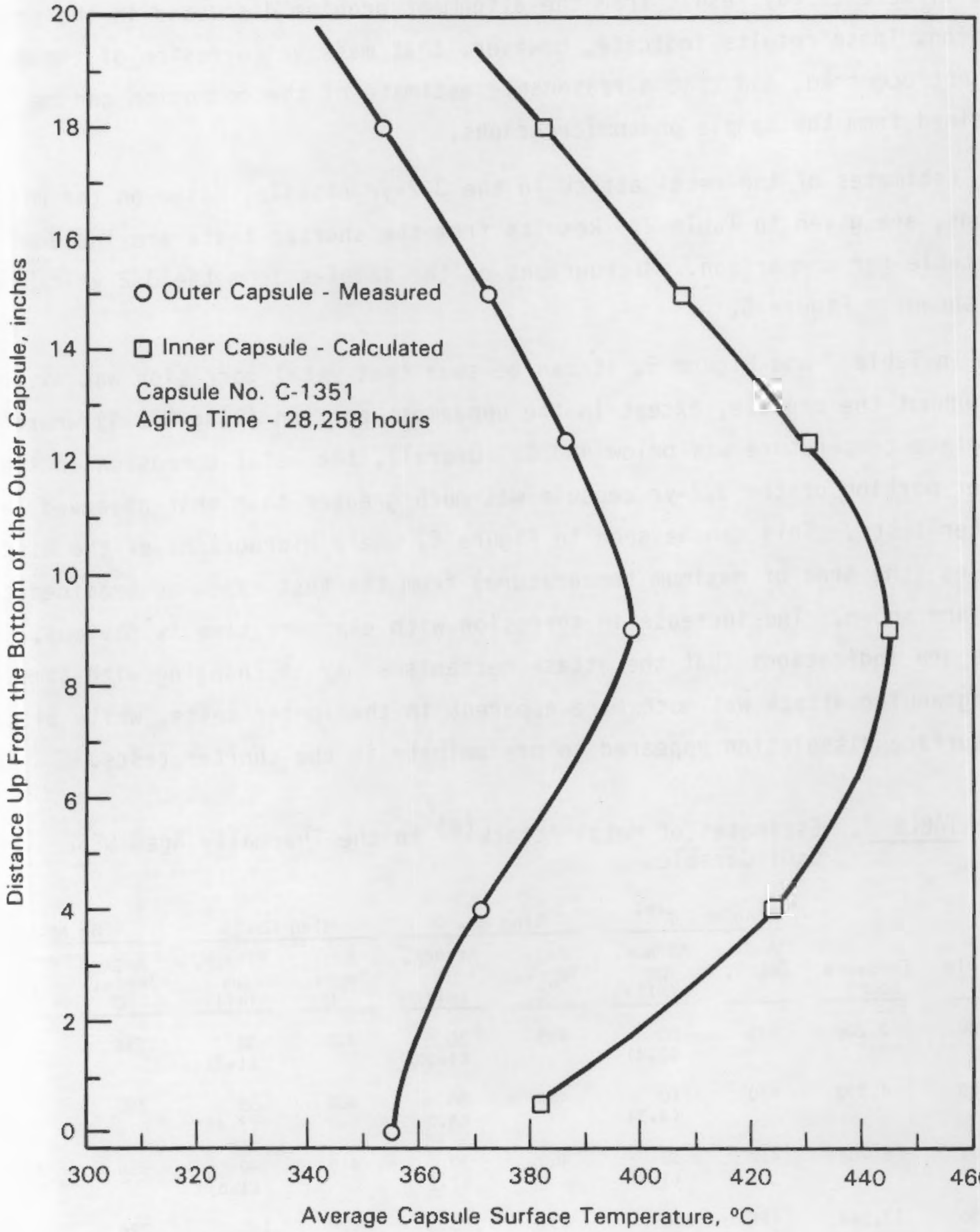


FIGURE 4. Average Temperature Profiles for the WESF Capsule Held at Temperature for 28,268 h

This difference may result from the alignment problem discussed in the previous section. These results indicate, however, that massive corrosion of the metal had not occurred, and that a reasonable estimate of the corrosion can be obtained from the sample photomicrographs.

Estimates of the metal attack in the 3.2-yr capsule, based on the micrographs, are given in Table 2. Results from the shorter tests are included in the table for comparison. Micrographs of the samples from the 3.2 yr capsule are shown in Figure 5.

