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Compatibility of Strontium-90 Fluoride with Containment Materials at Elevated Temperatures

H. T. Fullam

August 1981

Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
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Richland, Washington 99352

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SUMMARY

The Strontium Heat Source Development Program has been underway at the Pacific Northwest Laboratory since 1972 to obtain the data needed to permit the licensing of $^{90}\text{SrF}_2$ as a radioisotope heat-source fuel for terrestrial applications. The program is currently funded by the Space and Terrestrial Systems Division of the U.S. Department of Energy.

The use of $^{90}\text{SrF}_2$ as a heat-source fuel requires that the strontium-90 be adequately contained during heat-source service. A major portion of the Pacific Northwest Laboratory program is directed at determining the compatibility of $^{90}\text{SrF}_2$ with containment materials at heat-source operating temperatures. The primary emphasis of the research has been on the $^{90}\text{SrF}_2$ produced at the Waste Encapsulation and Storage Facility (WESF), which is the only major domestic source of $^{90}\text{SrF}_2$. The Pacific Northwest Laboratory compatibility studies are divided into five phases:

- initial screening tests
- supplemental screening tests
- WESF $^{90}\text{SrF}_2$ capsule demonstration tests
- thermal gradient test
- long-term tests.

The various phases are designed to complement each other and to provide a comprehensive evaluation of the compatibility of $^{90}\text{SrF}_2$ with containment materials.

The two sets of screening tests showed that most of the metals exposed at 800° to 1100°C to $^{90}\text{SrF}_2$ or inert SrF_2 that contained similar impurities suffered extensive attack. Of the 38 metallic materials screened, iridium, In-0.3 wt%, tungsten, rhenium, and TZM provided the best resistance to fluoride attack. As a general rule, the precious metals and refractory metals were more resistant to attack than were the base metals and their alloys. The screening tests also indicated that the metal attack was due primarily to impurity fluorides in the strontium fluoride.

For a variety of reasons, TZM, Haynes Alloy 25, and Hastelloy C-276 were the three materials selected for evaluation with WESF $^{90}\text{SrF}_2$ in the long-term compatibility tests. The long-term tests were carried out at 600° , 800° and 1000°C and lasted up to 30,000 h. Results obtained in the tests showed that all three alloys suffered substantial attack when exposed to the $^{90}\text{SrF}_2$, although the TZM was more resistant to attack than the Hastelloy C-276 and Haynes Alloy 25. In the case of the latter two alloys, they appeared to provide about equal resistance to fluoride attack for exposures longer than about 12,000 h.

All of the test data show that attack of the TZM, Haynes Alloy 25, and Hastelloy C-276 by the $^{90}\text{SrF}_2$ is due primarily to impurities in the fluoride. The fluorides of iron and chromium are the two principal contributors to the metal attack. The data also show that once the critical impurities in the $^{90}\text{SrF}_2$ have reacted with the metal, the rate of metal attack decreases to a very low level. In most of the tests, the critical impurities reacted within 6,000 to 12,000 h, and specimens exposed to the WESF $^{90}\text{SrF}_2$ for 20,000 and 30,000 h suffered no greater attack than specimens tested for 6,000 and 12,000 h.

Evaluation of the experimental data shows that WESF $^{90}\text{SrF}_2$ can be safely contained in TZM, Haynes Alloy 25 or Hastelloy C-276 for the nominal 10-year life of a heat source. However, all three alloys suffer significant attack by the $^{90}\text{SrF}_2$ at 600° to 1000°C , which places certain limitations and restraints on the heat-source design and use. The heat source must provide at least double containment of the $^{90}\text{SrF}_2$ with the inner capsule fabricated from TZM, Haynes Alloy 25, or Hastelloy C-276. The outer capsule(s) of the heat source must provide all of the structural strength needed to meet licensing requirements without support from the inner capsule. The inner capsule serves only as the primary containment barrier for the $^{90}\text{SrF}_2$ and provides no structural support. If Hastelloy C-276 or Haynes Alloy 25 is used for the inner capsule, the $^{90}\text{SrF}_2$ /capsule interface temperature should be limited to 800°C . If TZM is used for the inner capsule, the interface temperature should be limited to 1000°C . The TZM must be protected from external oxidation if it is used as the inner capsule.

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1.0 INTRODUCTION

Waste management planning at Hanford, Washington, calls for the recovery of radioactive fission-product strontium and cesium from stored high-level-fuel reprocessing wastes. The separated strontium and cesium are purified, converted to stable compounds, individually encapsulated in small, double-walled metallic canisters, and stored in a water basin on the Hanford Reservation. The respective storage forms selected for strontium and cesium were strontium fluoride and cesium chloride. The preparation, encapsulation, and storage of the SrF_2 and CsCl take place in the Waste Encapsulation and Storage Facility (WESF) operated for the U.S. Department of Energy (DOE) by Rockwell International (RHO).

The strontium recovered from the Hanford high-level wastes consists of a mixture of the radioisotope strontium-90 and several stable strontium isotopes. The ^{90}Sr isotopic content of the recovered strontium can vary from ~55% to as low as 25%, depending primarily on the time since the strontium was discharged from the nuclear reactor. Even though the stable isotopes make up 45% or more of the fission-product strontium, the product is typically referred to as ^{90}Sr , and compounds prepared from fission-product strontium are referred to as ^{90}Sr compounds (e.g., $^{90}\text{SrTiO}_3$ and $^{90}\text{SrF}_2$).

Strontium-90, in the form of strontium titanate (SrTiO_3) and strontium orthotitanate (Sr_2TiO_4), has been used as a radioisotope heat-source fuel in terrestrial applications since about 1960. The strontium titanates used in these applications were prepared from radioactive strontium recovered from the high-level wastes stored at Hanford. Once the strontium stored at Hanford is converted to SrF_2 , it will no longer be available for conversion to the titanate form. Therefore, the only major source of ^{90}Sr available for use as a radioisotope heat-source fuel will be the encapsulated $^{90}\text{SrF}_2$ stored at WESF.

The use of $^{90}\text{SrF}_2$ as a radioisotope heat-source fuel requires qualification testing and licensing of the $^{90}\text{SrF}_2$ fuel form. The Strontium Heat Source Development Program has been underway at the Pacific Northwest Laboratory (PNL) since 1972 to develop the data and technology needed to permit the licensing of $^{90}\text{SrF}_2$ -fueled heat sources by the cognizant national and international regulatory agencies. The PNL program is currently funded by the Space and Terrestrial Systems Division of the U.S. Department of Energy.

The Strontium Heat Source Development Program has three general tasks:

- determination of the pertinent chemical and physical properties of $^{90}\text{SrF}_2$;
- $^{90}\text{SrF}_2$ compatibility studies;
- heat-source design and qualification testing.

Work is being carried out concurrently on all three tasks.

A primary requirement in the licensing of a radioisotope heat source is that the fuel form must be safely contained from the time the heat source is fabricated until final disposal. A major portion of the PNL Strontium Heat Source Development Program has been directed at evaluating the compatibility of $^{90}\text{SrF}_2$ with potential containment materials at anticipated heat-source operating temperatures to obtain sufficient data to show that the $^{90}\text{SrF}_2$

can be adequately contained during heat-source service. Since the $^{90}\text{SrF}_2$ produced at WESF is the only major domestic source of ^{90}Sr for heat-source service, the PNL $^{90}\text{SrF}_2$ compatibility studies were directed primarily at WESF-produced $^{90}\text{SrF}_2$.

The $^{90}\text{SrF}_2$ compatibility studies were divided into several phases that were designed to complement each other and provide a comprehensive evaluation of the compatibility of $^{90}\text{SrF}_2$ with containment materials:

- initial scouting tests (Fullam 1975);
- supplemental screening tests (Fullam 1977b);
- WESF $^{90}\text{SrF}_2$ -capsule demonstration tests (Fullam 1980);
- thermal gradient test (Fullam 1977a);
- long-term tests.

Complete details of the first four phases of the work are presented in the reports referenced. Details of the long-term tests are provided in this report together with an overall evaluation of the results obtained in all of the compatibility studies. In order to assemble all of the $^{90}\text{SrF}_2$ compatibility data into a single source, details of the first four phases of the work are summarized in the appendix of this report.

2.0 CONCLUSIONS AND RECOMMENDATIONS

Results obtained in the strontium fluoride compatibility tests carried out at PNL show that attack of metallic containment materials at 600⁰ to 1100⁰C is primarily due to fluoride impurities in the strontium fluoride. The fluorides of iron and chromium contribute principally to the metal attack. The data also show that once the critical impurities in the ⁹⁰SrF₂ have been consumed by reaction with the metal, the rate of metal attack decreases to a very low level. In general, the critical impurities react with the metal within 6,000 to 12,000 h, and metal specimens exposed to ⁹⁰SrF₂ for periods of 20,000 to 30,000 h show no more chemical attack than the specimen tested for 6,000 to 12,000 h.

Evaluation of the test data show that WESF-produced ⁹⁰SrF₂ can be adequately contained for the nominal 10-year service life of a heat source by using Hastelloy C-276,[®] Haynes Alloy 25,[®] or TZM as the primary containment material. However, all three alloys suffer significant attack by the ⁹⁰SrF₂ at heat-source operating temperatures, which places certain limitations and requirements on the design and use of the heat source. Thermal aging reactions that affect the microstructure and mechanical properties of Hastelloy C-276 and Haynes Alloy 25 place additional restraints on the heat-source design if either alloy is used in the construction of the heat source. Restraints and limitations on the heat source due to ⁹⁰SrF₂ compatibility and alloy aging considerations include the following:

- The heat source must provide at least double containment of the ⁹⁰SrF₂ with the inner capsule fabricated from Hastelloy C-276, Haynes Alloy 25, or TZM.
- The outer capsule(s) of the heat source must provide all of the structural strength needed to meet licensing requirements without support from the inner capsule. The inner capsule should only serve as the primary containment barrier for the ⁹⁰SrF₂ since fluoride attack and aging reactions serve to reduce its structural strength. Once the heat source has been at temperatures of 600⁰C or higher for an extended period of time, mechanical stressing of the inner capsule could result in its fracture and release of radioactivity.
- If Hastelloy C-276 or Haynes Alloy 25 is used as the inner capsule material, the capsule/⁹⁰SrF₂ interface temperature should be limited to a maximum of 800⁰C. If TZM is used for the inner capsule, the interface temperature should be limited to 1000⁰C. If TZM is used, assurance must be provided that the inner capsule is protected from external oxidation.
- The service life of the heat source should be limited to 10 years if Hastelloy C-276 or Haynes Alloy 25 is used for the inner capsule, and 20 years if TZM is used.

Because iron and chromium fluorides in the ⁹⁰SrF₂ are principal causes of metal attack, operational changes at WESF that reduce their concentrations in the fluoride would improve the compatibility of the ⁹⁰SrF₂ with containment materials in heat-source service. Replacement of the

[®] Cabot Corp., Kokomo, Indiana.

[®] Cabot Corp., Kokomo, Indiana.

Inconel® boats used in firing the $^{90}\text{SrF}_2$ with a more corrosion-resistant material, or a material free of iron and chromium, should serve to effectively reduce the iron and chromium content of the $^{90}\text{SrF}_2$.

Results obtained in short-term screening tests (lasting up to 4400 h) with 38 metallic materials show that most metals suffered extensive attack when exposed to $^{90}\text{SrF}_2$, or to inert SrF_2 containing similar impurities, at 800° to 1100°C . Of the materials tested, iridium, Ir-0.3 wt% W, tungsten, rhenium and TZM provided the greatest resistance to fluoride attack. As a general rule, the precious metals and refractory metals were more corrosion-resistant than the base metals and their alloys. Exceptions to the rule were platinum and gold which suffered catastrophic attack.

For large-scale heat-source applications, material costs would preclude the use of iridium, rhenium or Ir-0.3 wt% W as the containment material for the $^{90}\text{SrF}_2$. The three materials could find use, however, in small-scale applications. The data obtained in the short-term screening tests are insufficient to show that Ir, Rh, or Ir-0.3 wt% W would safely contain WESF $^{90}\text{SrF}_2$ for long periods of time. If small-scale applications for $^{90}\text{SrF}_2$ heat sources should develop, it is recommended that additional compatibility testing of WESF $^{90}\text{SrF}_2$ with Ir, Rh and Ir-0.3 wt% W be carried out. The data obtained would allow any of the three materials to be used as the primary containment for the $^{90}\text{SrF}_2$ and would probably allow the heat source to operate at higher temperatures than is possible using Haynes Alloy 25, Hastelloy C-276 or even TZM as the primary containment material.

3.0 WESF FLOWSHEET FOR $^{90}\text{SrF}_2$ PRODUCTION

At Hanford, spent fuel from production reactors was reprocessed using the Purex process. The ^{90}Sr and other fission products from the spent fuel exited the Purex process in the high-level acid waste stream which was neutralized and stored in tanks. The simplified flowsheet for recovery of the strontium from the fuel reprocessing waste and its purification is shown in Figure 1. The flowsheet for conversion of the strontium to $^{90}\text{SrF}_2$ and its subsequent encapsulation is shown in Figure 2. The strontium recovery and purification take place in B-Plant, while the fluoride conversion, encapsulation and storage take place at WESF. Both facilities are currently operated by RHO.

FIGURE 1. Simplified Flowsheet for Strontium Recovery and Purification

FIGURE 2. WESF Flowsheet for Preparation and Encapsulation of $^{90}\text{SrF}_2$

In the $^{90}\text{SrF}_2$ process, the strontium is recovered from current Purex acid waste (CAW) or Purex acid sludge (PAS) by solvent extraction. The extractant used is di-2-ethylhexylphosphoric acid (HDEHP) and tributyl phosphate (TBP) in normal paraffin hydrocarbon (NPH). The strontium is stripped from the organic phase by dilute nitric acid and purified using a series of sulfate and hydroxide precipitation steps. The purified strontium is stored in a dilute nitric acid solution until it is converted to SrF_2 .

All steps in the fluoride conversion and encapsulation process are batch operations. A volume of aqueous feed solution containing 3 to 5 kg of strontium is neutralized to a pH of 8 to 9 with sodium hydroxide solution. Solid sodium fluoride is added to the solution to precipitate SrF_2 . The resulting slurry is digested at $\sim 80^\circ\text{C}$ for 1 h with air sparging and is then filtered. The filter cake is washed with water and fired at $\sim 1100^\circ\text{C}$ in argon in Inconel boats for several hours. After cooling, the SrF_2 is pulverized to minus 1/2-in. granules and loaded into a Hastelloy C-276 capsule by impact consolidation, which is essentially a cold-step-pressing operation. The capsule is closed by tungsten-inert-gas (TIG)-welding a lid in place. Then, the capsule is leak-checked and decontaminated, and the cleaned capsule is sealed, by TIG welding, in an outer capsule of 316 L stainless steel. The weld integrity of the outer capsule is checked using ultrasonic techniques. After weighing and calorimetry to determine the heat output, the capsule is stored in a water-filled basin.

The $^{90}\text{SrF}_2$ produced at WESF will contain substantial quantities of cation impurities and much lesser amounts of anion impurities. The impurity concentrations can vary over a considerable range. Strontium recovered from different waste tanks will, in general, contain the same kinds of impurities, but the concentrations may vary. Since the procedures for purifying the strontium are only partially effective, the impurity concentrations of the $^{90}\text{SrF}_2$ product will vary with the source of the strontium. Corrosion of process equipment, especially in the fluoride-firing operation, will also contribute to the impurities in the WESF $^{90}\text{SrF}_2$ and some product nonhomogeneity will result. The impurities normally found in WESF-produced $^{90}\text{SrF}_2$ and their probable concentration ranges are presented in Table 1. Zirconium-90 is a stable decay product of ^{90}Sr , and its concentration in the SrF_2 will increase with time as the ^{90}Sr decays.

The radiochemical purity of fission-product strontium will depend primarily on the time since discharge from the reactor and on the effectiveness of the purification procedures used in strontium recovery. Strontium recovered from Hanford wastes has been reported to contain up to 0.03% of the total activity as ^{144}Ce and 0.003% as ^{137}Cs . Analysis of strontium fluoride produced at WESF shows the only measurable activity other than ^{90}Sr - ^{90}Y is ^{137}Cs . WESF $^{90}\text{SrF}_2$, which was about 18 mo old at the time of analysis, contained $\sim 2.8 \times 10^{-5}$ Ci of ^{137}Cs per Ci of ^{90}Sr (Fullam 1977c). The $^{90}\text{SrF}_2$ will contain ^{90}Y , which is the decay daughter of ^{90}Sr . The ^{90}Y decays, in turn, to stable ^{90}Zr . Once secular equilibrium is established, the $^{90}\text{Y}/^{90}\text{Sr}$ atomic ratio in the $^{90}\text{SrF}_2$ is 2.56×10^{-4} .

The ^{90}Sr isotopic content of the encapsulated WESF $^{90}\text{SrF}_2$ can vary from ~ 25 to 55%, depending on the age of strontium. Pertinent data for a typical WESF storage capsule

TABLE 1. Typical Impurities Found in WESF-Produced $^{90}\text{SrF}_2$ and Their Probable Concentration Ranges

Component	wt%	Component	wt%
Sr	66 (nominal)	Mn	<0.1
F	30 (nominal)	Na	1 to 4
		Ni	<0.5
Al	<0.5	Pb	<0.2
Ba	0.1 to 2.0	RE ^(a)	<2.0
Ca	0.1 to 2.0	Si	<0.02
Cd	<0.1	Zr ^(b)	Variable
Cr	<0.5	H	<0.01
Cu	<0.01	O	<0.05
Fe	<0.5	NO ₃ ⁻	<0.05
K	<0.01	SO ₄ ⁻²	<0.01
Mg	0.05 to 0.5		

(a) RE--Rare Earth Elements

(b) Decay product--will increase as ^{90}Sr decays

containing SrF_2 having an initial ^{90}Sr isotopic content of 55% are given in Figure 3. The heat output, power density, and activity of the capsules will vary from the nominal values listed, depending on the initial ^{90}Sr content, and will decrease with time as the ^{90}Sr decays.

	INNER CAPSULE	OUTER CAPSULE
1. MATERIAL	HASTELLOY C-276	316L STAINLESS STEEL
2. INNER DIAMETER	2.01 in.	2.39 in.
3. OUTER DIAMETER	2.25 in.	2.63 in.
4. TOTAL LENGTH	19.05 in.	20.10 in.

STRONTIUM FLUORIDE DATA:

1. AMOUNT~2.8 kg/CAPSULE
2. CHEMICAL PURITY~95%
3. ^{90}Sr ISOTOPIC CONTENT~55%
4. BULK DENSITY~70% OF THEORETICAL DENSITY
5. ACTIVITY~140,000 Ci/CAPSULE
6. HEAT LOAD~960 W/CAPSULE
7. POWER DENSITY~1.0 W/cm³

FIGURE 3. Typical Data at the Time of Encapsulation for a WESF $^{90}\text{SrF}_2$ Storage Capsule

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4.0 PREVIOUS WORK WITH STRONTIUM FLUORIDE AS A HEAT SOURCE FUEL

In the early 1960's, the Martin Marietta Corporation first considered using strontium fluoride as the ^{90}Sr fuel form for radioisotope heat sources. Martin Marietta investigated the potential use of several strontium compounds, including strontium fluoride, to fuel various SNAP^(a) devices for terrestrial applications. As part of the Martin Marietta program, the compatibility of nonradioactive SrF_2 with a number of superalloys was investigated at temperatures up to 950°C for 19 mo (Maraglia 1966). Based on the limited amount of data obtained with nonradioactive SrF_2 , Hastelloy C, Hastelloy X, and Haynes Alloy 25 were identified to be the most resistant to attack by the nonradioactive SrF_2 at elevated temperatures.

In the late 1960's, the Atomic Energy Commission (AEC) decided to recover the radioactive strontium and cesium from the stored high-level wastes at Hanford and to store each element individually in metal canisters in a water basin. Strontium fluoride was selected as the storage form for the strontium, and CsCl was chosen as the storage form for the cesium. Once SrF_2 had been selected as the storage compound, PNL carried out a program to study the compatibility of SrF_2 , prepared by the WESF flowsheet, with containment materials and to identify the best material for the SrF_2 storage canister (Fullam 1972). Compatibility studies with radioactive and inert SrF_2 lasting up to 3 yr were carried out at temperatures up to 800°C . A large number of potential containment materials were investigated with principal emphasis on Hastelloy C, Hastelloy C-276, Hastelloy X, Haynes Alloy 25, and 316 L stainless steel.

Results obtained showed that of the five principal containment materials studied, Haynes Alloy 25 exhibited the greatest resistance to attack by the SrF_2 . Hastelloy C and Hastelloy C-276 were slightly less resistant to attack than the Haynes Alloy 25. Extrapolation of the short-term test data indicated that Haynes Alloy 25, Hastelloy C, or Hastelloy C-276 could be used to contain the WESF SrF_2 for long periods of time at temperatures up to 400°C , which was the maximum SrF_2 -canister interface temperature expected in the WESF operations. PNL recommended that Haynes Alloy 25 be used as the WESF SrF_2 canister material. For a variety of reasons, which included cost, availability, and fabricability, the Atlantic Richfield Hanford Company (which operated WESF at the time) and the AEC selected Hastelloy C-276 as the inner canister material for SrF_2 .

(a) SNAP--Systems for Nuclear Auxiliary Power

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5.0 THEORETICAL CONSIDERATIONS

Potential reactions between SrF_2 and a containment material 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. A thermodynamic analysis of possible reactions between SrF_2 and potential containment materials can be useful in selecting candidate materials for compatibility testing. However, for the analysis to be of real value, it is necessary that every possible reaction be considered. Carrying out a rigorous thermodynamic analysis can be relatively easy for simple systems that have only a few components, but may be very difficult or impossible for complex systems.

Consider a system involving WESF $^{90}\text{SrF}_2$ and a metal alloy such as Hastelloy C-276. A rigorous thermodynamic analysis of the system is virtually impossible because of the very many components involved and the lack of chemical and thermodynamic data. By making a number of simplifying assumptions, however, it is possible to carry out elementary thermodynamic analyses of such systems. These analyses can be useful in selecting candidate materials for compatibility testing, in spotlighting potential problem areas, and, more importantly, in analyzing and interpreting the results obtained in the compatibility tests. Simplified analyses were carried out on a number of systems involving WESF $^{90}\text{SrF}_2$ and metal alloys. The results obtained were presented in PNL-1967 (Fullam 1975). The thermodynamic factors that influence the compatibility of WESF $^{90}\text{SrF}_2$ with containment materials are discussed below.

5.1 THERMODYNAMIC FACTORS

Strontium is reported to form two fluorides: SrF and SrF_2 . The monofluoride SrF exists only in the gas phase at high temperatures and would not be stable at the temperatures encountered in a $^{90}\text{SrF}_2$ heat source ($<1200^\circ\text{C}$). Therefore, only SrF_2 needs to be considered in thermodynamic analyses of $^{90}\text{SrF}_2$ systems.

For a simple system containing SrF_2 and a pure metal, the reaction of interest is

The free-energy change (ΔG_R) of the reaction is a measure of 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

$$\Delta G_R = \Delta G_R^0 + RT \ln \frac{A^a(\text{Sr}) \cdot A(\text{MF}_{2a})}{A^a(\text{SrF}_2) \cdot A(\text{M})} \quad (2)$$

where

ΔG_R^0 = the standard free-energy change of the reaction
 $A()$ = the activity of a given component
 T = absolute temperature, $^{\circ}\text{K}$
 R = gas constant.

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

$$\Delta G_R^0 = \Delta G_f^0(\text{MF}_{2a}) - a\Delta G_f^0(\text{SrF}_2) \quad (3)$$

where

$\Delta G_f^0()$ = the 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

$$\Delta G_R = \Delta G_R^0. \quad (4)$$

If ΔG_f^0 for MF_{2a} is more negative than $a\Delta G_f^0$ for SrF_2 , ΔG_R^0 will be negative, and reaction (1) as written will proceed spontaneously.

In Table 2, standard free energy of formation (ΔG_f^0) values as a function of temperature are given for a number of inorganic fluorides. The more negative the value of ΔG_f^0 , the more stable the fluoride. From Table 2 it can be seen that SrF_2 is one of the most stable fluorides known. Assuming the reactants and products are in their standard states at unit activity, SrF_2 would not react spontaneously at temperatures up to 1200°C with any of the metals whose fluorides are given in Table 2, except calcium and possibly barium at temperatures above about 1000°C . In the case of nickel, for example, ΔG_R^0 for the reaction

would range from +128 kcal at 25°C to +122 kcal at 1200°C , and the reaction would not proceed spontaneously at any temperature up to 1200°C .

A valuable method of utilizing the standard free energy of formation data is to prepare an affinity diagram, of the type first proposed by Ellingham (Ellingham 1944), for the inorganic fluorides. In the diagram, ΔG_f^0 values for the fluorides are plotted as a function of temperature. Figure 4 shows such a diagram for several of the fluorides listed in Table 2 (in the diagram ΔG_f^0 is given as kcal/g-mol of fluorine). Assuming all reactants and products are in their standard states, at a given temperature a metal is able to displace from its fluoride any other metal that appears above it on the diagram.

TABLE 2. Free Energies of Formation of Inorganic Fluorides

Compound	$-\Delta G_F^0$, kcal/g-atom of Fluorine					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
AlF ₃	113	101	97	93	91	89
BF ₃	90	87	86	85	85	84
BaF ₂	137	125	122	119	117	116
CF ₄	40	36	35	34	33	32
CaF ₂	140	129	125	121	119	117
CbF ₅	64	59	58	57	56	55
CdF ₂	77	66	63	56	53	50
CoF ₂	74	65	61	58	57	55
CrF ₂	86	77	74	70	69	68
CrF ₃	83	73	70	67	65	64
CuF	56	48	45	43	43	42
CuF ₂	59	50	47	45	44	43
FeF ₂	79	70	67	64	62	61
FeF ₃	73	63	60	57	55	54
HF	65	65	66	66	67	67
KF	129	114	109	102	99	95
LaF ₃	134	124	120	117	115	113
MgF ₂	128	116	112	108	106	103
MnF ₂	90	81	78	76	75	74
MnF ₃	74	64	61	58	57	56
MoF ₅	63	58	57	56	55	54
MoF ₆	64	58	56	54	53	52
NaF	129	115	110	104	101	97
NiF ₂	74	64	61	58	57	55
PF ₃	54	50	48	47	46	45
PbF ₂	74	62	59	55	54	53
RF ₃ ^(a)	131	120	117	113	111	109
SF ₆	40	33	28	25	23	22
SiF ₄	94	89	87	86	85	84
SrF ₂	138	127	123	119	118	116
TiF ₃	100	90	86	83	81	79
TiF ₄	93	86	85	83	83	82
VF ₃	85	75	72	68	67	65
VF ₄	76	70	68	67	67	66
WF ₄	58	48	47	45	45	44
WF ₅	52	47	46	45	45	44
WF ₆	47	41	39	37	36	35
ZrF ₂	109	99	96	92	90	89
ZrF ₄	108	97	93	91	90	89

(a) RF₃ = rare earth fluoride--typically NdF₃

FIGURE 4. Standard Free Energies of Formation for Metal Fluorides as a Function of Temperature

The ΔG_f^0 data given in Figure 4 and Table 2 were compiled from several sources (Glassner 1957; Kubaschewski and Alcock 1979; Lindsay 1979; Rosenquist 1970; Smithells 1976) and were selected as being the most reliable data available on inorganic fluorides. Some of the ΔG_f^0 data were determined experimentally, while the remainder were calculated using standard thermodynamic techniques. The accuracy of the data varies with the fluoride considered, and in some cases the errors may be quite large, especially at the higher temperatures. Errors of ± 10 kcal/g-mol of fluorine would not be uncommon with some fluorides. Despite the questionable accuracy of some of the data, the ΔG_f^0 values can be used in preliminary assessments of the compatibility of SrF_2 with metallic materials. Even allowing for substantial errors in some of the data, it is obvious from Table 2 and Figure 4 that SrF_2 would not react spontaneously with most of the metals listed when the constituents are in their standard states.

Since SrF is not stable at the conditions encountered in an operating $^{90}\text{SrF}_2$ heat source, reactions of the type shown in Equation (6) need not be considered:

Strontium does form complex fluorides, but in every case the strontium has an oxidation state of +2. Therefore, reactions such as Equation (7) are not possible:

It is possible that reactions of the type shown by Equation (8) could occur:

For reaction (8) to proceed spontaneously when the constituents are in their standard sizes, ΔG_f^0 (per g-mol of fluorine) for the complex metal fluoride would have to be more negative than ΔG_f^0 for SrF_2 , which seems highly unlikely.

The possibility of reactions involving the formation of intermetallic compounds must also be considered:

For Equation (9) to proceed spontaneously when the constituents are in their standard states, ΔG_f^0 for the intermetallic compound must be sufficiently negative to overcome the difference in the free energies of formation of SrF_2 and the metal fluoride. The more negative ΔG_f^0 of the metal fluoride, the less negative ΔG_f^0 of the intermetallic compound has to be for Equation (9) to proceed spontaneously. Magnesium forms a very stable fluoride and is one of the few metals that is reported to form an intermetallic compound with strontium (Smithells 1976):

For Equation (10) to proceed spontaneously at 25°C, ΔG_f^0 for Mg_2Sr would have to be greater than -20 kcal/mol. ΔG_f^0 for Mg_2Sr has not been reported in the literature, but the heat of formation (ΔH_f^0) for Mg_2Sr is reported to be only -5.1 kcal/mol (Smithells 1976). Therefore, at 25°C, ΔG_f^0 for Mg_2Sr would be <-20 kcal/mol, and reaction (10) would not proceed spontaneously. Although data on other strontium intermetallic compounds are limited, it appears unlikely that reactions involving strontium intermetallics would be important in $^{90}\text{SrF}_2$ systems.

It is possible that the metal phase could dissolve in the strontium fluoride. Little is known of the solubility of metals in SrF_2 , but it is doubtful if the metal dissolution would occur to a significant degree at temperatures below the melting point of SrF_2 (1742°K).

WESF-produced $^{90}\text{SrF}_2$ contains a great many cation impurities (see Table 1). The concentrations of the impurities in the WESF $^{90}\text{SrF}_2$ can vary over fairly wide ranges. The bulk of the impurities will be present as fluorides, although trace amounts of oxides, nitrates, and sulfates may also be present. Referring to Table 2 and Figure 4, it can be seen that all of the impurity fluorides, except CaF_2 and possibly BaF_2 , have less negative free energies of formation and are less stable than SrF_2 . The less stable the impurity fluoride, the more likely it is to react spontaneously with the containment metals. Of the impurity fluorides present in

WESF $^{90}\text{SrF}_2$, the fluorides of cadmium, chromium, copper, iron, manganese, nickel, and lead are the least stable, and the most likely to react with containment materials. Assume, for example, that the $^{90}\text{SrF}_2$ contains FeF_3 and NiF_2 as impurities and is in contact with chromium metal:

If the reactants and products are in their standard states, it is apparent from Figure 4 that the chromium could reduce FeF_3 and NiF_2 to their respective metals, but would not react spontaneously with SrF_2 .

Reactions involving the formation of lower valence fluorides, complex fluorides, and intermetallic compounds would all have to be considered when analyzing $^{90}\text{SrF}_2$ systems containing impurity fluorides. For example:

Depending on the containment material under consideration, any of the reactions might be important in analyzing the compatibility of the WESF $^{90}\text{SrF}_2$ with the containment material. As a general rule, the less stable the impurity fluoride, the more likely it is to react spontaneously with a containment material in one way or another. Fortunately, chemical analyses of numerous batches of WESF-produced $^{90}\text{SrF}_2$ indicate that the less stable impurity fluorides are generally present in the lowest concentrations. Once the less stable fluorides present in a $^{90}\text{SrF}_2$ heat source are consumed by reaction with the capsule material, subsequent attack of the capsule should decrease to a very low level.

Another factor to be considered in evaluating $^{90}\text{SrF}_2$ systems is the decay of the ^{90}Sr . Strontium-90 decays by beta emission to ^{90}Y , which, in turn, decays by beta emission to stable ^{90}Zr :

The half-life for ^{90}Sr is 28.6 yr, while the half-life for ^{90}Y is 64 h. Once secular equilibrium is established, the $^{90}\text{Y}/^{90}\text{Sr}$ atomic ratio is 2.6×10^{-4} . Yttrium-90 does not have to be considered in the thermodynamic analysis, but the stable ^{90}Zr does have to be considered. The chemical species resulting from decay of the ^{90}Sr in the SrF_2 has not been identified. The $^{90}\text{SrF}_2$ should decay to the difluoride of stable ^{90}Zr :

Zirconium difluoride has been reported in the literature (McTaggart and Turnbull 1964) but is said to disproportionate at elevated temperatures to zirconium tetrafluoride and zirconium metal:

Any ZrF_2 formed as a decay product in an operating $^{90}\text{SrF}_2$ heat source should disproportionate according to Equation (18), but this has not been demonstrated experimentally. It is possible that the ZrF_2 , as it forms, could react with any SrF_2 or impurity fluorides present to form a stable complex fluoride or stable solid solution.

If ZrF_2 or zirconium metal is present in the system due to ^{90}Sr decay, it would act as a powerful reducing agent. From Figure 4 and Table 2, it is apparent that either ZrF_2 or Zr could reduce many of the less stable impurity fluorides to the corresponding metals. The overall effect would be for the ZrF_2 or zirconium metal to act as a gettering agent for the impurity fluorides and reduce the amount of material available to react with the containment material.

