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CESIUM CHLORIDE COMPATIBILITY TESTING PROGRAM - ANNUAL REPORT, FISCAL YEAR 1982

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DEC 82

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February 9, 1983

Recipients of PNL-4556

Dear Recipients:

Re: Cesium Chloride Compatibility Testing Program
Annual Report - Fiscal Year 1982

Figures 1 and 2 (pages 9 and 12) were reversed in the printing of the document. Please replace the incorrect pages (9-12) with the enclosed pages.

Sincerely,

H. T. Fullam

H. T. Fullam
Staff Engineer
Nuclear Fuel Cycle
Chemistry Section

HTF:lm

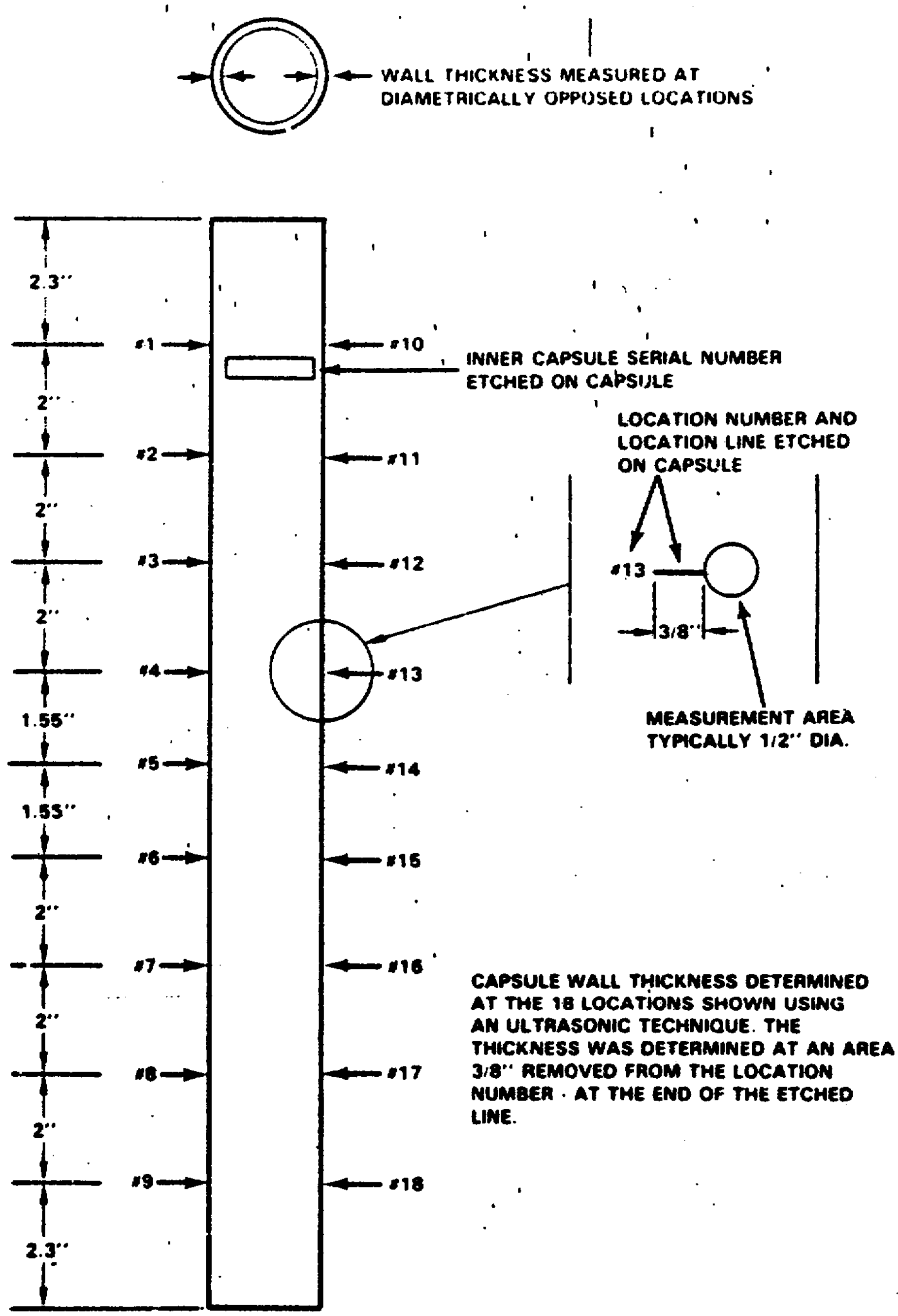

FIGURE 1. Locations Where the Wall Thickness of the Inner WESF Capsules Was Measured

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

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

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

TABLE 2. Pertinent Data on the Six WESF CsCl Capsules Used in the Thermal Aging Tests[a]

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

(a) As of 4-5-82.

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

4.4 CAPSULE AGING

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

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

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

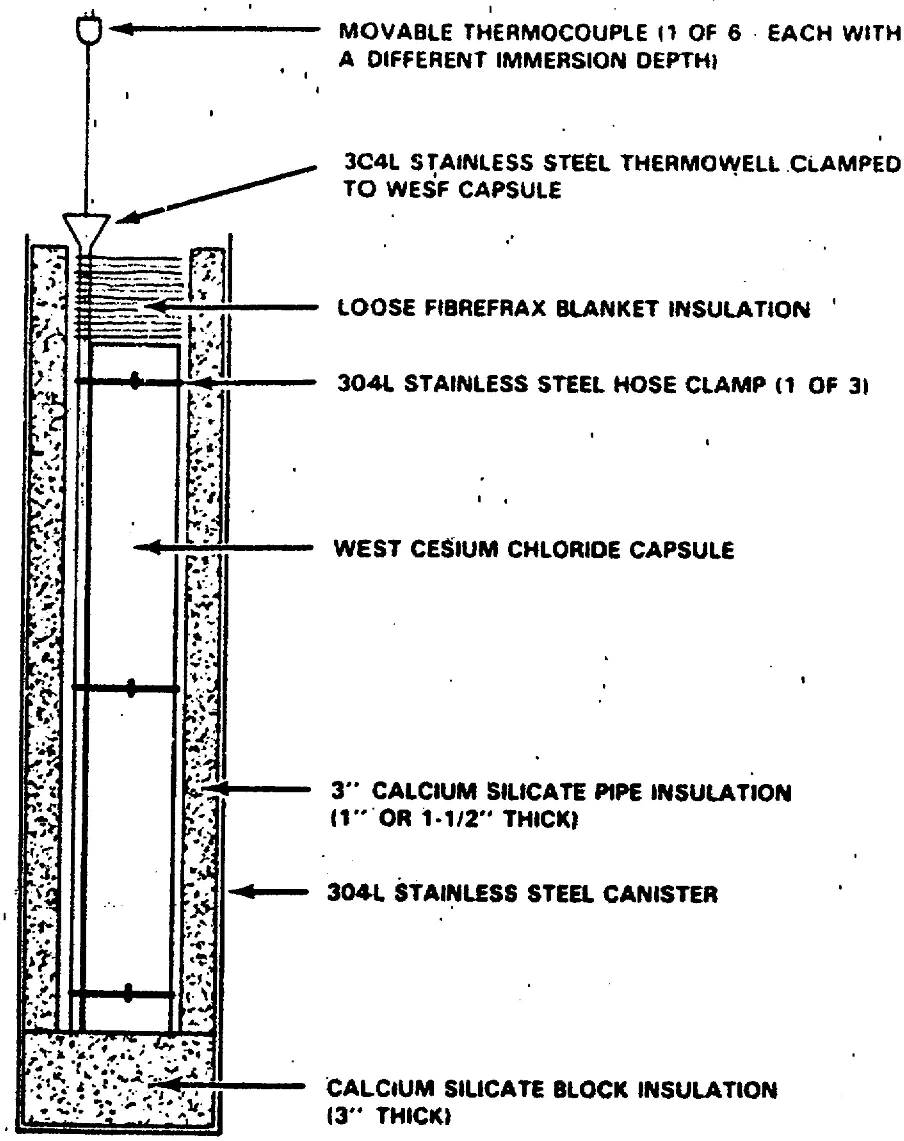

FIGURE 2. Sketch of a WESF Capsule in Its Insulated Container

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Cesium Chloride Compatibility Testing Program Annual Report - Fiscal Year 1982

H. T. Fullam

December 1982

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

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ABSTRACT

A program was started in FY 1982 to evaluate the compatibility of WESF-produced CsCl with 316 L stainless steel under the thermal conditions that would be encountered in a geologic repository. The program is funded through the Long-Term High-Level Defense Waste Program of the Department of Energy. The major part of the program involves compatibility testing of six standard WESF CsCl capsules at a maximum CsCl/metal interface temperature of 450°C. The capsules are allowed to self-heat to the test temperature in insulated containers and then held at temperature for 2,200 to 32,000 hours. After thermal aging, the capsules are destructively examined to determine the extent of the metal attack by the CsCl. This report describes the testing procedure and summarizes the activities completed during the first year of the program.

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1.0 INTRODUCTION

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

The cesium chloride is loaded into the inner 316L stainless steel capsules by melt casting. Each capsule, which has an I.D. of two inches and an inner length of about 19 inches, contains up to three kilograms of cesium chloride. The capsules contain up to about 70,000 Ci of cesium-137, depending on the age and purity of the fission product cesium chloride.

Recovery of the cesium from the high-level waste and its subsequent purification take place in B-Plant. Conversion of the purified cesium to cesium chloride, encapsulation of the cesium chloride, and storage of the cesium chloride capsules take place in the Waste Encapsulation and Storage Facility (WESF). Both facilities are currently operated for the Department of Energy (DOE) by the Rockwell Hanford Operation (RHO).

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

2.0 OBJECTIVES

The primary objective of the cesium chloride compatibility testing program is to evaluate the compatibility of WESF-produced cesium chloride with the 316L stainless steel capsule material under the conditions that would be encountered in a geologic repository. Sufficient short-term compatibility data are to be obtained with the WESF produced cesium chloride to permit useful estimates of long-term attack of the 316L stainless steel by the CsCl under repository conditions.

Secondary objectives of the program are to:

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

3.0 TESTING CRITERIA

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

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

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

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

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

The cesium chloride compatibility testing program is divided into five tasks:

1. radioactive compatibility data lasting up to 32,000 hours using standard WESF CsCl capsules,

2. heat transfer studies to define the relationship between the surface temperature of the inner and outer capsules of the WESF CsCl capsule,

3. chemical analysis of the CsCl from a batch of WESF produced CsCl (the CsCl product from WESF is not analyzed, although the Cs feed solution to WESF is analyzed),

4. a thermodynamic analysis of the WESF CsCl/316L stainless steel system,

5. physical property measurements on CsCl-impurity mixtures.

The major emphasis throughout the duration of the program is on the first task.

