Cesium Chloride Compatibility Testing Program Annual Report— Fiscal Year 1984

**G. H. Bryan
J. R. Divine**

January 1985

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Richland, Washington 99352

SUMMARY

A program was started in FY 1982 to evaluate the compatibility of WESF-produced cesium chloride (CsCl) with 316L stainless steel (SS) under the thermal conditions that will 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 $\sim 450^{\circ}\text{C}$. The capsules are placed vertically in insulated containers and allowed to self-heat to the test temperature, where they are maintained for intervals from 2200 to 32,000 h. After monitored thermal aging, the capsules are destructively examined to determine the extent of metal attack by the cesium chloride. The 17,544 h capsule was examined in FY 1984.

During the course of a prior examination, it was found that one of the aged test capsules exhibited discoloration and pitting on the outer surface of the inner capsule. The damage was attributed to problems encountered in the electropolishing operation, which is used to decontaminate the inner capsule after it is loaded with the CsCl and welded shut. A study was carried out in FY 1984 to a) determine if the pitting was associated with the electropolishing operation, b) identify acceptable solution(s) to the problem, and c) establish the effect, if any, on the long-term integrity of the capsule.

Another special study performed in FY 1984 was that of examining two capsules from the Waste Encapsulation and Storage Facility (WESF) storage pool. The objective was to establish the extent of capsule corrosion while in storage. This report summarizes program accomplishments in FY 1984.

Test capsule No. C-1486 was removed from its insulated container after being held at temperature for 17,544 h. The average maximum metal/CsCl interface temperature for the test period was 454°C . The capsule was shipped to ORNL for sectioning and metallographic examination. ORNL completed the metallographic examination of the capsule, as well as the 8784 h test capsule (C-1451), which had been shipped to ORNL in FY 1983. Metal attack observed in the 8784 h capsule was much less than that observed in the 17,544 h capsule or in the capsule tested for 4392 h. The maximum attack in the 8784 h capsule

was estimated to be about 40 μm (0.0016 in.); whereas the maximum attack in the 17,544 h capsule was estimated to be about 260 μm (0.010 in.).

Although, it is not unusual in compatibility testing to have wide variations in attack with replicate tests, the difference in the level of attack between the 8784 h capsule and the 17,544 h and 4382 h capsule appears to be greater than the variations usually encountered. A plot of the intergranular metal attack observed in each test capsule as a function of exposure time shows that the attack rate appears to decrease with time, as expected. Additional data points are needed, however, to determine with more certainty the form of the corrosion rate equation; the data will be generated from capsules already under test.

It should be noted that the original selection of the 450°C test temperature was based on a projected maximum area/thermal loading limitation of 30 kW/acre in a hypothetical repository. This thermal environment (i.e., 450°C) would never be realized during possible beneficial use applications of CsCl capsules in an irradiator.

The operating parameters for the electropolishing process at WESF were examined for their possible effect on capsule pitting. Within a reasonable range of conditions during normal operations, pitting is not expected. A chloride concentration of 100 ppm, more than believed to be reasonably present in the electropolishing bath, only slightly roughened the surface. Variations in temperature, current density, time, dissolved metal and phosphoric acid concentrations over the expected ranges were also shown to be unlikely causes for the pitting process. The most likely cause of the observed pitting is believed to be the deterioration, with use, of the rack, which leads to non-uniform current distribution. The presence of point contacts between the capsule supports and the capsule leads to rapid localized dissolution of the capsule and the formation of "pits."

The maximum pit depth achieved under worst case laboratory conditions was about 30% of the capsule wall thickness. The strength and ductility of the pitted specimens appear to be sufficient to ensure that the integrity of the WESF capsules is not threatened during service because of the pitting even

consideration was taken of any corrosion of the inner capsule surface by the cesium chloride in the strength and ductility evaluation.

Two WESF cesium chloride capsules were taken from the WESF storage pool and shipped to ORNL for sectioning and examination. Each capsule contained >70 kCi of ^{137}Cs at the time of loading. The two capsules had been in the pool for five and eight years, respectively, at the time of removal. Very little metal attack (25 μm or less) was observed on the interior surface of the inner capsules. Overall, attack observed in the storage pool capsules was about the same as that which occurs during the capsule loading operation. This indicates that the capsules could be stored in a water pool for long periods of time without suffering significant attack.

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1.0 INTRODUCTION

At Hanford, fission product cesium, containing 20-40% ^{137}Cs , has been recovered from the high-level waste (HLW) and converted to cesium chloride (CsCl). Recovery of the Cs, as the 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 storage of the CsCl capsules takes 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 small high-integrity 316L stainless steel (SS) capsules. The CsCl capsules are then stored in water basins on the Hanford Reservation. The CsCl is loaded into the inner 316L SS capsules by melt casting. Each capsule, which has an ID of 2 in. (50.8 mm) and an inner length of of ~19 in. (483 mm), contains up to 3 kg of CsCl . The capsules contain up to ~70,000 Ci of ^{137}Cs , depending on the age and purity of the fission product CsCl .

In order to evaluate the potential hazards associated with the geologic disposal of the WESF CsCl capsules, reliable estimates of long-term attack of the capsule material by the CsCl under disposal conditions are required. Available data on the compatibility of WESF-produced CsCl with 316L SS are not adequate for making the required estimates. The Cesium Chloride Compatibility Testing Program was started at the Pacific Northwest Laboratory (PNL) in FY 1982 to obtain the needed compatibility data. The program will take approximately 5 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 1984.

2.0 OBJECTIVES

The primary objective of the Cesium Chloride Compatibility Testing Program is to evaluate the compatibility of WESF-produced CsCl with the 316L SS capsule material under the conditions that could be encountered in a geologic repository. Sufficient short-term (5 yr) compatibility data are to be obtained with WESF-produced CsCl to permit useful estimates of long-term attack. Secondary efforts during FY 1984 involved: a) defining of the magnitude, severity, and origin of pitting found on the outer surface of some inner capsules, and b) the destructive examination of two WESF storage pool capsules in the same manner as those capsules being aged under potential maximum repository temperature conditions in order to confirm that a corrosion mechanism is not a threat to continued safe storage in a water basin.