In most $^{90}\text{SrF}_2$ systems of practical interest, one or more of the components would probably not be in their standard states, and ΔG_R would have to be determined using Equation (2). Considering the $\text{SrF}_2\text{-Ni}$ systems shown in Equation (5),

$$\Delta G_R = \Delta G_R^0 + RT \ln \frac{A_{\text{Sr}} \cdot A_{\text{NiF}_2}}{A_{\text{SrF}_2} \cdot A_{\text{Ni}}}. \quad (19)$$

From Equation (19), it is obvious that factors that reduce the activities of the reactants make ΔG_R more positive and reduce the driving force for the reaction to proceed as written. Similarly, reducing the activities of the products makes ΔG_R more negative and increases the potential for the reaction to proceed spontaneously. If the nickel is present as the constituent of an alloy, its activity will be less than unity, making ΔG_R more positive than when nickel is present in its standard state. In general, the lower the concentration of nickel in the alloy, the smaller its activity. If the other constituents of the $\text{SrF}_2\text{-Ni(alloy)}$ system are assumed to be at unit activity, then

$$\Delta G_R = \Delta G_R^0 - RT \ln A_{\text{Ni}}, \quad (20)$$

and ΔG_R at 25° and 1200°C would vary with the activity of the nickel in the following manner:

A_{Ni}	$\Delta G_R, \text{ kcal}$	
	25°C	1200°C
1.0	128.0	122.0
0.9	128.1	122.8
0.1	129.4	128.7
0.01	130.7	135.5
0.001	132.1	142.2
0.0001	133.5	149.0

Only a limited amount of data are available in the literature on the activities of metal alloy constituents, although methods are available for estimating the activities from other thermodynamic data. If the alloy is a solid solution, the activity (A_i) of a given component is given by the equation

$$\Delta \bar{G}_i = RT \ln A_i$$

where $\Delta \bar{G}_i$ is the partial molar free energy of solution (mixing) for the component. Methods are available for estimating the partial molar free energies of solution for metallic solid solutions (Hildebrand and Scott 1950; Kubaschewski and Alcock 1979).

Many of the nickel- and cobalt-base superalloys, considered as potential containment materials for $^{90}\text{SrF}_2$, are available in solution heat-treated form. As a first approximation, these materials can be assumed to be solid solution alloys. By calculating the partial molar free energies of solution for the various components of a given alloy, it is possible to estimate if the alloy constituents will react spontaneously with the constituents of the WESF $^{90}\text{SrF}_2$. Analyses of such systems show one or more of the constituents of a nickel- or cobalt-base alloy will probably react spontaneously with some of the impurity fluorides in the WESF $^{90}\text{SrF}_2$ at the temperatures encountered in an operating $^{90}\text{SrF}_2$ heat source (Fullam 1975). Chromium, in particular, is one component of most nickel- and cobalt-base alloys that is likely to react with the less stable impurity fluorides.

In analyzing systems involving WESF $^{90}\text{SrF}_2$ and a nickel- or cobalt-base alloy, it soon becomes obvious that if it is assumed the alloys are solid solutions, then, on a thermodynamic basis, the systems are very similar. The alloys generally contain a number of common components. Even though the concentration of a common component may vary over a wide range between alloys, the free energy of solution ($\Delta \bar{G}_i$) of the component generally does not vary markedly between alloys. This means that reactions involving common alloy components that are thermodynamically possible in one alloy-fluoride system will probably also be possible in other alloy systems. The only major differences between the systems, therefore, will be when the alloys contain different components.

When a nickel- or cobalt-base alloy is held at elevated temperatures for an extended period of time, it generally undergoes aging reactions, and the alloy can no longer be assumed

to be a solid solution. The effects of the aging reactions on the activities of the alloy constituents must be considered if the $^{90}\text{SrF}_2$ -alloy system is to be analyzed in a rigorous manner. Unfortunately, simple reliable methods for estimating the activities of components in the aged alloys are not available, and the value of carrying out rigorous analyses of aged alloy systems does not warrant the degree of effort required.

The $^{90}\text{SrF}_2$ produced at WESF is fired at $\sim 1100^\circ\text{C}$ before encapsulation. At this temperature, it is likely that a portion of the fluoride mixture is in the liquid phase. When the fluoride is cooled, it is impossible to tell what solid phases are present. It is very unlikely that the impurity fluorides are present in their standard states at unit activity. Rather, it is more reasonable to assume that the impurity fluorides are present as complex fluorides and/or solid solutions with SrF_2 or each other. Unfortunately, it has not been possible to determine experimentally how the fluorides exist in the WESF $^{90}\text{SrF}_2$. If the fluorides exist as complex fluorides and/or solid solutions, the net effect is a reduction of their activities. Since SrF_2 represents greater than 90% of WESF $^{90}\text{SrF}_2$, the impurity fluorides would have minimal effect on the activity of the SrF_2 . On the other hand, the formation of complex fluorides and/or solid solutions could produce a marked decrease in the effective activities of the impurity fluorides since they are present in low concentrations. The net result would be to reduce the potential for reactions to occur spontaneously between the impurity fluorides and the containment materials.

Factors that decrease the activities of the products increase the potential for reactions to occur between the fluorides and a containment material. Decreases in the activities of the products could result if 1) the product fluorides form complex fluorides and/or solid solutions with residual SrF_2 , impurity fluorides, or each other; and 2) the metal products dissolve in the fluoride phases and/or dissolve in or form intermetallic phases with components of the containment material.

The WESF-produced $^{90}\text{SrF}_2$ contains small amounts of oxide impurities. The reasoning applied above to the fluoride systems is generally applicable to the oxides. Free energy of formation data show that SrO is one of the most stable oxides known, and the SrO should not react spontaneously with the components of the containment materials (see Table 3). In addition, any SrO that is present in the WESF $^{90}\text{SrF}_2$ should be converted to SrF_2 by the impurity fluorides:

For reaction (21), ΔG_R^0 at 25° and 1200° would be -46 and -40 kcal, respectively, and the reaction, as written, would proceed spontaneously. Similarly, for reaction (22) ΔG_R^0 at 25° and 1200°C would be -177 and -171 kcal, respectively, and the reaction (22), as written, would proceed spontaneously. If the less stable oxide impurities are present in the WESF $^{90}\text{SrF}_2$ (i.e., Fe_2O_3 , NiO , etc.), they could react spontaneously with the containment materials in much the same manner as the less stable fluoride impurities.

TABLE 3. Free Energies of Formation of Inorganic Oxides

Compound	$-\Delta G_f^0$, kcal/g-atom of Oxygen					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
Al ₂ O ₃	126	112	106	101	99	96
B ₂ O ₃	94	83	80	77	75	73
BaO	129	116	111	105	103	100
CO	33	45	49	53	56	58
CO ₂	47	47	47	47	47	47
CaO	144	131	126	121	118	116
CbO	92	80	77	73	71	69
CdO	54	41	36	25	20	16
CoO	51	41	36	34	33	31
Co ₃ O ₄	46	34	30	25	23	21
Cr ₂ O ₃	83	71	67	63	61	59
Cu ₂ O	35	24	21	18	16	14
CuO	30	19	15	11	9	7
FeO	58	49	46	43	42	40
Fe ₃ O ₄	60	49	45	41	39	38
Fe ₂ O ₃	59	48	43	39	37	35
K ₂ O	76	58	52	44	40	36
La ₂ O ₃	136	125	121	117	115	112
MgO	137	122	117	112	109	104
MnO	87	77	73	70	68	66
Mn ₃ O ₄	77	64	60	56	53	52
Mn ₂ O ₃	72	59	55	51	49	47
MoO ₂	64	52	46	44	42	40
MoO ₃	54	42	38	35	34	33
Na ₂ O	90	70	64	51	46	40
Nb ₂ O ₅	85	75	68	64	62	60
NiO	52	38	33	29	26	24
P ₂ O ₃	81	70	67	64	62	60
P ₂ O ₅	66	53	49	45	43	42
PbO	45	31	26	23	21	19
R ₂ O ₃ (a)	137	125	121	117	115	113
SO ₂	41	36	34	32	32	31
SiO ₂	102	90	86	81	79	77
SrO	134	121	116	111	108	106
TiO	116	103	99	93	92	90
Ti ₂ O ₃	113	102	98	92	91	89
TiO ₂	103	93	89	84	83	81
VO	97	90	86	82	79	77
V ₂ O ₃	93	82	78	74	72	70
WO ₂	64	54	50	46	44	42
WO ₃	61	49	46	42	40	38
ZrO ₂	123	110	105	101	99	97
H ₂ O	55	48	45	42	41	39

(a) Rare earth oxide--typically Nd₂O₃

Analysis of inert SrF_2 fired at 1100°C for several hours showed it contained trace amounts of water. The water could react with some of the impurity fluorides to form hydrogen fluoride and the corresponding metal oxides, which could react with the containment materials.

WESF-produced SrF_2 also contains trace amounts of nitrate and sulfate. Depending on the compounds present, the sulfates and nitrates could react directly with the containment materials. A wide variety of metathesis reactions are possible between the nitrates, sulfates, oxides, and fluorides, and it is impossible to identify the nitrate and sulfate species present in the fluoride after it has been fired at high temperatures.

5.2 PHYSICAL FACTORS

Pure strontium fluoride melts at 1742°K , but the impurities found in WESF $^{90}\text{SrF}_2$ can produce phases that melt at much lower temperatures. The SrF_2 -NaF system, for example, exhibits a minimum melting point of 856°C (Berezhnaya and Bukhalova 1960). Differential thermal analysis of inert SrF_2 that contains impurities approximating those found in WESF $^{90}\text{SrF}_2$ shows the existence of a low melting phase that has a melting point of $851^\circ \pm 5^\circ\text{C}$ (Fullam 1977c). The amount of liquid phase appears to be small, amounting to less than 1% of the total mass at temperatures up to 1100°C . If a liquid fluoride phase is present in a WESF $^{90}\text{SrF}_2$ system, it could have a marked effect on the compatibility of a containment material with the fluoride for the following reasons:

- Thermodynamic considerations show that containment materials are more likely to react with the impurities in the SrF_2 than with the SrF_2 itself. Although the WESF $^{90}\text{SrF}_2$ is heterogeneous, the impurity fluorides are distributed fairly uniformly throughout the mass of a given batch of fluoride. Diffusion of impurity fluorides through the solid fluoride mixture to the fluoride-metal interface would be relatively slow at heat-source operating temperatures, and reactions between the metal and the impurity fluorides could be diffusion-limited. The presence of even a small amount of liquid phase in the fluoride mixture could drastically increase diffusion of the impurities to the fluoride-metal interface, which could, in turn, increase the rates at which the impurities and the containment material react.
- As a general rule, reaction rates are much slower when the reactants are all solids than when one or more of the reactants is a liquid or gas. Thus, the presence of a liquid phase that contains impurity fluorides could greatly increase reaction rates between the containment materials and the impurities.
- Product fluorides could dissolve in the liquid phase, effectively decreasing their activities. It is also possible that the metal phases could dissolve in the liquid phase, decreasing their activities, but this seems less likely to occur.

Thus, the overall effect of the presence of a liquid phase in the WESF $^{90}\text{SrF}_2$ would probably be to increase the potential for a given reaction to occur between the containment material and an impurity fluoride and to increase the rate at which the reactions could proceed.

Impact consolidation is used to load the granular $^{90}\text{SrF}_2$ into the WESF storage capsule. The bulk density of the $^{90}\text{SrF}_2$ in the capsule is in the range of 65 to 70% of theoretical density. As a result, void spaces are present, and there are areas in which the solid fluoride is not in direct contact with the capsule wall. A similar situation could occur in a $^{90}\text{SrF}_2$ heat source if the heat-source capsule is loaded with the $^{90}\text{SrF}_2$ in a similar manner. Even with a small amount of liquid phase present, it is possible that portions of the capsule surface would not be in direct contact with the fluoride. This could result in uneven attack of the capsule surface by the fluoride mixture.

Depending on the temperature, it is possible that some of the impurity fluorides in WESF $^{90}\text{SrF}_2$ would have significant vapor pressures. This could lead to an increase in the rate at which the impurity fluoride would react with a containment material. Because of the complexity of the WESF $^{90}\text{SrF}_2$ mixture, it is impossible to determine what the partial pressures of the individual fluoride components would be as a function of temperature.

In summary, thermodynamic considerations show that SrF_2 is a very stable fluoride, and it would not react spontaneously with normal containment materials at heat-source operation temperatures. The WESF-produced $^{90}\text{SrF}_2$ contains a number of less stable fluoride impurities (as well as oxides, nitrates, and sulfates), and some of these impurities could react spontaneously with some containment materials. Fortunately, the impurities that are most likely to react with the containment materials are generally present in the $^{90}\text{SrF}_2$ in low concentrations. Once these impurities have reacted, attack of the containment material by the remaining fluoride should decrease to a very low rate.

6.0 COMPATIBILITY TESTING OF STRONTIUM-90 FLUORIDE

The compatibility tests carried out during the development of the WESF were adequate to demonstrate that Hastelloy C-276 and Haynes Alloy 25 would safely contain $^{90}\text{SrF}_2$ for long periods of time (up to 600 yr) under the conditions encountered in the WESF operation. However, the data were not adequate for demonstrating the safe containment of $^{90}\text{SrF}_2$ under the conditions that a radioisotope heat source would encounter in service. The maximum $^{90}\text{SrF}_2$ -canister interface temperature encountered in the WESF operation is not expected to exceed $\sim 400^\circ\text{C}$, whereas fuel-clad interface temperatures approaching 1000°C were postulated for $^{90}\text{SrF}_2$ heat-source service. Therefore, detailed compatibility studies with $^{90}\text{SrF}_2$ were needed to show that the fluoride could be safely contained when it was used as a heat-source fuel. In carrying out the required compatibility studies, the primary emphasis was on the $^{90}\text{SrF}_2$ produced at WESF.

A detailed research plan for the $^{90}\text{SrF}_2$ compatibility studies was prepared at the start of the program. At the request of PNL, the research plan was reviewed by experts in radioisotopes containment at various government facilities including the Oak Ridge National Laboratory (ORNL), Savannah River Laboratory (SRL), and Mound Laboratory. The plan was also reviewed and approved, before testing started, by the Division of Applied Technology of the AEC, the original sponsor of the program. The work was subsequently sponsored by the Space Nuclear Systems Division of the Energy Research and Development Administration and is currently funded by the Space and Terrestrial Systems Division of the DOE. The research plan and all compatibility testing was reviewed and approved, in turn, by each sponsoring organization.

The program to evaluate the compatibility of $^{90}\text{SrF}_2$ with containment materials was divided into five major phases:

- initial scouting tests;
- supplemental screening tests;
- WESF $^{90}\text{SrF}_2$ capsule demonstration tests;
- thermal gradient test;
- long-term tests with WESF $^{90}\text{SrF}_2$.

The various tests were designed to complement each other and provide a comprehensive evaluation of the compatibility of $^{90}\text{SrF}_2$ with selected containment materials. Experimental details of the first four phases of the program are provided in Section 10.0, and details of the long-term tests are presented in Section 7.0.

6.1 INITIAL SCOUTING TESTS

Details of the initial scouting tests are presented in Section 10.1 and summarized below. The objectives of the initial scouting tests were twofold:

- to evaluate a number of containment materials with SrF_2 in short-term tests and to identify the best materials for long-term testing; and

- to determine the effects of impurities on the compatibility of SrF_2 with containment materials and to determine if additional purification steps were needed in the WESF operation to produce a $^{90}\text{SrF}_2$ product that could be safely contained in heat-source applications.

By sponsor directive, the containment materials evaluated in the initial scouting tests were limited to materials that could be adapted for use as the inner capsule in the WESF operation. This effectively eliminated from consideration materials such as precious metals (iridium, etc.) because of the costs involved, and protective deposits (vapor-deposited coatings, sputtered coatings, electrodeposited layers, etc.) because of the mechanical stresses encountered in the capsule-loading operation at WESF.

The scouting tests were carried out at 800° , 1000° and 1100°C and lasted 1500 and 4400 h. Nine metallic containment materials were evaluated in the tests: tungsten, TZM, Haynes Alloy 25, Haynes Alloy 188, Hastelloy C-276, Hastelloy X, Hastelloy N, Inconel 600 and Inconel 625. Selection of the nine materials was based on a number of factors, which included: the results of the earlier compatibility studies at Martin Marietta and PNL (see Section 4.0); other experimental programs involving metal fluorides at high temperatures; theoretical considerations; and heat-source operating requirements.

The nine containment materials were evaluated with four grades of strontium fluoride:

- high-purity nonradioactive SrF_2 containing <1000 ppm total impurities;
- high-purity nonradioactive SrF_2 containing controlled levels of individual added impurities;
- high-purity $^{90}\text{SrF}_2$;
- WESF-grade $^{90}\text{SrF}_2$.

The high-purity inert SrF_2 was tested as a reference material against which the other fluoride compositions could be compared. Impurities tested included NaF, MnF_2 , PbF_2 , CuF_2 , FeF_3 , AlF_3 , CaF_2 , MgF_2 , BaF_2 , SrO, $\text{Sr}(\text{NO}_3)_2$ and H_2O . Each impurity, except CaF_2 , MgF_2 , and BaF_2 , was tested individually by adding a controlled amount (up to 5 wt%) to the high-purity inert SrF_2 . The CaF_2 , MgF_2 and BaF_2 were tested in combination with the inert SrF_2 . When the tests were started, $^{90}\text{SrF}_2$ was not yet available from WESF. Instead, WESF-grade $^{90}\text{SrF}_2$ was prepared at PNL using the WESF flowsheet and a typical ^{90}Sr feed solution obtained from WESF. The WESF-grade $^{90}\text{SrF}_2$ contained about 4.5 wt% impurities typical of those later found to be present in WESF-produced $^{90}\text{SrF}_2$. The high-purity $^{90}\text{SrF}_2$ was prepared at PNL from the same ^{90}Sr solution used to prepare the WESF-grade ^{90}Sr . The solution was purified by chromatographic ion exchange before preparation of the fluoride. Unfortunately, the high-purity $^{90}\text{SrF}_2$ contained about 1.9 wt% impurities, with NaF the principal contaminant.

The nine containment materials were tested with each of the fluoride compositions. The tests with inert SrF_2 that contained controlled levels of added impurities were carried out at 1000°C ; all of the other fluoride compositions were tested at 800° , 1000° and 1100°C .

In the scouting tests, tungsten and TZM exhibited the greatest resistance to attack by the different fluoride mixtures. Haynes Alloy 25 was the most resistant of the nickel- and cobalt-base alloys to fluoride attack, with Hastelloy C-276 the best of the remaining nickel- and cobalt-base alloys. The presence of SrO , FeF_3 , and CuF_2 in the strontium fluoride generally produced increased attack of the containment materials. The presence of nitrate and water in the fluoride had surprisingly little effect on the attack.

Based on the results obtained in the scouting tests, TZM, Haynes Alloy 25 and Hastelloy C-276 were selected for long-term testing with $^{90}\text{SrF}_2$. Tungsten was not selected because of problems in the WESF operation related to fabricating, loading and welding tungsten capsules.

6.2 SUPPLEMENTAL SCREENING TESTS

The scouting tests were directed at containment materials that could be used in the WESF operation. However, certain applications for $^{90}\text{SrF}_2$ heat sources could arise that could not use the WESF $^{90}\text{SrF}_2$ capsule or modifications thereof. In such applications, containment materials other than those evaluated in the long-term tests may be preferred. The objective of the supplemental screening tests was to evaluate a large number of containment materials in a cursory manner and to determine their relative resistance to attack by SrF_2 . It was not intended that the screening tests provide sufficient compatibility data to allow licensing of $^{90}\text{SrF}_2$ sources using any of the materials evaluated. The actual licensing and deployment of $^{90}\text{SrF}_2$ sources fabricated from the materials screened would require additional testing with $^{90}\text{SrF}_2$. The screening tests would simply provide a guideline as to which materials should be considered for additional testing.

The supplemental screening tests were carried out at 800°C using inert SrF_2 that contained impurities similar to those found in WESF $^{90}\text{SrF}_2$. The tests lasted 1500 and 4400 h. A total of 33 materials, including two grades of ductile cast iron, were evaluated in the tests (see Table 4). Haynes Alloy 25, Hastelloy C-276 and TZM were tested as reference materials to allow the results obtained in the supplemental screening tests to be compared with results obtained in the other compatibility tests.

In general, the materials tested can be divided into three basic groups: precious metals, refractory metals, and base metals and alloys. Potential compatibility with SrF_2 was the prime consideration in the selection of the materials to be tested. Cost, availability, fabricability, mechanical properties, etc., were not considered in the selection.

Details of the tests and the results obtained are given in Section 10.2.

6.3 WESF $^{90}\text{SrF}_2$ CAPSULE DEMONSTRATION TESTS

The long-term tests with WESF $^{90}\text{SrF}_2$ and Hastelloy C-276 do not completely duplicate the conditions encountered in the WESF $^{90}\text{SrF}_2$ capsule, particularly with regard to the exposed metal surface-to- SrF_2 volume (S/V) ratio. Therefore, demonstration tests were carried out

TABLE 4. Containment Materials Evaluated in the Supplemental Screening Tests

1. Hastelloy Alloy C-276	17. Ductile Cast Iron ^(a)
2. Haynes Alloy 25	18. 316L Stainless Steel
3. TZM	19. JS-777
4. Hastelloy Alloy C-4	20. Molybdenum
5. Hastelloy Alloy S	21. Niobium
6. Hastelloy Alloy B	22. Hafnialloy 2525
7. Hastelloy Alloy B-2	23. Ta-10% W
8. Inconel 617	24. Mo-50% Re
9. Inconel 671	25. W-26% Re
10. Incoloy 800	26. Rhenium
11. Haynes Alloy 556	27. Iridium
12. René 41	28. Ir-0.3% W
13. Udimet 700	29. Platinum
14. Monel 400	30. Gold
15. Nickel 200	31. Titanium
16. Ingot Iron	32. Copper

(a) Two grades of ductile cast iron were evaluated--one grade had a pearlite matrix and the other a ferrite matrix.

with two full-size WESF $^{90}\text{SrF}_2$ capsules. The objective of the demonstration tests was to determine if attack of the Hastelloy C-276 by the $^{90}\text{SrF}_2$ in the demonstration capsules was significantly different from the attack observed with Hastelloy C-276 in the long-term tests with WESF $^{90}\text{SrF}_2$.

In the demonstration tests, two standard WESF $^{90}\text{SrF}_2$ capsules were placed individually in insulated containers and allowed to self-heat to a $^{90}\text{SrF}_2$ -Hastelloy C-276 interface temperature of $\sim 800^\circ\text{C}$. Because of uneven heat losses from the insulated containers, temperature gradients existed between the center and ends of the capsules and the interface temperatures varied by about 80°C between the capsule center and ends. One test lasted for 5000 h and the second test for 3 yr. At the conclusion of each test, the WESF capsule was sectioned, and samples were taken from various locations in the Hastelloy C-276 inner capsule and examined to determine the extent of attack by the $^{90}\text{SrF}_2$.

Details of the tests and the results obtained are given in Section 10.3.

6.4 THERMAL GRADIENT TEST

In the thermal gradient test, a Hastelloy C-276 capsule containing SrF_2 was subjected to a thermal gradient for ~ 6 mo. The inert SrF_2 used in the test contained impurities similar to those found in the $^{90}\text{SrF}_2$ produced at WESF. The objectives of the test were as follows:

- to determine the effect of temperature on the attack of the Hastelloy C-276 by the SrF_2 ;
- to identify the reaction mechanisms involved in the attack of the Hastelloy C-276 by the fluoride;
- to determine if the thermal gradient affected diffusion of the impurities in the SrF_2 .

The test capsule, fabricated from 1-1/2-in. Sch. 40 seamless Hastelloy C-276 pipes, was 26 in. long. The SrF_2 was cold-pressed into the capsule to $\sim 70\%$ of theoretical density. The capsule was closed by TIG-welding the end cap in place. The capsule had an S/V of $\sim 1.0 \text{ cm}^{-1}$, which compares with a value of $\sim 0.9 \text{ cm}^{-1}$ for the WESF capsule.

The capsule was heated in a three-zone tube furnace for 4400 h. The furnace was controlled so that the temperature of the capsule varied from 360°C at one end to 920°C at the opposite end, giving a temperature gradient of 560°C . At the conclusion of the test, the capsule was sectioned, and samples taken from various locations in the capsule were examined to determine the extent of metal attack and the reaction mechanisms involved. The SrF_2 from various locations in the capsule was also analyzed.

Details of the thermal gradient test are summarized in Section 10.4.

6.5 LONG-TERM TESTS WITH WESF $^{90}\text{SrF}_2$

The basic objective of the long-term tests was to obtain sufficient compatibility data with WESF-produced $^{90}\text{SrF}_2$ to show that the fluoride could be safely contained during heat-source service. The three preferred containment materials identified in the initial scouting tests (TZM, Haynes Alloy 25, and Hastelloy C-276) were tested with WESF-produced $^{90}\text{SrF}_2$ and inert $^{90}\text{SrF}_2$ that contained impurities similar to those found in the WESF $^{90}\text{SrF}_2$. The tests were carried out at 600° , 800° and 1000°C and lasted up to 30,000 h. Complete details of the long-term tests are given in Section 7.0.

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7.0 LONG-TERM COMPATIBILITY TESTS WITH WESF $^{90}\text{SrF}_2$

7.1 TEST OBJECTIVES

The long-term compatibility tests with WESF $^{90}\text{SrF}_2$ were carried out using the three preferred containment materials identified in the initial scouting tests--Hastelloy C-276, Haynes Alloy 25, and TZM. The basic objective of the tests was to obtain sufficient compatibility data with WESF $^{90}\text{SrF}_2$ and the three alloys to show that the $^{90}\text{SrF}_2$ could be safely contained during heat-source service. In order to accomplish this basic objective, it was necessary to meet the following specific objectives:

- obtain sufficient data on reaction kinetics to accurately estimate the metal attack that would occur during the service life of the $^{90}\text{SrF}_2$ heat source, which is assumed to be 10 yr;
- determine the effects of fluoride attack on the mechanical properties of the three alloys;
- identify as completely as possible with the funds available the reaction mechanisms involved in the attack of the three alloys by the WESF $^{90}\text{SrF}_2$;
- determine the principal factors that affect the attack of the three alloys by the $^{90}\text{SrF}_2$.

Since the WESF operation represents the only major domestic source of $^{90}\text{SrF}_2$, the emphasis of the long-term tests was on the $^{90}\text{SrF}_2$ produced at WESF. All of the radioactive tests were carried out using $^{90}\text{SrF}_2$ obtained from WESF.

7.2 TEST CONDITIONS

The Hastelloy C-276, Haynes Alloy 25 and TZM were evaluated with three grades of SrF_2 : WESF-produced $^{90}\text{SrF}_2$; WESF-produced $^{90}\text{SrF}_2$ spiked with Zr and ZrF_4 to simulate 10-yr decay of the $^{90}\text{SrF}_2$; and inert SrF_2 that contained impurities similar to those in the WESF $^{90}\text{SrF}_2$. The tests were carried out at 600° , 800° , and 1000°C and lasted up to 30,000 h. Three types of metal specimens were tested: compatibility specimens, tensile specimens, and Charpy V notch (CVN) specimens. The compatibility specimens, which were simply small discs of each alloy, were tested at three different S/V ratios. The tensile and CVN specimens were tested to determine the effect of fluoride attack on the mechanical properties of the three alloys. In addition, control specimens of each alloy were tested without fluoride present to determine the effects of aging, at various temperatures, on the microstructure and mechanical properties of the three materials.

Because of the many variables to be considered, it was impossible to test capsules for each possible set of conditions. A complete test matrix would have required several hundred $^{90}\text{SrF}_2$ capsules and a similar number of inert SrF_2 capsules. To hold the capsules required to a reasonable number, the test matrix shown in Table 5 was used for evaluating Hastelloy C-276, and identical test matrices were used for evaluating the Haynes Alloy 25 and TZM. The

TABLE 5. Conditions for the Long-Term Compatibility Tests With Hastelloy C-276(a)

Specimen Design Tested	Grade of SrF_2 Used	S/V, cm^{-1}	Exposure, h	No. of Capsules Tested		
				600°C	800°C	1000°C
Compatibility	Inert $\text{SrF}_2^{(b)}$	4.5	1,000	2	2	2
			6,000	2	2	2
			12,000	2	2	2
			20,000	2	2	2
			30,000	2	2	2
Compatibility	Inert SrF_2	2.5	1,000	1	1	1
			6,000	1	1	1
Compatibility	Inert SrF_2	0.9	1,000	1	1	1
			6,000	1	1	1
			12,000	1	1	1
			20,000	1	1	1
Compatibility	WESF $^{90}\text{SrF}_2$	4.5	1,000	2	2	2
			6,000	2	2	2
			12,000	2	2	2
			20,000	2	2	2
			30,000	2	2	2
Compatibility	WESF $^{90}\text{SrF}_2$	2.5	1,000	1	1	1
			6,000	1	1	1
Compatibility	WESF $^{90}\text{SrF}_2 + \text{Zr}^{(c)}$	4.5	1,000	1	1	1
			6,000	1	1	1
Control	None	---	1,000	1	1	1
			6,000	1	1	1
			12,000	1	1	1
			20,000	1	1	1
			30,000	1	1	1
Tensile	WESF $^{90}\text{SrF}_2$	2.8	6,000	2	2	2
			12,000	2	2	2
Tensile (Control)	None	---	6,000	4	4	4
			12,000	4	4	4
Charpy	WESF $^{90}\text{SrF}_2$	2.8	6,000	2	2	2
			12,000	2	2	2
Charpy (Control)	None	---	6,000	4	4	4
			12,000	4	4	4

(a) Conditions for the long-term tests with Haynes Alloy 25 and TZM were identical to those for the Hastelloy C-276.

(b) Nonradioactive SrF_2 containing impurities similar to those found in WESF $^{90}\text{SrF}_2$.

(c) Zirconium and ZrF_4 added to the WESF $^{90}\text{SrF}_2$ to simulate 10-yr decay of the $^{90}\text{SrF}_2$.

Hastelloy C-276 test matrix required 66 $^{90}\text{SrF}_2$ capsules, 48 inert SrF_2 capsules, and 63 control specimens. The Haynes Alloy 25 and TZM test matrices required like numbers of capsules and control specimens. A total of 108 tensile and 108 CVN specimens were required for the tests.

To be prepared for possible problems in the fabrication of the test capsules several extra capsules and lids were machined from each alloy. When the required test capsules had been fabricated, any extra capsules were also loaded with $^{90}\text{SrF}_2$ and compatibility specimens. The extra capsules were tested at 800°C . Thus, the total number of $^{90}\text{SrF}_2$ capsules tested was 210 instead of the 198 (3 x 66) required by the three test matrices. Approximately 7.5 kg of WESF $^{90}\text{SrF}_2$ ($\sim 350,000$ Ci) were needed in the fabrication of the $^{90}\text{SrF}_2$ test capsules.

It would have been highly desirable to carry out tests with $^{90}\text{SrF}_2$ at an S/V of 0.9 cm^{-1} , equivalent to the S/V of the WESF capsule. However, even a limited number of such tests would have required a very large volume of $^{90}\text{SrF}_2$ (at least 0.7 kg of $^{90}\text{SrF}_2$ per test capsule). This could not be attempted with the program funds available. Instead, the tests at an S/V of 0.9 cm^{-1} were carried out by using inert SrF_2 that contained impurities similar to those in WESF $^{90}\text{SrF}_2$.

7.3 TEST PROCEDURES

The same general procedures as those in the initial scouting test were used in the long-term tests. The basic procedure consisted of burying the test specimen in SrF_2 within the test capsule. The test capsule was closed by TIG-welding the lid in place and was sealed in a protective jacket to prevent oxidation. Then, the capsule was tested in an air atmosphere muffle furnace. After the test was completed, the capsule was sectioned and the test specimen removed and examined. Fabrication and testing of the $^{90}\text{SrF}_2$ capsules was carried out remotely in a heavily shielded facility (hot cell). The test specimens exposed to $^{90}\text{SrF}_2$ were sent to ORNL for examination.

7.3.1 Preparation of Test Capsules

Several capsule designs were used in the tests to accommodate the different types of test specimens and to allow different S/V ratios to be evaluated. With one exception, all metallic components of a test capsule were fabricated from the same alloy. The one exception involved the testing of TZM specimens and inert SrF_2 at an S/V of 0.9 cm^{-1} ; in these tests, the capsule bodies and lids were fabricated from Haynes Alloy 25 because of the difficulties and excessive costs involved in fabricating them from TZM.

Figure 5 shows the capsule design used in testing the compatibility specimens. Three different-size capsule bodies were used to provide the different S/V ratios needed-- 0.9 , 2.5 and 4.5 cm^{-1} . The two smaller size capsules and lids were machined from bar stock, while the largest capsule was fabricated from 2-1/2-in. Sch. 40 pipe and plate. The compatibility specimens were fabricated from bar stock. Each specimen was 0.5 in. dia by $\sim 1/4$ in. to $3/8$ in. thick. The flat faces of the specimens were ground and polished using $0.3\text{-}\mu\text{m}$ alumina for the final polish.

Figure 6 shows the capsule design used with the tensile specimens. The capsule bodies and lids were machined from bar stock. The tensile specimens were subsize specimens

NOTES:

1. CAPSULE, LID AND TEST SPECIMEN ARE SAME MATERIAL (EXCEPT AS NOTED IN TEXT)
2. SrF_2 COMPACTED TO $\sim 75\%$ OF THEORETICAL DENSITY
3. THREE DIFFERENT SIZE CAPSULES WERE USED TO GIVE THREE DIFFERENT S/V RATIOS.

THE CAPSULE DIMENSIONS WERE AS FOLLOWS.

CAPSULE	S/V, cm^{-1}	X, cm	Y, cm	O.D., cm
A	4.5	2.03	1.78	2.54
B	2.5	3.30	1.78	3.81
C	0.9	6.10	7.62	6.60

FIGURE 5. Capsule Design Used With the Compatibility Test Specimens

NOTES:

1. CAPSULE, LID AND TENSILE SPECIMEN ARE SAME MATERIAL
2. TENSILE SPECIMEN DESIGN CORRESPONDS TO ASTM SPECIFICATION E8-69 (0.287-cm-DIAMETER ROUND SPECIMEN)
3. SrF_2 IS COMPACTED TO $\sim 70\%$
4. $S/V \cong 2.8 \text{ cm}^{-1}$

FIGURE 6. Capsule Design Used With the Tensile Specimens

fabricated in accordance to ASTM Specification E8-69 (Anon 1974). The specimens had a diameter of 0.113 in. (0.287 cm) and were machined from 0.5-in.-dia barstock. The S/V for the test capsules was $\sim 2.8 \text{ cm}^{-1}$.

The capsule design used with the Charpy V notch (CVN) specimens is shown in Figure 7. The CVN specimens were subsize specimens fabricated according to ASTM Specification E23-72 (Anon 1974). Each specimen was 10 mm wide by 2.5 mm thick. The specimens were fabricated from 0.125-in. sheet and were oriented with the specimen notch parallel to the rolling direction and perpendicular to the plane of the sheet. The capsule bodies and lids were machined from bar stock. The S/V for the test capsules containing the CVN specimens was $\sim 2.8 \text{ cm}^{-1}$.