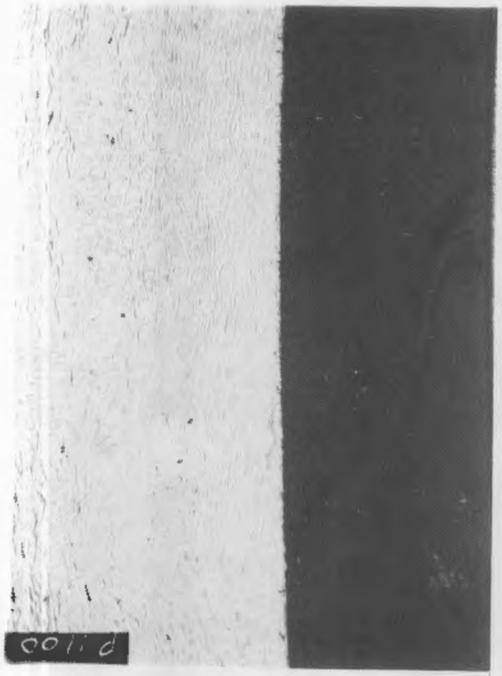
In Table 2 and Figure 5, it can be seen that metal corrosion was extensive throughout the capsule, except in the uppermost portion (Ring No. 4) where the interface temperature was below 400°C. Overall, the metal corrosion in the hotter portion of the 3.2-yr capsule was much greater than that observed in the shorter tests. This can be seen in Figure 6, where micrographs of the Ring 2 samples (the area of maximum temperature) from the test capsules examined to date are shown. The increase in corrosion with exposure time is obvious. There are indications that the attack mechanisms may be changing with time. Intergranular attack was much more apparent in the longer tests, while pitting and surface dissolution appeared to predominate in the shorter tests.

TABLE 2. Estimates of Metal Attack[(a)] in the Thermally Aged WESF CsCl Capsules

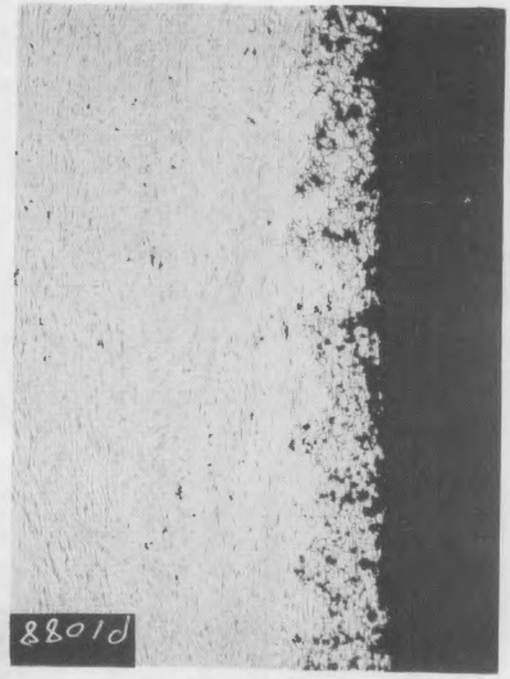
		Ring No. 1[(b)]		Ring No. 2		Ring No. 3		Ring No. 4	
Capsule No.	Exposure Hours	Avg. Temp., °C	Attack, µm (mil)	Avg. Temp., °C	Attack, µm (mil)	Avg. Temp., °C	Attack, µm (mil)	Avg. Temp., °C	Attack, µm (mil)
C-1266	2,208	415	60 (2.4)	455	30 (1.2)	420	30 (1.2)	354	35 (1.4)
C-1365	4,392	430	110 (4.3)	449	80 (3.2)	400	85 (3.4)	350	50 (2.0)
C-1451	8,784	432	30 (1.2)	460	30 (1.2)	415	40 (1.6)	356	20 (0.8)
C-1486	17,544	431	200 (7.9)	454	260 (10.2)	428	160 (6.3)	386	40 (1.6)
C-1351	28,268	426	430 (17)	445	460 (18)	421	360 (14)	387	35 (1.4)

(a) Attack estimated from photomicrographs; see discussion in text.
(b) See Figure 1 for ring locations on capsules.