3.0 TESTING CRITERIA

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

- the reaction temperature (316L SS/CsCl interface temperature)
- impurities in the WESF-produced CsCl
- changes in the microstructure of the 316L 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 include a detailed testing program to evaluate all of the variables which affect 316L SS/CsCl compatibility, especially with regard to impurity effects. The limited testing program now underway was designed on the following bases:

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

The uncertainties imposed by the last limitation can have a significant effect on 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 ICP results, and an elementary thermodynamic analysis of the 316L/WESF CsCl system were reported in the annual report for 1982 (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, as originally planned, was divided into five tasks.

- radioactive compatibility data lasting up to 32,000 h using standard WESF CsCl capsules aged at elevated temperatures
- heat transfer studies to define the relationship between the surface temperature of the inner and outer capsules of the WESF CsCl capsule
- 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)
- a thermodynamic analysis of the WESF CsCl/316L SS system
- physical property measurements on CsCl-impurity mixtures.

The major emphasis throughout the duration of the program is on the first task. Tasks 2 thru 5 were completed in FY 1982 and the results were reported in the annual report for FY 1982 (Fullam 1982). Activities completed in FY 1984 and discussed in this report include: a) a study of the pitting observed on the outer surface of some WESF inner capsules, and b) the metallographic examination of two cesium chloride capsules taken from the WESF storage pool.

4.0 RADIOACTIVE COMPATIBILITY TESTS

The radioactive compatibility tests are designed to provide the short-term data needed to estimate long-term attack of 316L SS by WESF-produced CsCl at a maximum metal/CsCl interface temperature of 450°C. The data obtained from the tests should meet this requirement within the limitations described in the previous section. Details of the testing procedures and preliminary results are presented in earlier reports (Fullam 1982, Bryan 1983) and are summarized below.

4.1 TESTING PROCEDURES

In the compatibility tests, six standard radioactive 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 2200, 4400, 8800, 17,500, 24,000, or 32,000 h. When thermal aging of a capsule is completed, it is removed from the insulated container, cooled, and shipped to the Oak Ridge National Laboratory (ORNL) for sectioning and examination. At ORNL, small samples are taken from the inner capsule at various locations and subjected to metallographic examination to determine the extent of metal attack by the CsCl.

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

The CsCl capsules used in the compatibility tests are typical WESF-production capsules prepared in the normal manner and meeting all Rockwell and DOE QC and QA requirements. All capsule components were fabricated in the usual manner with one additional step. In order to accurately determine metal attack by the CsCl, it is necessary to know the initial wall thickness of the inner capsules at the points where the samples are taken for metallographic examination. Therefore, the wall thickness of each of the eight inner capsules used in the tests was measured at 18 locations before the capsule was filled

with CsCl. An ultrasonic procedure was used to determine the wall thickness. The results obtained show the wall thickness of an inner capsule is fairly uniform over the length of the capsule along any given longitudinal surface element, with the thickness variations rarely exceeding 0.003 in. The tubing 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 these variations, the initial wall thickness of the inner test capsules are only known, accurately, at the locations where the thickness measurements were made.

Because of the test configuration used, substantial temperature gradients exist between the middles and ends of each capsule. Calibrated chromel-alumel thermocouples are used to measure the temperature profile of the outer capsule. Temperature readings are normally taken on a weekly basis. The inner capsule/CsCl interface temperatures are calculated from the measured outer capsule temperatures using the procedure described in the FY 1982 annual report (Fullam 1982). Figure 1 shows typical temperature profiles for an aged capsule. The temperatures shown in Figure 1 are average values, and some fluctuations, due to other hot cell activities, were observed in the weekly temperature measurements (Fullam 1982, Bryan 1983). Because the capsule temperature is dependent on decay of the radioactive cesium, the temperature will gradually decrease as the cesium decays.

When thermal aging of a test capsule is completed, it is removed from the insulated container, cooled, and shipped to ORNL, where the inner capsule is sectioned for metallographic examination. Four ring sections are cut from each capsule for examination at locations where the initial wall thickness is known (see Figure 2). Referring to Figure 2, Section 2 is taken from the capsule at a point of maximum interface temperature. In each case, this point occurs somewhere between thickness measurement points 5 and 6. Since the variation in wall thickness rarely exceeds 0.001 in. between adjacent longitudinal measurement points on a surface element, the wall thickness for Ring 2 between these points 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 loaded

FIGURE 1. Average Temperature Profile for the WESF Capsule Held at Temperature for 4392 hours

from a different batch of CsCl. Therefore, the chemical composition and cesium isotopic composition of the CsCl in the different test capsules can vary significantly. Table 1 gives the pertinent data on the six capsules used in the thermal aging tests. From the data, one can calculate an approximate ^{137}Cs isotopic concentration for each capsule, but the amount and types of impurities present in each capsule are unknown.

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" 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

NOS. 1-9 INDICATE AREAS WHERE WALL THICKNESS WAS MEASURED

FIGURE 2. Sectioning of the Aged Inner Capsules

TABLE 1. Pertinent Data on the Six WESF CsCl Capsules
Used in the Thermal Aging Tests^(a)

<u>Outer Capsule No.</u>	<u>Inner Capsule No.</u>	<u>CsCl, kg</u>	<u>¹³⁷Cs, Curies</u>	<u>Watts, t</u>
C-1266 (2200 h)	19073-G	2.388	45,870	220
C-1272	19073-B	2.701	56,930	273
C-1351	19073-E	2.597	52,520	252
C-1365 (4400 h)	19073-D	2.472	44,740	214
C-1451 (8800 h)	19073-C	2.756	54,380	261
C-1486 (17,500 h)	19073-H	2.716	51,140	245

(a) As of April 5, 1982.

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

When 316L SS is held in contact with WESF-produced CsCl at temperatures up to 450°C for extended periods of time, it is possible that chemical attack by the CsCl could be enhanced by changes in the microstructure of the metal as a result of thermal aging [i.e., low temperature sensitization (LTS)]. To help determine if thermal aging does result in microstructural changes, control samples of 316L SS are being aged in Argon at 400°C, 450°C, and 500°C for varying times up to 32,000 h. The aged samples are subjected to metallographic examination. The photomicrographs obtained will show what microstructural changes result from the thermal aging.

The control samples were cut from a rejected WESF SS inner capsule. Each sample was sealed in an argon-filled quartz envelope. The samples are heated in muffle furnaces whose temperatures are maintained within $\pm 2^\circ\text{C}$ of the control temperatures using solid state proportioning controllers. The samples are maintained at temperatures for 2200, 4400, 8800, 17,500, 24,000, or 32,000 h (the same time as the radioactive test capsules).