All metallic components of the test capsules were thoroughly cleaned with trichloroethylene and acetone before assembly. The SrF_2 was compacted into the capsules by cold-step pressing, using a hydraulic press. A small amount of SrF_2 (4 to 5 g) was placed in the capsule and compacted using the press and a steel plunger. The plunger was removed from the capsule, and a second increment of SrF_2 was added to the capsule and compacted. The test specimen was placed in the capsule on top of the fluoride layer and centered to prevent contact with the capsule wall. Then, additional fluoride was added to the capsule in 4 to 5 g increments and compacted until the capsule was filled to the desired level. (Special fixtures were used

NOTES.

1. CAPSULE, LID AND CHARPY SPECIMEN ARE SAME MATERIAL
2. CHARPY SPECIMEN DESIGN CORRESPONDS TO ASTM SPECIFICATION E23 (10-mm x 2.5-mm SUBSIZE IMPACT SPECIMEN)
3. SrF_2 IS COMPACTED TO $\sim 70\%$ OF THEORETICAL DENSITY
4. $S/V \cong 2.8 \text{ cm}^{-1}$

FIGURE 7. Capsule Design Used with the Charpy Test Specimens

to center the tensile and CVN specimens in the capsules and compact the fluoride around the test specimens.) When the capsule was filled with SrF_2 , the lid was pressed into the capsule and the capsule sealed by TIG-welding the lid in place. Finally, the test capsules were sealed in protective jackets of Inconel 600 to prevent oxidation during testing. Each protective jacket contained up to six test capsules. Alumina tubes and spacers were used to prevent contact between the test capsules and the jackets.

In the loading operation, the SrF_2 was compacted to about 70% of theoretical density, which is approximately the density of the $^{90}\text{SrF}_2$ in the WESF $^{90}\text{SrF}_2$ storage capsule. A pressure of 8 to 10 TSI was adequate to give the desired fluoride density.

The control specimens, which were tested without SrF_2 present, were sealed in evacuated quartz envelopes to prevent oxidation during testing.

Loading, welding, and heating of the capsules containing $^{90}\text{SrF}_2$ were carried out in heavily shielded hot cells. A small press constructed from a hydraulic jack was used to load the capsules in the cell. A small aircraft turntable and torch were used to TIG-weld the capsules in the cell and seal the capsules in their protective jackets.

7.3.2 Containment Materials

The three containment materials evaluated in the long-term tests were TZM, Haynes Alloy 25 and Hastelloy C-276. In preparing the test capsules of a given material, several lots of the alloy were needed to fabricate the capsule components because of the various sizes of capsules required. Table 6 shows the various forms from which the capsule components were fabricated. All of the compatibility specimens and tensile specimens of a given alloy were fabricated from

TABLE 6. Materials Used to Fabricate the Components of the Test Capsules

Material	Capsule Component	Component Fabricated From
Hastelloy C-276	Compatibility Specimen	0.5-in.-dia Bar Stock
	Tensile Specimen	0.5-in.-dia Bar Stock
	Charpy V Notch Specimen	0.125-in. Sheet
	1-in.-dia Capsule and Lid	1.0-in.-dia Bar Stock
	1-1/2-in.-dia Capsule and Lid	1.75-in.-dia Bar Stock
	2.6-in.-dia Capsule and Lid	2-1/2-in. Sch. 40 Pipe and 0.125-in. Sheet
Haynes Alloy 25	Compatibility Specimen	0.5-in.-dia Bar Stock
	Tensile Specimen	0.5-in.-dia Bar Stock
	Charpy V Notch Specimen	0.125-in. Sheet
	1-in.-dia Capsule and Lid	1.0-in.-dia Bar Stock
	1-1/2-in.-dia Capsule and Lid	1.625-in.-dia Bar Stock
	2.6-in.-dia Capsule and Lid	2-1/2-in. Sch. 40 Pipe and 0.125-in. Sheet
TZM	Compatibility Specimen	0.5-in.-dia Bar Stock
	Tensile Specimen	0.5-in.-dia Bar Stock
	Charpy V Notch Specimen	0.125-in. Sheet
	1-in.-dia Capsule and Lid	1-in.-dia Bar Stock
	1-1/2-in.-dia Capsule and Lid	1-1/2-in.-dia Bar Stock
	2.6-in.-dia Capsule and Lid	(a)

(a) Capsule and lid fabricated from Haynes Alloy 25 2-1/2-in. Sch. 40 pipe and 0.125-in. sheet (see text).

a single lot of the material. Similarly, all of the Charpy specimens of a given alloy were prepared from a single lot of the material. The compositions and mechanical properties of the materials used in fabricating the test specimens are shown in Table 7. The bar stock and pipe used to fabricate the Haynes Alloy 25 and Hastelloy C-276 capsules and lids were the standard solution heat-treated and rapid-quenched alloys. The bar stock used in preparing the TZM capsules and lids was stress-relieved wrought bar that had been heated for 3/4 h at 2300°F.

The test capsules were sealed in protective jackets of Inconel 600 to prevent oxidation during testing. The Inconel 600 jackets were fabricated from 1.5- and 3-in. Sch. 40 pipe and 0.25-in. plate.

7.3.3 Strontium Fluoride

The $^{90}\text{SrF}_2$ used in the long-term tests was obtained from WESF and was typical-production $^{90}\text{SrF}_2$. Approximately 7.5 kg of $^{90}\text{SrF}_2$ (~350,000 Ci) was required for the tests. The $^{90}\text{SrF}_2$ powder was loosely packaged in five Hastelloy C-276 WESF inner capsules that were sealed by TIG welding. These capsules were then sealed in 316 L stainless steel WESF outer capsules and shipped to PNL. At PNL, the capsules were opened, and the $^{90}\text{SrF}_2$ removed from the five capsules was blended to provide reasonable homogeneity. Several samples of the $^{90}\text{SrF}_2$ were taken and analyzed by various techniques. The average composition of the $^{90}\text{SrF}_2$ is given in Table 8.

The ^{90}Sr isotopic content of the $^{90}\text{SrF}_2$ was 50.6%, and the impurity content was ~5.5 wt%. The impurities were primarily metal fluorides. Although the $^{90}\text{SrF}_2$ was blended before sampling, some nonhomogeneity was evident from the analyses, particularly with regard to the iron, chromium and nickel content. Analysis of the replicate samples showed significant variations in the concentrations of the three elements, and the values given in Table 8 are average values. In addition to the variations observed, the iron, chromium and nickel concentrations were much higher in the $^{90}\text{SrF}_2$ than were their concentrations in the ^{90}Sr feed solution used in preparing the $^{90}\text{SrF}_2$. The iron, chromium and nickel in the $^{90}\text{SrF}_2$ resulted primarily from corrosion of the process equipment, especially the Inconel boats in which the $^{90}\text{SrF}_2$ was fired before encapsulation. Scaling of the Inconel boats introduced iron, chromium and nickel fluorides into the $^{90}\text{SrF}_2$ as discrete particles and produced the nonhomogeneity observed in the $^{90}\text{SrF}_2$ with regard to the three elements. Analysis of other production batches of $^{90}\text{SrF}_2$ showed that their iron, chromium, and nickel concentrations were generally lower than the values given in Table 8.

The nonradioactive SrF_2 used in the long-term tests was prepared using the WESF flow-sheet and contained impurities similar to those found in WESF $^{90}\text{SrF}_2$. The SrF_2 was prepared in several batches that were thoroughly blended before firing the SrF_2 at 1100°C. After firing, the SrF_2 was analyzed by several techniques, including spark-source mass spectroscopy, emission spectroscopy, flame photometry, and atomic absorption. The composition of the inert SrF_2 is given in Table 9. The SrF_2 contained about 5 wt% impurities, primarily metal fluorides. The composition of the inert SrF_2 was similar to that of the WESF $^{90}\text{SrF}_2$ used in the long-term tests with three exceptions:

TABLE 7. Compositions and Mechanical Properties of the Alloys Used in Fabricating the Test Specimens

Composition, wt%	Hastelloy C-276		Haynes Alloy 25		TZM	
	1/2-in.-dia Bar Stock Solution Heat-Treated at 2100°F and Rapid Quenched	0.125-in. Sheet Solution Heat- Treated at 2100°F and Rapid Quenched	1/2-in.-dia Bar Stock Solution Heat Treated at 2250°F and Water Quenched	0.125-in. Sheet Solution Heat Treated at 2200°F and Water Quenched	1/2-in.-dia Bar Stock-Stress- Relieved 3/4 h at 2300°F (ASTM Spec. B-387-69)	0.125-in. Sheet Stress-Relieved 3/4 h at 2300°F (ASTM Spec. B-387-69)
C	0.003	0.002	0.09	0.12	0.026	0.019
Co	2.06	2.23	Balance	Balance		
Cr	15.35	15.15	20.09	19.77		
Fe	6.45	6.14	2.10	2.20	0.003	0.003
Mn	0.53	0.56	1.73	1.67		
Mo	15.17	15.88			Balance	Balance
Ni	Balance	Balance	10.35	10.36	<0.001	<0.001
P	0.017	0.025	0.017	0.021		
S	<0.005	0.005	0.009	0.008		
Si	0.03	0.04	0.29	0.25	0.001	
Ti					0.41	0.46
V	0.21	0.21				
W	3.40	3.26	14.48	14.76		
Zr					0.09	0.089
O ₂					<0.0003	0.0004
H ₂					<0.0001	<0.0001
N ₂					<0.0001	<0.0001
<u>Tensile</u>						
UTS, MPa	745	755	934	1017	848 to 883	798 to 802
Yield, MPa	317	345	438	483	778 to 803	730 to 738
% Elong. in 4D	67.4		66.2		31 to 39	
% Elong. in 2 in.		56.2		59.0		35 to 38

TABLE 8. Composition of the WESF $^{90}\text{SrF}_2$ Used in the Long-Term Compatibility Tests

Element	wt%	Element	wt%
Sr	66.0	Mg	0.05
Al	0.30	Mn	0.01
Ba	0.84	Na	2.3
Ca	0.42	Ni	0.25
Cd	0.02	Pb	0.02
Cr	0.36	RE ^(a)	1.1
Fe	0.42	Zr	1.6

^{90}Sr Isotopic Content--50.6%

(a) RE--Rare earth elements

TABLE 9. Composition of the Inert SrF_2 Used in the Long-Term Compatibility Tests

Element	wt%	Element	wt%
Sr	65.9	Mn	0.01
F	29.0	Na	2.4
Al	0.26	Nd	1.0
Ba	0.70	Ni	0.02
Ca	0.21	Pb	0.06
Cd	0.01	Si	0.02
Cr	0.050	H_2O	<0.01
Fe	0.020	NO_3^-	<0.01
K	0.01	O^{2-}	<0.01
Mg	0.13		

- The iron, chromium, and nickel content of the inert SrF_2 was lower than in the $^{90}\text{SrF}_2$ used in the tests.
- Neodymium was used as a stand-in in the inert SrF_2 for the mixture of rare earths found in the $^{90}\text{SrF}_2$.
- Zirconium was eliminated from the inert SrF_2 .

The inert SrF_2 was prepared before the $^{90}\text{SrF}_2$ was obtained from WESF and analyzed. The iron, chromium and nickel content of the inert SrF_2 was based on typical batch analyses of the $^{90}\text{SrF}_2$ produced at WESF, and these values proved to be much lower than the iron, chromium and nickel concentrations in the batch of $^{90}\text{SrF}_2$ used for the long-term tests. Unfortunately, the long-term tests with the inert SrF_2 were started before the analyses of the WESF $^{90}\text{SrF}_2$ used in the tests were available. Program fundings did not permit the tests to be repeated using inert SrF_2 having the higher iron, chromium, and nickel concentrations.

In some of the tests, the SrF_2 was spiked with ZrF_4 and zirconium metal to simulate decay product buildup. The zirconium was added to the fluoride as -325 mesh powder of 99% purity; the ZrF_4 was added as -200 mesh powder of 98% purity. The composition of the mixture used was as follows:

- WESF $^{90}\text{SrF}_2$ --89.50 wt%
- Zr metal--3.75 wt%
- ZrF_4 --6.75 wt%.

The above mixture corresponds to ~10 yr decay of the WESF $^{90}\text{SrF}_2$. The mixture was thoroughly blended before being loaded into the test capsules.

7.3.4 Testing and Evaluation

The test capsules and control specimens were heated in air-atmosphere muffle furnaces. A total of 11 furnaces were required because of the large number of capsules to be tested, the different temperature requirements, and the need to test radioactive and inert capsules. Each furnace was equipped with a solid-state proportioning controller and a Platinel II or Pt/Pt-13% Rh thermocouple capable of maintaining the temperature within $\pm 2^\circ\text{C}$ of the set point. In addition, each furnace was equipped with a second calibrated thermocouple whose output was monitored continuously with a strip chart recorder and intermittently with a digital millivoltmeter. Each furnace controller was equipped with thermocouple break protection and an overtemperature protection circuit (OTP). A second overtemperature protection was installed in the strip chart recorder. The OTPs were set to turn off power to the furnace if the furnace temperature exceeded the control temperature by more than a specified amount (nominally 20°C).

In testing the capsules containing $^{90}\text{SrF}_2$, the problem existed of determining the actual metal/ $^{90}\text{SrF}_2$ interface temperatures. These temperatures were substantially above the furnace temperature and depended on the capsule designs. The use of a protective jacket served to increase the difference between the interface temperature and the furnace temperature. Heat transfer calculations showed that the furnace control temperatures should be 25 to 45°C below the desired test temperatures of 600° , 800° , and 1000°C , depending on the type of capsules in the furnace.

When a series of tests was completed, the capsules were removed from the furnace, cooled to ambient temperature, and the protective jacket removed. Each capsule was examined for signs of external oxidation and then sectioned, with care taken not to damage the test specimen. The SrF_2 and test specimen were removed from the capsule and separated. In almost every case, some fluoride adhered to the test specimen and could not be completely removed without damage to the specimen surface. The problem was more severe with the $^{90}\text{SrF}_2$ than with the inert SrF_2 .

The nonradioactive compatibility specimens were sectioned radially, and one half of the specimen was subjected to analysis. Attack of the three alloys by the inert fluoride was determined primarily by metallographic examination of the specimens. A number of the

specimens was also subjected to electron microprobe (EM) analysis and scanning electron microscopy (SEM). Some of the sectioned capsules were also subjected to metallographic examination to see if attack of the weld metal had occurred.

The radioactive compatibility specimens were placed on edge in mounting compound, ground down to the midpoint and then examined. Attack of the alloys by the $^{90}\text{SrF}_2$ was determined primarily by metallographic examination of the test specimens, although a limited number of the specimens were subjected to EM analysis. All mounting, grinding and examination of the radioactive test specimens were provided by the Electron and Radiation Metallography Group at ORNL.

The control specimens were treated in the same manner as the specimens exposed to the inert SrF_2 .

The tensile and CVN specimens exposed to the $^{90}\text{SrF}_2$ were washed with water in an ultrasonic cleaner to remove as much of the fluoride as possible that had adhered to the specimen surfaces. The specimens were then tested at room temperature. The control specimens were tested under similar conditions. All mechanical testing of the radioactive tensile and CVN specimens was carried out at ORNL, while testing of the control tensile and CVN specimens was carried out at ORNL and PNL.

The SrF_2 that adhered to the compatibility specimens made weight change measurements of the specimens, before and after exposure to the fluoride, of little value. Similarly, it was impossible to obtain meaningful dimensional data from most of the specimens because of the fluoride that adhered to their surfaces. Dimensional measurements did provide evidence, however, that no gross attack of the specimens had occurred, which might not be evident from the photomicrographs.

7.4 TEST RESULTS

Many of the metal specimens exposed to SrF_2 in the long-term tests suffered two distinctly different types of attack that have been designated as a) chemical attack and b) microstructural changes:

- Chemical attack is metal attack that can be directly attributed to reaction of the metal with components of the SrF_2 . This attack includes dissolution of the metal, selective leaching of alloy components, grain boundary attack, pitting, subsurface void formation, etc. Typical examples of chemical attack are shown in Figure 8. The chemical attack is most readily apparent in photomicrographs of the unetched test specimens.
- Microstructural changes are those instances where the metal test specimen exhibits areas in which the morphology differs significantly from that of the body of the specimen and from that of control specimens aged in vacuum at the same temperature without fluoride present. The microstructural changes usually consist of one or more of the following: the disappearance of normal alloy precipitates, the formation of abnormal precipitates, changes in the alloy matrix, and marked changes

TZM

HAYNES ALLOY 25

HASTELLOY C-276

HASTELLOY C-276

FIGURE 8. Typical Examples of Chemical Attack of Metal Specimens Exposed to WESF $^{90}\text{SrF}_2$

in the grain size. The microstructural changes do not include the normal changes in alloy morphology that occur when the alloys are aged at elevated temperatures. Figure 9 shows typical examples of microstructural changes. Generally, the test specimens had to be etched before the microstructural changes were apparent.

Specimen photomicrographs provide no direct evidence that the microstructural changes were the result of fluoride attack. Since these changes did not occur in the control specimens, they must have resulted, at least indirectly, from the chemical attack by the fluoride. In addition, the microstructural changes rarely occurred unless a specimen had suffered some degree of chemical attack.

The extent of the metal attack was determined primarily from photomicrographs of the test specimens. In many of specimens, the attack was nonuniform across the specimen surface, and photomicrographs were obtained of the areas showing maximum attack. The values reported in the following tables represent the maximum attack observed in the different specimens. It was difficult to obtain, from the micrographs, an exact measure of the attack, and attack greater than 25 μm was reported in 25- μm increments. A zero value was reported when the surface of a test specimen in contact with the fluoride was essentially unchanged from those of the control specimens tested without fluoride present. Where very slight attack was observed, an arbitrary value of $<25 \mu\text{m}$ or $<25 \mu\text{m}$ was reported.

Three serious problems were encountered in the testing and examination of the various capsules, which affected the results obtained:

- A number of the $^{90}\text{SrF}_2$ capsules held at 800°C for 6,000 and 12,000 h failed. The problem was detected when the 6,000-h capsules were removed from the furnace. The Inconel 600 jackets used to protect the capsules from oxidation were badly corroded, as were the test capsules they contained. The capsules that were lost were those containing most of the tensile and CVN specimens tested at 800°C. All of the failed capsules were from one furnace, while other $^{90}\text{SrF}_2$ capsules held in a second furnace at 800°C were unaffected.

The furnace holding the failed capsules showed no indication of a malfunction during the tests and was in good working condition when the failure was discovered. The furnace temperature was monitored continuously with the strip chart recorder, and the furnace and controller were equipped with two separate OTP circuits operating off separate thermocouples. Each OTP circuit was designed to shut off power to the furnace if the $^{90}\text{SrF}_2$ /metal interface temperature exceeded $\sim 800^\circ\text{C}$ or the thermocouple failed. Neither the temperature recorder nor the OTP circuits provided any indication that the furnace had overheated.

Specimens from the failed Inconel 600 jackets were subjected to metallographic examination. The micrographs obtained showed that the Inconel 600 was badly oxidized, and the microstructure indicated that the alloy had been heated to at least 1100°C. No explanation has been found that could account for the apparent overheating of the capsules without the furnace control system giving an indication of a temperature excursion.

TZM

HAYNES ALLOY 25

HASTELLOY C-276

HAYNES ALLOY 25

FIGURE 9. Typical Examples of Microstructural Changes in Metal Specimens Exposed to WESF $^{90}\text{SrF}_2$

- A similar problem was encountered with the six $^{90}\text{SrF}_2$ capsules tested at 1000°C for 30,000 h. The Inconel 600 jackets containing the test capsules failed shortly before the tests were to be terminated. Both the jackets and the contained capsules were badly corroded. The failure was very similar to that which occurred in the 800°C tests. The furnace and its control system were functioning properly when the failure was detected, and the control instrumentation provided no indication of a temperature excursion.
- A different problem was encountered with the CVN specimens that were successfully tested with $^{90}\text{SrF}_2$. It was found that the $^{90}\text{SrF}_2$ adhered strongly to the surface of the specimens and could not be removed without unacceptable damage to the specimens. A shielded instrument was available at ORNL for testing radioactive CVN specimens. The instrument required contact maintenance, however, and could not be used with the CVN specimens because of the excessive ^{90}Sr contamination that resulted when the specimens were fractured. Attempts to find another shielded instrument capable of testing the $^{90}\text{SrF}_2$ specimens were unsuccessful. Since the specimens could not be adequately decontaminated of $^{90}\text{SrF}_2$ to permit testing in the ORNL instrument, it was not possible to test the CVN specimens exposed to $^{90}\text{SrF}_2$. The $^{90}\text{SrF}_2$ also adhered to the tensile specimens. However, ORNL was able to test the tensile specimens in a shielded instrument, except for two specimens in which the $^{90}\text{SrF}_2$ adhered to the shoulders of the specimens, preventing proper gripping for testing.

Because of time restraints and the costs involved, it was not possible to fabricate and test replacement capsules for the capsules that failed, nor to set up shielded equipment for testing the contaminated CVN specimens.

7.4.1 Metal Attack

Results obtained in the long-term tests with Hastelloy C-276 are presented in Table 10. All of the specimens exposed to the fluoride suffered significant levels of attack, both chemically and microstructurally. In a number of instances, marked differences were evident in the extent of metal attack between replicate specimens. Some specimens tested for long periods of time exhibited less attack than specimens tested for shorter periods under identical conditions. The variations in the level of attack between replicate specimens, while significant, are not unusual in compatibility tests where extensive attack occurs.

Despite the apparent anomalies in the Hastelloy C-276 data, certain trends are apparent from the results obtained:

- The WESF $^{90}\text{SrF}_2$ was much more corrosive to Hastelloy C-276 than the inert SrF_2 .
- The addition of zirconium metal and ZrF_4 to the $^{90}\text{SrF}_2$, to simulate decay of the $^{90}\text{SrF}_2$, produced a marked decrease in the attack of the Hastelloy C-276 by the WESF $^{90}\text{SrF}_2$.

TABLE 10. Attack of Hastelloy C-276 Exposed to Radioactive or Inert Strontium Fluoride

Grade of SrF ₂ Used	Temp., °C	Capsule S/V, cm ⁻¹	Depth of Metal Affected, μ m									
			Chemical Attack					Microstructural Changes				
			1,000 h	6,000 h	12,000 h	20,000 h	30,000 h	1,000 h	6,000 h	12,000 h	20,000 h	30,000 h
Inert SrF ₂	600	4.5	<25	75	50	25	25	0	100	200	150	125
		4.5	25	100	50	25	25	125	125	175	100	75
		2.5	<25	125				50	125			
		0.9	25	150	75	150		100	150	150	150	
	800	4.5	<25	50	50	75	25	<25	75	75	100	50
		4.5	25	50	50	50	50	75	75	50	50	50
		2.5	<25	50				50	50			
		0.9	250	250	175	225		375	375	200	275	
	1,000	4.5	50	50	100	75	75	100	175	175	150	100
		4.5	75	75	50	75	75	100	150	200	125	150
		2.5	75	175				125	250			
		0.9	100	200	175	200		150	300	300	275	
WESF ⁹⁰ SrF ₂	600	4.5	75	75	225	200	75	100	100	175	250	550
		4.5	75	175	175	100	225	125	125	250	150	700
		2.5	250	175				300	250			
	800	4.5	175	200	300	175	300	300	500	625	250	500
		4.5	150	(a)	275	250	350	275	(a)	450	300	900
		2.5	750	600				875	>750			
	1,000	4.5	175	200	500	875	(a)	375	600	>1500	>1000	(a)
		4.5	250	300		750	(a)	375	>750		>1000	(a)
		2.5	300	625				375	>875			
WESF ⁹⁰ SrF ₂ + Zr + ZrF ₄ (b)	600	4.5	25	<25				50	50			
	800	4.5	50	25				125	125			
	1,000	4.5	75	100				175	>750			

(a) Specimen lost.

(b) WESF ⁹⁰SrF₂ containing Zr + ZrF₄ to simulate 10-yr decay of the ⁹⁰SrF₂.

- Attack of the Hastelloy C-276 increased with increasing exposure temperature. Chemical attack by $^{90}\text{SrF}_2$ showed a greater temperature dependence than chemical attack by the inert SrF_2 . Microstructural changes were less temperature dependent than the chemical attack.
- Decreasing the S/V of the test capsules greatly increased the attack of the Hastelloy C-276.
- With one major exception, the rate of attack decreased with increasing exposure time, and in many of the tests, the specimens exposed for 20,000 and 30,000 h exhibited no greater attack than specimens exposed for 6,000 and 12,000 h. The one exception involved the tests at $1,000^\circ\text{C}$ with $^{90}\text{SrF}_2$. Although the 30,000-h specimens were lost, the specimens tested for 20,000 h showed far more attack than the specimens tested for 6,000 and 12,000 h.

Micrographs of the various Hastelloy C-276 specimens showed that the types of attack appeared to vary with exposure temperature and time. These variations are discussed in Section 7.5.1.

Results obtained in the long-term tests with Haynes Alloy 25 are presented in Table 11. On an overall basis, attack of the Haynes Alloy 25 was very similar to that observed with Hastelloy C-276. The erratic behavior observed in the Hastelloy C-276 tests was also apparent in the tests with Haynes Alloy 25. In many of the tests, replicate specimens showed significantly different levels of attack, and many of the specimens exposed for long periods of time showed less attack than specimens tested for shorter periods. The same general trends observed with the Hastelloy C-276 were also apparent with the Haynes Alloy 25. Most importantly, the Haynes Alloy 25 showed the same decrease in rate of attack with increasing exposure time that was observed with the Hastelloy C-276. Most of the specimens tested for 20,000 and 30,000 h exhibited no greater attack than the specimens tested for 6,000 h under similar conditions. Unlike the Hastelloy C-276, attack of the Haynes Alloy 25 specimens tested at $1,000^\circ\text{C}$ with $^{90}\text{SrF}_2$ did not increase appreciably after 6,000 h exposure. One unusual problem was observed with the specimens tested with inert SrF_2 at $1,000^\circ\text{C}$: all of the specimens exposed for 20,000 and 30,000 h exhibited a very few isolated voids to considerable depths (up to $625\text{ }\mu\text{m}$). This type of attack was not observed in any of the other tests with Haynes Alloy 25. Micrographs of the various specimens and a discussion of attack mechanisms is presented in Section 7.5.2.

Results obtained with TZM in the long-term tests are presented in Table 12. The TZM specimens exposed to SrF_2 suffered far less attack than the Haynes Alloy 25 and Hastelloy C-276 specimens. With a few notable exceptions, microstructural changes were not a problem with TZM (the exceptions are discussed in Section 7.5.3). Evaluation of the data provides several general conclusions:

- Chemical attack of the TZM was substantially greater with the $^{90}\text{SrF}_2$ than with the inert SrF_2 .
- Decreasing the S/V of the test capsules increased the chemical attack of the TZM significantly.

TABLE 11. Attack of Haynes Alloy 25 Exposed to Radioactive or Inert Strontium Fluoride

Grade of SrF ₂ Used	Temp., °C	Capsule S/V, cm ⁻¹	Depth of Metal Affected, μ m									
			Chemical Attack					Microstructural Changes				
			1,000 h	6,000 h	12,000 h	20,000 h	30,000 h	1,000 h	6,000 h	12,000 h	20,000 h	30,000 h
Inert SrF ₂	600	4.5	<25	50	50	50	25	125	75	50	0	0
		4.5	<25	25	50	50	50	75	50	<25	0	0
		2.5	<25	50				50	75			
		0.9	25	75	50	100		50	75	0	100	
	800	4.5	<25	75	75	50	50	75	150	100	50	75
		4.5	<25	75	75	75	75	25	100	125	50	100
		2.5	<25	50				25	75			
		0.9	25	125	100	225		50	425	125	150	
	1,000	4.5	50	75	100	625(a)	550(a)	25	175	100	100	100
		4.5	50	75	75	450(a)	500(a)	25	100	300	125	125
		2.5	50	150				0	200			
		0.9	75	300	350	275		50	375	400	425	
	600	4.5	25	75	100	75	125	0	0	100	125	500
		4.5	50	125	75	175	125	0	0	100	200	500
		2.5	50	200				0	0			
	800	4.5	125	250	150	125	300	250	400	200	200	300
		4.5	100	275	175	175	250	150	450	250	300	375
		2.5	450	750				250	850			
	1,000	4.5	150	300	250	250	(b)	200	875	625	>750	(b)
		4.5	175	250		325	(b)	225	875		100	(b)
		2.5	250	500				300	625			
WESF ⁹⁰ SrF ₂	600	4.5	25	75	100	75	125	0	0	100	125	500
		4.5	50	125	75	175	125	0	0	100	200	500
		2.5	50	200				0	0			
WESF ⁹⁰ SrF ₂ + Zr + ZrF ₄ (c)	600	4.5	<<25	25				0	0			
		4.5	50	125				125	200			
		4.5	125	100				75	200			

(a) Specimen exhibited a few isolated voids to a considerable depth.

(b) Specimen lost.

(c) WESF ⁹⁰SrF₂ containing Zr + ZrF₄ to simulate 10-yr decay of the ⁹⁰SrF₂.

TABLE 12. Attack of TZM Exposed to Radioactive or Inert Strontium Fluoride

Grade of SrF ₂ Used	Temp., °C	Capsule S/V, cm ⁻¹	Depth of Metal Affected, μm									
			Chemical Attack					Microstructural Changes				
			1,000 h	6,000 h	12,000 h	20,000 h	30,000 h	1,000 h	6,000 h	12,000 h	20,000 h	30,000 h
Inert SrF ₂	600	4.5	0	<25	0	<25	<25	0	0	0	0	0
		4.5	<25	<25	(a)	<25	<25	0	0	(a)	0	0
		2.5	<25	25				0	0			
		0.9	<25	50	50	50		0	0	0	0	0
	800	4.5	<25	<25	<25	<25	<25	0	0	0	0	0
		4.5	<25	<25	<25	<25	<25	0	0	0	0	0
		2.5	<25	25				0	0			
		0.9	25	100	50	75		0	0	0	0	
	1,000	4.5	<25	<25	<25	<25	<25	0	0	0	0	<25
		4.5	<25	<25	<25	<25	<25	0	0	0	0	<25
		2.5	<25	<25				0	0			
		0.9	<25	25	25	25		0	0	0	50	
WESF ⁹⁰ SrF ₂	600	4.5	25	100	25	50	50	0	0	0	75	100
		4.5	50	25	50	75	25	0	0	0	75	0
		2.5	75	125				0	0			
	800	4.5	50	50	50	50	50	0	0	50	75	0
		4.5	50	50	50	50	50	0	0	0	75	75
		2.5	75	200				0	0			
	1,000	4.5	50	50	75	50	(a)	0	875	0	>750	(a)
		4.5	25	50		75	(a)	0	875		100	(a)
		2.5	50	50				0	0			
WESF ⁹⁰ SrF ₂ + Zr + ZrF ₄ (b)	600	4.5	0	<25				0	0			
	800	4.5	25	<25				0	0			
	1,000	4.5	25	<25				0	500			

(a) Specimen lost.

(b) WESF ⁹⁰SrF₂ containing Zr + ZrF₄ to simulate 10-yr decay of the ⁹⁰SrF₂.

- Chemical attack of the TZM was essentially independent of the exposure temperature.
- The addition of Zr and ZrF_2 to the $^{90}\text{SrF}_2$, to simulate decay product buildup, produced a slight decrease in the chemical attack of the TZM by the $^{90}\text{SrF}_2$.
- On an overall basis, chemical attack of the TZM specimens did not increase appreciably after the first 1000 to 6000 h exposure.

Micrographs of the test specimens and a discussion of attack mechanisms are presented in Section 7.5.3.

Several test capsules of each alloy were sectioned and the weld areas subjected to metallographic examination to see if attack had occurred. Although the design of the test capsules was such that the weld metal was not in direct contact with the fluoride, it was possible that fluoride material could diffuse to the weld zone. In none of the capsules examined was there any evidence of substantial attack of the weld metal by the fluoride, although very slight attack was observed in some of the capsules.

7.4.2 Effect of Metal Attack on Mechanical Properties

As discussed earlier, problems were encountered in the testing and evaluation of a number of the tensile and CVN specimens. Some of the specimens were lost during testing due to failure of the Inconel 600 protective jackets. Others could not be subjected to the mechanical property tests because the $^{90}\text{SrF}_2$ could not be adequately removed from the specimen surface. Because of the loss of test specimens, it was not possible to determine the effect of fluoride attack on the mechanical properties of the three alloys to the extent originally planned. Sufficient data were obtained, however, to indicate the general effect of fluoride attack on the tensile properties of the alloys, but no data were obtained on the effects of the attack on their Charpy impact energies.

Table 13 shows the room temperature tensile properties of Hastelloy C-276 specimens exposed to $^{90}\text{SrF}_2$ at 600° to 1000°C and of control specimens heated in vacuum. Aging of the control specimens at 600°C results in a large increase in the tensile strength and a marked decrease in the ductility of Hastelloy C-276 compared to the solution heat-treated alloy. Aging at 800°C produced a slight increase in tensile strength but a very sharp decrease in ductility. The control specimen aged at 1000°C showed a slight decrease in both tensile strength and ductility. On an overall basis, the Hastelloy C-276 specimens exposed to $^{90}\text{SrF}_2$ showed a large decrease in tensile strength and ductility compared to the control specimens aged in vacuum.