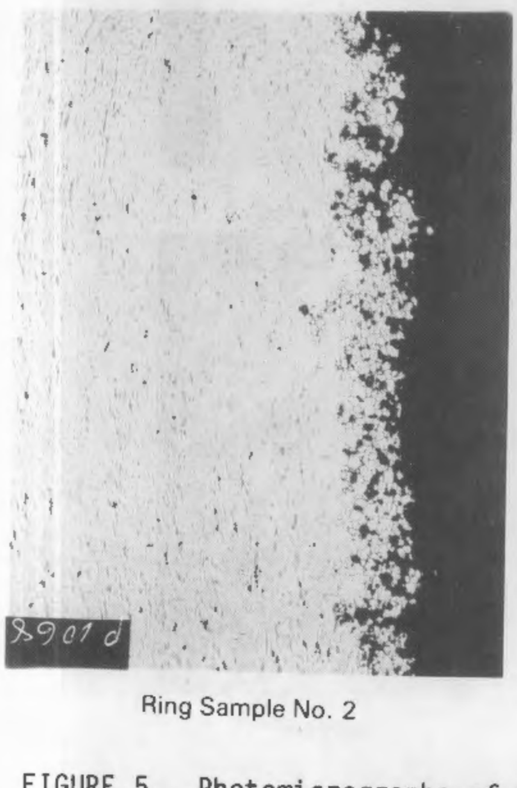
50X 400 μm



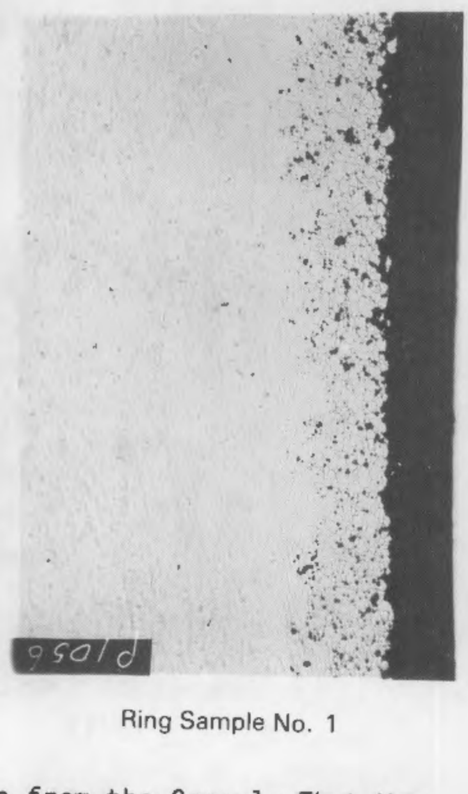
Ring Sample No. 4



Ring Sample No. 3



Ring Sample No. 2



Ring Sample No. 1

FIGURE 5. Photomicrographs of Samples Taken from the Capsule That Was Thermally Aged for 28,268 h

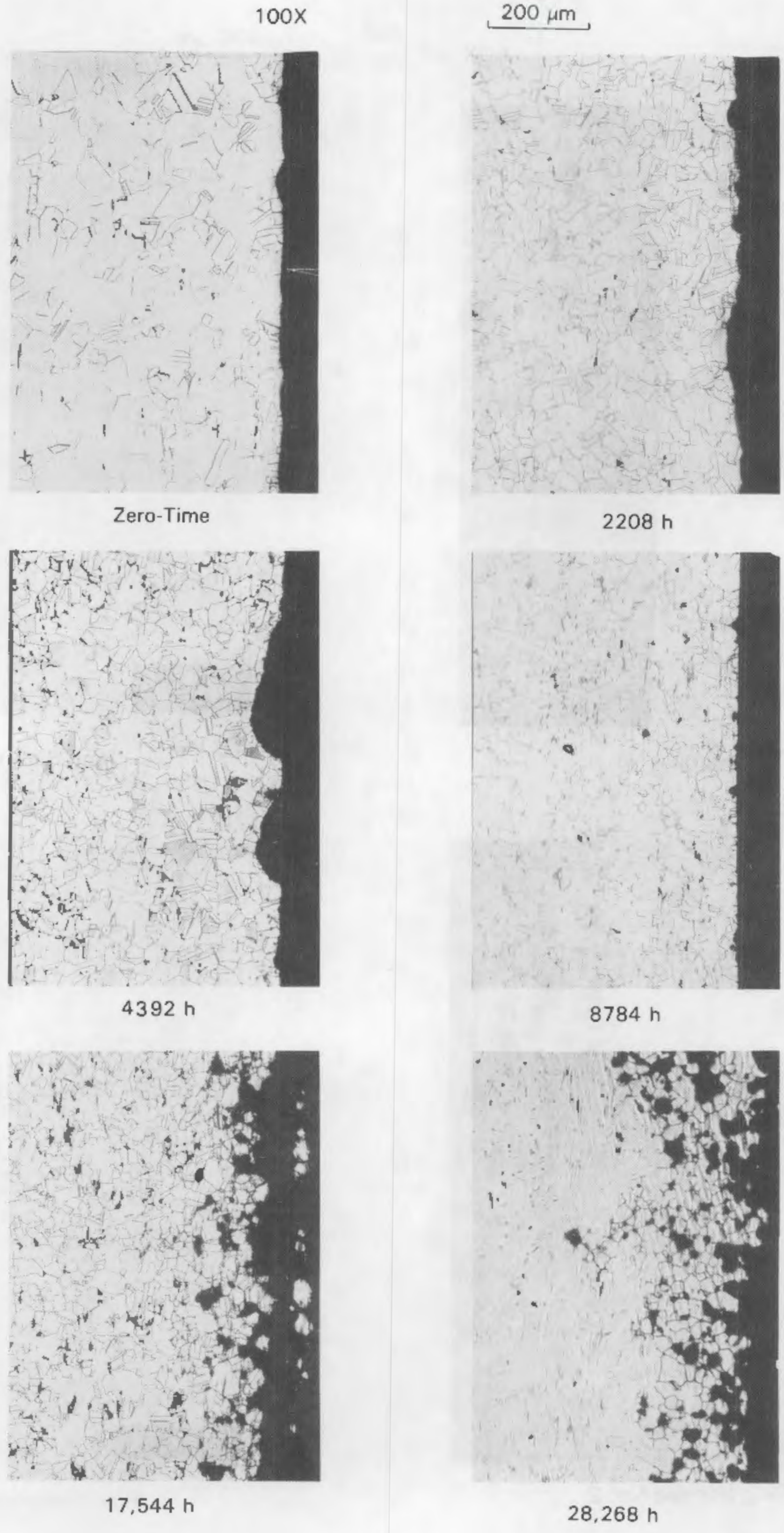


FIGURE 6. Effect of Exposure Time on Metal Corrosion at the Maximum Metal/CsCl Interface Temperature--Ring No. 2

In the portion of the capsule where the temperature is below 400°C (Ring No. 4) the corrosion rate is greatly reduced. The metal attack observed in the Ring 4 samples from both the 2- and 3.2-yr capsules appears no greater than that found in the shorter tests, even though the average interface temperatures are about 30°C higher in the longer tests (see Figure 7).