4.2 TEST RESULTS

In examining the test capsules to determine the extent of metal attack by the WESF CsCl, it was not possible to obtain a precise measure of the corrosion. Although the wall thickness of the inner capsule was accurately measured at 18 locations before testing, it was not possible to obtain similar measurements after testing. Adhesion of CsCl to the capsule surface makes it difficult to measure the wall thickness accurately using a micrometer or similar instrument. Determining the wall thickness of mounted specimens was also difficult because of alignment problems. For example, when the metal sample is mounted in plastic, in the hot cell for metallographic examination, the sample alignment could be off from the vertical plane. This mounting alignment error would result in an increase in the measured wall thickness ($15^\circ \approx 5$ mil).

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

4.2.1 "Zero Time" Capsules

Four sections were cut from each "zero time" capsule for examination. The sections were cut from the capsules as shown in Figure 2, except that Ring No. 2 was taken from the area which included thickness measurement location 6. Each sample was subjected to metallographic examination. Estimates of the metal attack, based on the photomicrographs obtained, are given in Table 2. The photomicrographs indicate that filling the capsules with molten CsCl produces relatively little attack of the 316L SS (<0.001 in.). The attack

TABLE 2. Estimates of Metal Attack in the "Zero Time" Capsules

Capsule No.	Depth of Attack, μm (mils)			
	Ring No. 1	Ring No. 2	Ring No. 3	Ring No. 4
19459	10 (0.4)	8 (0.3)	25 (1.0)	25 (1.0)
19073F	18 (0.7)	18 (0.7)	25 (1.0)	18 (0.7)

seems to be somewhat greater in the upper part of the capsules. The attack appears to involve general surface dissolution with some limited grain boundary attack at some locations.

4.2.2 Thermally Aged Capsules

Capsule No. C-1486 was removed from the insulated container after aging for 17,544 h. The capsule was sent to ORNL for sectioning and metallographic examination. Figure 3 shows the average temperature profiles for the capsule during aging.

Oak Ridge National Laboratory completed the metallographic examination of the 17,544 h test capsule, as well as the 8,784 h test capsule (C-1451), which had been shipped to ORNL in FY 1983. Metal attack in the two capsules was estimated from the photomicrographs obtained, and the results are presented in Table 3. Results obtained in the shorter duration test are also included in Table 3. Photomicrographs of the sample taken from the 8784 h and 17,544 h capsules are shown in Figures 4 and 5.

Referring to Table 3, it can be seen that the capsule tested for 8784 h exhibited much less attack than the capsules tested for 4392 and 17,544 h and exhibited obvious intergranular corrosion. Although it is difficult to make quantitative judgment, based on the photomicrographs, it appears that the attack mechanism(s) may be different between the 8784 h and the other two capsules. Both the overall amount and type of attack observed in the 8784 h capsule was similar to that observed in the 2208 h test capsule (Bryan 1983).

Although it is not uncommon, in compatibility testing, to observe wide variations in attack in replicate tests, the difference in the degree of attack between the 8784 h capsule and the 4392 h and 17,544 h capsules are far greater than the variations usually observed. It is difficult to explain, with the

FIGURE 3. Average Temperature Profiles for the WESF Capsule Held at Temperature for 17,544 Hours

TABLE 3. Estimates of Metal Attack^(a) in the Thermally Aged WESF CsCl Capsules

Capsule No.	Exposure Hours	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	415	60 (2.4)	455	30 (.12)	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)	392	40 (1.6)

(a) Minimum attack estimated from photomicrographs, see discussion in text on page 12.

(b) See Figure 2 for ring locations on capsules.

Ring 4 - Location 1

Ring 3 - Location 3

Ring 2 - Location 5

40 μ m

Ring 1 - Location 8

500X

FIGURE 4. Photomicrographs of Samples Taken From the Capsule That was Thermally Aged for 8784 Hours, Showing the Metal CsCl Interface

Ring 4 - Location 1

Ring 3 - Location 3

Ring 2 - Location 5

Ring 1 - Location 8

200 μ m

100X

FIGURE 5. Photomicrographs of Samples Taken From the Capsule That was Thermally Aged for 17,544 Hours, Showing the Metal CsCl Interface

limited data available, why the attack was so much less in the 8784 h capsule. Possible reasons for the reduced attack are as follows:

1. The cesium chloride in the capsule may have contained fewer impurities, which promote metal attack, than the CsCl in the other thermally aged capsules, which have been examined. This is possible because each of the test capsules were filled from a different batch of CsCl.
2. As discussed in an earlier section, it is not possible to tell from the photomicrographs if there has been extensive corrosion of the surface, which markedly reduced the capsule wall thickness. It is possible that this could have occurred with the 8784 h capsule and not with the other aged capsules. Because of the difficulties in measuring the residual wall thickness of the test samples accurately (see page 12), it is difficult to tell if this has taken place. The wall thickness data, as shown below, indicates the inner surface has not moved by dissolution of the metal in the 8784 h capsule, and that the estimates of the attack given in Table 3 are realistic estimates of the total attack.

Ring No.	Wall Thickness		Difference μm (mil)
	Before Loading μm (mil)	After Loading μm (mil)	
1	3350 (132)	3600 (142)	250 (10)
2	3310 (130)	3590 (141)	280 (11)
3	3340 (132)	3630 (143)	290 (11)
4	3420 (135)	3610 (142)	190 (8)

After loading wall thickness measurements of the samples from the 17,544 h capsules produced similar results, again indicating that the attack data given in Table 3 for the 17,544 h capsule are realistic estimates of the total attack.

3. Photomicrographs of the capsule specimens taken from the 8784 h capsule show the presence of a distinct zone several hundred μm deep, adjacent to the inner surface exposed to the CsCl (see Figure 6). A similar zone was not observed at the outer surface of the specimens, and was not observed on any of the samples taken from the other test

Ring 4 - Location 1

Ring 3 - Location 3

Ring 2 - Location 5

Ring 1 - Location 8

400 μ m

50X

FIGURE 6. Photomicrographs of Samples Taken From the Capsule That was Aged for 8784 Hours, Showing an Undefined Zone Adjacent to the Surfaces Exposed to the Cesium Chloride

capsules. The factor(s) which produced the zone and the zones effect on the resistance of the metal to attack by the CsCl have not been resolved. If the microstructure of the zone is significantly different from the typical microstructure of the annealed 316L SS, it could have a pronounced effect on the resistance of the surface to attack by the cesium chloride. Additional work is needed to identify the cause and nature of the zone and its effect on compatibility.