Table 14 gives the room temperature tensile data for Haynes Alloy 25 specimens exposed to $^{90}\text{SrF}_2$ at 600° to 1000°C and the control specimens aged in vacuum. Control specimens aged at 600°C for 6000 h exhibited a marked decrease in ultimate tensile strength and ductility compared to the solution heat-treated alloy. The specimens aged for 12,000 h also exhibited a marked decrease in ductility but an increase in ultimate tensile strength. The specimen aged at 800°C exhibited an increase in tensile strength and a very large decrease in ductility. Aging at 1000°C produced a moderate decrease in tensile strength and a large decrease in

TABLE 13. Room Temperature Tensile Properties of Hastelloy C-276 Specimens After Exposure to $^{90}\text{SrF}_2$, or Aged in Vacuum, at 600° to 1000°C

Aging Temp., °C	Aging Time, h	Control Specimens Aged in Vacuum					Specimens Exposed to ⁹⁰ SrF ₂				
		Stress, MPa			Elongation, %		Stress, MPa			Elongation, %	
		Ultimate	Yield	Fracture	Uniform	Total	Ultimate	Yield	Fracture	Uniform	Total
As Received(a)		779	360		48.9	59.0					
600	6,000	1,112	610	1,112	27.5	27.5	569	439	569	2.5	2.8
	6,000	1,014	580	1,014	26.2	26.2	480	370	489	5.8	5.8
	12,000	1,103	---	1,103	32.9	32.9	745	518	745	3.6	3.6
	12,000	1,034	---	1,034	42.8	42.8	663	474	663	4.5	4.6
800	6,000	832	457	832	9.6	9.6	556	280	556	4.8	4.8
	6,000	839	428	839	9.8	9.9	(b)	(b)	(b)	(b)	(b)
	12,000	814	431	814	9.0	9.0	(b)	(b)	(b)	(b)	(b)
	12,000	798	392	798	9.6	9.6	(b)	(b)	(b)	(b)	(b)
1,000	6,000	709	374	709	24.1	24.1	(c)	(c)	845	0	0
	6,000	678	311	678	20.5	20.5	261	260	261	0.3	0.5
	12,000	724	310	724	43.3	46.7	(d)	(d)	(d)	(d)	(d)
	12,000	721	307	721	41.4	43.2	(d)	(d)	(d)	(d)	(d)

(a) Solution heat-treated alloy as received from the vendor.

(b) Test specimen lost due to capsule failure during testing.

(c) Specimen failed while still within its elastic limit.

(d) Strontium fluoride could not be removed from shoulders of specimen to permit gripping them for tensile test.

TABLE 14. Room Temperature Tensile Properties of Haynes Alloy 25 Specimens After Exposure to $^{90}\text{SrF}_2$, or Aged in Vacuum, at 600° to 1000°C

Aging Temp., °C	Aging Time, h	Control Specimens Aged in Vacuum					Specimens Exposed to ⁹⁰ SrF ₂				
		Stress, MPa			Elongation, %		Stress, MPa			Elongation, %	
		Ultimate	Yield	Fracture	Uniform	Total	Ultimate	Yield	Fracture	Uniform	Total
As Received(a)		938	445		56.2	60.2					
600	6,000	806	545	806	31.1	31.1	(b)	(b)	786	0	0
	6,000	788	562	788	29.5	29.5	487	238	403	39.5	41.7
	12,000	958	---	958	26.2	26.2	855	(b)	855	0	0
	12,000	978	---	978	30.9	30.9	855	(b)	855	0	0
800	6,000	1,027	649	1,027	5.5	5.5	(c)	(c)	(c)	(c)	(c)
	6,000	1,056	659	1,056	6.7	6.7	(c)	(c)	(c)	(c)	(c)
	12,000	1,017	618	1,017	5.5	5.5	664	535	664	1.6	1.6
	12,000	808		808	3.8	3.8	731	478	731	3.0	3.0
1,000	6,000	855	474	855	8.2	8.2	659	392	659	15.0	15.0
	6,000	865	471	865	9.9	9.9	766	342	766	19.7	19.7
	12,000	850	430	850	10.4	10.4	561	374	557	11.2	11.7
	12,000	907	435	907	21.4	21.4	501	370	501	6.3	6.3

(a) Solution heat-treated alloy as received from the vendor.

(b) Specimen failed while still within its elastic limit.

(c) Specimen lost due to capsule failure during testing.

ductility. The specimens exposed to $^{90}\text{SrF}_2$ all exhibited a decrease in tensile strength compared to the control specimens. The effect of fluoride attack on ductility was less consistent; some specimens exposed to $^{90}\text{SrF}_2$ exhibited a higher ductility than the control specimens, while others exhibited a lower ductility.

Table 15 gives the room temperature tensile data for TZM control specimens heated in vacuum and specimens exposed to $^{90}\text{SrF}_2$ at 600° to 1000°C. Aging of the control specimens at 600° to 1000°C had, with one exception, little effect on the ultimate tensile strength of TZM. The one exception was the specimens aged at 600°C for 12,000 h, which exhibited a markedly lower ultimate tensile strength than the stress-relieved alloy. Several of the aged control specimens had higher yield strengths than the stress-relieved alloys. The aged control specimens were unusual in that their yield strengths were only slightly lower than the ultimate tensile strengths. The ductilities of the aged specimens were substantially lower than those of the stress-relieved alloy. Exposure of the TZM specimens to $^{90}\text{SrF}_2$ at 600° to 1000°C produced a general decrease in the tensile properties of the specimens, although two of the specimens exhibited higher tensile strengths than the control specimens.

As mentioned earlier, it was not possible to test the CVN specimens exposed to $^{90}\text{SrF}_2$ because the $^{90}\text{SrF}_2$ could not be adequately removed from the surfaces of the specimens. The control specimens aged at 600°, 800° and 1000°C in vacuum were tested at room temperature, however, and the results obtained are shown in Table 16. Both the Haynes Alloy 25 and Hastelloy C-276 showed marked decreases in Charpy impact strength when aged at 600° to 1000°C. The results obtained with the Haynes Alloy 25 are in good general agreement with published data, although direct comparisons are difficult because most of the data in the literature were obtained with full-size CVN specimens (McCoy and Bourgette 1973; Ferry 1969). Little information has been published on the Charpy impact strength of aged Hastelloy C-276. Unpublished data from the Cabot Corp. show the Charpy impact energy decreases sharply when the alloy is aged at 540° to 760°C. Full-size specimens aged at 760°C for 8000 h had an impact energy of only 4 ft-lb compared to >240 ft-lb for the solution-annealed alloy. Considering the difference in specimen size, the Cabot data for Hastelloy C-276 agree fairly well with the results obtained in this work.

Very erratic results were obtained with the TZM specimens. The impact energy for duplicate specimen varied by as much as 50%. Overall, thermal aging at 600° to 1000°C appeared to have little effect on the impact energy of TZM.

Although the CVN specimens exposed to $^{90}\text{SrF}_2$ were not tested, one can predict, based on results obtained with the tensile specimens, that attack of the three alloys by the $^{90}\text{SrF}_2$ would reduce the Charpy impact energy of the specimens. It is not possible to predict, however, to what extent the impact energy would be reduced. Since aging reactions at 600° to 1000°C effectively reduce the impact energy of the Haynes Alloy 25 and Hastelloy C-276 to very low levels, further reductions resulting from fluoride attack would be of minor significance. In the case of TZM, however, loss of impact energy resulting from fluoride attack could be quite important.

TABLE 15. Room Temperature Tensile Properties of TZM Specimens Exposed to $^{90}\text{SrF}_2$, or Aged in Vacuum, at 600° to 1000°C

Aging Temp., °C	Aging Time, h	Control Specimens Aged in Vacuum					Specimens Exposed to ⁹⁰ SrF ₂				
		Stress, MPa			Elongation, %		Stress, MPa			Elongation, %	
		Ultimate	Yield	Fracture	Uniform	Total	Ultimate	Yield	Fracture	Uniform	Total
As Received(a)		863	786				34.7				
600	6,000	886	851	521	0.5	26.0	500	494	288	0.5	27.1
	6,000						418	409	254	0.5	23.3
	12,000	703		703	2.4	2.4	876	855	523	0.5	24.5
	12,000	400		400	3.0	3.0	602	(b)	602	0	0
800	6,000	884	849	877	0.5	0.7	(c)	(c)	(c)	(c)	(c)
	6,000	676	669	300	0.4	16.8	(c)	(c)	(c)	(c)	(c)
	12,000	866	852	522	0.5	24.5	(c)	(c)	(c)	(c)	(c)
	12,000	876	851	521	0.4	23.4	(c)	(c)	(c)	(c)	(c)
1,000	6,000	883	832	534	0.7	26.0	814	669	783	11.3	15.8
	6,000	692	681	152	0.5	16.8	478	423	478	7.0	7.0
	12,000	838	804	511	0.5	26.6	779	545	779	12.0	12.0
	12,000	840	822	515	0.5	25.1	586	447	586	3.6	3.6

(a) Stress-relieved alloy as received from vendor.

(b) Specimen failed while still within its elastic limit.

(c) Specimens lost due to failure of capsule during testing.

TABLE 16. Room Temperature Charpy Impact Energy of Control Specimens Aged in Vacuum at 600° to 1000°C

Aging Temperature, °C	Aging Time, h	Charpy Impact Energy, (a) ft-lb		
		Hastelloy C-276	Haynes Alloy 25	TZM
As Received(b)	---	26.2(c)	21.5(c)	17.6(d)
600	6,000	5.2	16.4	10.7
	6,000	4.9	16.3	19.2
	12,000	3.2	4.2	18.1
	12,000	4.3	2.8	15.7
800	6,000	1.2	1.5	12.3
	6,000	<1.0	2.4	19.6
	12,000	<1.0	<1.0	18.0
	12,000	<1.0	<1.0	17.4
1,000	6,000	18.6	3.1	17.6
	6,000	16.9	4.7	14.2
	12,000	15.4	2.7	13.7
	12,000	16.9	2.6	19.8

(a) Subsize CVN specimens--2.5 mm thick x 10 mm wide.

(b) As-received from the vendor.

(c) Average value for four specimens.

(d) Average value for three specimens.

7.5 DISCUSSION

Examination of the test specimens showed that, in many instances, the reactions involved in the attack of each alloy appeared to vary with both exposure temperature and time. The attack mechanisms also appeared to differ between the specimens exposed to $^{90}\text{SrF}_2$ and specimens exposed to inert SrF_2 . In some instances, there appeared to be marked differences in the attack of duplicate specimens. An attempt was made to identify the attack mechanisms by using EM analyses and SEM. The systems are so complex, however, and so many tests were conducted that it was impossible to study the specimens in sufficient detail to define the specific reactions involved in the attack. All that could be achieved was to identify the general types of metal attack. Similarly, it was not possible to carry out phase identification analyses to determine the specific phases that formed in the alloys due to thermal aging and chemical attack. It was possible, however, to make some educated guesses as to the phases formed based on the EM and SEM analyses of the precipitates and published information on the thermal stabilities of the three alloys. It must be realized that the reaction mechanisms discussed in the following sections represent estimates of the most probable reactions based on a limited amount of data.

7.5.1 Hastelloy C-276- SrF_2 System

Aging of Hastelloy C-276 at 600° to 1000°C for extended periods of time resulted in extensive precipitate formation. Figure 10 shows the microstructures of the solution heat-treated

FIGURE 10. Effect of Thermal Aging on the Microstructure of Hastelloy C-276

alloy and control specimens held in vacuum at 600⁰, 800⁰, and 1,000⁰C for 1,000 and 30,000 h. There was little evidence of precipitates in the solution-annealed alloy (Figure 10a). The matrix was gamma-solid solution, and the annealing twins were the predominate feature. Aging of the alloy at 600⁰C initially produced some discontinuous grain boundary precipitation that could not be identified but may be M₆C carbides (Figure 10b). Continued aging at 600⁰C resulted in additional grain boundary and intragranular precipitation and the alloy appeared heavily aged (Figure 10c). Matthews (Matthews 1976) reports that Hastelloy C-276 undergoes an A₂B ordering reaction when aged at 1,000⁰F (538⁰C), and the specimens aged at 600⁰C for periods in excess of 12,000 h showed a similar microstructure. The precipitates were composed primarily of nickel, molybdenum and tungsten, and appear to be predominately an Ni₇Mo₆-type phase.

Control specimens of Hastelloy C-276 aged at 800⁰C showed extensive grain boundary and intragranular precipitation (Figure 10d-e). Analysis of the precipitates showed that they consisted primarily of nickel, molybdenum and tungsten with a small amount of iron. They appeared to be predominately the Ni₇Mo₆-type phase, which agrees with the results reported by Leonard (Leonard 1969). Aging of the alloy at 1000⁰C produced some precipitation but less than was observed at 800⁰C (Figure 10f-g). Continuous grain boundary precipitates formed initially at 1000⁰C, but continued aging resulted in the formation of discrete globular precipitates. Analyses showed that the precipitates were composed of nickel, molybdenum and tungsten and they appeared to be of the Ni₇Mo₆-type phase.

Figures 11 through 13 show micrographs of Hastelloy C-276 specimens exposed to inert SrF₂ at 600⁰ to 1000⁰C for up to 30,000 h, while Figures 14 through 16 show specimens exposed to ⁹⁰SrF₂ at the same conditions. In each case, the S/V of the test capsule was 4.5 cm⁻¹. Figures 17 and 18 show the effects that varying the S/V had on the attack of Hastelloy C-276 exposed to inert SrF₂ and ⁹⁰SrF₂. Figure 19 shows Hastelloy C-276 specimens exposed to ⁹⁰SrF₂ containing Zr + ZrF₄. The micrographs indicate that the type of chemical attack and the microstructural changes suffered by the Hastelloy C-276 varied with the test temperature. They also show that the specimens exposed to the ⁹⁰SrF₂ suffered much greater attack than the specimens exposed to inert SrF₂, but at a given temperature the type of attack appeared to be similar. Despite the apparent differences in the various micrographs, microprobe and SEM analysis of various samples indicated that the chemical attack mechanisms were similar in all cases and involved leaching of chromium, molybdenum, iron, tungsten and possibly cobalt from the alloy matrix. There was little indication that SrF₂ was directly involved in the attack of the Hastelloy C-276.

At 600⁰C, chemical attack of the specimens exposed to inert SrF₂ and ⁹⁰SrF₂ was fairly uniform across the surface and a reaction layer formed at the surface. There was little evidence of grain boundary attack in the specimens tested at 600⁰C. What appears to be grain boundary attack in the specimens exposed to inert SrF₂ is actually grain boundary precipitation (Figure 11). Microprobe analysis of the specimens showed that chromium, molybdenum, iron and possibly tungsten and cobalt were leached from the alloy. Figure 20 shows an elemental analysis of the reaction layer and underlying metal of a specimen exposed to inert SrF₂ at

100X
400 μm

1,000 h

6,000 h

12,000 h

20,000 h

30,000 h

FIGURE 11. Hastelloy C-276 Specimens Exposed to Inert SrF_2 at 600°C --S/V = 4.5 cm^{-1}

FIGURE 12. Hastelloy C-276 Specimens Exposed to Inert SrF_2 at 800°C -- $\text{S/V} = 4.5 \text{ cm}^{-1}$

FIGURE 13. Hastelloy C-276 Specimens Exposed to Inert SrF_2 at 1000°C -- $\text{S/V} = 4.5 \text{ cm}^{-1}$

FIGURE 14. Hastelloy C-276 Specimens Exposed to WESF $^{90}\text{SrF}_2$ at 600°C --
 $\text{S/V} = 4.5 \text{ cm}^{-1}$

FIGURE 15. Hastelloy C-276 Specimens Exposed to WESF $^{90}\text{SrF}_2$ at 800°C --
 $\text{S/V} = 4.5 \text{ cm}^{-1}$

FIGURE 16. Hastelloy C-276 Specimens Exposed to WESF $^{90}\text{SrF}_2$ at 1000°C --S/V = 4.5 cm^{-1}

FIGURE 17. Effect of S/V on the Attack of Hastelloy C-276 Specimens Exposed to Inert SrF_2 for 6000 h

FIGURE 18. Effect of S/V on the Attack of Hastelloy C-276 Exposed to WESF $^{90}\text{SrF}_2$ for 6000 h

100X
400 μm

500X
80 μm

FIGURE 19. Hastelloy C-276 Specimens Exposed to WESF $^{90}\text{SrF}_2$ Containing Zr + ZrF_4 for 6000 h--S/V = 4.5 cm^{-1}

FIGURE 20. Elemental Analysis of the Reaction Layer and Underlying Metal of a Hastelloy C-276 Specimen Exposed to Inert SrF_2 at 600°C for 30,000 h--S/V 4.5 cm^{-1}

600°C for 30,000 h. The data show that the reaction layer is enriched in chromium, iron, molybdenum, tungsten and cobalt and depleted in nickel. An unusual feature is that the outer surface of the reaction layer had a composition similar to that of the alloy matrix. This was also observed with other specimens tested at 600°C . No trace of strontium was found in the reaction layer or metal matrix. Microprobe scans of specimens exposed to $^{90}\text{SrF}_2$ showed a leaching of chromium, iron, and molybdenum from the alloy, but the cobalt and nickel were unaffected.

At 600°C , the microstructural changes consisted primarily of increased grain boundary precipitation. Analysis of the precipitates showed that they were composed primarily of chromium, iron, and molybdenum and are probably M_6C carbides. The specimens exposed to $^{90}\text{SrF}_2$ for 30,000 h exhibited a broad zone adjacent to the reaction layer that had a heavily aged appearance. This probably resulted from an increase in the A_2B ordering reaction.

Chemical attack of specimens tested at 800°C was fairly uniform across the surface, and a reaction layer formed at the surface. The reaction layer was quite thin on specimens exposed to inert SrF_2 , and much of the layer was leached away when the specimens were etched. The

reaction layer was much thicker on the specimens exposed to $^{90}\text{SrF}_2$ and contained grains of unreacted metal. Etching of the radioactive specimens had little effect on the reaction layer. The concentration and size of the unreacted metal grains increased from the outer edge of the reaction layer to the unreacted metal surface.

Analysis of the specimens tested at 800°C showed a leaching of chromium, molybdenum, iron, and tungsten from the alloy matrix, and the reaction layer was enriched in the four elements. The grains of unreacted metal in the reaction layer were almost completely depleted of chromium, and the reaction layer adjacent to the grains was very rich in chromium. Some strontium was found at the outer edge of reaction layer but not in the body of the reaction layer or matrix of the alloy. The data indicate that chemical attack of the Hastelloy C-276 at 800°C proceeded primarily along grain boundaries, leaving free particles of metal that were then slowly depleted of chromium.

Chemical attack of the specimens tested at 1000°C involved a general dissolution of the specimen surface with extensive grain boundary attack, pitting and subsurface void formation. Except for one specimen tested with $^{90}\text{SrF}_2$ for 1000 h, there was no indication of the formation of a reaction layer on the surfaces of the specimens. Microprobe and SEM analysis of the specimens showed that the only discernible changes in the alloy composition were a depletion of chromium, molybdenum and cobalt in a broad zone adjacent to the specimen surface and a slight increase in the iron concentration at the surface. Microstructural changes consisted primarily of the disappearance of normal alloy precipitates in a wide zone adjacent to the specimen surface. It is impossible to tell if the precipitates, which are principally an Ni_7Mo_6 phase, redissolved in the matrix or reacted in some way with the fluoride.

In general, decreasing the S/V ratio of the test capsules increased the attack of the Hastelloy C-276 (Figures 17 and 18), but the attack mechanisms did not appear to be affected. Figure 21, for example, shows micrographs of a specimen exposed to inert SrF_2 at 800°C for 6000 h using an S/V of 0.9 cm^{-1} . The micrographs show an extensive reaction layer containing particles of unreacted metal. Much of the reaction layer leached away when the specimen was etched. Figure 21 also shows an elemental analysis of the reaction layer and underlying metal. The analysis shows leaching of chromium, molybdenum, iron, and tungsten from the alloy matrix, and high concentrations of the four elements in the reaction layer. The metal particles in the reaction layer were depleted of chromium. No strontium was found in the reaction layer or underlying metal. The results were very similar to those obtained at 800°C using larger S/V values.

Samples of inert SrF_2 and $^{90}\text{SrF}_2$ taken from various test capsules were analyzed to determine if the composition of the fluoride had changed during the tests. The results obtained showed that after about 6000 h exposure, the chromium and iron concentration in both the inert SrF_2 and $^{90}\text{SrF}_2$ were reduced to very low levels. None of the other impurities originally present in the fluoride showed significant changes in concentration.

The addition of Zr and ZrF_4 to the WESF $^{90}\text{SrF}_2$ produced a marked decrease in the attack of Hastelloy C-276 at all temperatures (see Figure 19). The specimens exposed to the $^{90}\text{SrF}_2$

FIGURE 21. Micrographs and Elemental Analysis of a Hastelloy C-276 Specimen Exposed to Inert SrF_2 at 800°C for 6000 h--
 $S/V = 0.9 \text{ cm}^{-1}$

containing Zr and ZrF_4 were not subjected to microprobe or SEM analysis. The strontium fluoride from the test capsules was analyzed, however, and the results obtained show that the iron and chromium concentrations in the fluoride were approximately the same as the initial concentrations. The data indicate that the zirconium metal reacted with the iron and chromium fluorides before they could react with the test specimens, and reduced them to the corresponding metals. As a result, chemical attack of the test specimens was reduced to low levels.

7.5.2 Haynes Alloy 25- SrF_2 System

Figure 22 shows the microstructure of the solution heat-treated Haynes Alloy 25 used in the long-term tests and the microstructures of the control specimens heated in vacuum at 600° , 800° and $1,000^\circ\text{C}$ for 1,000 and 30,000 h. The microstructure of the solution-annealed

FIGURE 22. Effect of Thermal Aging on the Microstructure of Haynes Alloy 25

alloy shows discrete globular precipitates in a face-centered cubic matrix (Figure 22a). Analysis of the precipitates indicates that they are primarily M_6C carbides (Co, Cr, W) with possibly traces of Laves phase (Co_2W) that failed to redissolve during annealing. Aging of the alloy at $600^{\circ}C$ for 1,000 h had little effect on the microstructure (Figure 22b). Continued aging of the alloy at $600^{\circ}C$ produced some grain boundary precipitation and a heavily aged appearance (Figure 22c). The precipitates appear to be a mixture of M_6C and $M_{23}C_6$ carbides and a Laves phase (Co_2W) in a mixed hexagonal-close-packed and face-centered cubic matrix. The mixed matrix was not apparent in the micrographs until the Haynes Alloy 25 had been aged for 12,000 h.

Aging of the Haynes Alloy 25 at $800^{\circ}C$ produced continuous grain boundary precipitation as well as intragranular precipitation (Figure 22d-e). The intragranular precipitation was still increasing after 30,000 h at temperature. The precipitates appeared to consist primarily of M_6C carbides, a Laves phase (Co_2W), a Co_7W_6 phase, and possibly $M_{23}C_6$ carbides.

Aging of the alloy at $1000^{\circ}C$ produced discontinuous grain boundary precipitates and discrete globular intragranular precipitates (Figure 22f-g). The precipitates are probably M_6C carbides, the Laves phase, and the Co_7W_6 phase.

Figures 23 through 25 show micrographs of the Haynes Alloy 25 specimens exposed to inert SrF_2 at 600° , 800° , and $1,000^{\circ}C$ for up to 30,000 h, while Figures 26 through 28 show specimens exposed to the $^{90}SrF_2$ under the same conditions. The S/V of the test capsules was 4.5 cm^{-1} . Figures 29 and 30 show the effects of varying the capsule S/V on attack of specimens exposed to inert SrF_2 and $^{90}SrF_2$. Figure 31 shows micrographs of specimens exposed to $^{90}SrF_2$ containing Zr and ZrF_4 .

The Haynes Alloy 25 appeared to react with the SrF_2 in the same general way as the Hastelloy C-276. The specimens tested at 600° and $800^{\circ}C$ suffered fairly uniform chemical attack across the specimen surface with formation of an adherent reaction layer. The reaction layers were much thicker on the radioactive specimens than on specimens exposed to the inert SrF_2 . The reaction layers contained particles of unreacted metal. The concentration of unreacted particles was much greater with the radioactive specimens than with the inert specimens. Etching of the nonradioactive specimens removed most of the reaction layer. The reaction layer on the radioactive specimens was less affected by the etching operation. There was little indication of grain boundary attack in most of the specimens tested at 600° and $800^{\circ}C$, although some specimens tested at $800^{\circ}C$ exhibited subsurface voids to a considerable depth.

The micrographs indicate that the specimens tested at $1,000^{\circ}C$ suffered a different type of chemical attack. The attack appeared to involve dissolution of the metal surface combined with pitting, intergranular attack and subsurface void formation. Except for a few specimens, a reaction layer did not form on the specimens tested at $1000^{\circ}C$. In a number of the micrographs, especially those of specimens exposed to $^{90}SrF_2$, what appear to be subsurface voids are actually precipitates. This was also true of some of the specimens tested at $800^{\circ}C$.

FIGURE 23. Haynes Alloy 25 Specimens Exposed to Inert SrF_2 at 600°C --
 $\text{S/V} = 4.5 \text{ cm}^{-1}$

1,000 h

6,000 h

12,000 h

20,000 h

30,000 h

FIGURE 24. Haynes Alloy 25 Specimens Exposed to Inert SrF_2 at 800°C --
 $\text{S/V} = 4.5 \text{ cm}^{-1}$

FIGURE 25. Haynes Alloy 25 Specimens Exposed to Inert SrF_2 at 1000°C --
 $\text{S/V} = 4.5 \text{ cm}^{-1}$

FIGURE 26. Haynes Alloy 25 Specimens Exposed to WESF $^{90}\text{SrF}_2$ at 600°C --
 $\text{S/V} = 4.5 \text{ cm}^{-1}$

FIGURE 27. Haynes Alloy 25 Specimens Exposed to WESF $^{90}\text{SrF}_2$ at 800°C --
 $\text{S/V} = 4.5 \text{ cm}^{-1}$

FIGURE 28. Haynes Alloy 25 Specimens Exposed to WESF $^{90}\text{SrF}_2$ at 1000°C--S/V = 4.5 cm^{-1}

FIGURE 29. Effect of S/V on the Attack of Haynes Alloy 25 Specimens Exposed to Inert SrF₂ for 6000 h

600°C

100X
400 μm

1,000°C

800°C

FIGURE 30. Haynes Alloy 25 Specimens Exposed to WESF $^{90}\text{SrF}_2$ for 6000 h--S/V = 2.5 cm^{-1}

100X
400 μm

FIGURE 31. Haynes Alloy 25 Specimens Exposed to WESF $^{90}\text{SrF}_2$ Containing Zr + ZrF_4 for 6000 h--S/V = 4.5 cm^{-1}

Despite the differences apparent in the micrographs, EM and SEM data indicate that the same types of reactions occurred at all temperature. The reactions involve a general dissolution of the alloy surface, leaching of chromium, cobalt, and manganese from the alloy matrix, and reaction with grain boundary precipitates.

With most of the Haynes Alloy 25 specimens, the microstructural changes consisted of the depletion of normal alloy precipitates in a zone adjacent to the exposed surface. Some of the specimens tested at the higher temperatures with $^{90}\text{SrF}_2$ also exhibited an inner zone containing precipitates not found in the body of the specimen or in the control specimens.

At 600°C , microprobe and SEM analysis showed that chemical attack of the Haynes Alloy 25 consisted of a general dissolution of the metal surface and leaching of chromium, cobalt and manganese from the alloy matrix. Figure 32 shows micrographs and elemental analyses of the surface layer and underlying metal of a specimen exposed to inert SrF_2 for 30,000 h (capsule $\text{S/V} = 4.5 \text{ cm}^{-1}$). The reaction layer appeared to be composed of metal fluoride since its cation content was only 60 to 70 wt%. Chromium was the major cation present in the reaction layer together with lesser amounts of cobalt, tungsten, nickel, manganese and iron. The outer edge of the reaction layer had a significant strontium content. The underlying metal adjacent to the reaction layer was depleted of chromium, cobalt and manganese and enriched in iron. The nickel and tungsten content of the underlying metal was essentially unchanged. There was some indication that silicon was also leached from the alloy matrix. There was no evidence of strontium diffusion into the alloy matrix. Analysis of the SrF_2 taken from the test capsule showed that it was completely depleted of chromium and iron. The evidence indicates that the iron and chromium fluorides in the SrF_2 diffused to the surface of the metal and reacted with components of the alloy.

Analyses of other specimens tested at 600°C gave similar results, although the data indicated that leaching of cobalt and manganese increased with the exposure time. Decreasing the S/V of the test capsules increased the chemical attack of the Haynes Alloy 25 at 600°C , especially with the $^{90}\text{SrF}_2$, but the data indicate that the reaction mechanisms were unchanged.

Figure 33 shows micrographs and elemental analysis of a Haynes Alloy 25 specimen exposed to inert SrF_2 at 800°C for 6000 h. The S/V of the test capsule was 0.9 cm^{-1} . The data indicate that the reaction layer is composed of metal fluorides and unreacted metal particles. Chromium and cobalt were the principal cation components of the layer. The outer edge of the reaction layer had a high concentration of strontium. Analyses of unreacted metal particles showed that they were almost depleted of chromium. The chromium and iron concentrations in the reaction layer were higher than their normal concentrations in the alloy. The other cations were present at lower concentrations in the reaction layer than their normal concentrations in the alloy. The underlying metal adjacent to the reaction layer was depleted of chromium and cobalt and enriched in iron. Unlike the specimens tested at 600°C , manganese was not leached from the alloy matrix. The tungsten and nickel concentrations in the underlying metal were unchanged from the normal

FIGURE 32. Micrographs and Elemental Analysis of a Haynes Alloy 25 Specimen Exposed to Inert SrF_2 at 600°C for 30,000 h-- $S/V = 4.5 \text{ cm}^{-1}$

alloy concentrations. Analysis of the fluoride from the test capsule showed it was depleted of chromium and iron, but was slightly enriched in nickel and manganese. Similar results were obtained with other specimens tested at 800°C .

Figure 34 shows micrographs and elemental analysis of a Haynes Alloy 25 exposed to inert SrF_2 at 1000°C for 6000 h. The test capsule had an S/V of 2.5 cm^{-1} . Like most of the specimens tested at 1000°C , no reaction layer formed on the specimen surface. Chemical attack consisted of a general dissolution of the surface with pitting, grain boundary attack, and subsurface void formation. The elemental analysis showed the presence of a thin layer of SrF_2 on the specimen surface. The SrF_2 layer contained small amounts of cobalt, tungsten, iron, nickel and silicon, but no chromium or manganese. The metal matrix below the surface was depleted in chromium, tungsten and manganese, and enriched in cobalt, nickel and iron. The increases in the cobalt and nickel concentrations resulted from the decrease in the chromium, tungsten and manganese content. The increase in the iron concentration, however, appears to be due to diffusion of iron from SrF_2 into the alloy matrix. There was no evidence of the diffusion of strontium into the alloy matrix. Strontium fluoride was found in some of

FIGURE 33. Micrographs and Elemental Analysis of a Haynes Alloy 25 Specimen Exposed to Inert SrF_2 at 800°C for 6000 h-- $S/V = 0.9 \text{ cm}^{-1}$

the voids in the alloy matrix. Although it was not proven, it appears that the SrF_2 in the pores was due to physical transfer from the specimen surface to the voids during the polishing operation. There was no evidence that the SrF_2 diffused through the grain boundaries.

As can be seen in Figure 34, the alloy matrix adjacent to the surface had a mottled appearance. Analysis of the different colored areas showed only minor differences in composition, except for the chromium and cobalt content. The lighter the coloration, the lower the chromium content and the higher the cobalt content, and conversely, the darker the color, the higher the chromium content and the lower the cobalt content.

Analyses of other specimens tested at 1000°C gave very similar results.

One unusual feature was observed with the specimens exposed to inert SrF_2 at 1000°C for 20,000 and 30,000 h. The specimens exhibited a few isolated voids to a considerable depth. Cause of the void formation was not identified. It seem unlikely that it resulted from

FIGURE 34. Micrographs and Elemental Analysis of a Haynes Alloy 25 Specimen Exposed to Inert SrF_2 at 1000°C for 6000 h-- $S/V = 2.5 \text{ cm}^{-1}$

fluoride attack since there was no indication that grain boundary attack had occurred to the depths at which the voids were found, and the alloy matrix showed no unusual compositional differences due to a fluoride attack.

Decreasing the S/V ratio of the test capsules increased the attack of the Haynes Alloy 25 specimens. The analytical data indicate, however, that the attack mechanisms were not affected to any marked degree by changing the S/V ratio.

The addition of Zr and ZrF_4 to the $^{90}\text{SrF}_2$ produced a marked decrease in the attack of the Haynes Alloy 25. Analysis of the fluoride from test capsules indicated that the zirconium reduced the impurity fluorides (Fe , Cr), which cause the metal attack, to the corresponding metals. After testing, iron and chromium concentrations in the $^{90}\text{SrF}_2$ were approximately the same as the initial concentrations. When the zirconium was not added to the $^{90}\text{SrF}_2$, the fluoride taken from the test capsules was almost completely depleted of iron and chromium.

As mentioned earlier, the microstructural changes that occurred when Haynes Alloy 25 specimens were exposed to SrF_2 consisted primarily of the disappearance of normal alloy precipitates. Figure 35 presents high magnification SEM micrographs of Haynes Alloy 25 samples tested at 600°C , 800°C , and 1000°C showing the normal precipitates found in the body of the specimens. The compositions of the precipitates and the alloy matrices were determined at the point shown using EM analysis. The results obtained are presented in Table 17. Tungsten, cobalt and chromium made up 83 to 93 wt% of the precipitates with the combined concentrations of three elements increasing with the aging temperature. Analysis of the alloy matrix showed that at 800°C and 1000°C the tungsten and chromium concentrations in the matrix were reduced significantly below the nominal concentration in the solution heat-treated alloy due to the precipitate formation. Phase identification studies were not carried out on the precipitates. Based on published information and the limited analytical data obtained, the precipitates formed at 600°C probably consist of M_{23}C_6 (Cr_{23}C_6) and M_6C phases and a Laves phase (Co_2W). The precipitates formed at 800°C are probably M_6C carbides, the Laves phase, and $(\text{Co,Cr})_7\text{W}_6$

FIGURE 35. SEM Micrographs of Haynes Alloy 25 Specimens Aged at 600°C to 1000°C for 6000 h--Showing the Precipitates Formed

TABLE 17. Compositions of the Alloy Matrices and Precipitates Formed When Haynes Alloy 25 Specimens were Aged at 600°C to 1000°C for 6000 h

Composition, wt%	600°C		800°C		1000°C	
	Precipitate (A) (a)	Alloy Matrix (B)	Precipitate (C)	Alloy Matrix (D)	Precipitate (E)	Alloy Matrix (F)
Co	17.5	50.0	17.0	50.7	18.0	50.7
Cr	12.4	20.6	14.8	19.3	13.1	19.6
Fe	0.9	2.2	0.8	3.0	0.7	2.6
Mn	0.3	2.1	0.2	2.0	0.4	1.7
Ni	2.8	10.0	3.0	10.5	2.5	10.8
S	0.3	<0.1	0.8	<0.1	0.8	<0.1
Si	<0.1	0.3	<0.1	0.2	<0.1	0.3
W	53.0	14.0	57.7	12.7	61.6	12.0
TOTAL	87.2%	99.3%	94.3%	98.5%	97.1%	97.7%

(a) Letters correspond to the locations shown in Figure 35.

phases. Similar phases are formed at 1000°C, except that the amount of Laves phase is reduced relative to the $(\text{Co,Cr})_7\text{W}_6$ phase. An unusual feature was the high concentration of sulfur in the precipitates at all three temperatures.