In Table 2 and Figure 6, one anomaly is apparent. Corrosion in the capsule tested for 1 yr was far less than would be predicted from the results of the other tests. Although it is not uncommon in compatibility tests to observe wide variations in attack in similar tests, the difference in the attack observed in the 1-yr capsule, compared with the other test results, is much greater than the variations usually encountered. Possible reasons (such as lower levels of impurities in the CsCl) for the reduced attack in the 1-yr capsule are discussed in the FY 1984 annual report (Bryan and Devine 1985).

If the metal attack is plotted as a function of time for each ring location, the corrosion appears to proceed linearly with time at the higher temperatures (above about 400°C). Figure 8 shows such a plot for the maximum metal/CsCl interface temperature (Ring 2). If metal corrosion at the higher temperatures continues at a linear rate for an extended period of time, it has serious implications for the geologic disposal, and possibly the potential utilization, of the WESF CsCl capsules. This is discussed in more detail in Section 4.2.3. Results obtained in the 6-yr test, which will be completed in FY 1988, will provide needed information as to whether the corrosion is continuing at a linear rate.

4.2.2 Corrosion Mechanisms

Potential reactions between CsCl and the 316L SS 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 reaction to occur, but provides no insight on reaction kinetics. Based on thermodynamic considerations, pure cesium chloride should not react with 316L SS. The WESF-produced CsCl contains a number of impurities, however, and reactions between certain impurities in the CsCl and components of the 316L SS are thermodynamically possible. A thermodynamic analysis of the WESF CsCl/316L SS system was given in the FY 1982 annual report (Fullam 1982).