A plot of the metal attack for each ring location observed in the test capsules as a function of exposure time results in the approximated curves shown in Figure 7. As the use of photomicrographs to measure metal attack is somewhat subjective in nature, each point is shown with an estimated error bar. There is some indication the corrosion process is decreasing with time and may be related to the square root of time (i.e., parabolic) with the

FIGURE 7. Metal Attack for Each Ring Location Observed in the Thermally Aged WESF Cesium Chloride Capsules as a Function of Time

possible exception of Ring 2, which could be represented by a straight line. If the corrosion process is assumed to be parabolic, the activation energy (ΔE) is in the neighborhood of 20 Kcal/mole. This number is very uncertain, however, because of the uncertainties in the data. These uncertainties are exaggerated by the short temperature range involved, possible variations in the cesium chloride impurities concentrations between capsules, effects of filling the capsule with molten cesium chloride, variable thermal history of the capsule material, and uncertainties in the corrosion layer measurements. Some improvement of the activation energy should be possible with acquisition of the corrosion data on the capsules that are being maintained at $\sim 450^\circ\text{C}$ for 3 and 4 years.

4.2.3 Metal Control Samples

The 316L SS control samples, which had been held at 400° , 450° , or 500°C for 17,544 h, were subjected to metallographic examinations. The micrographs obtained are presented in Figure 8. The micrographs indicate that aging the alloy at 400° or 450°C for 17,544 h has little effect on the microstructure of the 316L SS, while aging at 500°C produced some grain boundary precipitation. This agrees with results previously reported for the control samples tested for shorter time periods. It should be noted that there has been little indication of grain boundary precipitation in the test capsules held at temperatures up to a maximum of 450°C for 17,544 h.

The evidence of grain boundary precipitation, when the control samples are held at 500°C , suggests an upper operating limit for storage of the WESF CsCl capsules. The presence of grain boundary precipitates could lead to increased attack of the alloy by the CsCl. Therefore, the maximum metal/CsCl interface temperature should be limited to $\sim 450^\circ\text{C}$, where grain boundary precipitation does not appear to be a problem.

4.2.4 Pool Cell Capsules

Two cesium chloride capsules, which had been stored at WESF for five and eight years respectively, were removed from the storage pool and shipped to ORNL for sectioning and examination. Sectioning and examination of the capsules was carried out in the same manner that was used with the thermally-aged capsules.

400°C

450°C

500°C

FIGURE 8. Control Samples of 316 L Stainless Steel Aged for 17,544 Hours at Various Temperatures

The two stored capsules examined were typical WESF CsCl capsules, and each contained more than 70 kCi of ^{137}Cs at the time of loading. Since the capsules were stored in a water pool, the 316L SS/CsCl interface temperature, during storage, was much lower ($<150^\circ\text{C}$) than the interface temperature the test capsules encountered during thermal aging.

Estimates of metal attack in the stored capsules by the CsCl, based on the photomicrographs obtained, are given in Table 4. The photomicrographs of the capsules are shown in Figures 9 and 10. Very little metal attack was observed in the storage capsules. Comparing the results given in Table 4 with the results given in Table 2, for the two "zero time" capsules, indicates that most of the attack observed in the two stored capsules probably occurred during the CsCl loading operation. The results also indicate that the capsules could be stored in a water pool for long periods of time (>100 yr) without suffering significant attack by the CsCl.

TABLE 4. Estimates of Metal Attack in the WESF CsCl Capsules Taken from the Storage Pool

Capsule No.	Storage Time Years	Depth of Attack, ^(a) m (mils)			
		Ring No. 1 ^(b)	Ring No. 2	Ring No. 3	Ring No. 4
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 2 for ring locations on capsules.

4.3 CONCLUSIONS

An evaluation of WESF CsCl capsules subjected to thermal conditions, that might be encountered in a geologic repository, has shown that some attack on the 316L SS takes place at the CsCl/capsule interface. As expected, the rate of attack appears to decrease with time; however, additional data points are needed to project the rate for extended periods of time.

Variations in the level of attack between the 8784 h capsule and the 17,544 h and 4382 h capsules seems to be greater than expected. Additional work is needed to determine why the metal attack is so much less in the 8784 h capsule than in other thermally aged capsules.

Ring 4 - Location 1

Ring 3 - Location 3

Ring 2 - Location 5

200 μ m

Ring 1 - Location 8

100X

FIGURE 9. Photomicrographs of Samples Taken From the WESF CsCl Capsule Which Had Been Held in the Storage Pool for Five Years

Ring 4 - Location 1

Ring 3 - Location 3

Ring 2 - Location 5

200 μ m

Ring 1 - Location 8

100X

FIGURE 10. Photomicrographs of Samples Taken From the WESF CsCl Capsule Which Had Been Held in the Storage Pool for Eight Years

Control samples of 316L SS held in argon at 400°C and 450°C for up to 17,544 h show very little change in the alloy microstructure. Grain boundary precipitation observed in the sample aged at 500°C indicates the maximum capsule temperature should be limited to below ~450°C to preclude grain boundary precipitation that might lead to increased attack of the alloy by CsCl.

Very little attack was observed in the CsCl capsules that were stored in the WESF storage pool for periods of five and eight years. The overall attack observed in these capsules probably occurs during the loading of the capsule with molten CsCl. Water pool storage for extended periods of time (>100 y) without significant metal attack should be possible.

Figure 10. Photomicrographs of samples taken from the WESF CsCl capsules which had been held in the storage pool for eight years.

5.0 CAPSULE CORROSION STUDY

When the 4892 h capsule was opened at ORNL for metallographic examination, the outer surface of the inner capsule was found to be discolored and possibly pitted at several locations. Similar damage had not been observed with the two "zero time" capsules or the capsule aged for 2208 h. Additional work was authorized at ORNL to examine the affected areas and to determine the extent of the possible damage and identify the probable cause(s). A total of seven areas on the outer surface was examined. Photomicrographs of the affected areas were obtained. The photomicrographs indicated extensive pitting had occurred at most of the affected areas. The photomicrographs also indicated the formation of a second phase in most of the affected areas. The maximum attack observed was about 300 μm (0.012 in). This corresponded to about 9% of the initial capsule wall thickness (Bryan 1983).