In those areas where the alloy was depleted of the normal precipitate due to exposure to the fluoride, analysis of the alloy matrix showed that the composition was very similar to that of the solution heat-treated alloy, except for the chromium concentration. The chromium concentration was reduced significantly in the affected zone. The data indicate that chemical attack of the alloy resulted in leaching of chromium from the alloy matrix with the subsequent redissolution of the precipitates.

The abnormal precipitates that formed in some specimens exposed to SrF_2 were not identified. Analyses of the precipitates indicated a composition approximately $(\text{Co,Cr})_7\text{W}_6$, with the cobalt and chromium present in approximately a 4 to 3 atomic ratio.

7.5.3 TZM- SrF_2 System

Figure 36 shows the microstructure of the stress-relieved TZM used in the long-term tests and the microstructures of the control specimens aged at 600°C, 800°C and 1,000°C for 1,000 and 30,000 h. The TZM used to fabricate the test specimens was wrought bar that had been stress-relieved for 3/4 h at 2300°F. The TZM exhibited a highly elongated grain structure typical of the wrought material. Aging of the alloy at 600°C to 1,000°C for 30,000 h had no significant effect on the microstructure of the TZM.

Figures 37 through 39 show micrographs of the TZM specimens exposed to inert SrF_2 at 600°C, 800°C and 1,000°C for up to 30,000 h. Figures 40 through 42 show micrographs of specimens exposed to the WESF $^{90}\text{SrF}_2$ under similar conditions. In each case, the S/V of the test capsule

FIGURE 36. Effect of Thermal Aging on the Microstructure of TZM

FIGURE 37. TZM Specimens Exposed to Inert SrF_2 at 600°C -- $\text{S/V} = 4.5 \text{ cm}^{-1}$

FIGURE 38. TZM Specimens Exposed to Inert SrF_2 at 800°C --S/V = $4.5\ \text{cm}^{-1}$

FIGURE 39. TZM Specimens Exposed to Inert SrF₂ at 1000°C--S/V = 4.5 cm⁻¹

FIGURE 40. TBM Specimens Exposed to WESF $^{90}\text{SrF}_2$ at 600°C --S/V = 4.5 cm^{-1}

FIGURE 41. TBM Specimens Exposed to WESF $^{90}\text{SrF}_2$ at 800°C --S/V = 4.5 cm^{-1}

FIGURE 42. TBM Specimens Exposed to WESF $^{90}\text{SrF}_2$ at 1000°C --S/V = 4.5 cm^{-1}

was 4.5 cm^{-1} . Figures 43 and 44 show TZM specimens exposed to inert SrF_2 and $^{90}\text{SrF}_2$ at different S/V values, while Figure 45 shows TZM specimens exposed to $^{90}\text{SrF}_2$ containing Zr and ZrF_4 .

The TZM exposed to the inert SrF_2 and $^{90}\text{SrF}_2$ suffered much less chemical attack than the other two alloys. Microstructural changes were not a problem with TZM, except for a small fraction of the specimens. The microstructural changes occurred most often with specimens exposed to $^{90}\text{SrF}_2$. When the changes did occur, they appeared to involve recrystallization of the molybdenum, and in a few instances the changes occurred to considerable depths. It was never determined why the changes occurred in only a few of the specimens and not in others tested under similar conditions. It appears that the recrystallization may have resulted from the dissolution of chromium or iron in the alloy.

Chemical attack of the TZM was erratic, and the micrographs indicate that, in several instances, specimens tested at the same temperature suffered different types of attack. Overall, chemical attack was much greater with the specimens exposed to $^{90}\text{SrF}_2$ than with those exposed to inert SrF_2 . Temperature appeared to have little effect on the extent of the chemical attack, but did appear to influence the type of attack. In most instances, the attack appeared to involve a general dissolution of the specimen surface with formation of a reaction layer at the surface. Grain boundary attack was also apparent in most specimens tested at 600° and 800°C , but was less obvious at 1000°C .

It was difficult to determine the reactions involved in the chemical attack of the TZM. Electron microprobe and SEM data indicated a general dissolution of the alloy in the fluoride and the leaching of titanium and zirconium from the alloy matrix. Analysis of the reaction layers that formed on the surfaces of the specimens showed that they were primarily molybdenum that contained small amounts of chromium, iron, titanium, zirconium and strontium. Analyses of the SrF_2 in several of the test capsules showed that it contained molybdenum and titanium and was depleted in iron and chromium.

Figure 46 shows a micrograph and elemental analysis of the surface layer of a TZM specimen exposed to inert SrF_2 at 1000°C for 20,000 h. The test capsule had an S/V of 0.9 cm^{-1} . The results show that the reaction layer was molybdenum metal with small amounts of chromium, iron, titanium, and zirconium. The outer edge of the reaction layer contained some strontium. The alloy matrix immediately adjacent to the reaction layer was depleted of titanium and zirconium, and contained a small amount of chromium and iron. There was no indication of strontium in the alloy matrix. The data indicate the chromium and iron fluorides diffused to the specimen surface and were reduced to the corresponding metals by the titanium and zirconium. The chromium and iron then dissolved in the molybdenum, which apparently recrystallized. The microprobe and SEM data indicate that similar reactions were involved in the chemical attack of TZM specimens tested at 600° and 800°C .

As was the case with the other alloys tested, the addition of Zr and ZrF_4 to the $^{90}\text{SrF}_2$ produced a decrease in the chemical attack of the TZM. Again, it appeared that the zirconium metal reacted preferentially with the chromium and iron fluorides in the $^{90}\text{SrF}_2$, reducing them to the corresponding metals, and effectively reducing the chemical attack of the TZM.

FIGURE 43. Effect of S/V on the Attack of TZM Specimens Exposed to Inert SrF₂ for 6000 h

FIGURE 44. TZM Specimens Exposed to WESF $^{90}\text{SrF}_2$ for 6000 h--S/V = 2.5 cm^{-1}

500X
80 μm

FIGURE 45. TZM Specimens Exposed to WESF $^{90}\text{SrF}_2$ Containing Zr + ZrF_4 for 6000 h--
S/V = 4.5 cm^{-1}

FIGURE 46. Micrograph and Elemental Analysis of a TZM Specimen Exposed to Inert SrF_2 at 1000°C for 20,000 h--S/V = 0.9 cm^{-1}

8.0 EVALUATION OF THE COMPATIBILITY TEST RESULTS

Analysis of the data obtained in the various compatibility tests point out certain factors that are important in evaluating the high-temperature containment of $^{90}\text{SrF}_2$. Most of these factors are applicable to all of the materials screened with strontium fluoride, while others are specific to the three alloys evaluated in the long-term tests.

In a number of the tests, widely different results were obtained in replicate experiments. Attack of specimens tested under apparently identical conditions sometimes varied by as much as several hundred percent. This is not unusual in high-temperature compatibility testing, however, and similar differences have been observed in compatibility tests involving other radioisotopes. As a general rule, the more extensive the attack, the greater the variations that have been observed with replicate specimens.

The screening tests with 38 metallic materials and $^{90}\text{SrF}_2$, or inert SrF_2 containing similar impurities, showed that most of the materials exposed to the fluoride at 800° to 1100°C suffered extensive attack. Iridium, tungsten, and Ir-0.3% W provided the greatest resistance to fluoride attack, while rhenium and TZM were significantly better than the remaining materials. As a general rule, the precious metals and refractory metals provided much better corrosion resistance than the base metals and transition metal. Two exceptions to the rule were gold and platinum, which suffered catastrophic attack. Factors causing the very severe attack of the gold and platinum were never defined.

Most of the metals that were exposed to the strontium fluoride suffered the two distinctly different types of attack discussed in Section 7.4.1--chemical attack and microstructural changes. The microstructural changes were much more likely to occur with complex alloys than with "pure" metals, or simply alloys. All of the data indicate that the microstructural changes are a direct result of the chemical attack. In several hundred tests carried out under a variety of conditions, microstructural changes were rarely observed unless the metal had suffered substantial chemical attack. There were many instances, however, where extensive chemical attack occurred without microstructural changes being present. The data indicate that the microstructure changes are probably caused by changes in the composition of the metal matrix due to the chemical attack. For example, the leaching of chromium from the Hastelloy C-276 matrix could cause normal precipitates to redissolve.

Of the two types of metal attack, the chemical attack is more serious than the microstructural changes from a safety standpoint. Carried to the extreme, chemical attack can result in the breaching of the containment vessel and a subsequent release of radioactivity. The chemical attack may also result in a marked decrease in the structural strength of the containment vessel. The microstructural changes, while they may affect the structural strength of the vessel, would not directly result in a breach of the containment.

Photomicrographs of the various test specimens indicate that the mechanisms involved in the chemical attack of a given material varied with temperature and in some cases with the exposure time. Examination of a large number of specimens using electron microprobe analysis

and scanning electron microscopy indicates, however, that this is not generally true. The analytical data infer that the same general reactions are involved in the chemical attack of a given material regardless of the exposure temperature. Although a specific type of attack, grain boundary attack for example, may be more prevalent at one temperature than another, the chemical reactions involved appear to be similar at all temperatures.

All of the experimental data indicate that attack of metallic materials is due primarily to impurities in the strontium fluoride. Except for a few isolated cases, there was little indication that the strontium fluoride reacted directly with the metals. Analyses of the reaction layers which formed on the surfaces of many of the test specimens showed very low strontium concentrations, although some strontium was usually found on the outer edge of a reaction layer. Analysis of the metal substrates showed little indication of strontium diffusing into the metal matrices. In a few instances, strontium was found in metal grain boundaries where attack had occurred. There was no evidence, however, that the strontium was directly involved in the grain boundary attack.

Although some differences were observed with some metals, the bulk of the data show that iron and chromium fluorides are the prime contributors to the metal attack. While it was not possible to determine experimentally the valence states of the iron and chromium, they should be present in the strontium fluoride as FeF_3 and CrF_3 .

Results obtained in the initial scouting tests with SrF_2 containing SrO or CuF_2 showed that both impurities, especially the SrO , caused extensive metal attack. Fortunately, copper and oxygen are present in WESF $^{90}\text{SrF}_2$ in very low concentrations. The fluoride normally contains less than ~ 100 ppm oxygen. Some of the oxygen may be present as SrO , but the SrO concentration should be quite low.

Based on results obtained in the long-term tests, a number of general conclusions can be reached regarding the containment of WESF $^{90}\text{SrF}_2$ for extended periods of time. Results obtained in the other compatibility tests serve to reinforce these conclusions:

- The TZM exhibited much better resistance to fluoride attack at 600° to 1000°C than did Haynes Alloy 25 and Hastelloy C-276. Except for a few isolated specimens, microstructural changes due to fluoride attack were not a problem with TZM. Microstructural changes, when they did occur, appeared to involve recrystallization of the molybdenum, possibly caused by the diffusion of iron and/or chromium into the alloy.
- Both the Haynes Alloy 25 and Hastelloy C-276 suffered extensive attack when exposed to WESF $^{90}\text{SrF}_2$ at 600° to 1000°C . In the shorter duration tests, the Haynes Alloy 25 appeared to be more resistant to attack than the Hastelloy C-276. Long-term attack of the two alloys was very similar, however, and for exposures greater than 12,000 h, there was little reason to select one alloy over the other for $^{90}\text{SrF}_2$ containment based on resistance to fluoride attack.
- On an overall basis, metal specimens exposed to WESF $^{90}\text{SrF}_2$ suffered much greater attack than did the specimens exposed to the inert SrF_2 .

- All of the long-term test data indicate that chemical attack of the three alloys is due primarily to certain impurities in the strontium fluoride. Once the critical impurities in the fluoride are consumed by reaction with the metal, the rate of chemical attack decreases to a very low level. The test results show that the critical impurities are consumed in a relatively short period of time ($\leq 12,000$ h). Most of the specimens tested for 20,000 and 30,000 h suffered no greater chemical attack than did specimens tested for 6,000 and 12,000 h. Exceptions were the Hastelloy C-276 specimens tested at $1,000^{\circ}\text{C}$ with WESF $^{90}\text{SrF}_2$ where the chemical attack continued to increase with time.
- In several of the tests, microstructural changes continued to increase with time even though the chemical attack did not. This may indicate that the kinetics of the reactions involved in the microstructural changes are relatively slow (i.e., redissolution of normal precipitates or precipitation of abnormal precipitates).
- The data indicate that iron and chromium fluorides (probably FeF_3 and CrF_3) in the strontium fluoride were the principal contributors to the attack of the three alloys. The WESF $^{90}\text{SrF}_2$ contained much greater concentrations of iron and chromium fluorides than the inert SrF_2 , which could help explain why greater metal attack occurred with the $^{90}\text{SrF}_2$. Analyses of the WESF $^{90}\text{SrF}_2$ and inert SrF_2 taken from a number of the test capsules showed that the fluoride was almost completely depleted of iron and chromium. This indicates that the iron and chromium fluorides had diffused to the metal surface and reacted. The final concentrations of the other impurities in the fluoride were not significantly different from their initial concentrations.
- Decreasing the S/V of the test capsules increased the metal attack. This is to be expected if impurities in the strontium fluoride are the primary cause of the attack, since decreasing the S/V of the capsule increases the amount of impurities available for reaction per unit of metal surface area.
- In every test, the addition of $\text{Zr} + \text{ZrF}_4$ to the $^{90}\text{SrF}_2$, to simulate decay product buildup, produced a marked decrease in metal attack. The zirconium metal powder dispersed in the $^{90}\text{SrF}_2$ apparently reacted with the iron and chromium fluorides and reduced them to the corresponding metals before they could react with the test specimens. Analysis of the $^{90}\text{SrF}_2$ from capsules of each alloy containing $\text{Zr} + \text{ZrF}_4$ after testing showed that the iron and chromium concentrations were approximately the same as the initial concentrations.
- The tensile specimens exposed to $^{90}\text{SrF}_2$ exhibited marked decreases in room temperature tensile properties compared to control specimens heated in vacuum. Overall, tensile specimens of the three alloys exposed to the $^{90}\text{SrF}_2$ suffered losses in tensile strength and ductility of as much as 50%.
- Aging of Hastelloy C-276 and Haynes Alloy 25 at 600° to 1000°C produced very large decreases in the Charpy impact energy of the two alloys due to precipitate

formation. Aging of the TZM at 600⁰ to 1000⁰C appeared to have little effect on its impact energy. Although the CVN specimens exposed to ⁹⁰SrF₂ were not impact tested, one would predict, based on results of the tensile tests, that fluoride attack would decrease the impact energy of the three alloys. This should not be a major problem with the Hastelloy C-276 and Haynes Alloy 25 because the normal aging reactions at 600⁰ to 1000⁰C reduce their impact energy to very low levels, and any further reductions due to fluoride attack should be relatively insignificant. This would not be true, however, with the TZM. Aging of TZM at 600⁰ to 1000⁰C had no apparent effect on its impact energy, and fluoride attack could result in a significant loss of impact energy.

9.0 ESTIMATES OF LONG-TERM METAL ATTACK

The nominal design requirements for the $^{90}\text{SrF}_2$ heat source being developed at PNL call for a service life of 10 years. Safety considerations and licensing requirements dictate that the ^{90}Sr must be adequately contained throughout the service life of the heat source until final disposal. In order to ensure that the ^{90}Sr is contained during service, it is necessary that corrosion of the containment vessel be adequately known or definable. It is not practical to carry out compatibility tests with WESF $^{90}\text{SrF}_2$ lasting 10 years. It is necessary, therefore, to be able to reliably estimate long-term attack of the containment materials by extrapolating the WESF $^{90}\text{SrF}_2$ compatibility data obtained in this program.

In attempting to extrapolate the WESF $^{90}\text{SrF}_2$ compatibility data to long exposure times, certain factors must be considered:

- Chemical attack of the containment material is the critical factor since excessive chemical attack can corrode through the canister and result in a breach of containment. Microstructural changes are of minor importance because they do not directly result in a breach of containment, although they may affect the structural strength of the containment vessel.
- Chemical attack of the containment materials is due primarily to certain critical impurities in the WESF $^{90}\text{SrF}_2$. Once the critical impurities have been consumed by reaction with the containment material, the rate of attack of the containment material decreases to a very low level. Since the chemical attack is due primarily to impurities, the S/V of the heat source capsule will affect the extent of the chemical attack.
- Significant differences in chemical attack were observed with replicate specimens in some of the compatibility tests. Insufficient data were obtained at each set of conditions to permit a meaningful statistical evaluation of the test results.
- Analysis of the experimental data from the various compatibility tests with Haynes 25, Hastelloy C-276 and TZM showed that the chemical attack rates could not be correlated with any of the standard rate equations. Therefore, extrapolation of the compatibility data to long-exposure times must be made using conservative empirical methods.

Only the data from the long-term tests with WESF $^{90}\text{SrF}_2$ were used in estimating chemical attack for very long exposures. The procedure used in making the estimates is described below, using the 600°C data for Hastelloy C-276 for illustration.

Figure 47 shows the chemical attack as a function of exposure time for Hastelloy C-276 exposed to WESF $^{90}\text{SrF}_2$ at 600°C and an S/V of 4.5 cm⁻¹. The large differences in attack between duplicate specimens in some of the tests are obvious. If one uses an average value for the chemical attack at each exposure time, the data show there is no increase in the chemical attack of the Hastelloy C-276 between 12,000 and 30,000 h. This is not unrealistic if the attack is due primarily to impurities in the $^{90}\text{SrF}_2$ and the impurities are consumed in a

FIGURE 47. Chemical Attack of Hastelloy C-276 Specimens Exposed to WESF $^{90}\text{SrF}_2$ at 600°C --S/V = 4.5 cm^{-1}

relatively short period of time. Extrapolation of the average attack data would show that Hastelloy C-276 exposed to the WESF $^{90}\text{SrF}_2$ for 10 to 20 yr would not suffer significantly more attack than the Hastelloy C-276 specimens tested for 12,000 to 30,000 h. A more conservative approach would be to consider only the maximum chemical attack observed for each exposure time and to use this data in making the long-range extrapolations. This has been done with the data shown in Figure 47. A curve-fitting procedure was used to obtain the best fit with the experimental data, and the equation obtained was used to estimate the chemical attack for long exposures. For the case under consideration, a logarithmic curve provides the best fit with the experimental data:

$$d = 41.8 \ln T - 207$$

where

d = depth of metal affected by chemical attack, μm

T = exposure time, h

Using the equation, chemical attack of Hastelloy C-276 at 600°C and an S/V of 4.5 cm^{-1} was estimated for 5-, 10-, 15- and 20-yr exposures. The results obtained are shown in Table 18. A similar procedure was used to estimate chemical attack of the Hastelloy C-276 at 800° and 1000°C and Haynes Alloy 25 at 600° , 800° , and 1000°C , and the results obtained are also shown in Table 18. In the case of Hastelloy C-276 at 1000°C , the chemical attack appeared to continue at about a linear rate up to 20,000 h. The best fit with the experimental data was obtained with a linear equation. Use of this equation to predict long-term attack resulted in estimates that are probably unrealistic, but which indicate that Hastelloy C-276 should not be used at 1000°C to contain WESF $^{90}\text{SrF}_2$.

TABLE 18. Estimated Chemical Attack of Metals Exposed to WESF $^{90}\text{SrF}_2$ at 600 $^\circ$ to 1000 $^\circ$ C for Extended Periods of Time

Material	Exposure Time, yr	Depth of Metal Affected, μm					
		S/V = 4.5 cm^{-1}			S/V = 0.86 cm^{-1}		
		600 $^\circ$ C	800 $^\circ$ C	1000 $^\circ$ C	600 $^\circ$ C	800 $^\circ$ C	1000 $^\circ$ C
Hastelloy C-276	5	240	368	1,660	1,260	1,930	8,700
	10	268	403	3,100	1,400	2,110	16,200
	15	285	424	4,420	1,490	2,220	23,200
	20	297	439	6,000	1,560	2,300	31,400
Haynes 25	5	208	331	380	1,090	1,730	1,990
	10	237	367	415	1,240	1,920	2,170
	15	254	389	436	1,330	2,040	2,280
	20	266	403	451	1,390	2,110	2,360
TZM	5	75	75	75	400	400	400
	10	104	104	104	545	545	545
	15	134	134	134	700	700	700
	20	163	163	163	855	855	855

A somewhat different procedure was used to estimate long-term attack of the TZM by WESF $^{90}\text{SrF}_2$. Evaluation of the long-term compatibility data shows that attack of the TZM by WESF $^{90}\text{SrF}_2$ was essentially independent of temperature, and very little increase in attack was observed after 6,000 h exposure. In fact, at 800 $^\circ$ C the chemical attack was unchanged from 1,000 to 30,000 h. In estimating long-term attack of the TZM, all of test data obtained at an S/V of 4.5 cm^{-1} were considered as a group without regard to temperature. Curve fitting was applied to the data, and a single equation was used to estimate chemical attack of the TZM at all three temperatures. The results obtained are shown in Table 18.

The test data used in estimating the long-time metal attack were obtained at an S/V of 4.5 cm^{-1} . Since impurities in the $^{90}\text{SrF}_2$ are the principal cause of the chemical attack, the S/V of $^{90}\text{SrF}_2$ system will affect the extent of the chemical attack of the containment material. The smaller the S/V of the system, the more extensive the chemical attack that should occur.

The S/V of the WESF storage capsule is $\sim 0.86 \text{ cm}^{-1}$. Assuming that the bulk density and composition of the $^{90}\text{SrF}_2$ are the same in the two types of capsules, the amount of impurities available to react with the capsule materials, per unit of surface area, would be more than five times greater in the WESF storage capsule than in the capsule used in the long-term tests ($4.5/0.86 = 5.23$). Therefore, one would expect on the order of five times as much chemical attack in the WESF storage capsule as in the test capsules when all the impurities have been consumed.

In the long-term compatibility studies, some tests were run with inert SrF_2 using capsules having an S/V of 2.5 or 0.9 cm^{-1} and with $^{90}\text{SrF}_2$ using capsules having an S/V of 2.5 cm^{-1} . In the tests involving an S/V of 0.9 cm^{-1} , the chemical attack averaged about 3.5 times greater than the attack in the capsules having an S/V of 4.5 cm^{-1} (compared to an impurity ratio of $4.5/0.9 = 5.0$). Similarly, at an S/V of 2.5 cm^{-1} , the chemical attack averaged about twice as great as the attack at an S/V of 4.5 cm^{-1} (compared to an impurity ratio =

4.5/2.5 = 1.8). Based on these results, a reasonable estimate of long-term attack in a WESF capsule can be made by multiplying the estimated attack for an S/V of 4.5 cm^{-1} by a factor of 5.23. When this was done, the results shown in Table 18 were obtained.

The Hastelloy C-276 inner capsule of the WESF $^{90}\text{SrF}_2$ storage capsule has a minimum wall thickness of 0.124 in. (3150 μm), except for a small area near each end cap where the thickness is reduced to a minimum of 0.114 in. (2900 μm). From Table 18, it can be seen that the Hastelloy C-276 inner capsule should be able to contain the WESF $^{90}\text{SrF}_2$ at 600 $^\circ$ or 800 $^\circ\text{C}$ for at least 20 yr without a breach of the containment. The Hastelloy C-276 should not be used at 1000 $^\circ\text{C}$. The data also show that inner capsules of Haynes Alloy 25 or TZM should be able to contain the WESF $^{90}\text{SrF}_2$ at 600 $^\circ$ to 1000 $^\circ\text{C}$ for at least 20 yr without a loss of containment.

Although the estimate of long-term attack show that the $^{90}\text{SrF}_2$ can be safely contained in Hastelloy C-276, Haynes Alloy 25 or TZM or for up to 20 yr, certain factors must be taken into consideration:

- All three alloys suffer extensive chemical attack when exposed to the WESF $^{90}\text{SrF}_2$ for long periods of time. The chemical attack will reduce the structural strength of the containment vessel regardless of which alloy is used.
- Microstructural changes resulting from the chemical attack will affect the structural strength of the containment vessel, although it has not been determined whether the effect of the changes will be deleterious or beneficial. For example, the formation of abnormal precipitates could reduce the impact energy and ductility of an alloy, but the disappearance of normal precipitates could increase the impact energy and ductility.

Because of the extensive chemical attack of the three alloys by the WESF $^{90}\text{SrF}_2$ and the resulting loss of structural strength, any heat-source design would require at least double encapsulation of the $^{90}\text{SrF}_2$. The inner capsule, which could be fabricated from Hastelloy C-276, Haynes Alloy 25 and TZM, would provide the required containment of the $^{90}\text{SrF}_2$. The outer capsule(s) would provide all of the structural strength needed for the heat source to meet licensing requirements without support from the inner capsule.

One additional point should be considered. The demonstration tests with the standard WESF $^{90}\text{SrF}_2$ capsules were carried out at $\sim 800^\circ\text{C}$ and lasted up to 26,200 h (see Section 10.3). Chemical attack of the Hastelloy C-276 inner capsule after 26,200 h exposure was about the same as that observed in the long-term tests with capsules having an S/V of 4.5 cm^{-1} . Considering the differences in S/V, one would have expected much greater chemical attack to have occurred in the demonstration tests. The results of the demonstration tests are encouraging inasmuch as they indicate that attack of the Hastelloy C-276 in the WESF storage capsule at 800 $^\circ\text{C}$ may be much lower than the results of the long-term tests indicate should occur. This means that the estimates of long-time attack given in Table 18 may be overly conservative.

10.0 APPENDIX

The strontium fluoride compatibility studies carried out as part of the Strontium Heat Source Development Program were divided into five major phases:

- the initial scouting tests (Fullam 1975)
- the supplemental screening tests (Fullam 1977b)
- the WESF $^{90}\text{SrF}_2$ capsule demonstration tests (Fullam 1980)
- thermal gradient test (Fullam 1977a)
- the long-term tests.

Details of the first four studies were presented in the reports referenced; details of the long-term tests are presented in this report.

In order to assemble all of the strontium fluoride compatibility data developed at PNL into a single source, details of the first four studies are summarized in the following sections.

10.1 INITIAL SCOUTING TESTS

The initial scouting tests were the first strontium fluoride compatibility studies carried out as part of the Strontium Heat Source Development Program. The objectives of the tests were twofold:

- to evaluate a number of potential containment materials with strontium fluoride in a series of short-term tests and identify the best materials for long-term testing; and
- to evaluate the effects of impurities on the compatibility of strontium fluoride with containment materials, and determine if additional purification steps were needed in the WESF operation to produce a $^{90}\text{SrF}_2$ product that could be safely contained in heat-source applications.

In the scouting tests, nine different containment materials were evaluated with four different grades of strontium fluoride at temperatures of 800° , 1000° , and 1100°C . The tests lasted 1500 and 4400 h.

10.1.1 Parameters for the Initial Scouting Tests

The experimental conditions for the initial screening tests are summarized in Table 19. The tests were divided into four series of tests, each using a different grade of SrF_2 , plus a fifth series in which reference specimens of the containment materials were heated without SrF_2 present.

Four grades of strontium fluoride, as shown in Table 19, were used in the initial scouting tests to determine the effects of impurities, decay products, radiation, etc., on the compatibility of SrF_2 with containment materials. High-purity nonradioactive SrF_2 was tested as a reference material against which the other fluoride compositions could be compared. The high-purity SrF_2 was prepared from reagent-grade chemicals using the WESF flowsheet; its composition is given in Table 20. The material contained <1000 ppm total impurities with

TABLE 19. Experimental Conditions for the Initial Scouting Tests

1. Grades of Strontium Fluoride Tested
 - a. High-purity nonradioactive SrF_2 (<1000 ppm impurities)
 - b. WESF-purity $^{90}\text{SrF}_2$ (~4.5 wt% impurities)
 - c. High-purity $^{90}\text{SrF}_2$ (~1.9 wt% impurities)
 - d. High-purity nonradioactive SrF_2 with controlled levels of added impurities
2. Containment Materials Evaluated

a. Hastelloy C-276	d. Haynes Alloy 25	g. Inconel 625
b. Hastelloy X	e. Haynes Alloy 188	h. TZM
c. Hastelloy N	f. Inconel 600	i. Tungsten
3. Test Temperatures
 - a. 800°C (1472°F)
 - b. 1000°C (1832°F)
 - c. 1100°C (2012°F)
4. Test Duration
 - a. 1500 h (~2 mo)
 - b. 4400 h (~6 mo)
5. Metal Surface-to- SrF_2 Volume Ratio
 - a. 4.5 cm^{-1}

sodium (300 ppm) and calcium (220 ppm) the principal impurities. The high-purity inert SrF_2 was tested with each containment material at 800° , 1000° , and 1100°C . Duplicate tests were conducted for each set of conditions.

Mixtures of high-purity inert SrF_2 with controlled levels of added impurities were tested to determine the effects of specific impurities on SrF_2 compatibility. The SrF_2 -impurity mixtures used in the tests are shown in Table 21. The mixtures were prepared by blending the high-purity inert SrF_2 with the appropriate amount of reagent-grade impurity compound. The SrF_2 -water mixture was prepared by adding water to the SrF_2 , using a micropipette, as the SrF_2 was compacted into the test capsule. Selection of the impurities to be studied was based on analysis of $^{90}\text{SrF}_2$ prepared by the WESF flowheet at PNL using a typical ^{90}Sr feed solution obtained from ARHCO (WESF-produced $^{90}\text{SrF}_2$ was not available when the tests were started). The concentrations of impurities used in the test mixtures were greater than those expected in the WESF $^{90}\text{SrF}_2$ in order to accelerate possible effects. It was impossible to test all of the impurities expected in the WESF $^{90}\text{SrF}_2$ because of the large number of test couples required. The tests were limited to those impurities that should be present in the WESF $^{90}\text{SrF}_2$ in large concentrations, such as Na, Ca, and Ba, and those impurities that thermodynamic calculations indicated should be especially troublesome, such as Cu, Fe, and Mn. The tests with fluoride-impurity mixtures were carried out at only one temperature, 1000°C .

TABLE 20. Analysis of High-Purity Inert SrF_2 Used in the Initial Scouting Tests(a)

Element	Concentration, ppm	Element	Concentration, ppm	Element	Concentration, ppm
H	7	Ga	ND ^(b)	Nd	ND
Li	1	Ge	5	Sm	ND
Be	<1	As	5	Eu	ND
B	<1	Se	ND	Gd	ND
C	10	Br	ND	Tb	ND
N	5	Rb	2	Dy	ND
O	50	Y	40	Ho	ND
Na	300	Zn	<10	Er	ND
Mg	10	Nb	<10	Tm	ND
Al	70	Mo	ND	Yb	ND
Si	15	Te	ND	Lu	ND
P	1	Ru	ND	Hf	<10
S	10	Rh	ND	Ta	<10
Cl	4	Pd	ND	W	ND
K	20	Ag	<10	Re	ND
Ca	220	Cd	ND	Os	ND
Sc	<1	In	ND	Ir	ND
Ti	20	Sn	ND	Pt	ND
V	<1	Sb	ND	Au	<1
Cr	30	Te	ND	Hg	ND
Mn	10	I	<10	Tl	ND
Fe	75	Cs	15	Pb	ND
Co	15	Ba	20	Bi	ND
Ni	5	La	1	Th	ND
Cu	4	Ce	ND	U	ND
Zn	5	Pr	ND		

(a) Values given are the average values from the analysis of three separate samples (using two or more procedures for most elements).

(b) ND indicates element is below the detection limit. In most cases, the detection limit is <1 ppm.

WESF-grade $^{90}\text{SrF}_2$ was tested to allow an early evaluation of the potential problems in containing $^{90}\text{SrF}_2$ that contained significant amounts of process impurities as well as decay products. It would have been highly desirable to use WESF-produced $^{90}\text{SrF}_2$ for the tests, but the plant had not yet started production when the tests were begun. Instead, $^{90}\text{SrF}_2$ was prepared at PNL using the WESF-flowsheet and a typical ^{90}Sr feed solution obtained from the plant. The analysis of the ^{90}Sr feed solution is shown in Table 22, and the composition of the $^{90}\text{SrF}_2$ product is given in Table 23. The $^{90}\text{SrF}_2$ contained about 4.5 wt% cation impurities, with sodium and rare earths the principal contaminants. It was not possible to analyze for

TABLE 21. Compositions of SrF_2 -Impurity Mixtures Used in the Initial Scouting Tests

Composition	wt%
1. Sr^{+2} (as SrF_2) ^(a)	95
Na^+ (as NaF)	5
2. Sr^{+2} (as SrF_2)	95
Ca^{+2} (as CaF_2)	1.67
Mg^{+2} (as MgF_2)	1.67
Ba^{+2} (as BaF_2)	1.66
3. Sr^{+2} (as SrF_2)	98
Mn^{+2} (as MnF_2)	2
4. Sr^{+2} (as SrF_2)	98
Pb^{+2} (as PbF_2)	2
5. Sr^{+2} (as SrF_2)	98
Cu^{+2} (as CuF_2)	2
6. Sr^{+2} (as SrF_2)	98
Fe^{+3} (as FeF_3)	2
7. Sr^{+2} (as SrF_2)	98
Al^{+3} (as AlF_3)	2
8. Sr^{+2} (as SrF_2)	99
O^{-2} (as SrO)	1
9. Sr^{+2} (as SrF_2)	99.95
NO_3^- [as $\text{Sr}(\text{NO}_3)_2$]	0.05
10. SrF_2	99.95
H_2O	0.05

(a) High-purity nonradioactive SrF_2 , containing <1000 ppm total impurities, used in preparing the mixtures.

anion impurities because procedures were not available in shielded facilities. The ^{90}Sr isotopic content of the fluoride product was 55.1%. The WESF-grade $^{90}\text{SrF}_2$ was tested with each containment material at 800° , 1000° , and 1100°C .