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 stainless steel by WESF-produced CsCl at a maximum metal/CsCl interface temperature of 450°C. The data obtained from the tests should meet this requirement, within the limitations described in the previous section.

4.1 TESTING PROCEDURE

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

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

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

4.2 CAPSULE FABRICATION

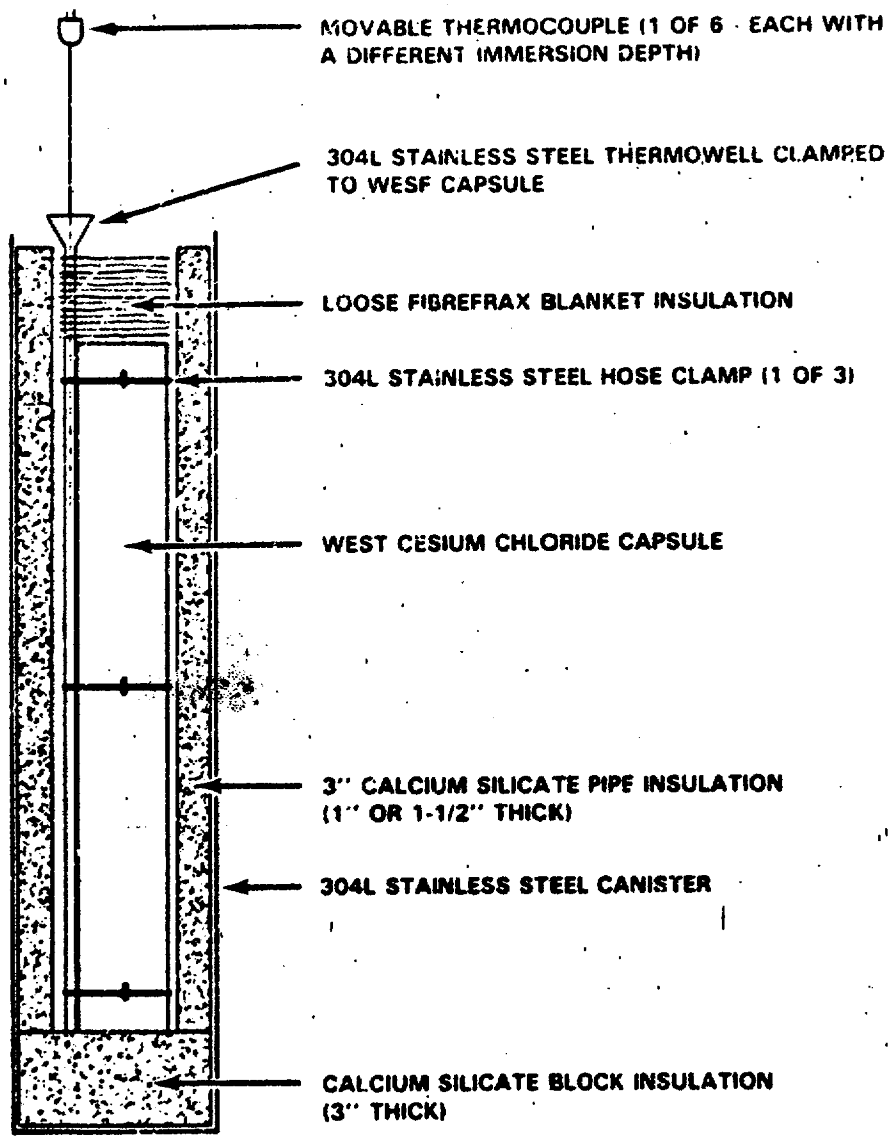
The CsCl capsules used in the radioactive compatibility tests are typical WESF-production capsules prepared in the normal manner and meeting all RHO and DOE QC and QA requirements. All capsule components were fabricated in the usual manner with one exception. In order to accurately determine metal attack by the CsCl, it is necessary to know the initial wall thickness of the inner capsules at the points were the samples are taken for metallographic examination. Therefore, the wall thickness of each of the eight inner capsules used in the tests was measured at the 18 locations shown in Figure 1 before the capsule was filled with CsCl. An ultrasonic procedure was used to determine the wall thickness.

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

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

4.3. ZERO-TIME CAPSULES

The two "zero-time" inner capsules were filled with CsCl in the normal manner. After removal from the loading apparatus, the CsCl was removed from the two capsules by water leaching. Each empty capsule was rinsed and 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



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	3	0.1330	12	0.1417
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	5	0.1315	14	0.1414
	6	0.1310	15	0.1419
	7	0.1315	16	0.1399
	8	0.1319	17	0.1411
	9	0.1307	18	0.1422
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	3	0.1458	12	0.1318
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(a) As of 4-5-82.