Prior to the problem observed with the 4392 h test capsule, pitting was observed on the outer surfaces of only a few other WESF CsCl inner capsules. Figure 11 shows the affected areas of one of the capsules.

Evaluation of the pitting problem by PNL and Rockwell personnel suggested that the pitting was associated with the electropolishing operation which is used to decontaminate the inner capsule after it is loaded with CsCl and welded shut. To confirm this, a study was carried out at PNL in FY 1984 to a) determine if the pitting problem was associated with the electropolishing operation, b) identify the probable cause, and c) identify acceptable solutions. Since the electropolishing operation is also used to decontaminate the $^{90}\text{SrF}_2$ capsules prepared at WESF, Hastelloy C-276 (the inner capsule material for the $^{90}\text{SrF}_2$), was studied as well as 316L SS.

The following sections provide the details of the study and summarizes the results obtained.

FIGURE 11. Pitted WESF Capsule. Magnification $\sim 2 \frac{1}{2} \times$

5.1 STUDY OBJECTIVES

The purposes of the PNL investigation of the WESF capsule pitting were the following:

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

5.2 BACKGROUND

Electropolishing procedures were developed in the mid-1970's (Arrowsmith 1978, Allen 1978) for use in decontaminating radioactively contaminated surfaces. Much of the effort was directed towards removal of plutonium from stainless steel (SS) surfaces. There was, however, a concerted effort to design a system for the decontamination of the Hastelloy C276 (SrF_2) capsules. The electropolishing system for the 316L SS CsCl capsules was designed using the information developed from both investigations.

The WESF electropolishing system for the CsCl capsules consists of a vessel with the necessary electrodes. The vessel is a 20 L stainless steel tank equipped with cooling coils. It contains a cylindrical concentric cathode, an air sparger, and a rack to hold the capsule (the racked capsule acts as the anode). The electrolyte is nominally 75% phosphoric acid and is recommended to be used at a temperature of 50°C. Chloride contamination of the bath is possible even though the capsule is thoroughly washed before electropolishing.

Comparison of photographs taken of the pitted WESF capsules, Figure 11, with those of the 4,392 h, 450°C exposure test capsules, Figure 12, shows a similarity in the structure of the "pits." In some cases, actual shallow holes are present. In the majority of the cases, however, the "pit" has a central mound surrounded by a circular channel. An example of the pit morphology is shown in Figure 13 from the 4,392 h test capsule.

FIGURE 12. Inner Capsule Tested at 450°C for 4,392 h, Cesium Chloride Compatibility Program

5.3 PROCEDURE

The cause of the pitting was originally believed to be due to electrical arcing, because the central portion of the pit was raised and resembled the type produced during arcing. Consequently, it was decided to look at a number of variables that might affect the process sufficiently to initiate arcing. Variables thought most likely to have an effect were the concentrations of chloride (direct pit formation as well as changes in film resistance), acid (change in solution conductivity, film properties), and metal ions in solution (formation of deposits), as well as high temperature (change in solution and/or film properties). Other possibilities not initially considered were the high gamma radiation flux (changes in film properties or current efficiency) and the total current passing through a given contact point (localized high rate electropolishing).

FIGURE 13. Pit From the 4,392 h, 450°C Test, Cesium Chloride Compatibility Program

With the exception of the metal ions, each parameter was varied independently of the others. By the nature of the process, the metal ions (iron, nickel, and chromium) built up in the solution as the electropolishing progressed. Three to five values of each parameter were tested within the range specified in Table 5.

All tests were performed on a laboratory scale. The initial tests used nominal 1-in. diameter 316L SS pipe. Later runs were performed with nominal 2 in. diameter 316L capsules rejected from WESF because of dimensional irregularities.

The test rack consisted of either a tantalum frame with four point contact or a tantalum frame with 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.

TABLE 5. Range of Conditions (Experimental Program)

H ₃ PO ₄	45% - 85%
Temperature	40°C - 70°C
Chloride	0 - 500 ppm (in solution; also solid CsCl on metal surface)
Dissolved Metal	0 - 25,000 ppm
Dose Rate	0, 1x10 ⁶ R/H
Current	14 - 80 A
Current Density	175 ASF (amperes per square foot, constant)
Voltage	~8V
Time	5 - 20 min

5.4 RESULTS

The results are given in two sections. Pit Formation describes the postulated growth mechanism and the laboratory efforts to evaluate operating parameters. Metallurgical Examination describes the tensile testing and the metallography of the pits and surrounding metal.

5.4.1 Pit Formation

5.4.1.1 Mechanism

Pitting appears to occur when a rack has suffered some degradation which results in loose connections or rough contacts and which, in turn, causes occasional nonuniform current flow through the capsule supports. It is further assumed that during the racking process or during the polishing, a point contact forms between the support contact and the capsule. This initial point contact is assumed to be on the order of ten mils in diameter (the central post diameter of typical pits is somewhat larger) and five mils high. A simple calculation, considering only heat losses through metallic conduction, shows that if a current of 10 to 80 A passes through a single contact point, the local temperature potentially can lead to concentration of the acid and localized boiling. The exact current temperature relationship is not known; the lower the current, the lower the final temperature will be.

Seventy-five percent phosphoric acid boils at about 130°C (266°F). As the temperature increases at the contact point, the acid concentrates locally; 100% acid boils at 220°C (428°F) as shown in Figure 14. If the published data

FIGURE 14. Isocorrosion Chart for Type 316 Stainless Steel in Furnace-Grade Phosphoric Acid Under Mildly Agitated Conditions (Corrosion Eng. Bulletin)
* Implies an excess of P_2O_5

(Corrosion Eng. Bulletin) on the corrosion rate of 316L SS in boiling phosphoric acid is extrapolated to 100% acid, a phenomenal corrosion rate of 250,000 mpy^(a) (0.5 mil/min) is estimated from the data in Figure 15. If the

FIGURE 15. Corrosion Tests on Nickel-Base Alloys and Type 316 Stainless Steel in Boiling Phosphoric Acid - 316 Stainless Steel data extrapolated to 100% Acid Concentration (Ibid)

(a) 1 mpy = 0.001 in. per year.

acid is concentrated an additional 10% by dehydration of the H_3PO_4 to P_2O_5 , the corrosion rate climbs to about 1,000,000 mpy. Therefore, in a 10 min run it is feasible to predict a penetration of 5 to 20 mils (0.2 to 0.5 mm).