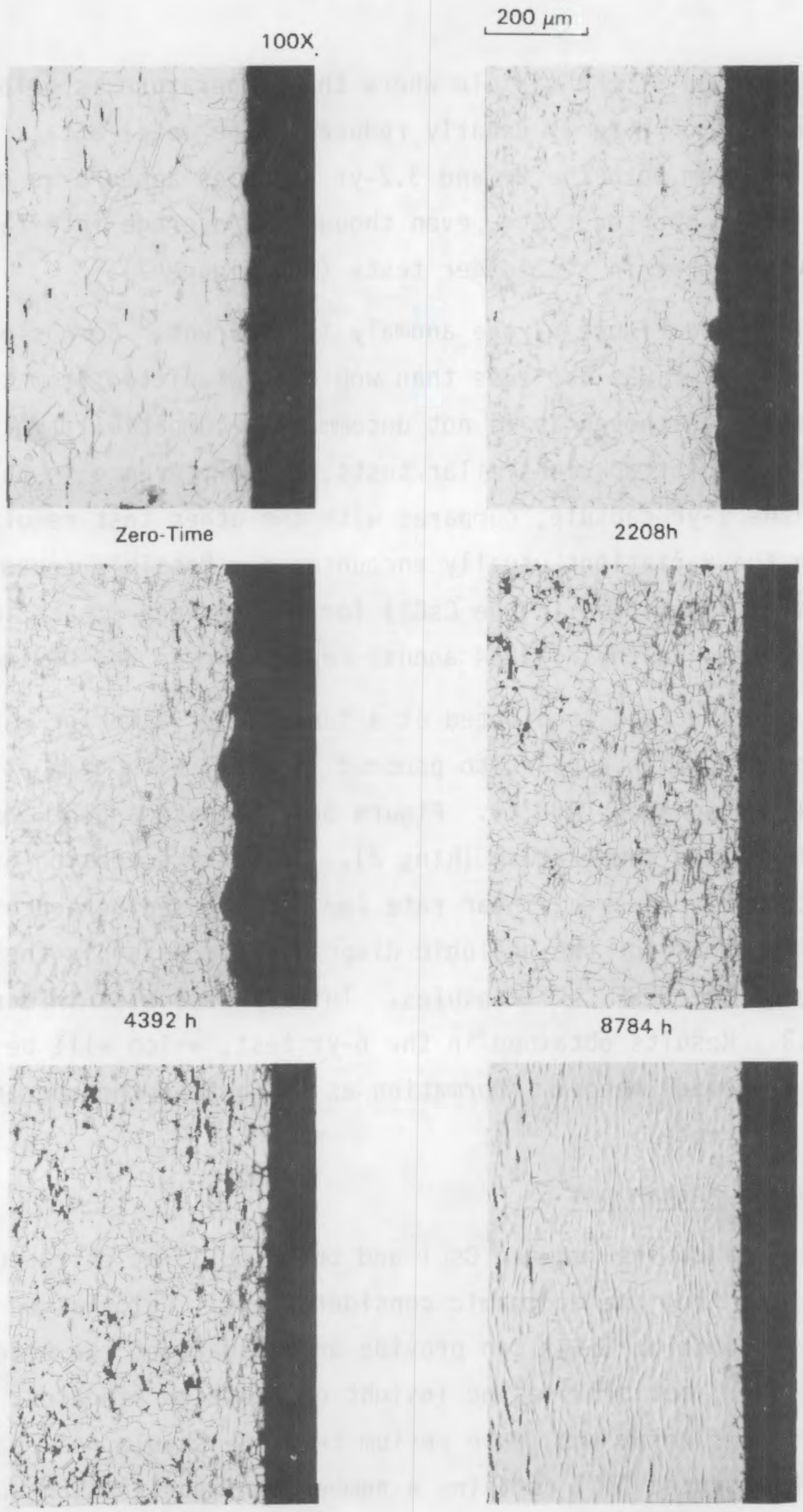


FIGURE 7. Effect of Exposure Time on Corrosion at Ring Location No. 4

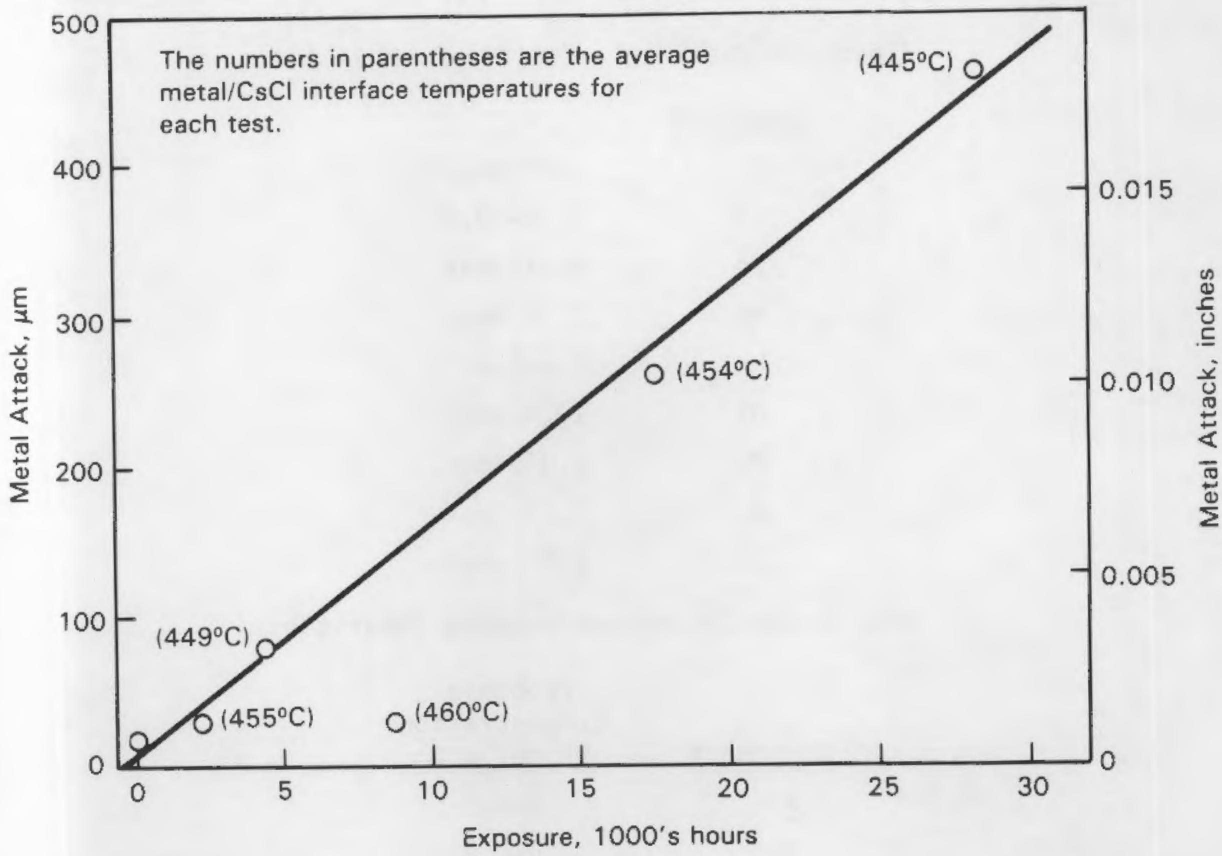


FIGURE 8. Metal Attack as a Function of Exposure Time at the Area of Maximum Metal/CsCl Interface Temperature--Ring No. 2

From a thermodynamic standpoint, the WESF CsCl/316 SS system is extremely complex because many components are contained in the system. Table 3 gives the nominal composition of the 316L SS and also lists the cation impurities that may be present in the WESF CsCl at greater than trace levels. Cation impurities in the CsCl are present primarily as chlorides, but small amounts of oxides may also be present. Oxides could be formed by hydrolysis of the metal chlorides during evaporation and melt casting. The CsCl may also contain a significant amount of water as well as small amounts of zeolite ion exchange material (complex aluminosilicates) carried over from the cesium purification operation.

TABLE 3. Components of the 316L Stainless Steel/WESF CsCl System

316 Stainless Steel--Nominal Composition

Component	wt%
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 Cesium Chloride--Probable Impurities

Component	Probable Concentration Range, wt%
Al	0-0.1
Ba[(a)]	0-0.2
Ca	0-0.2
Cr	0-1.0
Fe	0-1.0
K	0-3.0
Mg	0-0.2
Mn	0-0.2
Na	0-3.0
Ni	0-1.0
Pb	0-0.1
Rb	0-0.2
Si	0-0.5
Sr	0-0.2

(a) Initial barium concentration at the time of encapsulation--will increase with time due to decay of the ^{137}Cs.