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

4.4 CAPSULE AGING

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

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

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

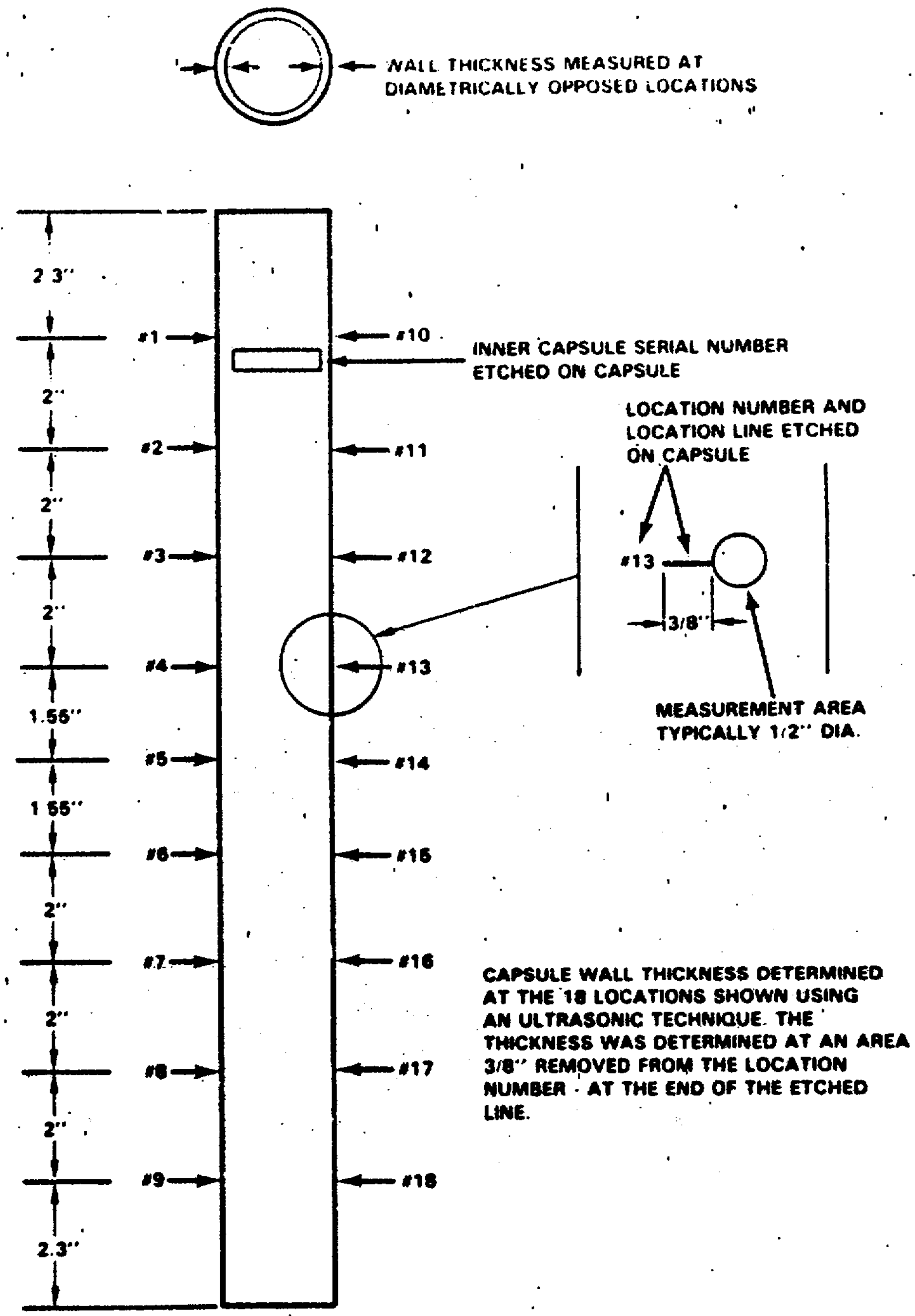

FIGURE 2.. Sketch of a WESF Capsule in Its Insulated Container

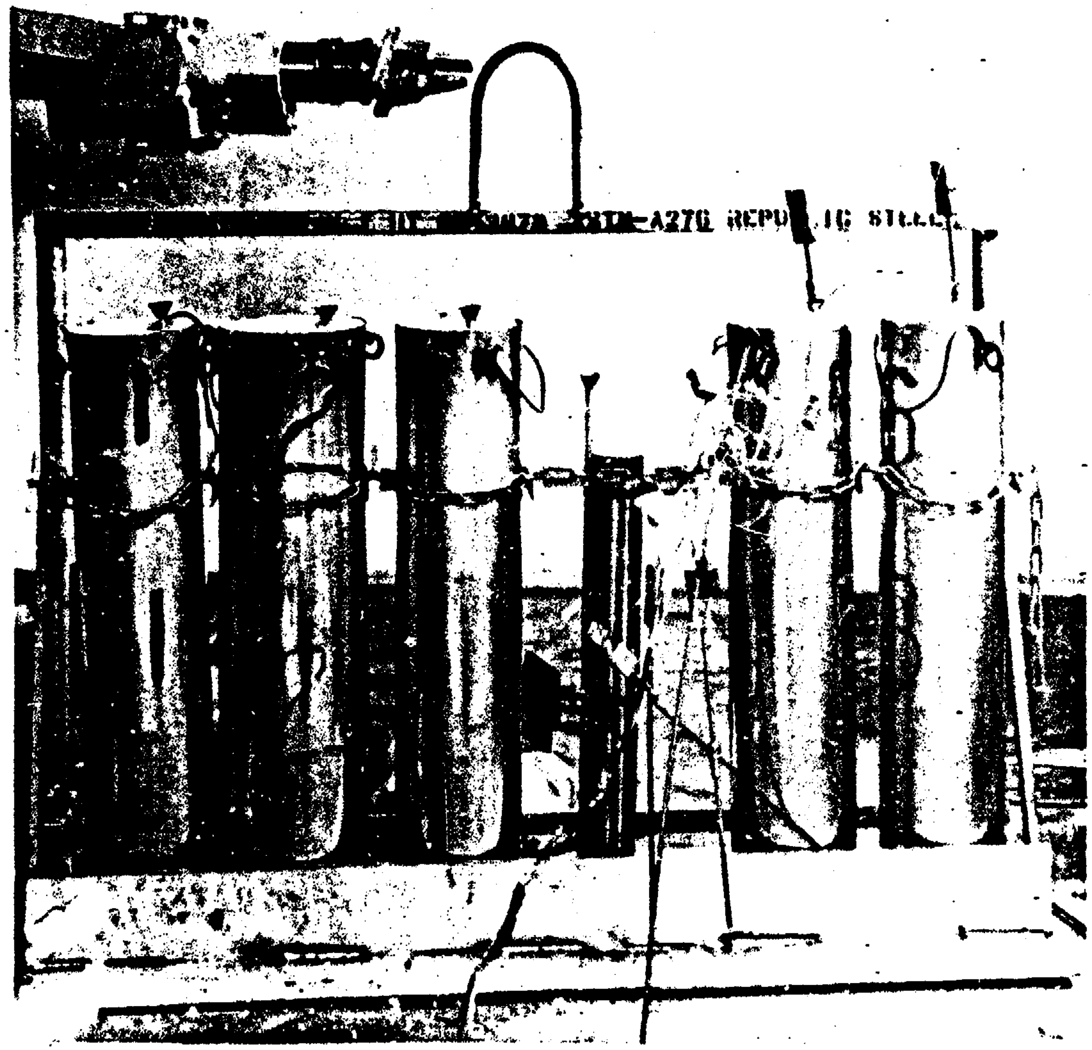

FIGURE 3. The Insulated Containers in a Holding Rack in the Hot Cell

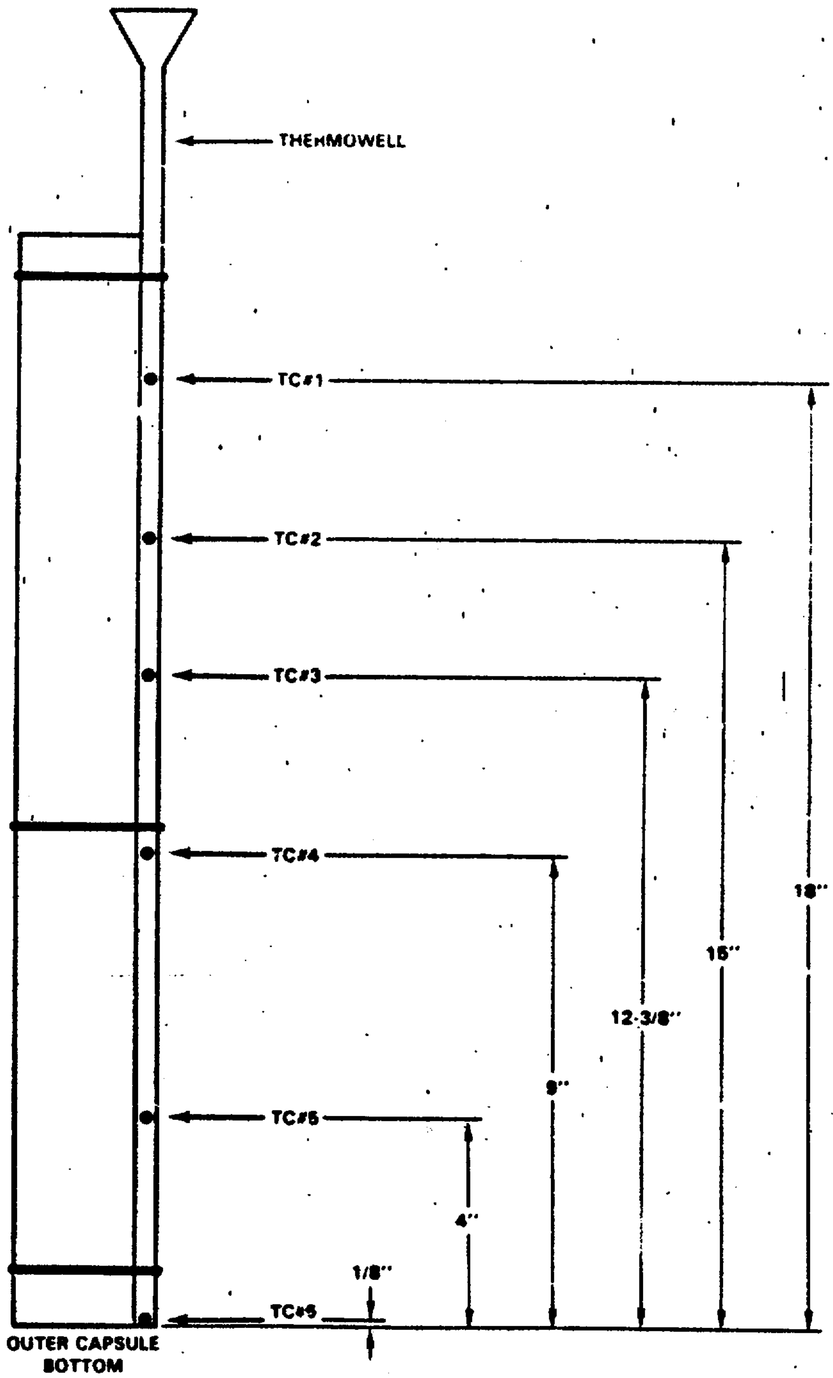

FIGURE 4. Locations Where the Capsule Surface Temperatures are Measured

obtained on a periodic basis. As will be shown later, substantial temperature gradients exist between the middle and ends of each capsule. The temperature readings are normally taken on a weekly basis.

The temperature readings obtained provide a measure of the surface temperature of the outer capsule. It was impossible to measure directly the inner capsule/CsCl interface temperature. Therefore, the inner capsule/CsCl interface temperature must be calculated from the outer capsule surface temperature. In order to determine the relationship between the outer capsule surface temperature and the inner capsule/CsCl interface temperature, extensive heat transfer studies were carried out with an electrically heated dummy WESF capsule. These studies are discussed in Section 4.7. Data from the heat transfer studies were also used to design the insulated containers to assure the test capsules reached the required aging temperature.

4.5 CAPSULE SECTIONING AND EXAMINATION

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

The thermally aged inner capsules will be sectioned in slightly different locations than the zero-time capsules. This is necessary because of the temperature gradients that exist over the length of the test capsules during aging. The maximum interface temperature does not correspond to any of the four locations where test samples were taken from the zero-time capsules. Sectioning of the aged capsules will be adjusted so that a sample is obtained at the surface element passing through the measurement areas and the point of maximum temperature. Since the initial wall thickness along a surface element of a capsule does not vary by more than 0.001-0.003 inches, the initial wall

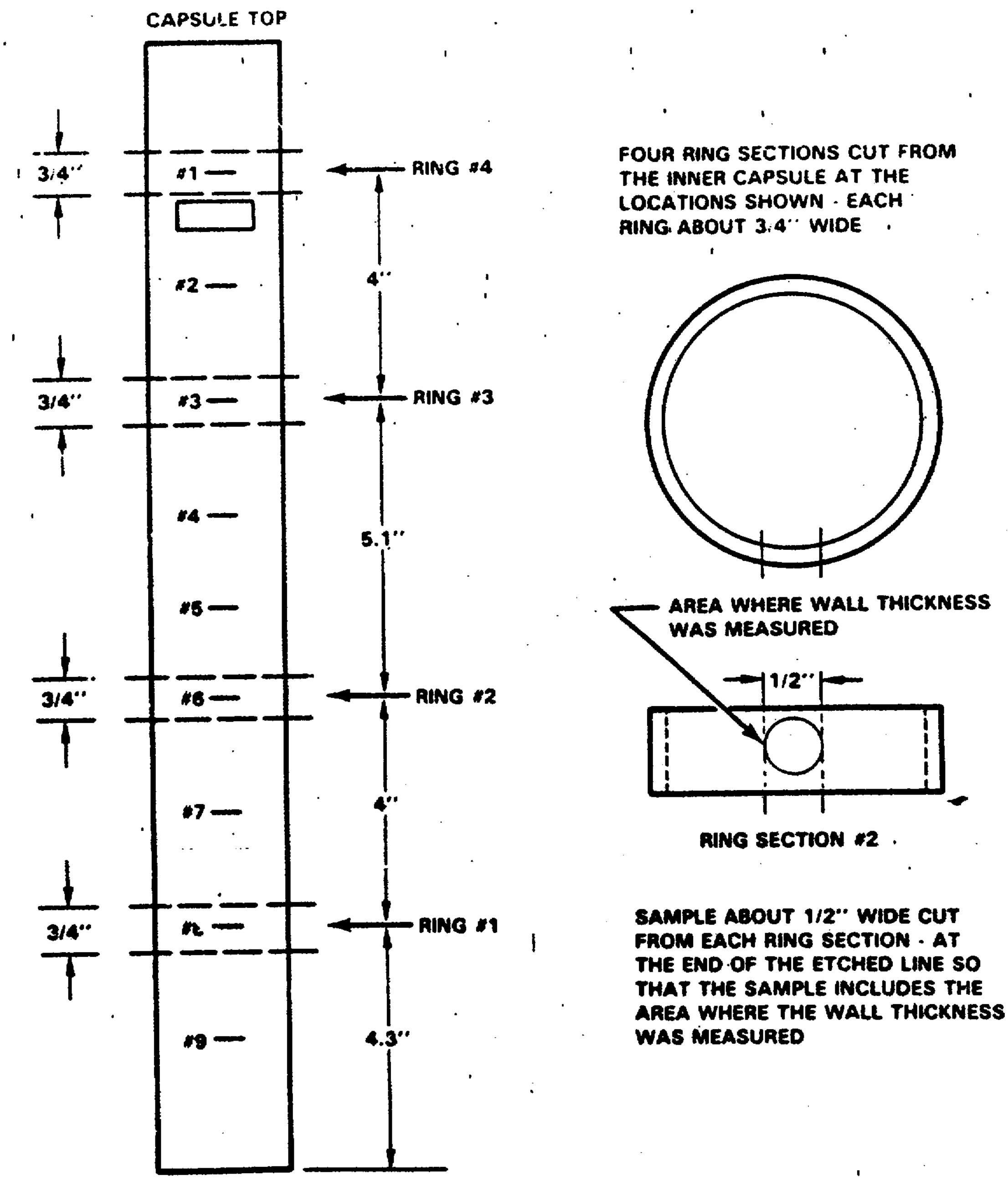

FIGURE 5. Sectioning of the Zero-Time Inner Capsules

thickness at the point where the sample is taken will be known with sufficient accuracy.