Two other factors are considered in explaining why the "pit" has a center post rather than simply being a hole. If the hot acid attempts to dissolve the center post, the post diameter decreases; the temperature increases to the point that solid phosphates precipitate (and are found in the crevice), inhibiting further dissolution. Continued dissolution of the outer wall of the crevice is inhibited by loss of heat to the bulk metal; the corrosion rate decreases rapidly with decreasing temperature, Figure 15.

As a consequence of the factors described above, the crevice continues to grow, perhaps at an increasing rate as it gets deeper, until it gets hot enough to dry out and stop growing. In some cases, particularly in the laboratory, it is postulated that the geometry is suitable to allow a gas bubble to form, which lifts the contact and allows it to slide and start a new pit.

5.4.1.2 Laboratory Results

In the first set of tests, the effect of dissolved metal buildup was considered. A total of eight samples was electropolished sequentially, with the total charge at the end of the experiment equivalent to 3,400 A min/L (25 g metal/L).^(a) All were polished at a rate of 0.104 ± 0.003 g metal/min and did not have any obvious differences in appearance. Consequently, no effect of dissolved metal on the surface finish, in the range examined, was seen, though the rate of metal dissolution did decrease slightly with time (Figure 16).

The second series of tests examined the effect of acid concentration. As shown in Figure 17, at, or below 75% acid, the amount of metal released per amount of electrical charge passed is essentially constant. Above 75% acid, this ratio, which is equivalent to current efficiency, decreases with increasing current. The conclusion drawn from this test is that 75% is the greatest acid concentration that should be used to effectively electropolish

(a) For a nominal processing of 20 capsules in the 20 L vessel at 175 A and 20 min each, a total of 3,500 A min is accumulated before replacing the solution. Because the anode efficiency is not 100%, less metal is removed than expected. The excess current is used to evolve oxygen.

FIGURE 16. Effect of Dissolved Metal on Polishing Time

FIGURE 17. Metal Dissolution Versus Acid Strength

316L SS and that 175 amperes per square foot (ASF) is an acceptable current density, though lower values would be more efficient. No obvious differences appeared in the specimens until the 45% acid was used. At this concentration the polish was not as uniform as at higher values.

In addition, it is possible to examine the effective resistance of the cell as a function of impressed current. The data in Figure 18 show effective resistance/current plots at two acid concentrations. The bend in the values occurs at ~100 ASF. Below this value, mass transport effects control the polishing; above, other reactions become more and more important. Thus, the current density used is acceptable, though a lower value would be better as is also indicated in Figure 17.

The effect of chloride and temperature were examined concomitantly. As noted in Figure 19, the effectiveness, in terms of metal dissolution rate, increased with increasing temperature. The range was not enough to significantly affect the polish, though the finish at 40°C was not as bright as at 50° and 60°C. At 70°C, the finish began to deteriorate, yielding a bright but roughened surface.

FIGURE 18. Variation of Effective Resistance With Current

FIGURE 19. Effect of Temperature on Polishing Rate at 175 ASF

In contrast, the chloride, though it had no apparent effect on metal removal rate, did affect the quality of the polish. At 40°C, chloride had no apparent effect. At 50°C, the nominal operating temperature, a very slight roughening of the surface was noted at 100 ppm Cl^- . At 60°C, the surface finish was similar to that at 50°C until 200 ppm Cl^- was reached. The surface remained bright, but the roughening was noticeably increased. The 70°C, 0 ppm Cl^- surface was similar to the 50°C, 100 ppm Cl^- , whereas the presence of Cl^- produced a surface roughness comparable to the 60°C, 200 ppm Cl^- . Despite the roughened surface, no sign of major pitting occurred. Slight intergranular corrosion occurred, in the presence of solid chloride, on the surface.

Tests were performed to determine the effect of radiation. Cobalt-60 gamma radiation at a dose rate of 1×10^6 R/H was used. The test specimens had been exposed to molten CsCl to simulate the capsule filling operation. No effect of gamma radiation was observed on the electropolishing step.

An attempt was also made to penetrate a piece of the 0.14 in. thick 316L capsule material using a single contact point. The test ended after 29 min (80 A contact current, nearly double the normal operating value) with a loss of the electrical contact. The estimated penetration was about 1 mm (40 mils) and is believed to be a worst case example.

5.4.2 Metallurgical Examinations

A number of laboratory-produced pits, in WESF-Type 316L capsule tubing and Hastelloy C276, have been examined to evaluate the WESF capsule pitting problem. The morphology and severity of the pitting attack was characterized by scanning electron microscopy (SEM) and optical metallography. Energy dispersive X-ray spectroscopy (EDS) was used to identify the corrosion products within the pits. Tensile tests of the 316L capsule material and electron fractography were used to evaluate the effect of pitting on capsule integrity. Results of these examinations are presented below.

5.4.2.1 Pit Characterization

Thirteen pits produced by PNL on WESF capsule material and three pits in Hastelloy C276 have been examined. The pitting conditions and examinations employed for each sample are summarized in Table 6.

Most of the examinations were conducted on samples that were pitted using a contact current of 80 amperes. This current was selected as a reasonable upper limit for the WESF capsule electropolishing process since it assumes nearly half of the total current used at WESF flows, through a single contact. Ten minutes exposure is twice the recommended interval for repositioning the WESF capsules during electropolishing and was used as the base exposure time for the experiments. Consequently, pits formed under these exaggerated conditions are expected to be more severe than those formed in actual WESF capsules.

Photomicrophotographs were taken to document the location and general characteristics of the pitting attack. Samples were then removed from the tubing for detailed examinations by SEM. Finally, selected samples were prepared, for examination by optical metallography, in cross section to estimate the depth and morphology of attack.