The barium concentration of the WESF CsCl will increase with time as the ^{137}Cs decays. The chemical form of the barium daughter is unknown. The monovalent cesium decays to divalent barium and only one chlorine atom is available per atom of barium formed.

$$^{137}CsCl \rightarrow {}^{137}BaCl \tag{2}$$

Barium monochloride is reported to exist at very high temperatures, but not at the temperatures encountered in a WESF capsule. If barium monochloride were to form, it would probably disproportionate to barium metal and barium chloride.

$$2\ BaCl \rightarrow Ba + BaCl_2 \tag{3}$$

The barium metal resulting from the disproportionation reaction would be extremely reactive and could reduce impurities in the chloride to lower valence states or metallic form.

If impurities in the WESF CsCl are the principal cause of the metal corrosion, the extent of the metal attack will be limited by the amount of impurities (with the exception of Ba) available to react with the 316L SS. As a result, the corrosion rate should be high initially and decrease with time as the impurities are consumed. Because of the large number of components in the 316L SS/WESF CsCl system, corrosion of the stainless steel probably involves a number of reactions. The rate-controlling step for each reaction is likely to involve diffusion of the reactant from the body of the CsCl to the metal/CsCl interface.

Pure cesium chloride has a melting point of 645°C. The presence of impurities in the CsCl can result in the formation of low melting phases. The $FeCl_3$-CsCl system, for example, has a minimum melting point of 270°C. The presence of a liquid phase in the storage capsule can adversely affect capsule corrosion in two ways.

- The presence of a liquid phase can facilitate diffusion of impurities from the bulk of the CsCl to the metal/CsCl interface.

- The presence of a liquid phase at the metal/CsCl interface could increase the corrosion rate because a liquid-solid reaction often proceeds at a faster rate than a solid-solid reaction.

The amount of liquid phase present will depend on the impurity content of the CsCl and the temperature. Since a temperature gradient would exist over the length of the storage capsule, the amount of liquid phase could vary in different portions of the capsule. In general, the amount of liquid phase in the storage capsule where the maximum interface temperature is 450°C should be quite low (<1 wt%), but even this small amount of liquid could facilitate the diffusion of impurities to the metal/CsCl interface.

In an attempt to identify the corrosion reaction(s), the samples from the 3.2-yr capsule are being analyzed by scanning electron microscopy (SEM). Insufficient data are currently available to identify probable reaction mechanisms from preliminary results obtained with Ring No. 2 samples; however, some trends are apparent. The data indicate that the bulk concentrations of the nickel, molybdenum, and silicon in the reaction zone are decreased. While the chromium concentration is increased slightly, the nickel concentration is increased at the edge of the reaction zone adjacent to the CsCl. The analysis of probable reaction products in void spaces in the reaction zone shows high concentrations of nickel, chromium, and molybdenum.

Work is continuing on the analyses of the samples to identify the probable reaction mechanisms; the results will be reported in the FY 1988 annual report.

If one assumes that the corrosion rate at a specific capsule 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, the rate equation obtained from the Ring No. 2 data is as follows:

$$y = 137\, t + 7$$

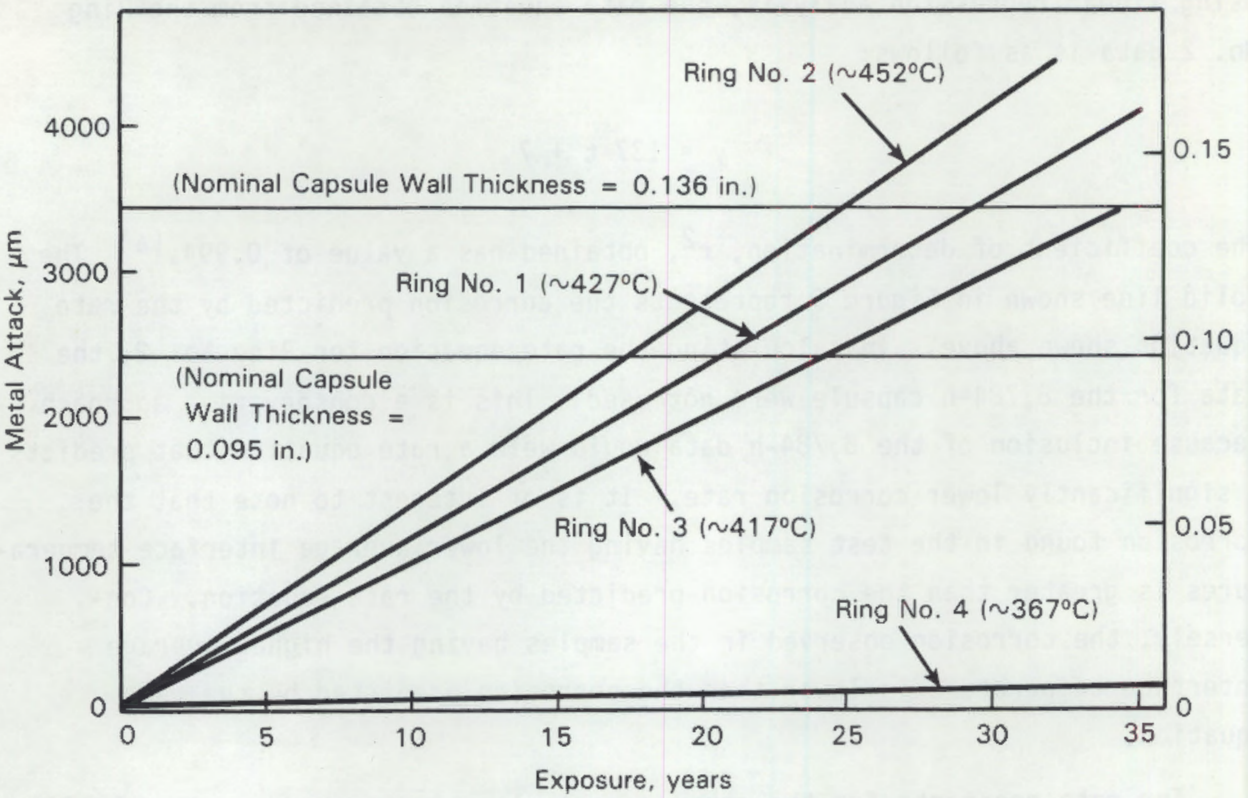
The coefficient of determination, r^2, obtained has a value of 0.994.[a] The solid line shown in Figure 9 represents the corrosion predicted by the rate equation shown above. In calculating the rate equation for Ring No. 2, the data for the 8,784-h capsule were not used. This is a conservative approach because inclusion of the 8,784-h data would weld a rate equation that predicts a significantly lower corrosion rate. It is of interest to note that the corrosion found in the test samples having the lower average interface temperatures is greater than the corrosion predicted by the rate equation. Conversely, the corrosion observed in the samples having the higher average interface temperature is lower than the corrosion predicted by the rate equation.