4.6 METAL CONTROL SPECIMENS

When 316L stainless steel is held in contact with WESF-produced CsCl at temperatures up to 450°C for extended periods of time, it is possible that chemical attack by the CsCl could produce changes in the microstructure of the metal. The thermal aging of the 316L stainless steel may also produce changes in its microstructure. To help differentiate between microstructural changes produced by thermal aging and those resulting from chemical attack, control samples of 316L stainless steel are being aged in argon at 400°, 450°, and 500°C for varying times up to 32,000 hr. 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 stainless steel inner capsule. Each sample was sealed in an argon-filled quartz envelope. The samples are heated in muffle furnaces whose temperatures are maintained within ±2°C of the control temperatures using solid state proportioning controllers. The samples are maintained at temperature for 2000, 4000, 8000, 16,000, 24,000, or 32,000 hours (the same times as the radioactive test capsules).

4.7 HEAT TRANSFER STUDIES

A large number of heat transfer studies were carried out using an electrically heated dummy WESF CsCl capsule. The objectives of the studies were to:

- determine the relationship between the outer capsule surface temperature and the inner capsule surface temperature (the inner capsule surface temperature and the inner capsule/CsCl interface temperature were assumed to be the same), and

- obtain the heat transfer data needed to design the insulated containers used in the radioactive compatibility tests.

The electrically heated dummy capsule was fabricated from standard 316L stainless steel WESF inner and outer capsules. The dummy capsule was mounted vertically in an insulated container for the heat transfer tests. A 0.5 in. dia. 500 watt cartridge heater was used to heat the capsule. The heater was inserted in the inner capsule through holes drilled in the tops of the inner and outer capsules. Power to the heater was controlled with a variable transformer. Heater voltage was measured with a digital voltmeter and the heater current with an AC ammeter. A narrow slot was machined the length of the outer surface of the inner capsule to serve as a thermowell. The slot was covered with a thin strip of 316L stainless steel sheet welded to the capsule surface. A movable thermocouple inserted in the slot served to measure the capsule temperature at various locations along its length. Small holes in the endcaps of the inner and outer capsules provided free movement of the thermocouple.

Four thermowells, fabricated from stainless steel tubing, were welded lengthwise to the outer capsule surface 90° apart. A fifth stainless steel thermowell was fastened to the outer capsule using three stainless steel hose clamps. Five movable thermocouples placed in the thermowells were used to measure the outer capsule surface temperature at various locations along the capsule length. A loose thermocouple was also placed in the space between the outer capsule and the pipe insulation around the capsule. Outputs of the seven thermocouples were monitored with a multipoint digital thermometer.

All of the thermometers and the measuring instruments were calibrated prior to use.

The dummy capsule was mounted vertically in the insulated container. The container was lined with three inches of block insulation on the bottom and pipe insulation on the side. The capsule was covered with loose blanket insulation. The thickness of the pipe insulation could be varied from one to three inches. Figures 6 and 7 show top and side views of the dummy capsule and insulated container.

In carrying out a test, a constant voltage was applied to the heater and the system was allowed to come to thermal equilibrium. When equilibrium was reached, the inner and outer capsule surface temperatures were measured. By moving the thermocouples up and down the length of the capsules, temperature profiles of the inner and outer capsules were obtained as a function of power

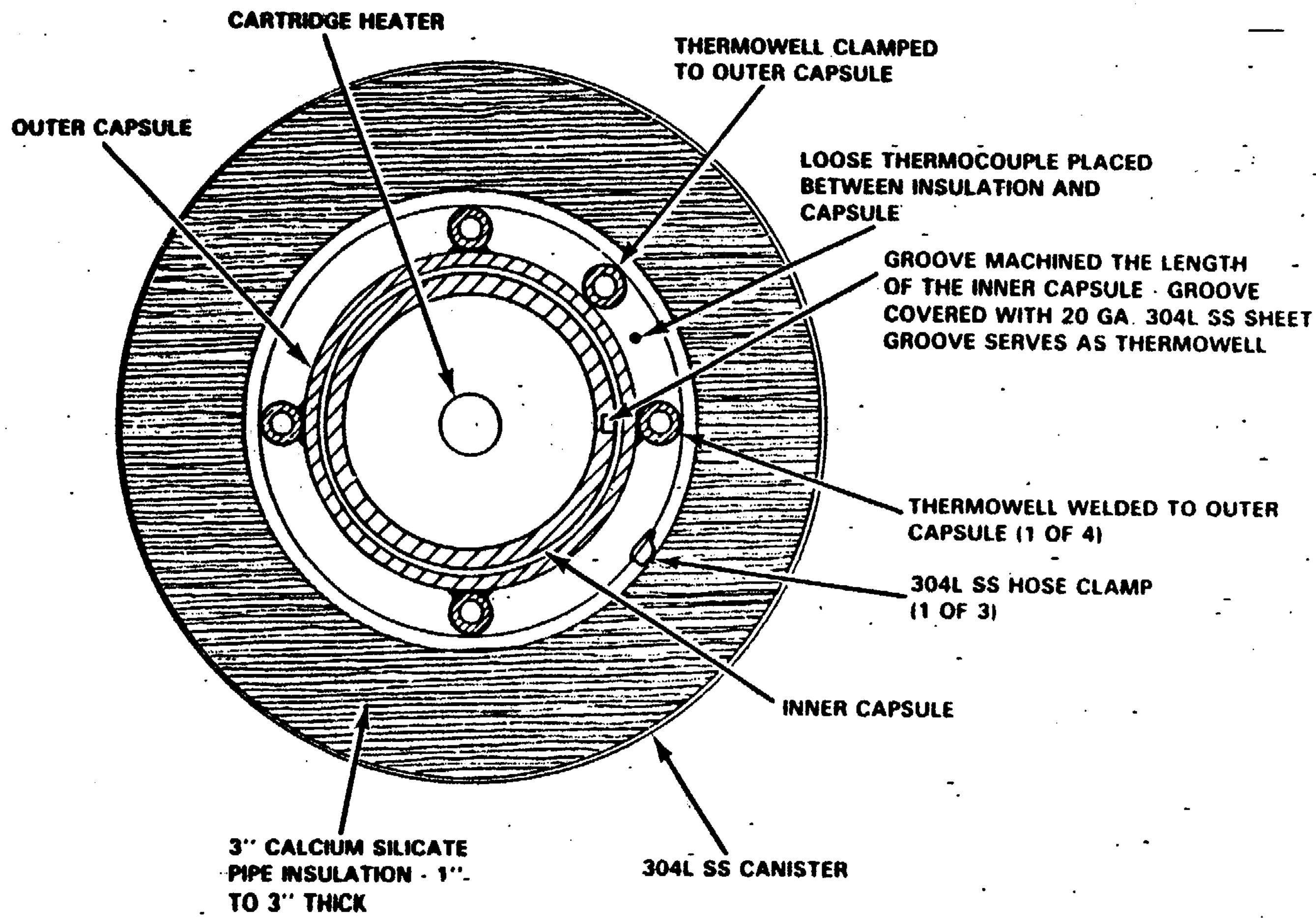

FIGURE 6. Top View of the Electrically Heated Dummy Capsule and Insulated Container

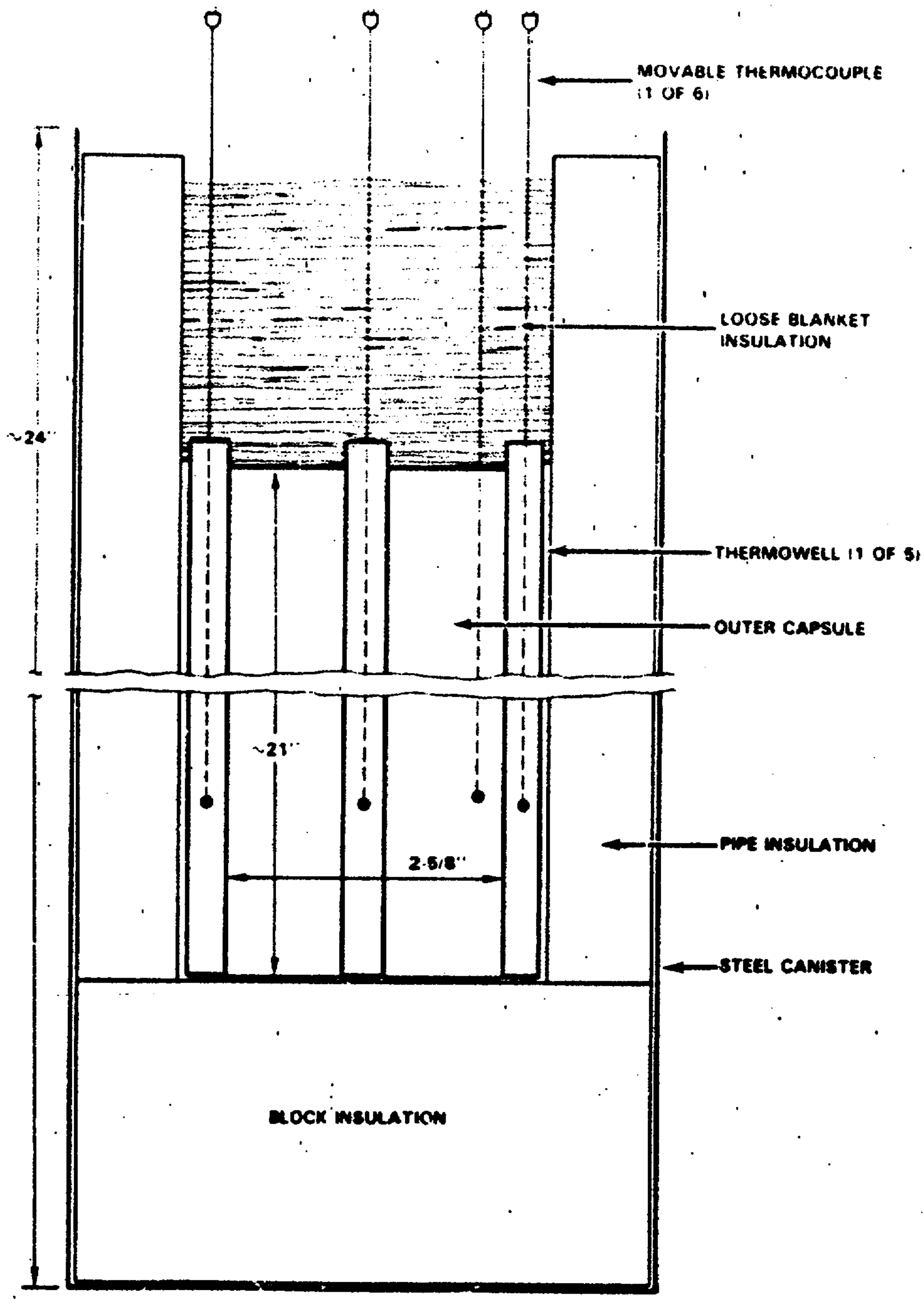

FIGURE 7. Side View of the Dummy Capsule and Insulated Container

input to the heater and insulation thickness. Figure 8 shows the results obtained at a power input of 141 watts using 1.5 inches of pipe insulation. Similarly shaped curves were obtained with other power inputs and thicknesses of insulation. The results show that a significant temperature gradient exists between the middle and ends of the capsules. The maximum temperature of both the inner and outer capsules occurs nine inches up from the bottom of the outer capsule regardless of the power input to the heater and the thickness of the pipe insulation around the capsule. At each elevation, the four thermocouples in the welded thermowells agreed with each other within 5°C. This was true even if the inner capsule was touching the outer capsule along one side. At a given elevation, the thermocouple in the thermowell clamped to the outer capsule read 7° to 14°C lower than the average of the four thermocouples in the welded thermowells, depending on the power input and insulation thickness. The loose thermocouple positioned between the capsule and the insulation gave the same reading, within ±1°C, as the thermocouple in the clamped thermowell at the same elevation.