TABLE 6. Summary of Pitting Conditions and Examinations Employed During Pit Characterization Studies

Material	Sample Number	Pitting Conditions			Examination/Technique		
		Contact Current amps	Bath Temperature °C	Time Minutes	Visual	Scanning Electron Microscopy	Optical Metallography (Cross Section)
Type 316L	5A	14	43-46	10	X	X	
"	5B	14	45-48	10	X	X	
"	5C	14	47-50	10	X	X	
"	5E	10	50-51	10	X	X	
"	5F	18	42-45	10	X	X	
"	9A	80	41-50	10	X	X	X
"	9B	80	43-50	10	X	X	X
"	9C	80	40-47	10	X	X	
"	15	80	22-24	5	X	X	X
"	16A	80	40-45	10	X	X	X
"	16B	80	45-51	10	X	X	
"	17A	80	45-60	20	X	X	X
"	17B	80	40-47	10	X	X	
Hastelloy C276	5	80	20-25	5	X	X	X
"	10	80	20-25	10	X	X	X
"	20	80	20-25	20	X	X	X

5.4.2.2 Type 316L Stainless Steel

A variety of pit configurations was observed in the 316L capsule material for samples prepared using a total current of 80 amperes for 5, 10, and 20 min, respectively. The pits, Figures 20, 21, and 22, form by rapid dissolution of the material around contact points with the tantalum support. Both single and multiple pits were observed and no correlation was evident between the pitting conditions and the number of pits on a sample. The pit configuration appeared to depend on the number of contact points and possibly on movement of the tantalum/capsule contact during processing. Similar pits were also produced with lower contact currents, although the pit size and severity of attack was reduced. The minimum contact current for producing pits was about 10 to 14 amperes.

The pitting attack was localized at the contact point. A circular crevice was produced around a central post where contact was made, see Figure 21. Corrosion products within the crevice were highly enriched in phosphorus, and tantalum deposits from the electrode were observed on the central post. Dissolution and undercutting of the central post were also observed in several instances, see Figure 23. This may affect the depth of the pitting attack, although the conditions promoting these processes are not known.

Individual pits (produced using a contact current of 80 amperes) varied from 0.3 to 0.7 mm in diameter and pitted regions up to 4 mm across were found in samples with multiple contact points. Pit crevice depths ranged from 0.5 to 1.0 mm for the five samples examined in cross section. The crevices tended to be rather broad and blunted in appearance. None of the crevices examined showed a crack-like morphology, which could lead to detrimental behavior in the mechanical properties. Crevice depth measurements may not represent the maximum depth because of the difficulty in locating the maximum depth in cross section. However, a depth of 1 mm appeared to be an upper limit for the crevices produced during an 80 ampere-10 min test and, therefore, is considered a near maximum depth for the pits in the WESF capsules. As noted, a similar depth was obtained after a 30 min test.

(a)

(b)

FIGURE 20. Pit Morphology of Type 316L, Sample No. 15 (80 amperes Contact Current-5 Minute Exposure): (a) SEM Micrograph of Tube Surface; (b) Optical Micrograph of Cross Section Through the Pits Shown in (a)

(a)

(b)

FIGURE 21. Pit Morphology of Type 316L, Sample No. 9A (80 amperes Contact Current-10 Minutes Exposure): (a) SEM Micrograph of Tube Surface; (b) Optical Micrograph of Cross Section Through Pit Shown in (a)

(a)

(b)

FIGURE 22. Pit Morphology of Type 316L, Sample No. 17A (80 amperes Contact Current-20 Minutes Exposure): (a) SEM Micrograph of tube surface; (b) Optical Micrograph of Cross Section Through Pits Shown in (a). Note corrosion product (CP) buildup in crevices. This corrosion product was highly enriched in phosphorus.

FIGURE 23. Optical Micrograph Showing Degradation and Undercutting of the Central Posts of Type 316L, Sample No. 16A (80 amperes contact current-10 minutes exposure)

Intergranular corrosion was observed in selected areas on the tube surfaces. This type of highly-localized attack can be particularly detrimental, since it can reach significant depths rapidly under certain material-environmental conditions, and is difficult to detect by cursory examination. Intergranular attack was most severe adjacent to the pits, but diminished rapidly with distance as shown in see Figure 24. Examination of the metallographic cross sections showed no evidence of significant intergranular attack near the base of the pits, Figure 25. Therefore, since most of the intergranular attack was shallow in nature ($\sim 10\ \mu\text{m}$ in depth), it is not expected to seriously affect capsule properties.

5.4.2.3 Hastelloy C276

Pitting attack in Hastelloy C276 was similar to that observed in the Type 316L capsule material. Pits produced during 5, 10, and 20 min exposure, using a contact current of 80 amperes, are illustrated in Figures 26, 27, and 28, respectively. As with the pits formed in 316L, both single and multiple pits were observed in the Hastelloy C276 samples. The pit crevice depth increased

FIGURE 24. SEM Micrograph Showing Intergranular Attack on Tubing Surface Near Pit Edge

from 0.3 to 0.4 mm with increasing exposure time. Attack depths were typically smaller in the Hastelloy C276 material than in 316L for identical exposure conditions. Severe undercutting was noted at longer exposure times in the Hastelloy samples, which may explain the small increase in penetration with increasing exposure time. Corrosion products, highly enriched in tantalum and/or phosphorus, were found in the crevices, consistent with the results from the Type 32 6L material. These observations indicate that the same pitting mechanism applies for both 316L SS and Hastelloy C276, although the details of the attack vary with material; the crevice depth for Hastelloy C276 is expected to be smaller than that of 316L, based on the information in Figure 15. Indications of intergranular attack were identified in the central post regions of many of the Hastelloy samples. This attack was only observed near the surface of the post and near the base of the pit.

Central
Post

Base of
Pit

(a)

(b)

FIGURE 25. Optical Micrographs Showing Smooth Attack Near the Base of Pits: (a) Type 316L, Sample No. 9B; (b) Type 316L, Sample No. 9A. No intergranular attack was observed within the crevice region of the pits.

(a)

(b)

FIGURE 26. Pit Morphology of Hastelloy C276, Sample No. 5 (80 amperes Contact-5 Minutes Exposure): (a) SEM Micrograph of Tube Surface; (b) Optical Micrograph of Cross Section Through the Pit Shown in (a). Slight intergranular attack can be seen in central post region in (b).

(a)

(b)

FIGURE 27. Pit Morphology of Hastelloy C276, Sample No. 10 (80 amperes Contact-10 Minutes Exposure): (a) SEM Micrograph of Tube Surface; (b) Optical Micrograph of Cross Section Through the Multiple Pits Shown in (a).