The rate constants for the other capsule locations, as determined by linear regression analysis, are shown below:

Capsule Location	K_1	K_2	Coefficient of Determination, r^2
Ring No. 1	116	26	0.953
Ring No. 2	137	7	0.994
Ring No. 3	99	13	0.949
Ring No. 4	3.7	27	0.363

The data for the 8,760-h capsule were not used in calculating the rate equations for Rings 1, 3, and 4. In the case of the Ring No. 4 corrosion data, where the average interface temperature is below 400°C, none of the standard forms of the rate equation provides a good fit with the experimental data. The

(a) The coefficient of determination indicates the quality of fit with the experimental data achieved by the regression analysis. Values of r^2 close to 1.0 indicate a better fit than values close to zero.



Note:

1. The nominal initial wall thickness of the WESF CsCl inner capsules varies from 0.095 in. to 0.135 in. depending on the 316L SS tubing used to fabricate the capsule.

2. The temperature shown for each ring location is the average interface temperature for all of the tests.

FIGURE 9. Estimated Long-Term Corrosion in the WESF CsCl Inner Capsule, Assuming Linear Corrosion Rates

use of a linear rate equation will overestimate the long-term corrosion for Ring No. 4 and represents a conservative analysis of the corrosion problem in the colder portion of the capsule.

Long-term corrosion of the 316L SS by the WESF CsCl at the four capsule locations, as predicted by the linear rate equations, is shown in Figure 9. The estimates show that corrosion through the inner capsule wall would be achieved in 17 to 25 years, depending on the initial capsule wall thickness,[a] if the corrosion proceeds at a linear rate.

It must be remembered that the use of linear rate equations to predict the long-term metal corrosion represents a very conservative approach for two major reasons.

- Over long time periods, the capsule interface temperature will decrease substantially as the radioactive cesium decays. Since the half-life of ^{137}Cs is about 30 yr, the heat generation in the capsule would be cut in half in 30 yr and the interface temperature would decrease accordingly.
- Corrosion of the 316L SS appears to be due primarily to impurities contained in the WESF CsCl. The impurity reactants are consumed as the corrosion reactions proceed, and the corrosion rate should decrease with time.

The actual long-term corrosion of the four capsule locations will, therefore, be less than that predicted in Figure 10; it is impossible to define how much less at this time. Nevertheless, the corrosion would still be sufficient to raise questions regarding the long-term integrity of the inner capsule if the initial maximum metal/CsCl interface temperature were allowed to reach 450°C. The seriousness of the problem would depend on the structural and containment requirements placed on the WESF CsCl capsule by the repository disposal criteria.

All of the experimental data attained to date indicate that the potential corrosion problem would be greatly reduced, or eliminated, if the initial maximum interface temperature for the storage capsule were reduced. Figure 10 shows the estimated corrosion for a 25-yr storage time as a function of the interface temperature,[b] assuming linear corrosion rates. From the figure it

(a) During the WESF operation, the nominal wall thickness specification for the 316L SS tubing used in fabricating the inner capsule 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.

(b) The average interface temperature assumed for each ring location is the average value for the five thermally aged capsules examined to date.