Referring to Figure 8, it can be seen that the ΔT between the inner and outer capsules varied with the elevation. The ΔT also varied with the power input to the heater and the thickness of the pipe insulation. It is interesting to note that even at the bottom of the capsule where the inner and outer capsules were in direct contact, there was still a ΔT of 10°-20°C between the two capsules.

Sufficient heat transfer tests were run to determine the ΔT between the inner and outer capsules as a function of elevation, power input, and insulation thickness. From these data, the insulated containers were designed to give the desired maximum 316L stainless steel/WESF CsCl interface temperature of 450°C. The design was complicated by two factors:

- the decay energy of the six WESF capsules varied from 214 to 273 watts (as of 4-5-82), thus requiring different thicknesses of insulation around the capsules, and

- there is marked disagreement between various sources on how much of the cesium-137/barium-137m decay energy is absorbed within the WESF capsule.

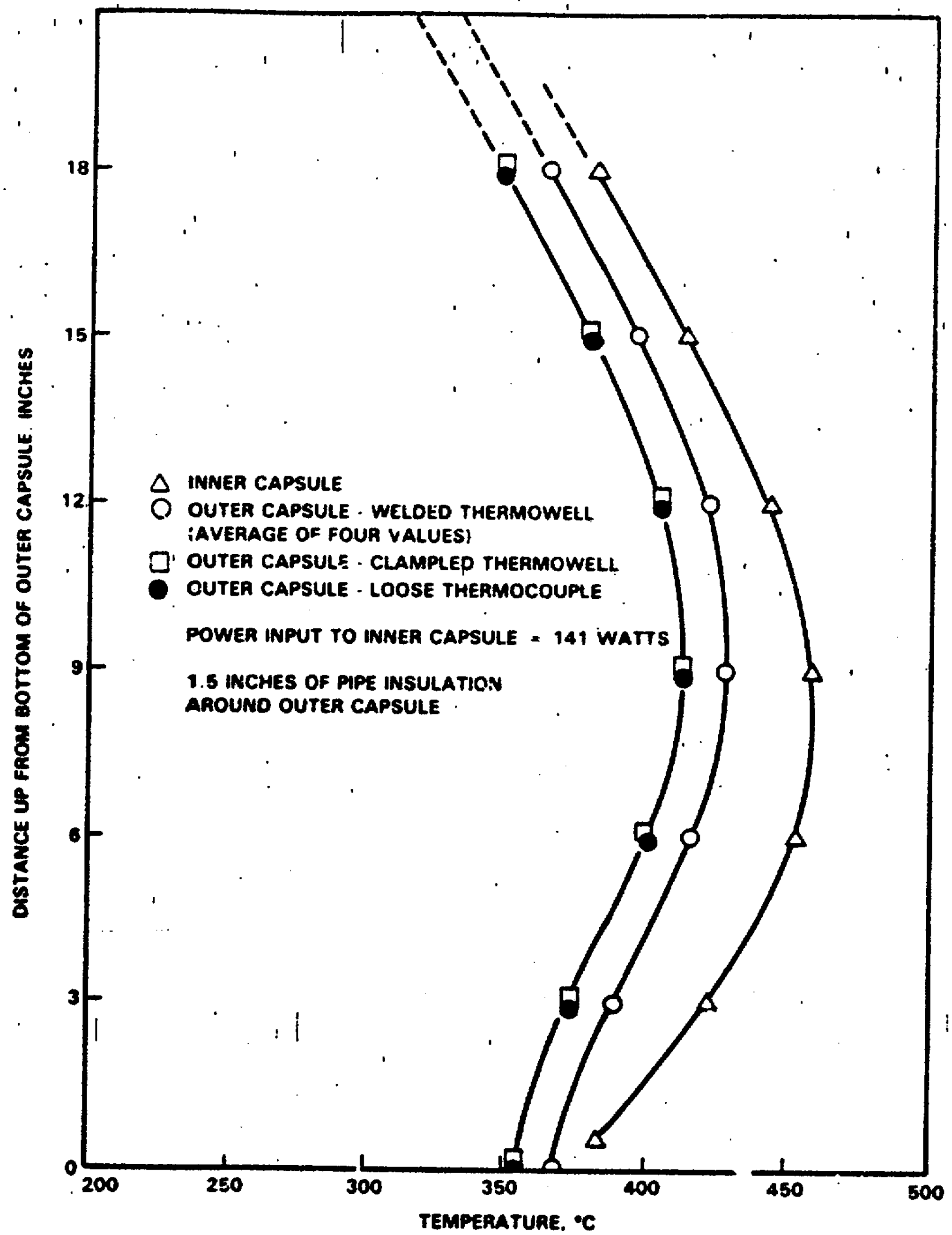

FIGURE 8. Typical Capsule Temperature Profiles Obtained Using the Dummy Capsule

In designing the insulated containers, it was assumed that 55-60% of the decay energy is absorbed in the capsule. Subsequent results with the six WESF capsules indicated that 57 to 62% of the energy was absorbed in the capsule. As will be shown in Section 4.8.2, the design of the six insulated containers was sufficient to maintain the average maximum metal/CsCl interface temperature of each capsule between 450° and 460°C.

4.8 PRELIMINARY TEST RESULTS

4.8.1 Zero-Time Capsules

The two zero-time capsules were shipped to ORNL in April for sectioning and examination. The capsules were sectioned as described in Section 4.5. Metallographic examination of the eight samples taken from the two capsules has been completed by ORNL. Prints of the photomicrographs obtained were not received at PNL, however, in time for inclusion in this report. Preliminary observations of ORNL staff indicated that none of the test samples exhibited significant attack. Detailed evaluation of the micrographs will be needed, however, to confirm this conclusion.

4.8.2 Thermal Aging Tests

Thermal aging of the six WESF capsules was started in April 1982. Aging of the 2000 hr capsule was completed in July 1982 (the capsule was actually maintained at temperature for 2208 hours). Shipment of the capsule to ORNL for sectioning was delayed until September because of problems with the in-cell transfer crane and unavailability of the NRBK-43 shipping cask. During the time between the end of the test and shipment to ORNL, the capsule was held in the hot cell; the maximum 316L stainless steel/CsCl interface temperature during the period averaged 130°C. Holding the capsule at a maximum temperature of 130°C for about two months is not expected to have a significant effect on the attack of the metal by the CsCl.

Sectioning and examination of the 2000 hr test capsule was scheduled to be completed by the end of FY 1982. The delays in shipping the capsule to ORNL prevented this milestone from being met. Examination of the capsule should be completed by the end of November 1982.

Figure 9 shows the temperature profiles for the capsule aged for 2208 hours. The temperature profiles are similar to those obtained with the electrically heated dummy capsules and are typical of the six WESF test capsules. The temperature profiles shown in Figure 9 represent the average surface temperatures for the test period (2208 hours). Considerable fluctuations in surface temperature were observed and continue to be observed between measurements. Figure 10 shows the inner capsule surface temperature for capsule No. 1486 which has been under test for 3192 hours. The temperature fluctuations observed with capsule No. 1486 represent the worst case situation. The other capsules exhibit similar temperature fluctuations, but they are less severe than those shown in Figure 10.

It is difficult to explain the rather large temperature fluctuations observed. Since the heat output of each capsule is essentially constant over the time spans under consideration, the variations cannot be explained by changes in the energy absorbed within a capsule. Fluctuations in cell air temperature and air flow could account for some of the variations, but it is unlikely they could account for the magnitude of the fluctuations observed. Tests with the electrically heated dummy capsule showed that the thermocouples used to measure the surface temperature reached a constant temperature within ten minutes after being inserted in the thermowell. Since the test thermocouples are placed in the thermowells at least 20 to 30 minutes before the readings are taken, they should have reached a constant temperature when the readings were taken. Overall, it appears likely that the the temperature fluctuations observed are the result of several unrelated factors.

The test criteria call for the capsules to be held at a maximum metal/CsCl interface temperature of 450°C. Because of the differences in the decay energies of the six capsules, it was impossible to bring all six capsules to exactly 450°C. As shown in Table 3, however, the average maximum temperatures of the six capsules are being maintained between 451°C and 458°C; which is adequate control for the tests.