High-purity $^{90}\text{SrF}_2$ was tested to estimate the effects of radiation and decay-product buildup on the compatibility of SrF_2 with containment materials. The high-purity $^{90}\text{SrF}_2$ was prepared from the same solution used to prepare the WESF-grade $^{90}\text{SrF}_2$. The Sr solution was purified by chromatographic ion exchange prior to preparation of the fluoride. The procedure

TABLE 22. Composition of ^{90}Sr Feed Solution

Total Sr	=	16.2 g/L
^{90}Sr	=	8.93 g/L
H^+	=	0.7 <u>M</u>
NO_3^-	=	2.5 <u>M</u>

Isotopic Analysis:

^{84}Sr	=	0.10 atom%
^{86}Sr	=	0.57
^{87}Sr	=	0.40
^{88}Sr	=	43.80
^{90}Sr	=	55.10

Impurity Analysis:

<u>Element</u>	<u>Moles/Mole Sr</u>
Al	0.013
Ba	0.003
Ca	0.015
Cd	<0.0006
Cr	<0.003
Cu	<0.0002
Fe	<0.003
Mg	<0.004
Mn	<0.001
Na	5.7
Ni	<0.005
Pb	0.007
RE ^(a)	0.010
Zr	<0.004

(a) RE--Rare Earths

used in preparing the high-purity $^{90}\text{SrF}_2$ was identical to that used in preparing the WESF-grade $^{90}\text{SrF}_2$. The analysis of the high-purity $^{90}\text{SrF}_2$ is given in Table 24. Unfortunately, the high-purity $^{90}\text{SrF}_2$ contained about 1.9 wt% impurities, principally Na, that could have affected the results obtained, making it difficult to estimate the effects of radiation and decay product buildup on compatibility. The high-purity $^{90}\text{SrF}_2$ was tested with each containment materials at 800 $^{\circ}$, 1000 $^{\circ}$, and 1100 $^{\circ}$ C.

The nine containment materials evaluated in the initial scouting tests, and their compositions, are given in Table 25. By sponsor directive, the materials evaluated were limited to materials that could be used as the inner capsule in the WESF operation. This effectively eliminated from consideration a wide variety of materials. For example, precious metals, such

TABLE 23. Analysis of WESF-Grade $^{90}\text{SrF}_2$ Used in the Initial Scouting Tests

Element	Concentration, wt%	Element	Concentration, wt%
Al	<0.01	Mn	<0.01
Ba	0.35	Na	2.0
Ca	0.48	Ni	<0.01
Cd	0.04	P	ND
Co	ND ^(a)	Pb	0.015
Cr	<0.01	Si	<0.005
Cu	0.01	Sn	ND
Fe	0.03	Zn	ND
K	ND	Zr	ND
Mg	0.20	RE ^(b)	1.7

(a) ND--not detected (the detection limit for most elements ~0.01%).

(b) RE--Rare earths.

TABLE 24. Analysis of High-Purity $^{90}\text{SrF}_2$ Used in the Initial Scouting Tests

Element	Concentration, wt%	Element	Concentration, wt%
Al	0.25	Mn	0.0005
Ba	0.002	Na	1.32
Ca	0.006	Ni	0.002
Cd	0.0007	P	ND
Co	ND ^(a)	Pb	0.006
Cr	0.003	Si	ND
Cu	<0.0005	Sn	ND
Fe	0.022	Zn	ND
K	0.004	Zr	ND
Mg	0.0036	RE ^(b)	ND

(a) ND--not detected (the detection limit for most elements ~0.01%).

(b) RE--rare earths.

as iridium, could not be considered because of the cost involved. The use of protective coatings on base metals (i.e., vapor-deposited coatings, sputtered coatings, electrodeposited coatings, etc.) could not be considered because of the mechanical stresses encountered in the WESF capsule loading operation.

Selection of the containment materials to be evaluated in the initial screening tests represented a critical decision point in the Strontium Heat Source Development Program. Cost

TABLE 25. Chemical Composition of Containment Materials Evaluated in the Initial Screening Tests^(a)

Element	Composition, wt%								
	Hastelloy C-276	Hastelloy X ASM-5754	Hastelloy N	Haynes Alloy 25 ASM 5759D	Haynes Alloy 188	Inconel 600 Hot Finished, Pickled and Annealed	Inconel 625 ASM-5666 Hot Finished and Annealed	TZM Wrought Bar Stress-Relieved 3/4 h at 2300°F	Tungsten Arc Cast
	Solution Heat- Treated at 2100°F	Solution Heat- Treated at 1950°F	Solution Heat- Treated at 2165°F	Solution Heat- Treated	Solution Heat- Treated at 2100°F				
Al			0.16				0.21		
B		0.001	0.01						
C	0.005	0.09	0.07	0.11	0.08	0.07	0.04	0.019	
Cb							3.62		
Co	1.36	1.85	0.16	Bal	Bal				
Cr	15.05	21.38	6.21	20.25	21.80	15.73	21.99		
Cu			0.30			0.12			
Fe	6.20	18.94	4.73	2.40	1.56	7.54	3.44	0.001	
La					0.05				
Mo	15.65	8.88	16.81				8.93		
Mn	0.49	0.62	0.59	1.65	1.12	0.17	0.05		
Ni	Bal	Bal	Bal	10.80	22.3	76.12	61.17	< 0.001	
P	0.015	0.015	0.01	0.014	0.010				
S	0.008	0.006	0.01	0.005	0.006	0.007	0.007		
Si	< 0.01	0.47	0.72	0.25	0.31	0.22	0.24		
Ti			0.24				0.28	0.44	
V	0.24								
W	3.50	0.44	0.42	14.90	14.05				99.9
Zr								0.087	

(a) Compositions listed are as given in the Certified Report of Chemical Analysis supplied with each lot of material.

considerations prevented the testing of a wide variety of materials, and time considerations made it imperative that the materials selected for initial testing provided the maximum possibility of achieving the program objectives. To be suitable as a containment material for $^{90}\text{SrF}_2$ in heat-source applications, a material should not only be compatible with the $^{90}\text{SrF}_2$ under source operating conditions but provide other heat-source requirements as well. These can include such requirements as oxidation resistance, seawater corrosion resistance, and good high-temperature strength characteristics. Containment materials that best meet the fluoride compatibility requirement may not provide other source and/or WESF-process requirements. Since the $^{90}\text{SrF}_2$ will be at least double-encapsulated in the heat source, consideration can be given to the use of dissimilar materials for the inner and outer capsules--the inner capsule material would provide fluoride compatibility and WESF process needs, and the outer material would provide other source requirements. Therefore, in selecting the materials for evaluation in the initial screening tests, primary emphasis was placed on fluoride compatibility and adaptability to the WESF process.

Selection of the materials to be tested from the many potential candidates was based on a review of the following considerations:

- an elementary thermodynamic analysis of SrF_2 containment;
- results obtained in earlier SrF_2 compatibility programs at the Martin Marietta Corp. (Maraglia 1966) and PNL (Fullam 1972);
- results obtained in other experimental programs involving metal fluorides at high temperatures, including the Molten Salt Reaction Program at ORNL, the fluoride volatility programs at ORNL, Argonne National Laboratory, and Battelle Memorial Institute, Columbus, and miscellaneous electrolytic studies involving fused fluoride salts;
- adaptability of the containment materials to the WESF process;
- potential heat-source operating requirements (i.e., temperature, etc.);
- probable $^{90}\text{SrF}_2$ heat-source licensing requirements.

Anticipated compatibility with $^{90}\text{SrF}_2$ was the primary basis for selecting the nine materials evaluated, and in some instances overrode other considerations. For example, earlier work had indicated that Haynes Alloy 25 was compatible with SrF_2 at 400° to 900°C , and it was selected for testing even though thermal aging reactions in the alloy at 650° to 900°C greatly reduce its Charpy impact energy and ductility (Ferry 1969; McCoy and Bourgette 1973).

The initial screening tests were carried out at temperatures of 800° , 1000° , and 1100°C . When the program was started, a review of potential applications for $^{90}\text{SrF}_2$ heat sources was made. This review indicated that $^{90}\text{SrF}_2$ could be used with both static and dynamic conversion systems. Advanced concepts for both types of systems called for capsule-fuel interface temperatures, under normal operating conditions, in the range of 800° to 1000°C , and temperatures up to 1100°C under accident conditions. The test temperatures were selected to bracket the range of expected capsule operating and accident temperatures.

The tests were conducted for 1500 and 4400 h. It was felt that 4400 h was the shortest test period that would provide a reasonable comparison of the various containment materials and allow a valid evaluation of the effects of impurities on compatibility. Two time periods were used to obtain preliminary estimates of reaction kinetics.

An important variable in the design of any compatibility test capsule is the ratio of exposed containment material surface to the SrF_2 volume (S/V). The WESF $^{90}\text{SrF}_2$ capsule has a surface to volume ratio of about 0.86 cm^{-1} . It was impractical to use this value in the initial screening tests because of the many capsules to be tested and the large amount of $^{90}\text{SrF}_2$ required if an S/V of 0.86 was used. The capsule design used for the tests had a S/V ratio of 4.5 cm^{-1} , and this was not varied. The effect of varying the S/V ratio on compatibility was evaluated in the long-term tests.

In addition to the fluoride compatibility tests, individual metal control samples were tested at each temperature to determine the effect of time and temperature on the microstructures of the containment materials. The samples were tested without SrF_2 present and served as references to compare with the metal specimens exposed to the fluoride.

10.1.2 Test Procedures

The procedures used in preparing the test capsules for the initial scouting studies were designed to duplicate the WESF process as closely as possible. While the design of the test capsules differed substantially from the WESF capsule, the procedures used to load and weld the capsules were similar to those used at WESF. All operations involving $^{90}\text{SrF}_2$ were carried out remotely in heavily shielded facilities (hot cells).

The design of the capsules used in the initial scouting tests is shown in Figure 48. Basically, the capsule consisted of a small metal test specimen packed in strontium fluoride within a metal capsule. The capsule and test specimen were the same material. All metal components of the capsules were machined from bar stock. All test capsules of a given material that were used in the tests were prepared from a single lot of material that was well characterized as to chemical composition and physical properties. Each test specimen was 1/2 in. dia and $\sim 3/8$ in. thick, and all the test specimens of a given material were prepared from a single lot. The flat faces of each specimen were ground and polished to a metallographic finish using $0.3\text{-}\mu\text{m}$ alumina for the final polish. After fabrication, the metal components of the capsules were cleaned in an ultrasonic bath using trichloroethylene, washed with acetone, dried in air, and stored in sealed containers until needed.

Strontium fluoride was loaded into the test capsules by step-pressing using a hydraulic press. The loading operations were carried out in an argon atmosphere glove box. The metal capsule was pressed into a steel die. A small increment of SrF_2 (4 to 5 g) was placed in the capsule and compacted using the hydraulic press and a steel plunger. The plunger was removed and a second increment of SrF_2 added to the capsule and compacted. The test specimen was placed on top of the fluoride layer and centered to prevent contact with the capsule wall. Additional fluoride was added to the capsule and compacted in 4- to 5-g increments

NOTES:

1. CAPSULE, LID AND TEST SPECIMEN ARE SAME MATERIAL
2. METAL COMPONENTS MACHINED FROM BAR STOCK
3. FLAT FACES OF TEST SPECIMENS POLISHED TO METALLOGRAPHIC FINISH
4. SrF_2 STEP PRESSED INTO CAPSULE

FIGURE 48. Design of the Capsules Used in the Initial Scouting Tests

until the capsule was filled to the desired level. The capsule lid was pressed into place and the capsule ejected from the die block. The capsule was then transferred in a sealed container to an argon-atmosphere welding box where it was closed by TIG-welding the lid in place. In the loading operations, the fluoride was compacted to a density of about 75% of theoretical density, approximately the density of the $^{90}\text{SrF}_2$ in the WESF capsule. A pressure of 9 to 10 TSI was sufficient to give the desired fluoride density. A similar procedure was used to fabricate the radioactive couples, except the loading and welding operations were carried out in air-atmosphere hot cells. A small press constructed from a hydraulic jack was used to compact the fluoride. The capsules were sealed by TIG welding.

Testing of the capsules was carried out in air-atmosphere muffle furnaces. To protect the capsules from external oxidation during testing, they were sealed in protective jackets of Inconel 600. Each jacket contained up to eight capsules. Alumina tubes and spacers were used to prevent contact between the capsules and the Inconel 600.

Several furnaces were required because of the large number of capsules to be tested, the different temperature requirements, and the need to test both radioactive and nonradioactive capsules. Each furnace was equipped with a solid-state proportioning controller and calibrated Platinel II thermocouple capable of maintaining the temperature within $\pm 2^\circ\text{C}$ of the set point. In addition, each furnace was equipped with a second calibrated thermocouple, either Platinel II or Pt/Pt-13% Rh, which was monitored continuously with a strip-chart recorder and periodically with a digital millivoltmeter. The second thermocouple was positioned in approximately

the same location in the furnace chamber as the controller thermocouple. Each controller was equipped with thermocouple break protection to turn off the power if the control thermocouple failed as well as an OTP circuit.

In testing capsules that contained radioactive compounds, the problem exists of determining the actual test specimen-compound interface temperature. This temperature can be substantially above the furnace temperature, depending on the design and heat output of the capsule. Use of a protective jacket serves to increase the temperature difference. Heat transfer calculations showed that the furnace control temperatures should be 762, 972, and 1077°C to give the desired average interface temperatures of 800°, 1000°, and 1100°C.

10.1.3 Evaluation of the Test Specimens

When a series of tests was completed, the capsules were cooled and removed from their protective jackets. Each capsule was examined for signs of external oxidation and then sectioned by using an abrasive saw while taking care not to damage the test specimen. The SrF₂ and test specimen were removed from the capsule and separated. In almost every case, some SrF₂ adhered to the test specimen and could not be removed completely without damage to the specimen surface. The problem was especially severe with the radioactive fluoride.

The nonradioactive test specimens were cut in half and one section subjected to metallographic examination. The radioactive specimens were placed on edge in mounting compound, ground to the midpoint, and subjected to metallographic examination. Some of the capsules were sectioned and their weld areas subjected to examination.

Attack of the nonradioactive test specimens was evaluated using optical microscopy, scanning electron microscopy and electron microprobe analysis. Microhardness measurements were obtained on some of the test specimens. Attack of the radioactive test specimens was evaluated primarily by optical microscopy.

Initially, it was hoped that additional data on fluoride-metal interaction could be obtained by chemical analyses of the SrF₂ and test specimens and by dimensional and weight changes of the test specimens, but these hopes proved to be unwarranted. Chemical analysis of the SrF₂ and metal specimens by various techniques provided little useful information. Any changes in composition observed were always less than the precision of the analytical procedures used. The use of X-ray diffraction to identify reaction products was also unsuccessful and was abandoned. Weight changes of the test specimens were of little value. Strontium fluoride adhering to the metal specimens made weight changes meaningless, and attempts to remove the fluoride without affecting the metal surface were unsuccessful. Dimensional measurements on the test specimens precluded the possibility of gross metal attack that might not be obvious from the metallographic examination but could not be used to get precise measurements of the attack.

10.1.4 Test Results

Examination of the test specimens showed that most of the material exposed to strontium fluoride suffered the two distinctly different types of attack described in Section 7.4:

a) chemical attack, and b) microstructural changes. Typical examples of chemical attack are shown in Figure 49, and typical examples of microstructural changes are shown in Figure 50. In presenting the experimental data, both types of attack are reported whenever they occur.

Metal attack by the SrF_2 was determined from photomicrographs of the test specimens and electron microprobe data, if available. It was difficult to obtain an exact measure of the attack from the photomicrographs, and the results presented in the following tables are estimates of the depth of metal affected. With most specimens, the attack was not uniform across the specimen surface. The photomicrographs and microprobe data were obtained from those areas of the specimens showing maximum attack, and, in every case, the data reported in the tables represent the maximum attack observed. Zero interaction was assumed when the specimen surface in contact with the fluoride was essentially unchanged from that of the control specimens

FIGURE 49. Typical Examples of Chemical Attack

FIGURE 50. Typical Examples of Changes in Specimen Microstructure

tested without fluoride present. Where very slight attack was found, an arbitrary value of $<25 \mu\text{m}$ was assigned, attack greater than $25 \mu\text{m}$ was reported in $25\text{-}\mu\text{m}$ increments.

Attack of the metal specimens exposed to the high-purity inert SrF_2 is summarized in Table 26. The data show that the refractory metals tungsten and TZM provide the greatest resistance to attack by the high-purity SrF_2 . There was no evidence of chemical attack of the tungsten and TZM and only slight indication of microstructural changes in 4400-h tests. Attack of the Ni- and Co-base alloys varied considerably with the Haynes Alloy 25 exhibiting the least attack. Surprisingly, the Haynes Alloy 188, which is also a Co-base alloy similar in composition to Haynes Alloy 25, showed considerably more attack than the latter alloy.

TABLE 26. Metal Attack Observed in Capsules Containing High-Purity Nonradioactive SrF_2

Material Tested	Test Temperature, °C	Depth of Metal Affected, μm			
		Chemical Attack		Change in Microstructure	
		1500 h	4400 h	1500 h	4400 h
Hastelloy C-276	800	25	50	25	25
	1000	100	175	25	50
	1100	150	200	0	50
Hastelloy X	800	25	<25	50	50
	1000	25	25	50	25
	1100	50	25	25	100
Hastelloy N	800	25	100	50	125
	1000	75	75	125	125
	1100	<25	25	125	150
Haynes Alloy 25	800	<<25	25	<25	<25
	1000	<<25	25	<25	25
	1100	<<25	25	25	50
Haynes Alloy 188	800	50	25	50	50
	1000	50	75	0	0
	1100	50	100	25	25
Inconel 600	800	0	<25	75	150
	1000	<25	<25	125	175
	1100	<25	25	0	100
Inconel 625	800	25	25	25	50
	1000	75	75	100	100
	1100	50	75	0	0
TZM	800	0	0	0	<25
	1000	0	0	0	<25
	1100	0	0	0	<25
Tungsten	800	0	0	0	<25
	1000	0	0	0	<25
	1100	0	0	0	<25

Except for the Hastelloy C-276, metal attack did not increase substantially with increasing exposure temperature. In the case of Hastelloy N, the chemical attack at 1100°C was less than at the lower temperatures. In several instances, microstructural changes were less at 1100°C than at the lower temperatures. These results are probably due to the fact that many of the normal precipitates found in the Ni- and Co-base alloys redissolve when the alloys are heated above 1000°C. Overall, metal attack did not increase appreciably with increasing exposure time. Microhardness measurements were obtained on all of the 1500-h and some of the 4400-h specimens, as well as the control specimens. The results showed a general softening of the Ni- and Co-base alloys with increasing exposure temperature. The effects of fluoride attack on hardness appeared to be quite complex and difficult to interpret. Overall, the microhardness measurements provided little meaningful data, and the hardness measurements were not made in the other series of compatibility tests.

Results obtained in the tests with high-purity $^{90}\text{SrF}_2$ are presented in Table 27. Overall, there was considerably more attack of the specimens exposed to the $^{90}\text{SrF}_2$ than the specimens exposed to the inert SrF_2 . In the case of the Ni- and Co-base alloys, microstructural changes occurred to much greater depths than was observed in the nonradioactive tests. In general, however, the results obtained with the high-purity $^{90}\text{SrF}_2$ confirm those obtained with the inert SrF_2 . Tungsten and TZM provided the greatest resistance to fluoride attack, and Haynes Alloy 25 was the best of the Ni- and Co-base alloys. Increasing the exposure temperature had little overall effect on metal attack, and a number of specimens exhibited less attack at 1100°C than at the lower temperatures. In general, metal attack did not increase appreciably with increasing exposure time, and a number of specimens tested for 4400 h exhibited less attack than the equivalent specimens tested for 1500 h.

TABLE 27. Metal Attack in Capsules Containing High-Purity $^{90}\text{SrF}_2$

Material Tested	Test Temperature, $^\circ\text{C}$	Depth of Metal Affected, μm			
		Chemical Attack		Change in Microstructure	
		1500 h	4400 h	1500 h	4400 h
Hastelloy C-276	800	100	50	150	150
	1000	50	100	125	375
	1100	100	150	300	150
Hastelloy X	800	25	50	125	125
	1000	50	100	250	375
	1100	125	100	500	550
Hastelloy N	800	100	50	250	200
	1000	150	200	400	400
	1100	50	(a)	125	(a)
Haynes Alloy 25	800	<25	<25	75	50
	1000	<25	25	75	75
	1100	25	50	100	75
Haynes Alloy 188	800	100	125	250	325
	1000	150	75	300	125
	1100	50	50	125	125
Inconel 600	800	25	75	100	200
	1000	50	(a)	150	(a)
	1100	50	50	100	100
Inconel 625	800	150	75	250	125
	1000	100	(a)	325	(a)
	1100	125	50	375	375
TZM	800	0	25	0	0
	1000	0	<25	0	0
	1100	<25	25	0	0
Tungsten	800	0	0	0	0
	1000	<25	<<25	0	0
	1100	<25	<25	0	0

(a) The test specimens were inadvertently destroyed before examination.

The results obtained with WESF-grade $^{90}\text{SrF}_2$ are presented in Table 28. In general, the results confirm those obtained with the high-purity fluorides. Although the WESF-grade $^{90}\text{SrF}_2$ contains substantially more impurities than the high-purity $^{90}\text{SrF}_2$, the overall metal attack was not appreciably greater. In the case of Hastelloy C-276, the specimens exposed to the WESF-grade $^{90}\text{SrF}_2$ exhibited less chemical attack than the specimens exposed to the high-purity fluorides. Again, tungsten and TZM exhibited the greatest resistance to attack, while Haynes Alloy 25 was the best of the Ni- and Co-base alloys. Overall, metal attack at 1100°C was not appreciably greater than at 1000°C , and the attack did not increase to any marked degree with exposure time.

The results obtained with the inert SrF_2 containing controlled levels of added impurities are presented in Table 29. In the 1500-h tests, a number of the test capsules were

TABLE 28. Metal Attack in Capsules Containing WESF-Grade $^{90}\text{SrF}_2$

Material Tested	Test Temperature, $^\circ\text{C}$	Depth of Metal Affected, μm			
		Chemical Attack		Change in Microstructure	
		1500 h	4400 h	1500 h	4400 h
Hastelloy C-276	800	50	50	75	75
	1000	50	75	125	200
	1100	75	75	125	150
Hastelloy X	800	25	75	100	100
	1000	25	25	150	100
	1100	75	75	150	250
Hastelloy N	800	100	150	175	150
	1000	175	225	500	300
	1100	150	(a)	200	(a)
Haynes Alloy 25	800	25	25	50	50
	1000	25	25	50	75
	1100	25	50	50	50
Haynes Alloy 188	800	25	50	50	100
	1000	75	100	175	250
	1100	25	50	200	125
Inconel 600	800	25	75	100	275
	1000	25	50	200	350
	1100	50	50	175	300
Inconel 625	800	25	100	100	200
	1000	50	125	500	450
	1100	100	125	450	350
TZM	800	<25	<25	0	0
	1000	<25	<25	25	0
	1100	<25	<25	0	0
Tungsten	800	0	0	0	0
	1000	0	<25	0	0
	1100	25	<25	0	0

(a) Test specimen inadvertently destroyed before examination.

TABLE 29. Metal Attack in Capsules Containing SrF₂-Impurity Mixtures at 1000°C

Material Tested	Impurity Added	Depth of Metal Affected, μm			
		Chemical Attack		Change in Microstructure	
		1500 h	4400 h	1500 h	4400 h
Hastelloy C-276	NaF	25(a)	25	---	75
	MnF ₂	50	25	75	100
	PbF ₂	50(a)	25	---	75
	CuF ₂	25	50	200	375
	FeF ₃	50	25	200	200
	AlF ₃	<25(a)	<25	---	100
	(Ca-Ba-Mg)F ₂	25	25	75	75
	SrO	300	250	300	250
	Sr(NO ₃) ₂	25(a)	25	---	250
	H ₂ O	100(a)	25	---	125
Hastelloy X	NaF	<25	<25	75	50
	MnF ₂	100(a)	25	---	125
	PbF ₂	25(a)	25	---	100
	CuF ₂	750(a)	100	---	300
	FeF ₃	25	75	300	550
	AlF ₃	<25	25	100	75
	(Ca-Ba-Mg)F ₂	<25(a)	25	---	100
	SrO	375(a)	200	---	250
	Sr(NO ₃) ₂	125(a)	25	---	100
	H ₂ O	25(a)	25	---	125
Hastelloy N	NaF	50	50	250	250
	MnF ₂	50	75	50	125
	PbF ₂	75	75	150	200
	CuF ₂	75(a)	100	---	500
	FeF ₃	150(a)	200	---	375
	AlF ₃	<25	25	75	250
	(Ca-Ba-Mg)F ₂	<25	25	75	100
	SrO	625	875	700	875
	Sr(NO ₃) ₂	50(a)	50	---	375
	H ₂ O	50	25	125	125
Haynes Alloy 25	NaF	<25	25	75	50
	MnF ₂	<25(a)	<25	---	75
	PbF ₂	<25	25	100	75
	CuF ₂	50(a)	25	---	450
	FeF ₃	50(a)	75	---	500
	AlF ₃	<25	<25	75	100
	(Ca-Ba-Mg)F ₂	<25	25	50	25
	SrO	125	175	0	75
	Sr(NO ₃) ₂	25(a)	50	---	0
	H ₂ O	25	25	0	0
Haynes Alloy 188	NaF	<25	25	0	75
	MnF ₂	<25(a)	25	---	125
	PbF ₂	25	50	125	100
	CuF ₂	25(a)	50	---	325
	FeF ₃	50(a)	25	---	175
	AlF ₃	<25	<25	<25	50
	(Ca-Ba-Mg)F ₂	<25	25	25	75
	SrO	300	500	0	250
	Sr(NO ₃) ₂	25(a)	<25	---	125
	H ₂ O	<25(a)	25	---	50

TABLE 29. (contd)

Material Tested	Impurity Added	Depth of Metal Affected, μm			
		Chemical Attack		Change in Microstructure	
		1500 h	4400 h	1500 h	4400 h
Inconel 600	NaF	25(a)	25	---	25
	MnF ₂	50	25	125	75
	PbF ₂	25	25	75	250
	CuF ₂	25	75	75	200
	FeF ₃	50(a)	100	---	200
	AlF ₃	25	25	0	25
	(Ca-Ba-Mg)F ₂	25	25	75	25
	SrO	500	250	0	0
	Sr(NO ₃) ₂	75(a)	25	---	300
	H ₂ O	25(a)	25	---	25
Inconel 625	NaF	25	25	100	300
	MnF ₂	25	50	200	250
	PbF ₂	25	25	150	150
	CuF ₂	150(a)	50	---	300
	FeF ₃	50(a)	100	---	325
	AlF ₃	25	25	150	150
	(Ca-Ba-Mg)F ₂	125(a)	25	---	250
	SrO	175(a)	250	---	450
	Sr(NO ₃) ₂	75(a)	25	---	250
	H ₂ O		50	---	125
TZM	NaF	<<25(a)	<<25	0	0
	MnF ₂	<<25(a)	<25	0	0
	PbF ₂	<25	<25	0	0
	CuF ₂	50(a)	150	50	150
	FeF ₃	50(a)	75	50	75
	AlF ₃	<<25	<25	0	0
	(Ca-Ba-Mg)F ₂	<<25	<<25	0	0
	SrO	<25	<25	0	0
	Sr(NO ₃) ₂	<<25(a)	<<25	0	0
	H ₂ O	<25	<<25	0	0
Tungsten	NaF	<<25	<25	0	0
	MnF ₂	<25(a)	<25	0	0
	PbF ₂	0(a)	<25	0	0
	CuF ₂	50	25	0	0
	FeF ₃	<<25	<25	0	0
	AlF ₃	0(a)	<25	0	0
	(Ca-Ba-Mg)F ₂	<<25	<25	0	0
	SrO	<25	<25	0	0
	Sr(NO ₃) ₂	0(a)	<25	0	0
	H ₂ O	<25(a)	0	0	0

(a) Indicates capsules accidentally overheated to 1200°C for about 4 h.
No meaningful estimate of microstructural changes possible because of overheating.

accidentally overheated to ~1200°C for about 4 h on the day the tests were to be terminated. Results obtained with the overheated capsules are indicated with an (a) in the table. The overheating produced marked changes in the microstructures of the Ni- and Co-base alloys, such as very large grain size and dissolution of precipitates, which made it impossible to evaluate the effect of strontium fluoride attack on the microstructure. Overheating the capsules for a

period of only 4 h at the end of a 1500-h tests would not be expected to increase the chemical attack of the tests specimens significantly. However, the overheating did make it difficult to estimate the degree of chemical attack of the Ni- and Co-base alloys because of the marked changes in the microstructure of the specimens. The values given in Table 29 for chemical attack of the overheated specimens are, at best, rough approximations of the depth of metal affected.

On an overall basis, the addition of impurities to high-purity inert SrF_2 increased metal attack, with microstructural changes in the Ni- and Co-base alloys especially sensitive to the presence of impurities in the SrF_2 . On an individual basis, SrO , CuF_2 and FeF_3 produced the most marked increase in metal attack. The addition of SrO to the fluoride resulted in a large increase in chemical attack of all the Ni- and Co-base alloys, while the addition of CuF_2 and FeF_3 resulted in substantial increases in the depth of metal exhibiting microstructural changes. The presence of CuF_2 or FeF_3 also increased the chemical attack of TZM several fold and tungsten to a lesser degree. The presence of nitrate ion or water in the fluoride had surprisingly small effect on metal attack. This may have been because both nitrate and water were added to the fluoride in relatively small concentrations.

On an overall basis, tungsten provided the greatest resistance to attack by the fluoride-impurity mixtures. TZM was almost as good, except when copper or iron was present in the fluoride. Of the Ni- and Co-base alloys, it was difficult to select one as providing the best overall resistance to the fluoride-impurity mixtures. Haynes Alloy 25 and Hastelloy C-276 probably provided the best overall resistance to chemical attack, but they suffered as badly as the other Ni- and Co-base alloys from changes in microstructure.

The weld areas of a number of test capsules were examined to see if attack of the weld metal had occurred. In the couple design used, there is no direct contact between the weld metal and the compacted strontium fluoride. It was possible, however, for strontium fluoride particles to penetrate the space between the capsule wall and lid and approach the weld zone. In addition, the possibility of gas-metal reactions exists that could lead to attack of the weld metal, while temperature gradients could lead to diffusion of reactants to the weld area.

In general, metal attack in the weld areas was found to be much less than that observed with the test specimens. There was very limited attack of the weld metal in the tests with high-purity SrF_2 . The only case where extensive attack of the weld metal was apparent was in the capsules containing CuF_2 or FeF_3 as impurities in the SrF_2 . The Ni- and Co-base alloy capsules containing the SrF_2 - SrO mixture showed little evidence of weld metal attack. This is surprising, considering the extensive attack of the test specimens exposed to the SrF_2 - SrO mixture. The results indicate that there was little movement or diffusion of the SrO in the test capsules, whereas considerable diffusion of the CuF_2 or FeF_3 must have occurred. Overall, attack of the weld metal in the various test capsules was much less than that observed with the metal specimens.

10.1.5 Discussion

The results presented in the previous section show the extent of metal attack that occurred in the various tests. The data provide no indication of the attack mechanisms involved. Using EM analysis, SEM, and micrographs of the test specimens, an attempt was made to identify the attack mechanisms involved. The systems involved are quite complex, however, and with the limited data available, it is difficult to define the reactions occurring in the various systems in more than qualitative terms. Discussions of each of the individual metal-SrF₂ systems are provided in Fullam (1975). As will be shown in Section 10.1.6, TZM, Haynes Alloy 25, and Hastelloy C-276 were the three materials selected for long-term testing. Discussions of these three materials are presented in the following sections.

10.1.5.1 TZM-SrF₂ System

The TZM test specimens were fabricated from wrought bar that had been stress-relieved at 2300°F for 3/4 h. Photomicrographs of the "as-received" material showed a highly elongated grain structure typical of wrought materials (Figure 51). Exposure to temperatures up to 1100°C for periods up to 4400 h produced no significant change in the microstructure (Figure 51). No grain growth was apparent in any of the specimens except possibly a slight amount in specimens heated for 4400 h at 1100°C.

Resistance of the TZM to fluoride attack approached that of tungsten. Very little reaction was observed with specimens exposed to the high-purity inert SrF₂. Electron microprobe data indicated a slight increase in titanium concentration at the surface of the specimens tested for 4400 h. Specimen exposed to high-purity ⁹⁰SrF₂ and WESF-grade ⁹⁰SrF₂ suffered slight chemical attack, but there was little indication of microstructural changes (see Figure 52). In most cases, the reaction involved a general dissolution of the molybdenum with some pitting and grain boundary attack.

In the tests with the SrF₂-impurity mixtures, only slight metal attack was observed, except for the mixtures containing CuF₂ and FeF₃. In the latter cases, the attack was several times greater than was observed in the other TZM tests (Figure 53). When CuF₂ or FeF₃ was present in the SrF₂, there was extensive chemical attack of the TZM with heavy pitting, grain boundary attack, and subsurface void formation. From the micrographs, it appears that some recrystallization of molybdenum has occurred at the surface of the specimens. Electron microprobe data showed extensive diffusion of iron or copper into the alloy matrix and along the grain boundaries. The data indicate that the copper and iron fluorides were reduced to the free metals at the specimen surface. The metals then diffused into the alloy. The presence of the impurity could account for the apparent recrystallization of the molybdenum at the surface. Much less attack was observed in the couples containing the other fluoride-impurity mixtures. Where attack did occur, it normally involved pitting and grain boundary attack.

10.1.5.2 Haynes Alloy 25-SrF₂ System

The Haynes Alloy 25 test specimens were fabricated from bar stock that had been solution heat-treated (per ASM 5759D). Microstructure of the "as-received" material was typical of the

FIGURE 51. Effect of Temperature on the Microstructure of TZM

solution heat-treated alloy showing scattered carbides not taken into solution and annealing twins in the grains (Figure 54a). Aging of the alloy at 800°C for up to 4400 h produced continuous precipitates along the grain boundaries, localized precipitates on twin boundaries and heavy bulk precipitation (Figure 54b). From EM data and the photomicrographs, the precipitates appear to consist primarily of M_6C carbide phase (W, Cr, Co) and Laves phase $[(Co)_2(W, Cr)]$ with some $M_{23}C_6$ carbide phase. The microprobe data also indicated the presence of a significant quantity of molybdenum (up to 1.8%) in the carbide and Laves phase; molybdenum is not reported as a constituent of the alloy by the manufacturer. Aging at 1000°C produced M_6C and some $M_{23}C_6$ carbides in the grain boundaries, along twin boundaries and in the grain

FIGURE 52. TZM Specimens Exposed to $^{90}\text{SrF}_2$

matrices; the Laves phase is more abundant (Figure 54c). Aging at 1100°C resulted in the disappearance of the twins and dissolution of most of the carbide phases, but the Laves phase remained (Figure 54d).