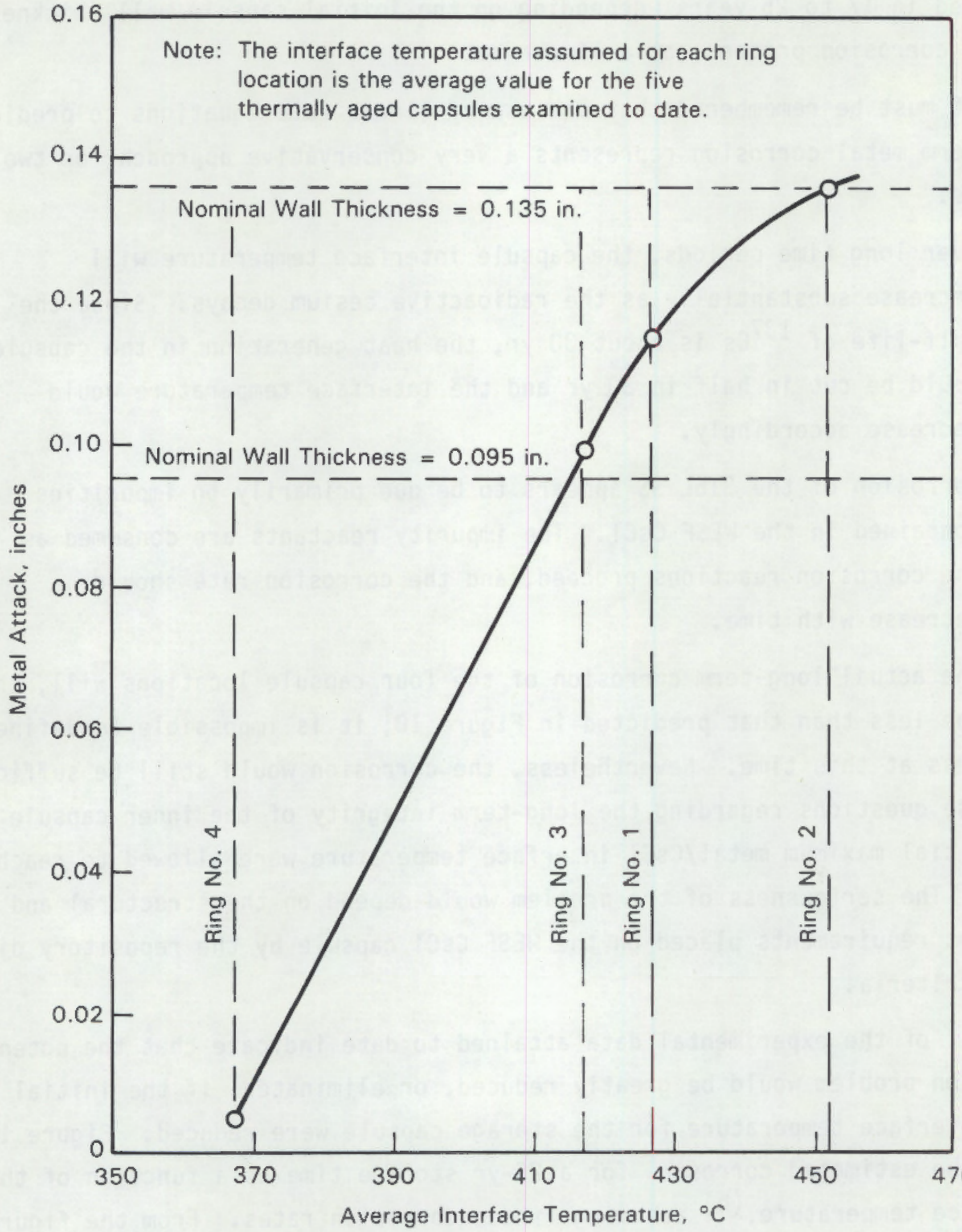


FIGURE 10. Estimated Corrosion as a Function of Interface Temperature for a 25-yr Storage Time, Assuming Linear Corrosion Rates

can be seen that reducing the maximum interface temperature to 350°C should essentially eliminate the corrosion problem.

4.2.3 Estimates of Long-Term Metal Attack

Safe disposal of the WESF CsCl capsules in a geologic repository requires containment of the chloride until the radioactive cesium decays to an innocuous level. Corrosion of the capsule by the cesium chloride at the temperature regime encountered in a repository can threaten the integrity of the WESF capsule. By making some conservative assumptions, the short-term compatibility data obtained to date can be used to estimate long-term corrosion of the WESF 316L SS inner capsule by the CsCl under proposed repository conditions.

It was assumed that the maximum metal/CsCl interface temperature in a repository would be limited to 450°C. The compatibility tests were designed to give the same initial maximum interface temperature. For the reasons discussed in Section 4.1, however, precise control of the interface temperature profile in each capsule was not possible. Therefore, the average interface temperature profile of a thermally aged capsule varied significantly from capsule to capsule. Because each aged capsule was sampled at the same locations, the average interface temperatures for the samples taken from the same capsule location varied over a substantial range (see Table 2). Despite these temperature variations, the compatibility data obtained to date indicate that corrosion of the 316L SS at a specific capsule location proceeds at a linear rate when the interface temperature exceeds about 400°C. This can be seen in Figure 8, where the corrosion data for the Ring 2 samples have been presented.

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