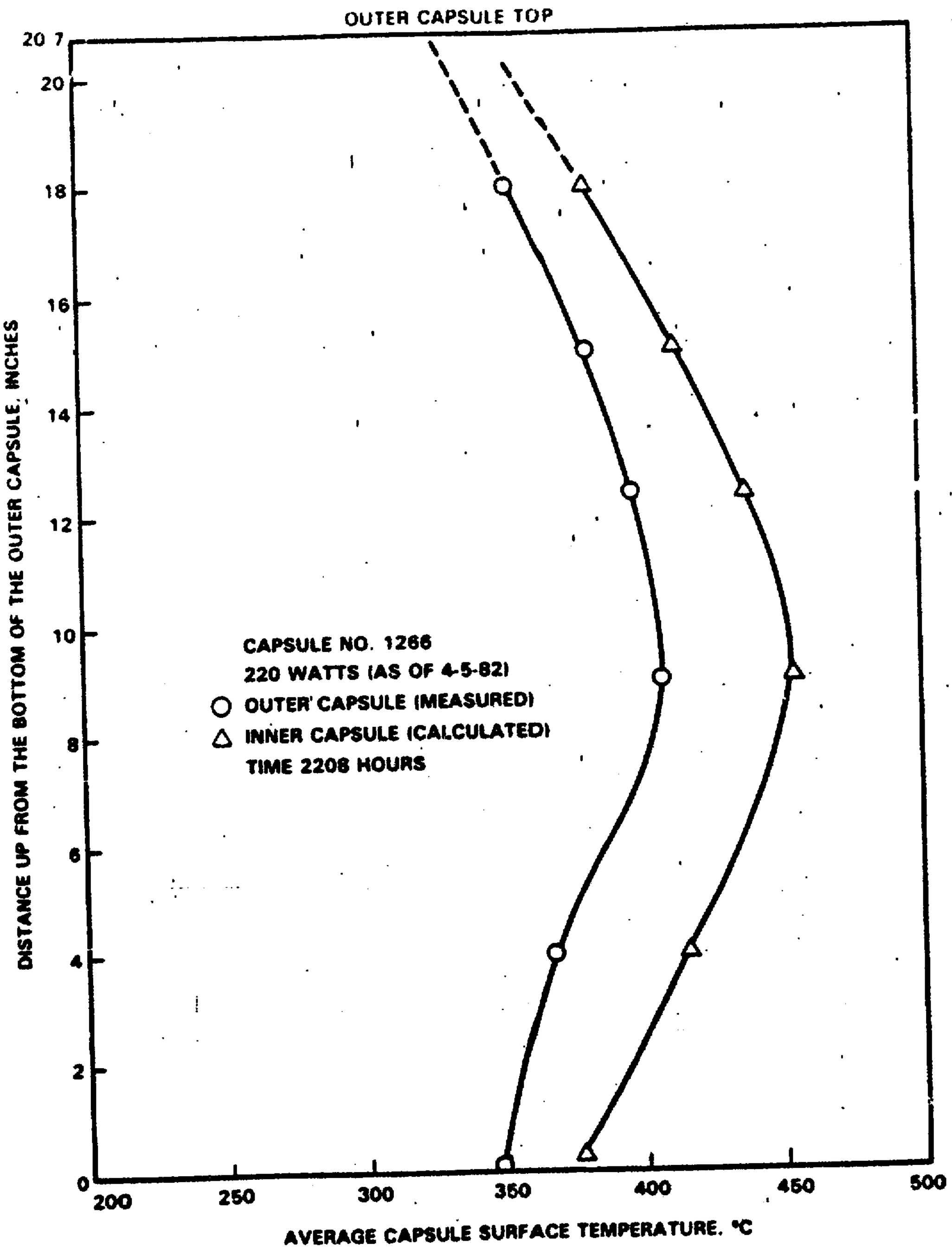

FIGURE 9. Average Temperature Profiles for the WESF Capsule Held at Temperature for 2208 Hours

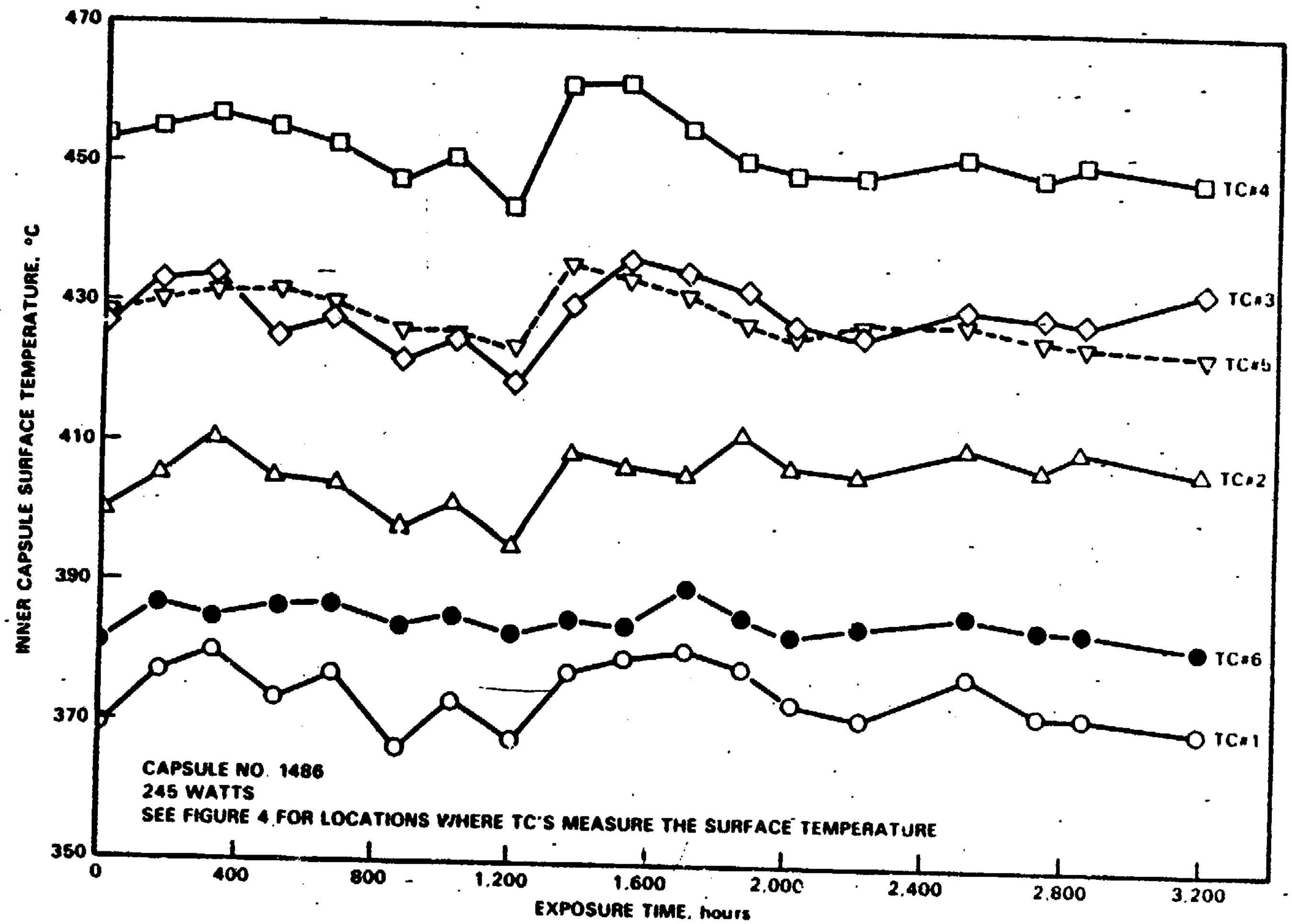

FIGURE 10. Temperature Fluctuations Observed With Capsule No. 1486 as a Function of Time

TABLE 3. Maximum Test Temperatures for the Six WESF Cesium Chloride Capsules

Capsule No.	Exposure Hours	Number of Readings	Average Maximum Temperature(a) °C
1266	2208	14	455±4
1272	3360	18	456±6
1351	3192	18	453±4
1365	3192	18	451±5
1461	3192	18	458±4
1486	3192	18	453±8

(a) Average maximum inner capsule surface temperature for the exposure time shown.

5.0 CHEMICAL ANALYSIS OF WESF-PRODUCED CESIUM CHLORIDE

The cesium chloride produced at WESF is not analyzed for impurities. The cesium feed solution to WESF is analyzed periodically, but it is impossible to tell from the feed solution data what is the impurity content of each batch of CsCl. The WESF specification for the feed solution requires that the molar ratio of Na + K + Rb to Cs be <0.15. If one assumes that the Na, K, and Rb are present in equimolar concentrations in the feed solution, the maximum permissible concentrations of NaCl, KCl, and RbCl in the CsCl would be about 1.6 wt%, 2.0 wt%, and 3.3 wt%, respectively. If potassium were the only impurity in the feed solution, its concentration in the CsCl would be <6.2 wt%. The problem is further complicated by the corrosion of process equipment in WESF whick can add impurities to the CsCl. Certain impurities, such as chlorides of iron and chromium, are expected to have a detrimental effect on the compatibility of the WESF CsCl with the 316 L stainless steel capsule, even when present in low concentrations.

Because of the high radiation levels associated with the ^{137}Cs, large dilutions are required prior to analysis of WESF CsCl solutions using the lightly shielded analytical equipment currently available at Hanford. This prevents the accurate determination of low level impurities in the WESF CsCl.

As part of the current program, a limited study was undertaken to see if the cesium could be adequately separated from the impurities to permit reliable analysis of the impurities using available analytical procedures. Several ion exchange and solvent extraction procedures were evaluated, but none provided the required separation.

In order to obtain some measure of the impurity content of the WESF CsCl, it was decided to use the dilution approach and have RHO analyze the diluted CsCl solution using the ICP. A single sample of CsCl was taken from one of the batches of CsCl used to fill the zero-time capsules. A weighed amount of the sample was dissolved in reagent grade nitric acid. A small aliquot of the solution was diluted with ultrahigh purity nitric acid, and samples of the diluted solution analyzed by ICP. A "blank" solution prepared in a similar manner was also analyzed using the ICP. The total cesium in the solution was determined chemically, and the cesium-137 content radiochemically. Estimates of the impurity content of WESF CsCl, based on the ICP results, are given in Table 4. The ICP data showed the iron content of the CsCl to be very high and nonreproducible; indicating probable contamination of the solution. The cesium-137 isotopic content of the CsCl sample was determined to be 26%.

Additional work on determining the impurity levels in the WESF-produced CsCl are needed, especially with regard to the iron content. The program's scope in FY 1983 does not include continuation of the analytical activities.

TABLE 4. Estimates of Impurity Levels in WESF CsCl as Determined by ICP

Element	wt%	Element	wt%
Al	0.14	Na	2.8
B	0.14	Ni	0.1
Ba	0.55	Pb	0.14
Cd	0.02	Si	0.21
Co	0.10	Sr	0.02
Cr	1 4	Ti	0.07
Fe	(a)	Zn	0.03
K	0.68		

(a) Iron content was very high and nonreproducible, indicating probable contamination of CsCl solution.

6.0 THERMODYNAMIC ANALYSIS OF THE 316L STAINLESS STEEL-WESF CESIUM CHLORIDE SYSTEM

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

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

$$2\ CsCl + Fe \rightleftharpoons 2\ Cs + FeCl_2. \qquad (1)$$

The free energy change of the reaction is the driving force for the reaction to occur under a given set of conditions. For reaction (1) the free energy change ΔG_R is given by the equation

$$\Delta G_R = \Delta G_R^0 + RT\ \ln \frac{A^2_{(Cs)} \bullet A_{(FeCl_2)}}{A^2_{(CsCl)} \bullet A_{(Fe)}}$$

Where, ΔG_R^0 = the standard free energy change of the reaction
$A_{(\ )}$ = the activity of a given component
T = absolute temperature, °K
R = gas constant

The standard free energy change (ΔG_R^0) is given by the equation

$$\Delta G_R^0 = \Delta G^0_{f(FeCl_2)} - 2\Delta G^0_{f(CsCl)}$$

where $\Delta G^0_{f(\ )}$ = standard free energy of formation of a given component

A negative value for the free energy change ΔG_R indicates that reaction (1), as written, is spontaneous. If the reactants and products are all in their standard states at unit activity, then

$$\Delta G_R = \Delta G_R^0$$
$$= \Delta G^0_{f(FeCl_2)} - 2\Delta G^0_{f(CsCl)}.$$

At 298°K, ΔG_f^0 for CsCl is -99 kcal/mole and for $FeCl_2$ it is -72 kcal/mole, therefore

$$\Delta G_R^0 = -72 - 2(-99) = + 126 \text{ kcal}.$$

Since ΔG_f^0 for equation (1) is positive, the equilibrium will favor the reverse reaction, and iron will not react with CsCl.