FIGURE 53. TBM Specimens Exposed to SrF_2 -Impurity Mixtures at 1000°C

Aging of Haynes Alloy 25 at 650 to 900°C results in a sharp loss in Charpy impact energy and ductility (Ferry 1969; McCoy and Bourgette 1973). Typically, the Charpy impact energy at 25°C decreases from 70 ft-lb to less than 10 ft-lb when the alloy is aged at 800°C for 100 h. The loss of impact energy and ductility is reported to be due to the presence of the Laves and carbide phases.

Haynes Alloy 25 showed the greatest overall resistance to fluoride attack of any of the Ni- and Co-base alloys tested but was considerably less resistant than tungsten or TBM. Only slight attack of the alloy was found in the tests with high-purity nonradioactive SrF_2 . The level of attack did not increase significantly with increasing exposure temperature. Chemical attack did not exceed $25\text{ }\mu\text{m}$ and consisted of pitting and grain boundary attack, with limited subsurface void formation in the specimens tested at 1100°C (Figure 55). There was no

FIGURE 54. The Effect of Temperature on the Microstructure of Haynes Alloy 25

indication of strontium diffusion into the grain boundaries or matrices, but some strontium was found in the voids. High-magnification photomicrographs (3000X) revealed very fine porosity to a depth of 25 μm in the 1100°C specimens, which was not present in specimens tested at lower temperatures. Electron microprobe data indicated a depletion of Laves phase to a depth of up to 50 μm in all specimens exposed to the high-purity nonradioactive SrF_2 . This depletion is not readily apparent in the photomicrographs.

Tests with WESF-grade and high-purity $^{90}\text{SrF}_2$ produced significantly more attack of the Haynes Alloy 25 than the nonradioactive SrF_2 . Chemical attack increased only slightly, but there was a marked increase in the depth of metal affected by changes in microstructure. Photomicrographs of Haynes Alloy 25 specimens exposed to $^{90}\text{SrF}_2$ are shown in Figure 56. Specimens exposed to the radioactive fluoride exhibited a general dissolution of the metal surface

FIGURE 55. Haynes Alloy 25 Specimens Exposed to High-Purity Nonradioactive SrF_2

with some grain boundary attack and pitting. Chemical attack appeared to increase slightly with increasing exposure temperature. The depth of metal affected by microstructural changes did not appear to increase to any marked degree with increasing temperature. Most of the specimens exposed to $^{90}\text{SrF}_2$ exhibited a thin surface layer where normal alloy precipitates were largely depleted. The affected layers also contained large discrete spheroidal precipitates which were not found in the body of the test specimens or in the reference specimens. The nature of the spheroidal precipitates was not determined.

The tests with SrF_2 -impurity mixtures showed that only two of the impurities increased the chemical attack of the Haynes Alloy 25 significantly, but most of them produced changes in the alloy microstructure. The addition of SrO to the SrF_2 greatly increased the chemical attack with the test specimen, exhibiting grain boundary attack and subsurface void formation to a depth of 100 to 200 μm (Figure 57a). Microprobe data showed diffusion of strontium along

FIGURE 56. Haynes Alloy 25 Specimens Exposed to $^{90}\text{SrF}_2$

the grain boundaries and a high concentration of strontium along the edges of the subsurface voids. The data indicate that the attack is probably due to reactions between the SrO and precipitates in the grain boundaries. The addition of FeF_3 to SrF_2 also increased the chemical attack (Figure 57b) but less so than the SrO . Specimens exposed to $\text{SrF}_2\text{-FeF}_3$ exhibited a

FIGURE 57. Haynes Alloy 25 Specimens Exposed to SrF_2 -Impurity Mixtures at 1000°C

general dissolution of the metal surface with grain boundary attack and subsurface void formation. Microprobe data showed iron diffusion into the alloy (Figure 58) and a decrease in the cobalt and chromium concentrations at the surface of the specimen (Figure 58). None of the other impurities added to the SrF_2 increased the chemical attack to any degree except possibly the nitrate ion. Four capsules were tested with the SrF_2 - $\text{Sr}(\text{NO}_3)_2$ mixture at 1000°C , and only one showed increased chemical attack compared to the SrF_2 without nitrate present.

The addition of impurities to the high-purity nonradioactive SrF_2 generally resulted in the formation of precipitates not normally found in Haynes Alloy 25. Copper and iron were especially bad in this regard, and abnormal precipitates were observed to depths of 400 to

FIGURE 58. Microstructure of Haynes Alloy 25 Exposed to $\text{SrF}_2\text{-FeF}_3$ at 1000°C and Electron Microprobe Scans of the Affected Areas

500 μm in specimens exposed to SrF_2 containing FeF_3 or CuF_2 for 4400 h at 1000°C (Figure 57b and c). The dark areas that appear to be voids are actually precipitates. In the case of specimens exposed to FeF_3 , EM data showed these precipitates to be composed primarily of chromium and manganese (Figure 58), while the precipitates in the specimens exposed to $\text{CuF}_2\text{-SrF}_2$ were high in chromium and tungsten. The microprobe data also showed copper had diffused into the grain boundaries and matrix of the alloy as had the iron.

Specimens exposed to the other impurity-fluoride mixtures also exhibited abnormal precipitates (for example, Figure 57d shows a test specimen exposed to $\text{SrF}_2\text{-PbF}_2$). However, there was no indication of diffusion of the cation associated with the impurity fluoride into any of

the test specimens, except those exposed to CuF_2 and FeF_3 . Microprobe data indicated no abnormalities in the composition of the Haynes Alloy 25, and the composition of the abnormal precipitates could not be identified.

The theoretical analysis of the Haynes Alloy 25- $^{90}\text{SrF}_2$ system predicted that the alloy should be resistant to attack by pure SrF_2 , but that the alloy should react with some impurities in the $^{90}\text{SrF}_2$ such as CuF_2 and FeF_3 . The experimental results tended to confirm these predictions, although the calculation would lead one to expect more attack of the alloy by the WESF-grade $^{90}\text{SrF}_2$ than was actually observed. The results do show that the presence of less stable fluorides, such as CuF_2 and FeF_3 , in the SrF_2 does increase attack of the alloy as predicted.

In addition to providing considerable resistance to attack by strontium fluoride, Haynes Alloy 25 possesses certain other features, such as good oxidation resistance and good sea-water corrosion resistance, which make it a desirable containment material for the fluoride. However, the potential usefulness of Haynes Alloy 25 as a containment material for $^{90}\text{SrF}_2$ is reduced by the aging reactions that occur when the alloy is heated to temperatures in the range of 650 to 900°C, which sharply reduce its Charpy impact energy and ductility.

10.1.5.3 Hastelloy C-276-SrF₂

The Hastelloy C-276 test specimens were fabricated from wrought bar stock that had been solution heat-treated at 2100°F and rapidly quenched. The microstructure of the "as-received" alloy is shown in Figure 59. There is very little indication of precipitated second phases, with annealing twins being the predominant feature. Grain size is relatively large. Thermal aging at 800°C produced continuous grain boundary precipitation and heavy bulk precipitation (Figure 59b). The precipitates appear to be predominantly carbide phase with possibly some Ni_7Mo_6 -type phase present. Microprobe data show the precipitates to be enriched in molybdenum, tungsten, and chromium with the molybdenum concentration of the matrix sharply reduced from the nominal concentrations (8 to 10% versus a nominal 16%). Aging at 1000°C resulted in less precipitate formation, and the composition of the precipitates was more indicative of a M_6C -type carbide and Ni_7Mo_6 phase (Figure 59c). Again, the precipitates were enriched in molybdenum, and the concentration of molybdenum in the matrix was reduced to 8 to 10%. When the alloy was aged at 1100°C for 1500 h, it was found that very little precipitate formation occurred (Figure 59d). Aging for 4400 h, however, resulted in significant precipitate formation but less than occurred at 1000°C (Figure 59e). The precipitates appear to be predominantly Ni_7Mo_6 phase with some M_6C -type carbide phase.

Exposure of Hastelloy C-276 to high-purity nonradioactive SrF_2 resulted in extensive metal attack that increased sharply with increased exposure temperature (Figure 60). Grain boundary attack and subsurface void formation were the predominant forms of attack at all temperatures. Changes in microstructure were less extensive, although some abnormal precipitates were present in the various specimens tested. These precipitates were high in chromium and nickel. Electron microprobe data showed extensive diffusion of strontium along the affected grain boundaries, and a very thin surface layer where strontium appeared to have diffused into

FIGURE 59. Effect of Thermal Aging on the Microstructure of Hastelloy C-276

the alloy matrix. The mechanism of the grain boundary attack was not identified but may have involved reaction of SrF_2 with carbides in the grain boundaries.

Hastelloy C-276 exposed to WESF-grade or high-purity $^{90}\text{SrF}_2$ exhibited less chemical attack than the specimens exposed to high-purity nonradioactive SrF_2 . However, microstructural changes occurred to much greater depths. Overall, less chemical attack was observed in the WESF-grade $^{90}\text{SrF}_2$ couples than in the couples containing high-purity $^{90}\text{SrF}_2$. Specimens exposed to the radioactive strontium fluoride suffered general surface dissolution with some grain boundary attack and subsurface void formation (Figure 61). Grain boundary attack was far less than that found in the nonradioactive couples, especially at the higher temperatures. Abnormal precipitates were found in all specimens but were more extensive at the higher temperatures. The nature of the precipitates was not determined. The effect of temperatures on metal attack was much less pronounced with the radioactive fluoride than with the nonradioactive SrF_2 .

FIGURE 60. Hastelloy C-276 Specimens Exposed to High-Purity Nonradioactive SrF_2

With one exception, the addition of impurities to the high-purity nonradioactive SrF_2 reduced the chemical attack of the Hastelloy C-276. The grain boundary attack and void formation that was so extensive in specimens exposed to high-purity nonradioactive SrF_2 were far less prevalent in the specimens exposed to the SrF_2 -impurity mixtures, except when SrO was present. However, the addition of impurities did serve to increase the depth of metal affected by microstructural changes. Typical examples of Hastelloy C-276 specimens exposed to SrF_2 -impurity mixtures are shown in Figure 62. In several of the photomicrographs, what appear to be voids are actually precipitates. These precipitates were not fully identified, but in almost every case they were high in chromium and nickel. Microprobe data indicated that there was little diffusion of Sr into the specimens, except for the specimens exposed to SrO . There was no evidence of diffusion of cation impurities into the Hastelloy C-276 except when iron

FIGURE 61. Hastelloy C-276 Specimens Exposed to $^{90}\text{SrF}_2$

or copper was present in the fluoride. When copper or iron was present, there was significant diffusion into the alloy matrix but not along grain boundaries. Strontium oxide was extremely corrosive to the alloy, and grain boundary attack and void formation occurred to a depth of up to 300 μm . Microprobe data indicated extensive diffusion of strontium along the grain boundaries.

10.1.6 Conclusions

Sufficient data were obtained in the initial scouting tests to accomplish the test objectives. Based on the overall results obtained, three materials were identified as the prime candidates for long-term testing. They are TZM, Haynes Alloy 25, and Hastelloy C-276. Selection of the three materials was based on the following considerations:

FIGURE 62. Hastelloy C-276 Specimens Exposed to SrF_2 -Impurity Mixtures at 1000°C for 4400 h

- Of all the containment materials evaluated, tungsten was the most compatible with the various grades of strontium fluoride at 800 to 1100°C . Chemical attack of the tungsten was very slight. The only tungsten specimens exhibiting significant chemical attack were those exposed to SrF_2 containing CuF_2 as an impurity. Exposure to the fluoride had almost no effect on the microstructure of the tungsten. Other properties of tungsten, such as its poor oxidation resistance and difficulties in fabrication and welding, reduce its usefulness as a container material for $^{90}\text{SrF}_2$. Because of its many limitations, tungsten is not considered to be a practical material to use in the WESF to contain the $^{90}\text{SrF}_2$, and it was not selected as one of the materials to be evaluated in the long-term compatibility tests. However, tungsten should be considered as a potential container material for $^{90}\text{SrF}_2$ in special applications.

- TZM is almost as resistant to attack by strontium fluoride as tungsten. Chemical attack of the TZM specimens was minimal except when exposed to strontium fluoride containing CuF_2 or FeF_3 . No significant effect on the microstructure was observed except in the specimens exposed to SrF_2 containing CuF_2 or FeF_3 . TZM suffers some of the same disadvantages as tungsten, such as poor oxidation resistance. However, TZM is more easily fabricated and welded than tungsten and can probably be adapted for use in the WESF process to contain the $^{90}\text{SrF}_2$. This would involve using TZM for the inner capsule and a different material that is oxidation resistant for the outer capsule. Because the TZM is compatible with $^{90}\text{SrF}_2$ and because it can probably be used in the WESF process, it was selected as one of the materials to be evaluated in the long-term tests.
- Of seven Ni- and Co-base alloys tested, Haynes Alloy 25 was the most resistant to fluoride attack. On an overall basis, both chemical attack and changes in microstructure were much less with the Haynes Alloy 25 specimens than with the other Ni- and Co-base alloys. However, the Haynes Alloy 25 specimens suffered considerably more attack than the tungsten and TZM specimens. Haynes Alloy 25 suffers a serious loss of toughness and ductility when thermally aged at 650 and 900°C, which reduces its usefulness as a container material for $^{90}\text{SrF}_2$ in heat-source applications. However, the alloy can be considered for use when the $^{90}\text{SrF}_2$ is doubly encapsulated. The Haynes Alloy 25 can be used for the inner capsule to provide $^{90}\text{SrF}_2$ compatibility, and a different material can be used for the outer capsule to provide the needed structural strength. In addition, the alloy can be used in the WESF production operation with a minimum of development effort. Based on the above consideration, Haynes Alloy 25 was selected as one of the materials to be evaluated in the long-term compatibility tests.
- The other six Ni- and Co-base alloys were less resistant to fluoride attack than the Haynes Alloy 25. Ranking the six in order of their resistance to fluoride attack is difficult because the ranking would vary depending on the grade of strontium fluoride being considered. Overall, the Hastelloy C-276, Inconel 600, and Hastelloy X appear to be about equal in their resistance to fluoride attack, while the other three alloys, Haynes Alloy 188, Inconel 625, and Hastelloy N, are substantially less resistant to attack. Because Hastelloy C-276 possesses many attractive properties, such as good oxidation resistance and excellent sea-water corrosion resistance, and since it is currently being used as the inner capsule at WESF to contain the $^{90}\text{SrF}_2$, it was selected as the third containment material to be evaluated in the long-term compatibility tests. Inconel 600 and Hastelloy X also possess certain desirable properties and should be considered as possible alternatives to Hastelloy C-276.

Overall, the experimental results show that the impurities that are normally present in the WESF $^{90}\text{SrF}_2$ in high concentration, i.e., Na, Ca, Ba, have relatively little effect on the compatibility of the strontium fluoride with the containment materials at 800 to 1100°C. The

results also show that certain impurities can have a serious adverse effect on strontium fluoride compatibility. Strontium oxide for example, when present in the SrF_2 , produces extensive chemical attack of the Ni- and Co-base alloys. Fluorides of the multivalent cations, such as Cu and Fe, generally cause increased chemical attack of the containment materials tested. They also produce substantial microstructural changes in the Ni- and Co-base alloys. Water and nitrate ion had a surprisingly small effect on compatibility, possibly because they were present in low concentrations. Fortunately, the impurities that were shown to have an adverse effect on compatibility are normally present in the WESF $^{90}\text{SrF}_2$ in low concentrations. It does not appear likely that additional purification steps will be needed in the WESF process to improve the quality of the $^{90}\text{SrF}_2$ product. However, close control of the purification steps and other process operations will be needed to ensure that the harmful impurities are reduced to the lowest practical levels. Corrosion of process equipment, especially during the $^{90}\text{SrF}_2$ firing operation, could result in iron, chromium, and nickel contamination of the $^{90}\text{SrF}_2$, and this could present a problem.

10.2 SUPPLEMENTAL SCREENING TESTS

The scouting tests discussed in the previous section evaluated potential containment materials that could be used in the WESF operation. The supplemental screening tests were carried out to evaluate materials not considered in the scouting tests. The primary objective of the screening tests was to evaluate a large number of materials in a cursory manner and to determine their relative resistances to attack by strontium fluoride. It was not intended that the tests provide sufficient compatibility data to allow the licensing of $^{90}\text{SrF}_2$ sources using any of the materials tested.

The supplemental screening tests were carried out at 800°C using inert strontium fluoride containing impurities similar to those found in WESF $^{90}\text{SrF}_2$. The tests lasted 1500 and 4400 h. A total of 33 materials, including two grades of ductile cast iron, were evaluated. Hastelloy C-276, Haynes Alloy 25, and TZM were included in the tests to serve as reference materials and to permit comparison of the results obtained in the screening tests with results obtained in the other compatibility studies.

10.2.1 Materials

The strontium fluoride used in the screening tests was similar in composition to the inert SrF_2 used in the long-term compatibility tests. The SrF_2 was prepared by a modified version of the WESF flowsheet using reagent grade chemicals, and the product contained impurities approximating those found in WESF-produced $^{90}\text{SrF}_2$. The SrF_2 was analyzed by several techniques, including spark-source mass spectroscopy, emission spectroscopy, flame photometry, and atomic absorption. The composition of SrF_2 is given in Table 30.

The containment materials evaluated in the screening tests are shown in Table 31. In general, the materials can be divided into three basic groups: precious metals, refractory metals, and base metals and alloys. Selection of a material for testing was based only on its

TABLE 30. Composition of the Nonradioactive SrF_2 Used in the Supplemental Screening Tests

Component	Wt%	Component	Wt%
Sr	66.0	Mg	0.3
F	29.5	Na	2.5
Al	0.3	Nd ^(a)	1.0
Ba	0.7	Ni	0.02
Ca	0.2	Pb	0.06
Cd	0.02	Si	0.02
Cr	0.05	H ₂ O	<0.01
Fe	0.02	NO ₃ ⁻	<0.01
K	0.01	O	<0.01

(a) Nd used as representative of the rare earths found in WESF $^{90}\text{SrF}_2$.

TABLE 31. Containment Materials Evaluated in the Supplemental Screening Tests

1. Hastelloy Alloy C-276	17. Ductile Cast Iron ^(a)
2. Haynes Alloy 25	18. 316L Stainless Steel
3. TZM	19. JS-777 [®]
4. Hastelloy Alloy C-4	20. Molybdenum
5. Hastelloy Alloy S	21. Niobium
6. Hastelloy Alloy B	22. Hafnialloy 2525
7. Hastelloy Alloy B-2	23. Ta-10% W
8. Inconel 617	24. Mo-50% Re
9. Inconel 671	25. W-26% Re
10. Incoloy 800 [®]	26. Rhenium
11. Haynes Alloy 556	27. Iridium
12. René 41 [®]	28. Ir-0.3% W
13. Udimet 700 [®]	29. Platinum
14. Monel 400 [®]	30. Gold
15. Nickel 200	31. Titanium
16. Ingot Iron	32. Copper

(a) Two grades of ductile cast iron were tested--one grade had a pearlite matrix and the other a ferrite matrix.

® Huntington Alloys, Huntington, West Virginia.

® General Electric, Detroit, Michigan.

® Kelsey Hayes, Utica, New York.

® Huntington Alloys, Huntington, West Virginia.

® Jessop Steel Company, Washington, Pennsylvania.

potential compatibility with SrF_2 , and other factors such as cost, availability, fabricability, mechanical properties, etc., were ignored in the selection. All of the materials tested are commercially available except for the Hafn alloy 2525 and Ir-0.3% W alloy, which are development alloys. The Ir-0.3% W alloy was obtained from the ORNL, which is developing iridium alloys for $^{238}\text{PuO}_2$ containment. The Hafn alloy 2525 was supplied by TWR, Inc. The compositions of the different materials are given in Tables 32 to 34. The compositions given are based on certificates of analysis supplied by the vendor, except for five materials: Ir-0.3% W, Hafn alloy 2525, copper 110, and the two ductile cast irons. In the latter cases, the compositions given are the nominal compositions of the materials. The materials were evaluated in the condition in which they were received from the vendor. No thermal conditioning was attempted to modify the materials in any way.

10.2.2 Capsule Fabrication

Three different compatibility capsule designs were used in the screening tests as shown in Figure 63. The different designs were necessary because of the different forms in which the containment materials were available. Figure 63a is the preferred design because the SrF_2 only contacts the material being tested. When the material was only available as sheet or foil (Ir, Ir-0.3% W, Pt, Re, Au), the design shown in Figure 63b was used. Use of the capsule liner prevented direct contact of the SrF_2 with the Inconel 600 capsule but did not preclude reaction of the fluoride with the capsule material. The composite design shown in Figure 63c is a poor choice for compatibility testing of different materials because of possible interactions between the materials. It had to be used in some of the screening tests because of cost and material availability. When the composite design was used, Hastelloy C-276, Haynes Alloy 25, and TZM specimens were always included in the capsule to serve as control specimens. The dimensions of the three capsules were such that the exposed metal surface-to- SrF_2 volume (S/V) ratio was approximately the same for all three designs.

The precious metals tested were generally in the form of thin foils and test specimens cut from the foil were tested without further treatment. Other specimens cut from plate or barstock were polished to a metallographic finish on the major flat faces using 0.3- μm alumina for the final polish. The test specimens and capsules were thoroughly cleaned with trichloroethylene and acetone and air dried prior to final capsule assembly.

The test capsules were assembled in air. The SrF_2 was compacted into the capsule by cold step-pressing. A compaction pressure of 8 to 10 TSI gave a fluoride density of 70 to 75% of theoretical density. When the capsule was filled with SrF_2 , the lid was pressed into place, and the capsule sealed by TIG welding. The capsule was then leak-checked to insure weld integrity.

10.2.3 Capsule Testing and Evaluation

The test capsules were sealed in protective jackets of Inconel 600 to prevent oxidation during testing. The tests were carried out in air-atmosphere muffle furnaces at 800°C for 1500 and 4400 h. Each furnace was equipped with a solid-state proportioning controller and calibrated Platel II thermocouple that could maintain the temperature within $\pm 2^\circ\text{C}$ of the

TABLE 32. Composition of the Base Metals and Alloys Evaluated in the Supplemental Screening Tests

Element	Concentration, wt%																		Ductile Cast Iron(a)	Ductile Cast Iron(b)
	Hastelloy C-276	Hastelloy C-4	Hastelloy S	Hastelloy B	Hastelloy B-2	Haynes Alloy 25	Haynes Alloy 556	Inconel 617	Inconel 671	Incoloy 800	Rene 41	Udimet 700	Monel 400	Nickel 200	Ingot Iron	316L SS	JS 777	Copper 110		
Al			0.16				0.21	0.09		0.22	1.46	4.51								
B			0.005								<0.004	0.03								
C	<0.002	<0.002	0.007	0.04	0.009	0.08	0.11	0.06	0.05	0.007	0.06	0.05	0.10	0.07	0.016	0.026	0.03		3.90	3.90
Ce															0.003					
Co	2.33	0.13	0.58	1.4	0.95	Bal	20.4	12.2			10.8	18.6								
Cr	15.1	15.8	15.9	0.94	0.88	19.9	21.7	22.3	47.3	21.9	19.3	15.3				17.34	20.8			
Cu			0.07								0.53	<0.10	30.9	0.03	0.38	0.18	1.64	99.90 min		
Fe	6.14	0.50	1.94	5.4	1.6	2.06	Bal		0.27	Bal		0.31	1.46	0.05		Bal	Bal	(0.04 O ₂)		
La			0.02																	
Mg																			0.05	0.07
Mn	0.56	0.10	0.65	0.64	0.46	1.30	1.3		0.03	0.87		<0.10	0.82	0.16	0.04	1.78	1.60		0.67	0.59
Mo	15.9	15.8	14.7	28.8	27.5		3.0	9.4			9.65	4.95			0.04	2.15	4.30			
Nb							0.06										0.26			
Ni	Bal	Bal	Bal	Bal	Bal	10.5	19.8	Bal	51.8	33.8	Bal	Bal	Bal	99.5		13.38	25.4			
P	0.025	0.016	<0.005	0.02	0.03	0.017									0.008	0.021	<0.008		<0.005	<0.005
S	0.005	0.008	<0.005	0.02	0.02	0.006			0.005	0.004		0.006	0.004	0.005	0.026	0.012	0.006		0.032	0.024
Si	0.04	0.02	0.31	0.42	<0.1	0.29	0.32	<0.1	0.24	0.63		<0.10	0.14	0.06	<0.01	0.012	0.42		2.25	1.55
Ta							0.8													
Ti		0.19							0.35	0.09	3.24	3.47								(0.95 Ca)
V	0.21			0.31																
W	3.26		0.22			14.6														
Zr																				

(a) Grade 60-45-12--pearlite matrix

(b) Grade 60-45-12--ferrite matrix

TABLE 33. Composition of Transition Metals and Refractory Metals Evaluated in the Supplemental Screening Tests

Element	Concentration, (a) wt%							
	Titanium	Molybdenum	TZM	Niobium	Hafnialloy 2525	Ta-10% W	Mo-50% Re	W-26% Re
C	0.04	<0.02	0.018	<0.005		0.0026		
Fe	0.22	0.007	0.003	0.005		<0.001	0.006	0.0021
H ₂	<0.01	<0.001	<0.0001	<0.001				
Hf					Ba1			
Mo		Ba1				<0.001	Ba1	<0.005
N ₂	0.03	0.001	0.0001	0.004		0.0016		
Nb				Ba1		<0.00025		
Ni		0.003	<0.001				0.001	
Pd					0.27			
Pt					0.24			
O ₂		0.001	0.0007	0.018		0.0026		
Re							46.9	Ba1
Si		0.004	0.001	0.002			0.001	
Ta				0.092		Ba1		
Ti	Ba1		0.53	0.003				
W						9.8		73.8
Zr			0.099	0.026				

(a) Trace elements not listed are <100 ppm.

set point. The furnace temperature was continuously monitored with a second calibrated Platine1 II thermocouple and a strip-chart recorder. Both the temperature controller and recorder were equipped with OTP circuits to turn off power to the furnace if the temperature exceeded ~820°C.

When the tests were completed, the capsules were sectioned with an abrasive saw. The test specimens were separated from the bulk of the SrF₂. Some SrF₂ always adhered to the specimens and could not be removed without damage to the specimen surface. This made weight and dimensional measurements on the specimens of little value in evaluating SrF₂ attack.

The test specimens were sectioned, and a sample from each specimen was subjected to metallographic examination. Attack of the test specimens by the SrF₂ was determined from the photomicrographs obtained. A few of the specimens were also subjected to EM analysis.

10.2.4 Results and Discussion

Most of the materials exposed to SrF₂ at 800°C suffered both chemical attack and microstructural changes. The extent of the attack was estimated from photomicrographs of the test specimens, and the results obtained with the various materials are presented in Table 35. In

TABLE 34. Composition of Precious Metals Used in the Supplemental Screening Tests

Element	Rhenium ^(a)	Iridium	Ir-0.3% W	Platinum	Gold
Au					99.99 min
C					<0.003
Fe	0.005	<0.001	0.002		
H ₂				<0.002	
Ir		99.9	Bal		
Mo	<0.005		0.001		
N ₂		<0.003			<0.001
O ₂		<0.002			<0.002
Pt				99.99 min	
Re	Bal				
Rh			0.002		
Ru			0.004		
S		0.001	0.002		
Si	<0.0001	0.004	0.001		
Ta		0.002			
Th			0.003		
W		0.080	0.30		

(a) Member of the manganese subgroup but listed in this table for convenience.

most cases, attack was not uniform across the specimen surface, and the values given in the table represent the maximum attack observed with a given specimen.

In the case of the Hastelloy C-276, Haynes Alloy 25, TZM, and Ir-0.3% W alloy, multiple samples of each material were tested for each time period using each of the three capsule designs shown in Figure 63. Table 36 shows the results obtained. While there are differences in the level of attack exhibited by individual specimens of a given material, the differences cannot be attributed to the capsule design. The results indicate that potential reactions between dissimilar metals in a composite capsule (Figure 63c) probably have minimal effect on the compatibility of the individual metals in the capsule with SrF₂ at 800°C. Therefore, the data presented in Table 35 should provide a good indication of the relative resistances of the different materials to attack by SrF₂ at 800°C that contains impurities similar to those found in WESF ⁹⁰SrF₂, even though the data were obtained using three different capsule designs.

A detailed discussion of the interaction of the SrF₂ with the individual containment materials, including photomicrographs of the test specimens, is included in Fullam (1977b). Micrographs of several of the test specimens are shown here to indicate the types of attack observed with the different materials. Hastelloy C-276 was tested as a reference material, and Figure 64 shows micrographs of the test specimens. Attack of the Hastelloy C-276

FIGURE 63. Capsule Designs Used in the Supplemental Screening Tests

specimens by the SrF_2 was similar to that observed in other tests with $^{90}\text{SrF}_2$ at 800°C . Chemical attack was fairly uniform across the specimen surface, and a reaction layer formed at the surface. The attack consisted primarily of leaching of alloy components and grain boundary attack with some subsurface void formation. The reaction layer contained grains of unreacted metal. Microprobe analysis of the specimens indicated that two reaction mechanisms were probably involved in the chemical attack: selective leaching of chromium, molybdenum and iron from the alloy matrix; and reaction of impurities in the SrF_2 , probably iron and chromium fluorides, with grain boundary precipitates. Microstructural changes in the Hastelloy Alloy C-276 specimens exposed to SrF_2 consisted of three distinct reaction zones: a narrow surface layer largely depleted of alloy precipitates; a central zone containing abnormally heavy intragranular precipitates; and an inner zone that is depleted of intragranular precipitates.

Figure 65 shows micrographs of the iridium tested as it was received from the vendor and after exposure to SrF_2 at 800°C for 4400 h. The test specimens were prepared from iridium sheet that had been annealed at 1500°C . Information on how the sheet was fabricated was not available. It has been reported that iridium metal that is commercially available contains several thousand parts per million tungsten, and it was this fact that led to the development of the Ir-0.3% W alloy at ORNL. Analysis of the iridium used in this study, however, showed that it contained only 800 ppm tungsten; and the material appeared to be much less ductile

TABLE 35. Attack of Test Specimens Exposed to Nonradioactive SrF₂ at 800°C

Containment Material	Depth of Metal Affected, ^(a) μm			
	Chemical Attack		Change in Microstructure	
	1500 h	4400 h	1500 h	4400 h
Hastelloy C-276 ^(b)	75	75	180	125
Haynes Alloy 25 ^(b)	50	25	75	50
TZM ^(b)	<25	<25	0	<25
Hastelloy C-4	125	100	305	330
Hastelloy S	180	75	380	305
Hastelloy B	100	100	380	280
Hastelloy B-2	255	150	460	460
Haynes Alloy 556	125	125	150	175
Inconel 617	180	205	360	360
Inconel 671	635	510	635	510
Incoloy 800	205	180	0	0
Rene 41	255	280	360	330
Udimet 700	>635	>635	0	>635
Monel 400	125	150	205	150
Nickel 200	180	205	255	205
Ingot Iron	75	100	0	175
Ductile Cast Iron (Pearlite Matrix)	75	100	50	125
Ductile Cast Iron (Ferrite Matrix)	75	100	50	175
316L SS	150	560	0	0
JS 777	150	125	175	150
Copper	>635	>635	0	0
Titanium	>635	>635	X ^(d)	X
Hafn alloy 2525	>635	CR ^(c)	X	X
Molybdenum	50	<25	0	<25
Niobium	75	50	50	50
Ta-10% W	255	50	0	0
Mo-50% Re	50	25	0	0
W-26% Re	20	25	0	0
Rhenium	<25	<25	0	0
Iridium	0	<<25	0	0
Ir-0.3% W	0	<<25	0	0
Platinum	>635	>635	X	X
Gold	>380	>380	X	X

(a) Estimated from photomicrographs.

(b) Tested as reference specimens.

(c) CR--complete reaction.

(d) X--could not be determined because of extensive chemical attack

TABLE 36. The Effect of Capsule Design on Metal Attack by Strontium Fluoride at 800°C

Material	Capsule Design Used ^(a)	Exposure Time, h	Depth of Metal Affected, μm	
			Chemical Attack	Change in Microstructure
Hastelloy C-276	1-A	1500	50	150
Hastelloy C-276	1-C	1500	75	175
Hastelloy C-276	1-A	4400	50	125
Hastelloy C-276	1-A	4400	75	100
Hastelloy C-276	1-C	4400	50	100
Haynes Alloy 25	1-A	1500	50	75
Haynes Alloy 25	1-C	1500	25	75
Haynes Alloy 25	1-A	4400	25	50
Haynes Alloy 25	1-C	4400	25	50
Haynes Alloy 25	1-C	4400	<25	25
TZM	1-A	1500	<25	0
TZM	1-C	1500	<25	0
TZM	1-A	4400	<25	<25
TZM	1-C	4400	<<25	<25
Ir-0.3% W	1-B	1500	0	0
Ir-0.3% W	1-C	1500	0	0
Ir-0.3% W	1-C	1500	0	0
Ir-0.3% W	1-B	4400	<<25	0
Ir-0.3% W	1-C	4400	0	0
Ir-0.3% W	1-C	4400	<<25	0

(a) See Figure 63 for capsule design used.

than the Ir-0.3% W alloy. The microstructure of the as-received iridium sheet is shown in Figure 65a. The structure exhibits the elongated pattern typical of rolled material indicating that recrystallization was not complete. The microstructure of the iridium was unaffected by aging at 800°C for 4400 h. The iridium was very resistant to chemical attack by SrF_2 at 800°C (Figure 65b and c). The 1500-h specimens were unaffected by exposure to the fluoride while the 4400-h specimens exhibited very slight surface roughening. The microstructure of the iridium was unchanged by exposure to the fluoride.