(a)

(b)

FIGURE 28. Pit Morphology of Hastelloy C276, Sample No. 20 (80 amperes Contact-20 Minutes Exposure): (a) SEM Micrograph of Tube Surface; (b) Optical Micrograph of Cross Section Through the Pit Shown in (a). Note heavy attack and undercutting of central post.

5.4.3 Mechanical Properties

Tensile tests of the WESF 316L capsule material were used to evaluate the effects of pitting on mechanical properties and indicate whether the pits may significantly reduce capsule integrity. Longitudinal tensile specimens containing 0, 1, or 3 pits along the 6.4 by 25 mm gage section and 3.6 mm in thickness were tested. Test temperatures of 25°, 200°, and 450°C were used to cover the maximum temperature range expected in service. Tensile strain rate was $2 \times 10^{-4} \text{ sec}^{-1}$ for all specimens. Temperature was continuously controlled and monitored by thermocouples along the gage section. All tests were performed in air.

The pits were produced using a contact current of 80 amperes for 10 min. A series of tensile specimens containing 0, 1, or 3 pits are shown in Figure 29. Pit depth varied from 0.7 to 0.9 mm (20-25% of wall thickness) while the variation in width was from 1.2 to 1.7 mm. These pit dimensions

FIGURE 29. Tensile Specimens Containing 0, 1, and 3 Pits Along The Gage Section

decreased the cross-sectional area of the tensile specimens by ~5%. Pit dimensions and the decrease in cross-sectional area are probably greater than would occur in an actual WESF capsule. Thus, they indicate an upper limit to the effect of pits on tensile properties.

The presence of pits had only a small effect on tensile properties as indicated in Table 7. The yield and ultimate tensile strengths are plotted as a function of test temperature in Figure 30. The data for a given test temperature varied by less than 10% with the greatest scatter observed for the yield strength measured at 25°C. Kenna and Schultz (Kenna 1983) reported the room temperature yield strength of WESF capsule material to be 328 ± 23 MPa, and the present results are within the scatter of their experimental results on unpitted specimens. Also, the decrease in strength with increasing test temperature follows the expected temperature dependence for Type 316L. Consequently, we conclude pitting will have no significant effect on the strength of the WESF capsules.

A somewhat greater effect of pitting on tensile ductility was observed as illustrated in Figure 31. Total elongation decreased by ~25% in specimens containing pits. Lower elongations were expected in the pitted specimens because of localized deformation in regions of decreased cross-sectional area, but it is difficult to estimate the expected reduction based on geometry. The minimum elongations measured from the pitted specimens were about 40%, which indicates the material retains considerable ductility.

Fracture morphology examinations showed that all tensile specimens failed in a ductile manner. Electron fractograph from pitted and unpitted samples are shown in Figure 32. Specimens tested at elevated temperatures failed by ductile shear rupture along planes orientated at about 45 degrees to the tensile axis. Some regions of normal dimple rupture were seen near the center of specimens tested at 25°C, but the majority of these fractures also occurred by dimple shear rupture. No distinct differences in the fracture surfaces were seen between specimens tested at a given temperature, which indicates pitting had little effect on the fracture mode.

TABLE 7. Longitudinal Tensile Properties of Pitted and Unpitted WESF
316 L Capsule Tubing

Specimen Number	Test Temperature °C	Number of Pits	0.2% ^(a) Yield Strength MPa	Ultimate Tensile Strength MPa	Uniform ^(b) Elongation %	Total Elongation %	Reduction in Area %
3	25	0	309	650	60.5	73.9	69.5
11	25	1	330	656	54.5	59.2	56.2
12	25	3	352	656	53.0	56.8	49.7
1	200	0	239	518	43.8	50.2	57.2
8	200	1	225	512	38.4	41.5	43.2
7	200	3	224	510	35.7	38.3	39.7
2	450	0	202	527	44.5	52.6	44.6
9	450	1	191	506	37.5	39.0	34.8
10	450	3	186	507	39.4	42.3	29.6

(a) 1 ksi = 6.895 MPa.

(b) Elongation at maximum tensile load.

FIGURE 30. Effect of Pitting on the 0.2% Yield and Ultimate Tensile Strength of 316L Capsule Material

In addition, detailed examination of the fracture surfaces near the base of the pits revealed no evidence of intergranular failure or brittle crack initiation in these regions. Typical electron fractographs showing the interface between the pit and the dimpled fracture surface are presented in Figure 33. Extensive deformation occurred prior to fracture, as evidenced by the slip lines and grain distortions in the interface region. This indicates crack nucleation was difficult and that the presence of preexisting pits does not promote brittle failure. The reduced cross-sectional area due to pitting is considered to be the primary cause for the lower ductility in the pitted specimens.

In summary, the tensile test results indicate pitting is harmful only to the extent that it reduced the cross-sectional area of the material. The strength and ductility of the pitted specimens were sufficient to ensure the integrity of the WESF capsules during service.

FIGURE 31. Effect of Pitting on the Total Elongation of 316L Capsule Material

FIGURE 32. Electron Fractographs of Pitted and Unpitted Type 316L Specimens Tested at: (a) and (b) 450°C; (c) and; (d) 200°C; (e) and (f) 25°C. All specimens failed in a ductile manner.

(a)

(b)

FIGURE 33. Electron Fractographs Illustrating Ductile Fracture Characteristics Near the Base of Pits: (a) Tested at 450°C; (b) Tested at 200°C. Both specimens show no indication of local brittle behavior due to the presence of the pit.

5.5 CONCLUSIONS

The study of cause and long-term consequences of the "pitting" on the WESF cesium chloride capsules has found:

- The pitting is caused by a nonuniform current distribution at the rack/capsule contact, which forms localized hot spots. The high temperature causes the acid to become more concentrated through boiling of the acid. The concentrated boiling phosphoric acid causes a high rate of corrosion which forms the crevice.
- The lack of intergranular attack at the base of the crevices and the favorable results of the mechanical testing leads to the conclusion that there will be no long-term failure mechanism accentuated by the pitting, beyond that of having a small hole in the capsule wall with a consequential thinner wall.
- An attempt to penetrate the capsule wall by electropolishing failed after 30 min with the loss of electrical contact. Consequently, the maximum wall penetration is ~40 mils (1 mm), out of a total thickness of 136 mil.
- No justification was found to require examination and repack of the existing capsules. A modification of the rack design is recommended for future work, however, to eliminate the pitting.

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