From a thermodynamic standpoint, the 316L stainless steel - WESF CsCl system is an extremely complex one because of the many components contained in the system. Table 5 gives the nominal composition of the 316L stainless steel and also lists the cation impurities that may be present in the CsCl at greater than trace levels. Cation impurities in the CsCl are probably present as metal chlorides, but small quantities of oxides may also be present. Oxides could be formed by hydrolysis of the chlorides during evaporation and melt casting.

A rigorous thermodynamic analysis of the 316L stainless steel - WESF CsCl system is extremely difficult, if not impossible, for several reasons. By making a number of simplifying assumptions, however, an elementary thermodynamic analysis of the system can be made which can help to identify potentially troublesome reactions. These assumptions are:

TABLE 5. Components of the 316L Stainless Steel/ Cesium Chloride System

316 Stainless Steel - Nominal Composition

Component	Weight %
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 Conc. Range Weight %
Al	0-0.1
Ba	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

- components of the stainless steel are present in their standard states at unit activity,

- the cation impurities in the CsCl are present as simple chlorides or oxides at unit activity, and

- each reaction product is at unit activity.

Using these assumptions, one can estimate the potential for a reaction to occur between a component of the CsCl and a constituent of the 316L stainless steel by calculating the standard free energy of reaction, as was done for equation (1) above.

Table 6 gives standard free energy of formation data for a number of chlorides at different temperatures. The data were obtained from a number of sources and were selected as being the most reliable data available. Figure 11 shows some of the standard free energy data from Table 6 in graphic form. From Table 6 it can be seen that CsCl is very stable, and it should not react with any of the components of the stainless steel up to at least 1000°C.

Other reactions may be possible, however, involving components of the stainless steel and CsCl. Assuming all reactants and products are in their standard states at unit activity, a metal can react with any chloride which has a standard free energy of formation more positive than its own chloride. This means that in Figure 11 a metal could react with any chloride that appears above it on the diagram. For example, consider the reaction of manganese in the stainless steel and ferrous chloride in the CsCl at 298°K.

$$FeCl_2 + Mn \rightleftharpoons MnCl_2 + Fe \qquad (2)$$

$$\Delta G^0_R = \Delta G^0_{f(MnCl_2)} - \Delta G^0_{f(FeCl_2)}$$

$$= -106 - (-72)$$

$$= -34 \text{ kcal}$$

TABLE 6. Standard Free Energy Formation Values for Selected Chlorides at Various Temperature.[a]

Compound	$-\Delta G_f^\circ$, kcal/g-atom of chlorine		
	298°K	500°K	1000°K
$AlCl_3$	50	46	43
$BaCl_2$	97	93	84
CCl_4	4	2	-2
$CaCl_2$	90	87	78
$CdCl_2$	42	33	25
$CrCl_2$	42	39	33
$CrCl_3$	38	35	25
$CsCl$	94	94	82
$FeCl_2$	36	33	26
$FeCl_3$	27	23	21
HCl	23	23	24
KCl	98	93	82
$MgCl_2$	71	67	58
$MnCl_2$	53	50	43
$MoCl_5$	20	17	13
$NaCl$	92	87	76
$NiCl_2$	31	28	20
PCl_3	21	20	19
$PbCl_2$	38	34	26
$RbCl$	96	92	80
S_2Cl_2	6	—	—
$SiCl_4$	37	35	32
$SrCl_2$	93	[illegible]	82

(a) References: Glassmer 1957, Kellogg 1950, Kubaschewski 1979, Lindsay 1979, Rosenqvist 1970, Smithells 1976, Villa 1950.

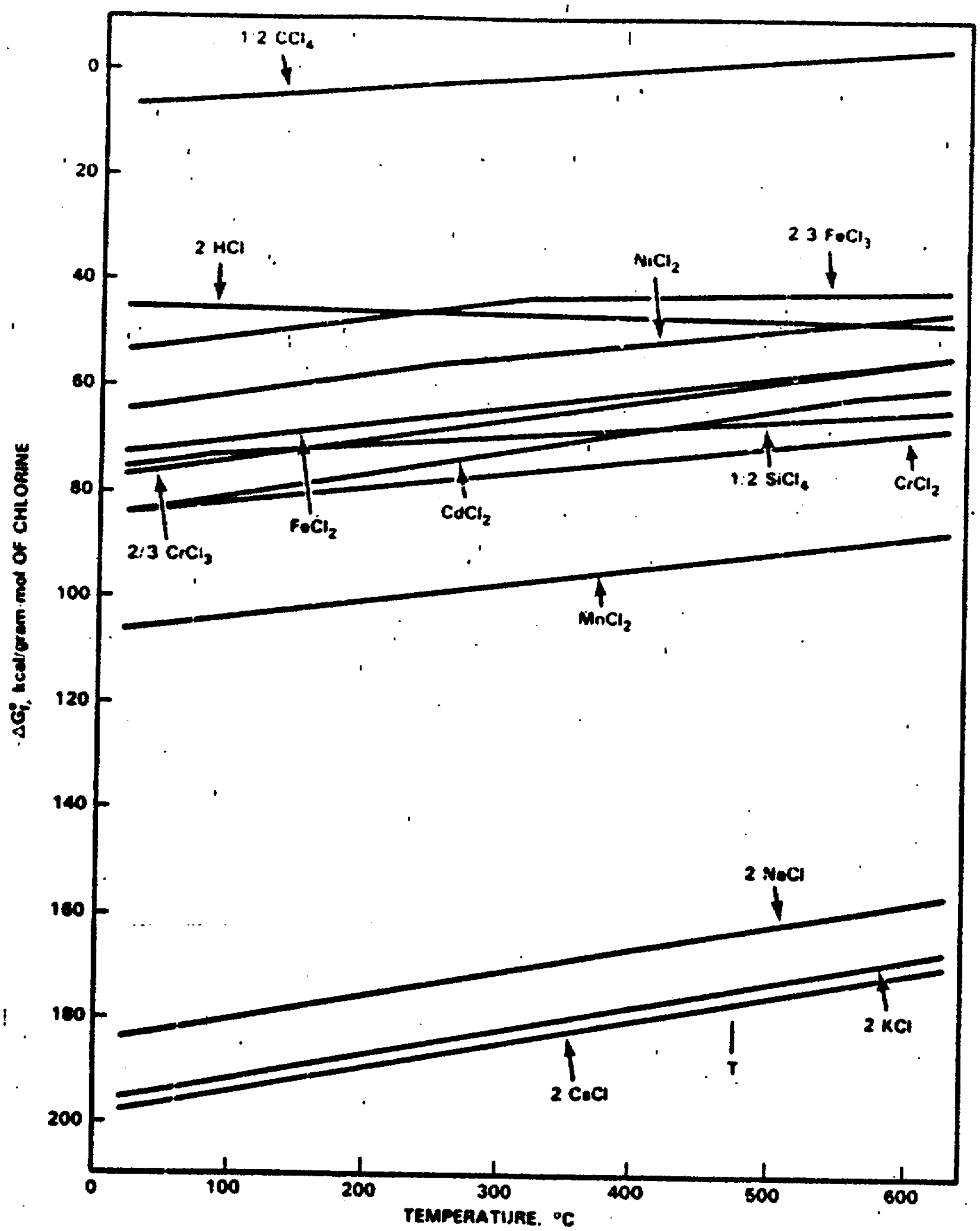

FIGURE 11. Standard Free Energy of Formation of Various Chlorides as a Function of Temperature

Since ΔG^0_R is negative, reaction (2), as written, could proceed spontaneously when the reactants and products are in their standard states at unit activity. In similar fashion, other potentially troublesome reactions can be identified for the WESF CsCl/316L stainless steel system. Some of these reactions are

$$Mn + CrCl_2 \rightarrow MnCl_2 + Cr$$
$$\Delta G^0_R = -30 \text{ kcal (at } 298^0\text{K)}$$

$$Mn + CdCl_2 \rightarrow MnCl_2 + Cd$$
$$\Delta G^0_R = -22 \text{ kcal (at } 298^0\text{K)}$$

$$Cr + FeCl_3 \rightarrow CrCl_3 + Fe$$
$$\Delta G^0_R = -33 \text{ kcal (at } 298^0\text{K)}$$

$$Fe + NiCl_2 \rightarrow FeCl_2 + Ni$$
$$\Delta G^0_R = -10 \text{ kcal (at } 298^0\text{K)}$$

These equations show that reactions are likely to occur between the less stable chloride impurities in the CsCl (i.e., $FeCl_2$, $CdCl_2$, $NiCl_2$) and the more reactive metals in the stainless steel (i.e., Mn, Cr). Similar reasoning applies to any oxide impurities which may be present in the CsCl.

In the actual system the components would not all be in their standard states at unit activity. Consider again equation (2). The free energy of the reaction is given by the equation

$$\Delta G_R = \Delta G^0_R + RT \ln \frac{A_{(MnCl)_2} \bullet A_{(Fe)}}{A_{(FeCl_2)} \bullet A_{(Mn)}}$$

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

$$\Delta\bar{G}_{Mn} = RT \ln A_{(Mn)}$$

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

$$\begin{aligned} \Delta G_R &= \Delta G_R^0 + RT \ln \frac{1}{A_{(Mn)}} \\ &= \Delta G_R^0 - RT \ln A_{(Mn)} \\ &= -106 - (-72) - (-2) \\ &= -32 \text{ kcal} \end{aligned}$$

Thus, the net effect of the manganese being present in the stainless steel in a solid solution is to make reaction (2), as written, slightly less favorable; although the reaction would still proceed spontaneously. Similarly, if the ferrous chloride were present in the CsCl as a component of a solid solution, equation (2) would be slightly less favorable by the partial molar free energy of solution of the $FeCl_2$. Therefore, it is apparent that factors that reduce the activities of the reactants make ΔG_R more positive and reduce the driving force for the reaction, as written to proceed. Similarly, reducing the activities of the products makes ΔG_R more negative and increases the potential for the reaction to proceed spontaneously.

7.0 PHYSICAL PROPERTY MEASUREMENTS

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

The addition of metal chlorides to the CsCl results in the formation of low melting phases and may affect the phase transition temperature. It was previously reported that the addition of KCl to CsCl can reduce the temperature at which a phase transition begins to as low as 315°C (Fullam 1971). Questions have been raised regarding the validity of these data. Therefore, additional work was carried out to: (1) confirm the effects of KCl additions on the phase transition temperature of CsCl, and (2) determine the effects of other impurities, which may be present in WESF-produced CsCl, on the CsCl phase transition and melting point. Thermal expansion measurements and differential scanning calorimetry (DSC) measurements were made using a duPont model 990 thermal analyzer with the model 943 thermomechanical analyzer and DSC cell.