Figure 66 shows platinum specimens before and after exposure to strontium fluoride at 800°C. The test specimens were fabricated from platinum tubing having a wall thickness of ~ 0.025 in. The microstructure of the platinum is shown in Figure 66a. Aging of the platinum at 800°C for up to 4400 h resulted in extensive grain growth and apparent recrystallization (Figure 66b). In some locations, very large single grains extended across the thickness of

FIGURE 64. Micrographs of Hastelloy Alloy C-276 Specimen Exposed to Inert SrF_2

the platinum. Exposure to SrF_2 at 800°C resulted in catastrophic attack of the platinum, and the pieces of platinum tubing were completely corroded through in places (see Figure 66c). The attack involved extensive subsurface void formation together with some grain boundary attack and general dissolution of the specimen surface (Figure 66d). The reacted platinum apparently dissolved in the fluoride since there was no indication of a reaction layer. The chemical attack of the platinum was so extensive it was impossible to tell if the microstructure of the platinum was modified by the SrF_2 attack.

Hastelloy S is the prime candidate for the outer capsule of the $^{90}\text{SrF}_2$ heat source, and it was evaluated in the supplemental screening tests to determine its relative resistance to SrF_2 attack. The Hastelloy Alloy S test specimens were prepared from wrought bar that had been solution heat-treated at 1950°F and air cooled. The microstructure of the solution

FIGURE 65. Micrographs of Iridium Specimens

heat-treated alloy is shown in Figure 67a. Aging of the alloy at 800°C produced a semicontinuous network of grain boundary precipitates (Figures 67b and c). Matthews indicates that the precipitates are probably a mixture of borides and carbides-- M_3B_2 , M_5B_4 , and M_6C (Matthews 1976). Grain size stability of the alloy was very good and aging at 800°C produced no discernible change in grain size.

The Hastelloy Alloy S specimens exposed to SrF_2 at 800°C suffered extensive attack. Both the chemical attack and the microstructural changes were more extensive in the 1500 h test than the 4400-h test, although the attack mechanisms appeared to be similar in both tests (see Figure 68). Chemical attack was fairly uniform across the specimen surface and consisted primarily of leaching of alloy components with formation of an adherent reaction layer. The reaction layer contained a large amount of unreacted metal particles. Some grain boundary attack and

FIGURE 66. Micrographs of Platinum Specimens

subsurface void formation were also observed in the specimens. Microstructural changes consisted of a narrow zone adjacent to the reaction layer in which normal alloy precipitates were largely depleted and a much broader zone that contained an extensive network of abnormal grain boundary precipitates.

Figure 69 shows micrographs of Inconel 671 specimens before and after exposure to strontium fluoride at 800°C. The specimens were fabricated from wrought bar stock that had been annealed at 2200°F for 1 h and cooled. The microstructure of the annealed alloy is shown in Figure 69a. The dark areas are a chromium-rich phase, and the light matrix is the nickel-rich phase. The microstructure appears more typical of a cast material than the wrought alloy. Aging of the alloy at 800°C for up to 4400 h produced the microstructure shown in Figures 69b and c. Again, the light phase is probably a nickel-rich phase while the dark phase is a chromium-rich phase.

FIGURE 67. Microstructure of Hastelloy Alloy S

The specimens of Inconel 671 exposed to SrF_2 at 800°C suffered very extensive attack (Figure 69d-f). The specimen tested for 1500 h suffered more attack than the 4400-h specimen, but the attack mechanisms appeared to be the same in each case. Chemical attack involved selective leaching of chromium from the alloy, particularly along stringers containing the chromium-rich phase, resulting in extensive subsurface void formation. Some general dissolution of the specimen surface was also evident. Microstructural changes consisted of a broad surface zone in which the basic structure of the alloy appeared to have been modified, probably due to the leaching of the chromium, and an adjacent zone containing an abnormally heavy concentration of the chromium-rich phase.

Except for the Hastelloy C-276 and Haynes Alloy 25 reference materials, the two ductile cast irons exhibited the greatest resistance to SrF_2 attack of all the base metals tested.

FIGURE 68. Hastelloy Alloy S Specimens Exposed to SrF_2 at 800°C

The microstructures of the as-received and thermally aged ductile cast-iron specimens are shown in Figure 70. The microstructure of the ferritic anneal ductile cast iron as received from the vendor consisted of spherical graphite nodules (spherulites) in a matrix of free ferrite. The microstructure of the as-received pearlitic anneal ductile cast iron consisted of spherical graphite nodules surrounded by an envelope of free ferrite in a pearlite matrix. Aging of the specimens at 800°C for 4400 h produced only a slight change in the microstructure of the pearlitic anneal specimen, but a marked change in the structure of the ferritic

FIGURE 69. Micrographs of Inconel 671 Specimens

anneal specimen. The structure of the aged ferritic anneal specimen was very similar to that of the aged pearlitic anneal material, although it contained somewhat more free ferrite, and the graphite nodules were slightly smaller. The ductile cast iron specimens exposed to SrF_2 at 800°C for 4400 h suffered a limited amount of chemical attack and microstructural changes (see Figures 71 and 72). The attack mechanisms were similar in each case, which is not surprising since the microstructures of the aged specimens were very similar. Chemical attack in each case consisted of general surface dissolution with some pitting, grain boundary attack,

FIGURE 70. The Microstructure of "As-Received" and Thermally Aged (800°C) Specimens of Ductile Cast Iron

and subsurface void formation. The microstructural changes consisted of a very thin surface layer that appeared to contain a high concentration of free ferrite and a narrow inner zone that was depleted of free ferrite.

10.2.5 Conclusions

Evaluation of the test data leads to several general qualitative conclusions regarding the compatibility of strontium fluoride with containment materials at 800°C:

- Except for 316L stainless steel, metal attack did not increase appreciably with increasing exposure time. In some cases, specimens exposed to SrF_2 for 4400 h exhibited less attack than similar specimens tested for 1500 h; except for the Ta-10% W, however, the differences were no greater than the spread of data usually encountered in compatibility testing. Although quantitative data on the reaction

FIGURE 71. Pearlitic Anneal Ductile Cast-Iron Specimen Exposed to WESF-Grade Nonradioactive SrF_2 for 4400 h at 800°C

mechanisms involved were not obtained, the results of the current tests provide additional evidence that metal attack is due primarily to impurities in the SrF_2 ; and the impurities which are initially present in low concentrations are consumed in a relatively short period of time. Apparently at 800°C , diffusion of the impurities in the SrF_2 matrix is fairly rapid, and the impurities diffuse to the metal surface and react within a few hundred or few thousand hours. The fluorides of iron and chromium appear to be prime factors in the metal attack.

- The base metal alloys tested were much more susceptible to microstructural changes arising from SrF_2 attack than the other materials tested.
- Of the 33 materials tested, iridium and Ir-0.3% W alloy provided the greatest resistance to SrF_2 at 800°C . Rhenium was only slightly less resistant to attack.

FIGURE 72. Ferritic Anneal Ductile Cast-Iron Specimen Exposed to WESF-Grade Nonradioactive SrF_2 for 4400 h at 800°C

Only tungsten, which was evaluated in the initial scouting tests, appears to be as resistant to SrF_2 attack as the iridium and Ir-0.3% W alloy.

- None of the refractory metals tested were as resistant to SrF_2 attack at 800°C as TZM, which was evaluated in the initial scouting tests.
- None of the base metals tested were as resistant to SrF_2 attack at 800°C as Haynes Alloy 25, which was evaluated in the initial scouting tests.
- Hastelloy Alloy C-276, which was also evaluated in the initial scouting tests, is less resistant to attack at 800°C than Haynes Alloy 25 but is better than the other base metals evaluated in the current tests. The ductile cast irons were the best of the remaining base metal alloys.

Based on the results of the supplemental screening tests, iridium and Ir-0.3% W are the best materials of those tested for containing strontium fluoride at 800°C . Rhenium, which is

only slightly less resistant to attack, would be the next choice. Tungsten, which was evaluated in the initial scouting tests, would rank with the iridium and Ir-0.3% W alloys as a containment material for SrF_2 . Each of the four materials possesses certain disadvantages that reduce their usefulness as a containment material for SrF_2 . All of them are relatively difficult to fabricate, especially the iridium and tungsten. The mechanical properties and welding difficulties associated with tungsten reduce its usefulness, while the rhenium, iridium, and Ir-0.3% W alloy are costly and in short supply. On an overall basis, excluding costs, the Ir-0.3% W alloy or rhenium would probably be the preferred containment material for SrF_2 at 800°C . For the large-scale application of $^{90}\text{SrF}_2$, cost considerations would probably rule out the use of iridium, rhenium or Ir-0.3% W alloy, except possibly as a thin coating on a base-metal substrate. However, their use may be acceptable in certain small-scale applications where material costs are not a prime consideration. Therefore, it appears that additional compatibility testing of the three materials with WESF-produced $^{90}\text{SrF}_2$ is justified if potential applications exist, and enough data should be generated to permit licensing of $^{90}\text{SrF}_2$ sources fabricated from the materials.

For large-scale applications where cost considerations preclude the use of precious metals, TZM, Haynes Alloy 25, and Hastelloy C-276 appear the best choices for SrF_2 containment at 800°C , since these materials were evaluated in the long-term tests. The only other materials that might warrant additional investigation would be the ductile cast irons and ingot iron.

10.3 WESF $^{90}\text{SrF}_2$ CAPSULE DEMONSTRATION TESTS

The demonstration tests were carried out using two typical WESF $^{90}\text{SrF}_2$ capsules taken from the storage pool. (A description of the WESF $^{90}\text{SrF}_2$ capsule is given in Section 3.0.) The WESF $^{90}\text{SrF}_2$ capsule has an exposed metal-to- $^{90}\text{SrF}_2$ volume (S/V) ratio of about 0.86 cm^{-1} . The smallest S/V ratio used in the long-term tests with $^{90}\text{SrF}_2$ was 2.5 cm^{-1} . The objective of the capsule demonstration tests was to determine if attack of the Hastelloy C-276 inner capsule by the $^{90}\text{SrF}_2$ was significantly different from that observed with Hastelloy C-276 in the long-term tests with WESF $^{90}\text{SrF}_2$.

Each test capsule was placed horizontally in an insulated container and allowed to self-heat to a temperature of $\sim 800^\circ\text{C}$. One capsule was held at temperature for 5000 h and the second for 26,200 h ($\sim 3\text{ yr}$). At the conclusion of the test, the 316L stainless steel outer capsule was removed, and the Hastelloy C-276 inner capsule was sectioned, and metal samples were taken at several locations. Figure 73 shows the locations where the Hastelloy C-276 capsule was sectioned. The samples were shipped to ORNL for metallographic examination, and attack of the Hastelloy C-276 by the $^{90}\text{SrF}_2$ was determined from the photomicrographs obtained.

The ^{90}Sr isotopic content of the SrF_2 in the capsules was $\sim 52\%$ at the start of testing. The heat output of each capsule was about 950 watts when the tests started. At the

FIGURE 73. Sketch Showing Locations Where Sections Were Cut From the Hastelloy C-276 Inner Capsule After Testing

conclusion of the 5000-h test, the heat output of the capsule was calculated to be about 940 watts, and at the end of the 3-yr test, the output of the capsule was ~ 885 watts.

A chemical analysis was not obtained on the fluoride in each test capsule. An analysis was obtained on the batch of strontium fluoride used to fill the capsules: the batch analysis is shown in Table 37. The fluoride contained ~ 6 wt% impurities. There is some nonhomogeneity in each batch of SrF_2 , principally in the iron, chromium, and nickel content. This nonhomogeneity results from the presence of corrosion products from the metallic equipment, primarily the Inconel X boats used in firing the fluoride. Therefore, the values given in Table 37 are only estimates of the iron, chromium, and nickel content of the SrF_2 in the capsules.

In the demonstration tests, it was not possible to measure the Hastelloy C-276/ $^{90}\text{SrF}_2$ interface temperature directly. Instead, the surface temperature of the 316L stainless steel outer capsule was measured using three movable calibrated chromel-alumel thermocouples. The $^{90}\text{SrF}_2$ -Hastelloy C-276 interface temperature profile was calculated from the outer capsule surface temperature using standard heat transfer techniques. Heat losses from the insulated containers were nonuniform, and temperature gradients existed between the midpoint and ends of each capsule. The calculated interface temperature profiles for the two capsules are shown in Figures 74 and 75. The interface temperatures at the locations where the sections were cut from the capsules are also shown in the figures. It was found that the temperature at any given capsule location fluctuated by as much as $\pm 6^\circ\text{C}$ during the course of the test. These fluctuations did not follow any set pattern and were random in nature. In the 5000-h test, there was no discernible decrease in the interface temperature profile with time, even though the heat output of the capsule had decreased by about 1% by the end of the test. In the 3-yr test, it appeared that the interface temperature profile had decreased by an average of about 12°C during the test, while the heat output of the capsule decreased about 7%. The interface temperature profiles given in Figures 74 and 75 represent best estimates of the average test temperatures.

TABLE 37. Analysis of the $^{90}\text{SrF}_2$ in the Test Capsules(a,b)

Element	wt%	Element	wt%	Element	wt%
Sr	66.6	Cr	0.25	Ni	0.22
Al	0.2	Fe	0.40	Pb	0.025
Ba	0.35	Mn	0.01	RE ^(c)	1.2
Ca	0.43	Na	1.9	Zr	1.2
Cd	<0.02				

- (a) Analysis of the batch of $^{90}\text{SrF}_2$ used to fill the test capsules.
 (b) ^{90}Sr Isotopic content--52%.
 (c) RE--rare earths.

FIGURE 74. Temperature Profile for the WESF $^{90}\text{SrF}_2$ Capsule Tested for 5000 h, Showing the Locations at Which the Capsule was Sectioned

FIGURE 75. Temperature Profile for the WESF $^{90}\text{SrF}_2$ Capsule Tested for 26,200 h, Showing the Locations at Which the Capsule was Sectioned

The samples taken from the capsules were subjected to metallographic examination, and the photomicrographs obtained are shown in Figures 76 and 77. Attack of the Hastelloy C-276 was estimated from the photomicrographs, and the results obtained are given in Table 38. Thickness measurements on the test specimens eliminated the possibility of gross attack that might not be apparent from the photomicrographs. The results show that chemical attack of the Hastelloy C-276 was not appreciably greater in the 3-yr test than in the 5000-h test. This confirms the results obtained in the other compatibility tests and is additional evidence that the attack is due primarily to impurities in the SrF_2 .

The data show that in each test the extent of chemical attack varied along the length of the capsule. The variation in attack cannot be directly attributed to temperature differences because the most extensive chemical attack occurred at intermediate interface temperatures. Examination of the micrographs shown in Figures 76 and 77 indicates that the type of chemical attack also varied somewhat along the length of the capsule. In addition, the chemical attack that occurred in the 5000-h test appeared to be quite different from that which occurred in the 3-yr test, even though the capsules' interface-temperature profiles were very similar. The chemical attack of the capsule tested for 3-yr was quite similar to that observed in other compatibility tests carried out at 800°C involving Hastelloy C-276 and $^{90}\text{SrF}_2$. The chemical attack of the capsule tested for 5000 h was more similar to that observed in other tests carried out at 600°C .

The micrographs of the sections from the two test capsules show that there are marked differences in the Hastelloy C-276 microstructure along the length of a capsule, even though the temperature gradient between the test sections in each case is at most 50° to 60°C . The micrographs also showed that precipitate formation was much heavier in the Hastelloy C-276 sections from the 3-yr test than in the sections from the 5000-h test. The microstructure of the Hastelloy C-276 specimens from the capsule tested for 3 yr was similar to that of other Hastelloy C-276 specimens aged at 750 to 850°C . On the other hand, the microstructure of the specimens from the capsule tested for 5000 h was similar to that of Hastelloy C-276 specimens aged at temperatures below 800°C . It is difficult to reconcile these results since the temperature measurements and heat transfer calculations show that two capsules were tested at approximately the same temperature.

The differences in the Hastelloy C-276 microstructure could help account for the differences in the extent and type of chemical attack observed between the two capsules and along the length of each capsule. Possible differences in the impurity content of the fluoride in each capsule could also help account for the differences in the attack observed between capsules. Since the $^{90}\text{SrF}_2$ is not homogeneous, the impurity content of the $^{90}\text{SrF}_2$ could also vary along the length of a capsule and affect the metal attack.

One unexpected result was the absence of microstructural changes due to fluoride attack in the capsule tested for 5000 h and in one section from the capsule tested for 3 yr. In all of the other PNL compatibility tests involving Hastelloy C-276 and strontium fluoride, the alloy suffered extensive microstructural changes. It was not determined why the microstructural changes did not occur as expected. In the 3-yr test, three of the Hastelloy C-276

FIGURE 76. Photomicrographs of the Sections From the Hastelloy C-276 Inner Capsule Tested for 5000 h

FIGURE 77. Photomicrographs of the Sections From the Hastelloy C-276 Inner Capsule Tested for 26,200 h

TABLE 38. Attack of the Hastelloy C-276 by $^{90}\text{SrF}_2$ in the WESF Capsule Demonstration Tests

Test Duration, h	Section No.	Interface Temperature, $^{\circ}\text{C}$	Depth of Hastelloy C-276 Affected, (a) μm	
			Chemical Attack	Change in Microstructure
5,000	1	762	80	0
	2	821	230	0
	3	813	210	0
	4	790	280	0
26,200	1	778	130	0
	2	831	180	310
	3	824	310	560
	4	800	230	510

(a) Estimated from photomicrographs.

sections exhibited extensive changes in microstructure. These changes consisted of a narrow surface layer largely depleted of normal alloy precipitates, and a much broader inner zone containing very heavy precipitation not found in the body of the alloy. The microstructural changes observed in the 3-yr tests were very similar to those observed in other tests carried out at 800°C with Hastelloy C-276 and $^{90}\text{SrF}_2$.

Assuming attack of the Hastelloy C-276 is due primarily to impurities in the strontium fluoride, the extent of metal attack should depend on the exposed metal surface-to- SrF_2 volume ratio (S/V) of the capsule. The smaller the S/V ratio the greater the metal attack should be. Based on the results obtained in the other compatibility tests with strontium fluoride and Hastelloy C-276 where much larger S/V ratios were used, one would expect much greater metal attack in the demonstration tests than was actually observed. Reasons for the lower than expected metal attack in the demonstration tests with the full-sized WESF $^{90}\text{SrF}_2$ capsules are not obvious from the data available. The most likely explanation is that the actual iron and chromium concentrations in the strontium fluoride in the two capsules were lower than the batch analysis indicated. The results obtained in the demonstration tests are encouraging inasmuch as they indicate that attack of Hastelloy C-276 at 800°C in the WESF $^{90}\text{SrF}_2$ storage capsule may be much lower than the results of the other PNL compatibility studies have indicated should occur.

10.4 THERMAL GRADIENT TEST

In the thermal gradient test, a Hastelloy C-276 capsule containing inert strontium fluoride was subjected to a temperature gradient of 560° (from 360° to 920°C) for a period of 4400 h. The nonradioactive SrF_2 contained impurities similar to those found in WESF-produced $^{90}\text{SrF}_2$. The objectives of the test were threefold:

- to determine the effect of temperature on the attack of the Hastelloy C-276 by the SrF_2 ;
- to determine if the thermal gradient affects diffusion of impurities in the SrF_2 ;

- to identify the reaction mechanisms involved in the attack of the Hastelloy C-276 by the fluoride.

The test capsule was fabricated from 1.5-in. Sch. 40 Hastelloy C-276 seamless pipe 26 in. in length. The capsule endcaps were fabricated from 0.125-in. Hastelloy C-276 sheet. The specifications for the pipe and sheet are given in Table 39. The SrF_2 was cold-pressed into the capsule to $\sim 70\%$ of theoretical density. The filled capsule was closed by TIG-welding the end cap in place. The exposed metal surface-to- SrF_2 volume ratio (S/V) for the capsule was $\sim 1.0 \text{ cm}^{-1}$ compared with a value of $\sim 0.86 \text{ cm}^{-1}$ for the WESF $^{90}\text{SrF}_2$ capsule.

The inert strontium fluoride used for the test was similar in composition to the typical $^{90}\text{SrF}_2$ produced at WESF. The composition of the fluoride is given in Table 40. The SrF_2 was prepared by the WESF flowsheet using reagent grade chemicals; it was analyzed by a variety of methods including spark-source mass spectrometry, emission spectroscopy, flame photometry, and atomic absorption. The data show that the cation impurities were present as fluorides. The SrF_2 was from the same batch of inert SrF_2 that was used in the long-term tests. After firing at 1100°C , the SrF_2 was light tan in color.

TABLE 39. Composition and Mechanical Properties of the Hastelloy C-276 Used in Fabricating the Test Capsule

Composition, wt%	1.5-in. Sch. 40 Seamless Pipe--Solution Heat-Treated at 2150°F and Rapid Quenched	0.125-in. Sheet Solution Heat-Treated at 2150°F and Rapid Quenched
C	<0.002	0.002
Co	1.69	2.23
Cr	15.64	15.15
Fe	6.90	6.14
Mn	0.56	0.56
Mo	15.19	15.88
Ni	Balance	Balance
P	0.016	0.025
S	0.003	0.005
Si	0.03	0.04
V	0.16	0.21
W	3.29	3.26
Mechanical Properties		
UTS, MPa	731	755
Yield, MPa	376	345
% Elong. in 2 in.	63.5	56.2

TABLE 40. Composition of the SrF₂ Used in the Thermal Gradient Test

Component	wt%	Component	wt%
Sr	65.9	Nd	1.0
Al	0.26	Ni	0.02
Ba	0.70	Pb	0.06
Ca	0.21	Si	0.02
Cd	0.01	F	29.0
Cr	0.050	H ₂ O	<0.01
Fe	0.022	NO ₃ ⁻	<0.01
K	0.010	O	<0.01
Mg	0.13	F	29.0
Mn	0.01		
Na	2.4		

Five calibrated chromel-alumel thermocouples were welded to the capsule at various locations to monitor the capsule surface temperature throughout the test. Capsule endcap temperatures were measured with removable thermocouples. Outputs of the thermocouples were measured using a calibrated digital multimeter. The test capsule was placed in a heavy-wall 316L stainless steel tube that was placed, in turn, in a horizontal three-zone tube furnace. Each zone of the furnace was controlled independently allowing a temperature gradient to be maintained along the length of the capsule. Figure 78 shows the capsule surface temperature at various locations along the length of the capsule. The temperature varied from 360° to 920°C over the length of the capsule, giving a temperature gradient of 560°C. Temperature control was quite stable, and the maximum temperature fluctuation observed at any location during the test was ±6°C. The capsule was held at temperature for 4400 h.

At the conclusion of the test, the capsule was cut into several sections using an abrasive saw. The sectioned capsule is shown in Figure 79. The temperatures indicated in the photograph are the approximate temperatures at the locations where the cuts were made. The strontium fluoride in the capsule varied from a compacted powder at the cold end of the capsule (<680°C) to a highly sintered porous mass at the hot end. The SrF₂ that had been held above about 850°C adhered strongly to the inner capsule surface. The SrF₂ that had been held between ~750 and 850°C appeared to have sintered and contracted away from the capsule wall and was easily removed from the capsule. The SrF₂ in the cold end had not sintered to any appreciable degree and was easily removed from the capsule. The color of the SrF₂ varied from white at the cold end of the capsule to pale blue at the hot end.

Specimens were cut from the capsule at various locations and subjected to metallographic examination to determine the extent of attack by the fluoride. At each location where a specimen was to be taken, a ring ~0.75 in. wide was cut from the capsule. The ring was then split as shown below to give two diametrically opposed specimens:

FIGURE 78. Capsule Surface Temperature at Various Locations

Each pair of specimens was examined and photomicrographs obtained of the surfaces in contact with the fluoride. The micrographs obtained are shown in Figure 80. Micrographs were also obtained of the body of each specimen to show how the microstructure of the Hastelloy C-276 varied with temperature due to aging reactions. These micrographs are shown in Figure 81. The micrographs show that aging Hastelloy C-276 at 450°C had no effect on its microstructure, and the microstructure of the aged alloy is identical to that of the solution-annealed alloy. Heating the alloy at temperatures of 680° to 918°C produced heavy grain boundary precipitation as well as intragranular precipitation. Leonard (1969) reports that aging Hastelloy C-276 at 650° to 1100°C results in the precipitation of a P-type phase that transforms to a Ni_7Mo_6 -type phase. Microprobe analyses of the precipitates formed at 680° to 918°C show that they are composed primarily of nickel, molybdenum and tungsten and have the approximate composition $\text{Ni}_7(\text{Mo,W})_6$, which agrees with the Leonard findings. The microprobe data showed that the nickel content of the precipitates was essentially independent of temperature, but the ratio of tungsten to molybdenum in the precipitates increased with increasing temperature. There was some indication that the precipitates contained some carbide phases at the lower temperature ($\leq 680^\circ\text{C}$), but not at the higher temperatures.

Attack of the Hastelloy C-276 by the fluoride was estimated from the micrographs, and the results obtained are shown in Table 41. The attack observed with each pair of specimens was quite similar; and the estimates provided in Table 41 represent the maximum attack observed

FIGURE 79. Sectioned Capsule from the Thermal Gradient Test

FIGURE 80. Hastelloy C-276 Specimens Exposed to Nonradioactive SrF_2 for 4400 h

FIGURE 81. The Microstructure of Hastelloy C-276 Held at Various Temperatures for 4400 h

with each pair. Chemical attack of the Hastelloy C-276 increased sharply with increasing exposure temperature. The type of attack observed also appeared to vary with the temperature. Very little attack was apparent at 448°C. At 680°C and above, there was extensive chemical attack, and a reaction layer formed on the surface of the alloy. At 680° to 780°C, the attack was relatively uniform across the surface with only slight indication of grain boundary attack. At the higher temperatures (>830°C), extensive grain boundary attack and subsurface void formation were observed, and the reaction layer contained free grains of unreacted metal. Contact with the fluoride also produced marked changes in the alloy microstructure. The depth of metal affected by the microstructural changes increased with increasing temperature up to about 870°C and then decreased at higher temperatures. At temperatures above about 780°C, the microstructural changes consisted of a zone at the surface depleted of normal alloy precipitates

TABLE 41. Attack of the Hastelloy C-276 at Various Locations in the Capsule After Exposure to SrF_2 ^(a) for 4400 h

Location No.	Approximate Interface Temperature, °C	Depth of Metal Affected, ^(b) μm	
		Chemical Attack	Microstructural Changes
1	448	<<25	<25
2	680	50	75
3	781	100	150
4	830	150	275
5	874	175	375
6	918	200	225

(a) Composition of the SrF_2 is given in Table 40.

(b) Estimated from photomicrographs of capsule specimens.

and an adjacent inner zone containing precipitates not found in the body of the specimen. At temperatures below about 780°C , the microstructural changes consisted of a zone at the surface depleted of normal precipitates.

Samples of the strontium fluoride were taken from various locations in the capsule and analyzed to determine if changes in the impurity levels had occurred due to the thermal gradient imposed on the capsule and/or to reactions with the Hastelloy C-276. The analytical results indicate that the impurity levels in the SrF_2 were essentially unchanged along the length of the capsule except for two elements: iron and chromium. Table 42 shows results obtained with several of the impurities in the SrF_2 . Both the iron and chromium exhibited concentration gradients over the length of the capsule, although the gradient directions were reversed for the two elements. The data show that the overall concentrations of iron and chromium in the SrF_2 after testing were much lower than the initial concentrations. The concentrations of the other impurities in the fluoride were unaffected by the test.

The test specimens were subjected to EM analysis in an attempt to identify the reactions involved in the attack. The results obtained show that attack apparently involved two principal mechanisms: selective leaching of chromium, molybdenum, iron and tungsten from the alloy matrix, and reaction of the iron and chromium fluoride in the SrF_2 with precipitates in the grain boundaries of the alloy. The grain boundary reactions were more prevalent at the higher temperatures. The microprobe data show a high concentration of chromium, molybdenum, iron and tungsten in the reaction layer at the specimen surface, and a depletion of chromium, molybdenum, iron and tungsten in the alloy matrix immediately adjacent to the reaction layer. The grains of unreacted metal in the reaction layer were largely depleted of chromium and partially depleted of molybdenum, iron, tungsten and cobalt. The leaching of the molybdenum, iron and tungsten appeared to decrease with increasing exposure temperature. There was no indication that the SrF_2 participates directly in the reactions, and no strontium was found in the alloy matrix. The microprobe data also indicate that the grain boundary attack observed at the higher temperatures involved the reaction of FeF_3 and CrF_2 with the $\text{Ni}_7(\text{Mo},\text{W})_6$ phase. There was no evidence of the diffusion of strontium into the grain boundaries of the alloy.

TABLE 42. Impurity Concentrations in SrF_2 Samples Taken From Various Locations in the Capsule

Element	Concentration, wt%						
	Initial SrF ₂	#1 (448°C)	#2 (680°C)	#3 (781°C)	#4 (830°C)	#5 (874°C)	#6 (918°C)
Ca	0.21	0.27	0.19	0.21	0.24	0.20	0.22
Cr	0.050	0.006	0.015	0.014	0.025	0.029	0.055
Fe	0.022	0.016	0.019	0.020	0.013	0.006	0.002
Mg	0.13	0.10	0.15	0.11	0.14	0.16	0.11
Na	2.4	2.7	2.5	2.9	2.4	2.4	2.4
Ni	0.020	0.022	0.015	0.019	0.025	0.022	0.022
Si	0.02	0.02	0.01	0.02	0.03	0.02	0.02

FIGURE 82. Elemental Analysis of the Hastelloy C-276 Specimen Exposed to Inert SrF_2 at 781°C for 4400 h--S/V = 1 cm^{-1}

Figure 82 shows an elemental analysis of the reaction layer and underlying metal of the Hastelloy C-276 sample exposed to the SrF_2 at 781°C . The data indicate that the reaction layer is composed of metal fluorides and unreacted metal particles. The reaction layer was enriched in chromium, molybdenum iron and tungsten; and the underlying metal, adjacent to the reaction layer, was depleted in the four elements. There was also an indication that some cobalt was leached from the alloy matrix to a very limited depth. Analyses of a particle of unreacted metal in the reaction layer showed the chromium content was less than 1 wt% while the nickel content exceeded 85 wt%. The outer edge of the reaction layer contained some strontium fluoride.

Examination of the specimens exposed to the SrF_2 at 680° , 830° and 918°C gave results similar to those presented above, except that the leaching of chromium from the alloy matrix was greater at the higher temperatures.

The following conclusions can be reached from the results obtained. The data show that chemical attack of Hastelloy C-276 by WESF-grade inert SrF_2 increases with temperature. Two reactions predominate: leaching of components from the alloy matrix and reaction of iron and chromium fluorides in the SrF_2 with the Ni_7Mo_6 phase grain boundary precipitate. The latter reaction occurs primarily at temperatures above 800°C . The only impurities involved in the chemical attack appear to be the iron and chromium fluorides. Analysis of the SrF_2 shows that the other impurities in the SrF_2 are unaffected by the metal attack. There was no evidence that SrF_2 was involved in the grain boundary attack, and there was no evidence of strontium diffusing into the alloy.

11.0 REFERENCES

- Anon. 1974. Annual Book of ASTM Standards - Part 10. American Society for Testing and Materials.
- Berezhnaya, V. T. and G. A. Bukhalova. 1960. Russ. J. Inorg. Chem. (English Trans). 5:445
Zr Neorgan. Khim. 5(4):925.
- Ellingham, H. J. T. 1944. J. Soc. Chem. Ind. May, page 125.
- Ferry, P. B. 1969. Effects of Thermal Treatments on the Energy Absorption Capability of Selected Superalloys. TI-734-25-001, Atomics International, Canoga Park, California.
- Fullam, H. T. 1972. Compatibility of Cesium Chloride and Strontium Fluoride With Containment Materials. BNWL-1673, Pacific Northwest Laboratory, Richland, Washington.
- Fullam, H. T. 1975. The Containment of $^{90}\text{SrF}_2$ at 800 to 1100°C Preliminary Results. BNWL-1967, Pacific Northwest Laboratory, Richland, Washington.
- Fullam, H. T. 1977a. Pacific Northwest Laboratory Monthly Report on the Strontium Heat Source Development Program, Division of Nuclear Research and Applications for January 1977. BNWL-1845-32, Pacific Northwest Laboratory, Richland, Washington.
- Fullam, H. T. 1977b. Containment of Strontium Fluoride at 800 C - Supplemental Screening Tests. BNWL-2259, Pacific Northwest Laboratory, Richland, Washington.
- Fullam, H. T. 1977c. Strontium-90 Fluoride Data Sheet. BNWL-2284, Pacific Northwest Laboratory, Richland, Washington.
- Fullam, H. T. 1980. Compatibility Testing of the WESF $^{90}\text{SrF}_2$ Storage Capsule at 800°C. PNL-3433, Pacific Northwest Laboratory, Richland, Washington.
- Glassner, A. 1957. The Thermodynamic Properties of the Oxides, Fluorides, and Chlorides to 2500°K. ANL-5750, Argonne National Laboratory, Argonne, Illinois.
- Hildebrand, J. H. and R. L. Scott. 1950. The Solubility of Nonelectrolytes. Reinhold Publishing Corp., New York, New York.
- Kubaschewski, O. and C. B. Alcock. 1979. Metallurgical Thermochemistry. Pergamon Press, New York, New York.
- Leonard, R. B. 1969. Corrosion. 25:222-228.
- Lindsay, W. L. 1979. Chemical Equilibria in Soils. John Wiley and Sons, New York, New York.
- Maraglia, F. J. 1966. Compatibility of Strontium Space Fuel Forms. MND-3062-27, Martin Marietta Corp., Baltimore, Maryland (declassified).
- Matthews, S. J. 1976. Thermal Stability of Solid Solution Strengthened High-Performance Alloys. Report No. 8979, Cabot Corp., Kokomo, Indiana.
- McCoy, H. E. and D. T. Bourgette. 1973. Influence of Aging on the Impact Properties of Hastelloy N, Haynes Alloy No. 25 and Haynes Alloy No. 188. ORNL-TM-4380, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- McTaggart, F. K. and A. G. Turnbull. 1964. Australian J. Chem. 17:727-30.
- Rosenqvist, T. 1970. Thermochemical Data for Metallurgists. University of Trondheim, Tapir Forlag.
- Smithells, C. J., Editor. 1976. Metals Reference Book. Butterworths, Boston, Massachusetts.

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