Figure 12 shows the results obtained in the earlier work with the CsCl-KCl system and those obtained in the current work. Figure 13 shows some of the actual thermal expansion scans obtained in the latest work with pure CsCl (>99.995%) and CsCl-KCl mixtures. The latest data confirm those previously reported, and show that the addition of as little as 3 wt% KCl to CsCl lowers the temperature at which the phase transition begins below 350°C.

A number of other CsCl-impurity chloride systems were studied including a simulated WESF CsCl mixture whose composition is given in Table 7. Results obtained are shown in Table 8. None of the individual impurity chlorides studies (except KCl) has a major effect on the phase transition temperature, but all formed low melting phases with the CsCl. No phase transition was detected with the CsCl-$FeCl_3$ system because the minimum melting point was about 270°C. The addition of Cs_2O (or CsOH) to the CsCl raised the phase transition temperature to about 494°C. The simulated WESF CsCl mixture, which contained 3 wt% KCl, exhibited a minimum melting point of about 452°C, and the phase transition started at about 343°C. This compares with a phase transition temperature of about 344°C for the CsCl-3.1 wt% KCl mixture. The

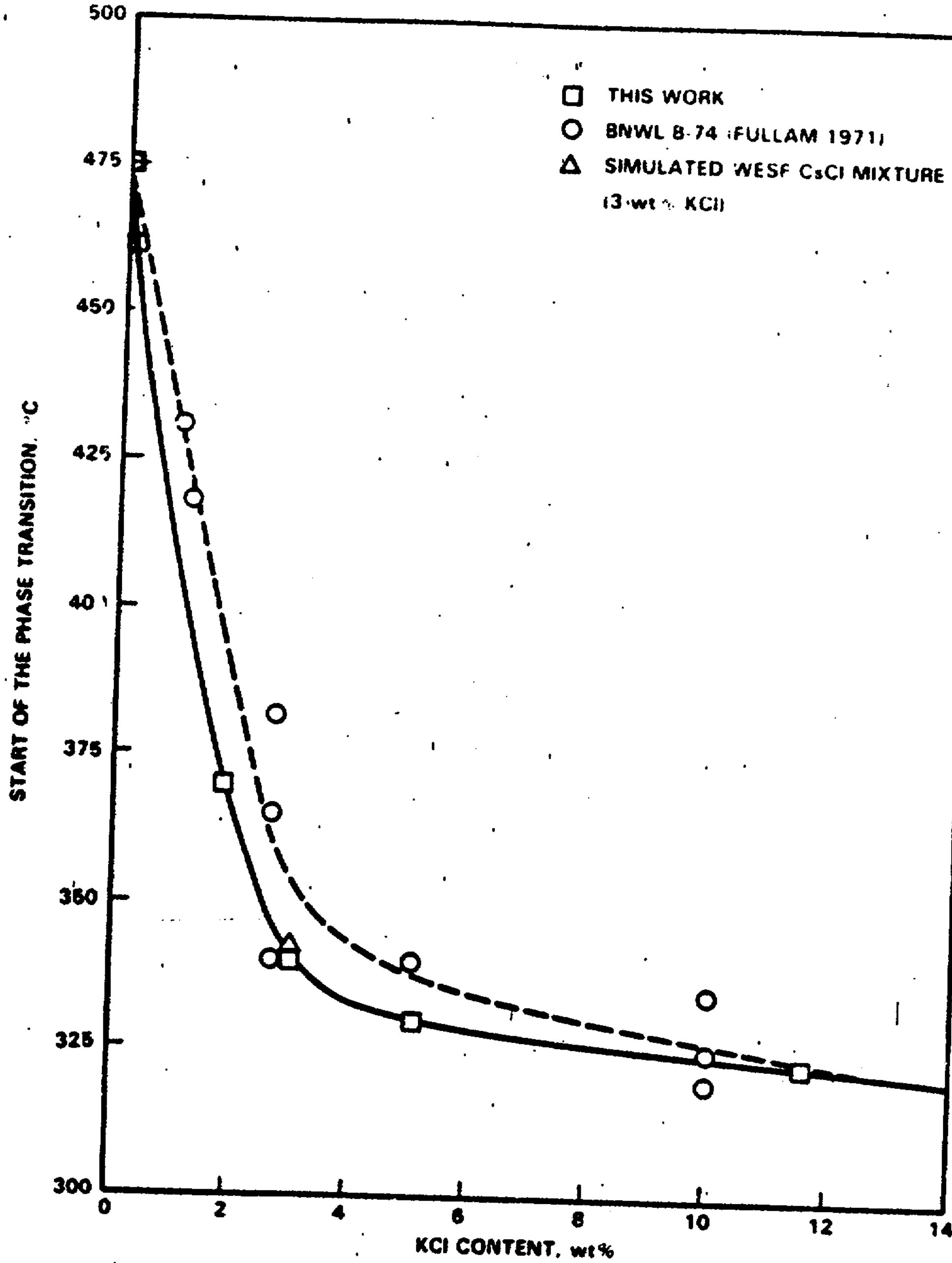

FIGURE 12. The Effects of KCl Content on the Phase Transition Temperature of Cesium Chloride - Determined by Thermal Expansion Measurements

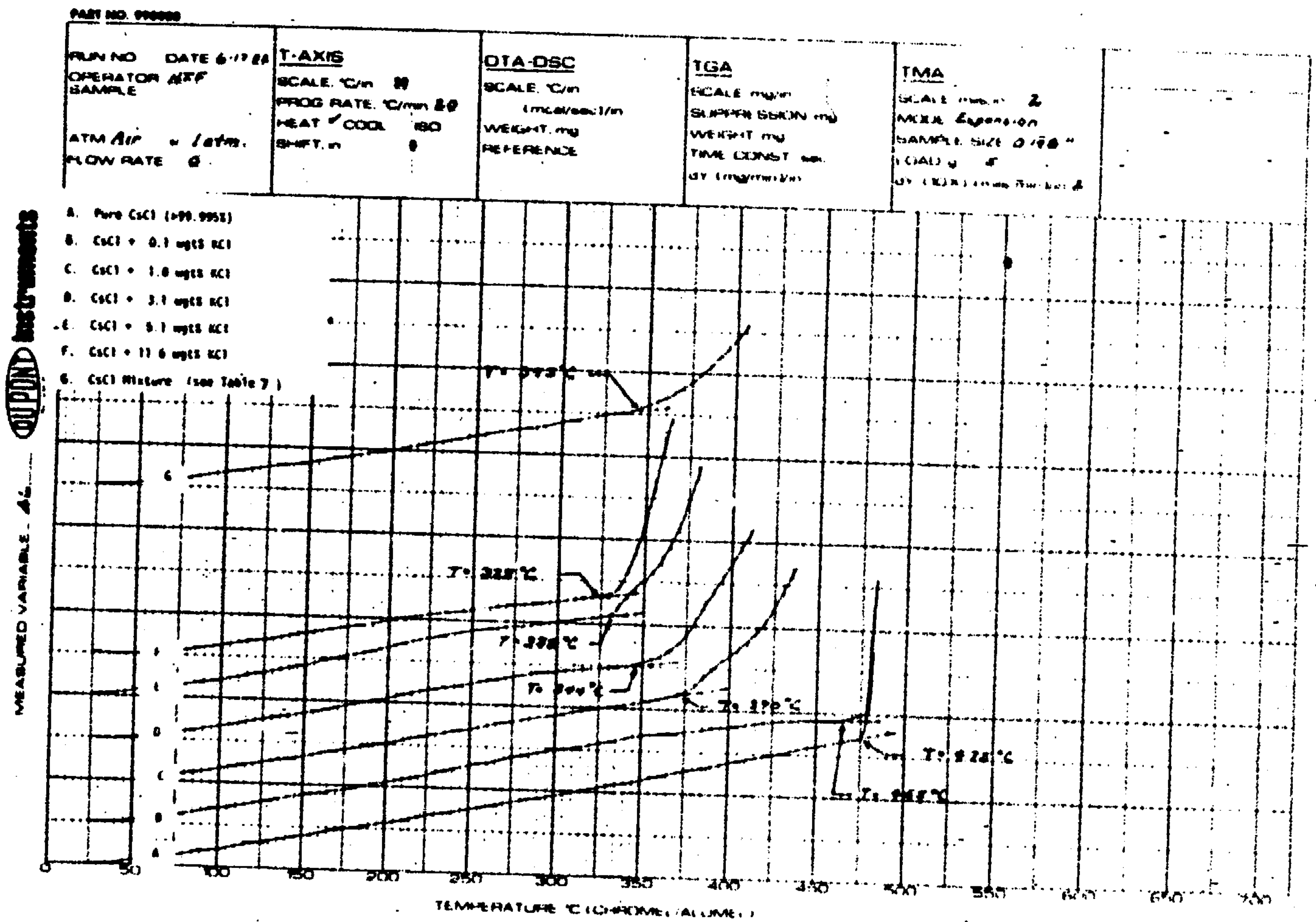

FIGURE 13. Thermal Expansion Scans for KCl-CsCl Mixtures

TABLE 7. Composition of the Simulated WESF Cesium Chloride Mixture Used in the Physical Property Measurements

Component	Wt%	Component	Wt%
CsCl	90.0	$FeCl_3$	0.2
NaCl	4.5	$CrCl_3$	0.2
KCl	3.0	$NiCl_2$	0.2
RbCl	0.5	$MnCl_2$	0.2
$BaCl_2$	0.5	$PbCl_2$	0.2
$CaCl_2$	0.5		

TABLE 8. The Effect of Impurities on the Phase Transition Temperature and Melting Point of CsCl

System[(a)]	Start of the Phase Transition °C	Minimum Melting Point °C
CsCl + 5% KCl	330	605
CsCl + 5% NaCl	470	493
CsCl + 5% KCl + 5% NaCl	332	478
CsCl + 5% $BaCl_2$	475	557
CsCl + 5% $CaCl_2$	468	610
CsCl + 3% $FeCl_3$	(c)	270
CsCl + 3% $CrCl_3$	475	622
CsCl + 3% $PbCl_2$	472	480
CsCl + 3% $MnCl_2$	477	489
CsCl + 3% $NiCl_2$	479	520
CsCl + 3% Cs_2O	494	
CsCl Mixture[(b)]	343	452

(a) Composition in wt%.

(b) See Table 9 for composition.

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

results show that in a CsCl system containing a number of impurity chlorides the phase transition temperature is determined by the KCl content.

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CESIUM CHLORIDE COMPATIBILITY TESTING PROGRAM - ANNUAL REPORT, FISCAL YEAR 1982

F.T. Fullam

Pacific Northwest Laboratory
Richland, WA

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