PACIFIC NORTHWEST LABORATORY
QUARTERLY REPORT
TO SPACE NUCLEAR SYSTEMS DIVISION
FOR OCTOBER - DECEMBER 1974

Battelle

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PACIFIC NORTHWEST LABORATORY
QUARTERLY REPORT
TO SPACE NUCLEAR SYSTEMS PROGRAMS
FOR OCTOBER - DECEMBER 1974

by

H. T. Fullam

January 1975

On January 19, 1975, research and development programs of the U.S. Atomic Energy Commission (AEC) became part of the newly formed Energy Research and Development Administration (ERDA). In this report, since it refers to work done in 1974, most references are to AEC programs.

ABSTRACT

The short-term compatibility tests with SrF_2 containing controlled levels of impurities have been completed and the test couples evaluated. With a few exceptions, the addition of impurities to the fluoride increased the metal attack.

Evaluation of the short-term $^{90}\text{SrF}_2$ test couples is approximately 60% completed. Examination of the remaining couples should be completed in January, 1975.

Dissolution rate measurements with nonradioactive SrF_2 , SrTiO_3 and Sr_2TiO_4 have been completed. The results show that in general, Sr_2TiO_4 dissolves at the highest rate, SrTiO_3 at the slowest rate and SrF_2 at an intermediate rate. The dissolution rate for each compound is highly dependent on the composition, surface area and thermal history.

The thermodynamic analysis of the $^{90}\text{SrF}_2\text{-W}$ system has been completed.

The final version of the program plan has been submitted to Space Nuclear Systems (SNS).

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STRONTIUM HEAT SOURCE DEVELOPMENT PROGRAM

At Hanford, strontium will be separated from the high-level waste, converted to the fluoride and doubly encapsulated in small, high-integrity containers for subsequent long-term storage. The fluoride conversion, encapsulation and storage will take place in the Waste Encapsulation and Storage Facilities (WESF). The encapsulated strontium fluoride represents an economical source of ^{90}Sr if the WESF capsule can be licensed for heat source applications under anticipated use conditions. The objectives of this program are to obtain the data needed to license $^{90}\text{SrF}_2$ heat sources and specifically the WESF $^{90}\text{SrF}_2$ capsules. The information needed for licensing can be divided into three general areas:

- 1. Long-term SrF_2 compatibility data.*
- 2. Chemical and physical property data on $^{90}\text{SrF}_2$.*
- 3. Capsule property data such as external corrosion resistance, crush strength, etc.*

The current program is designed to provide the required information.

SHORT-TERM COMPATIBILITY TESTS

The short-term compatibility tests consisted of four series of tests, each using a different fuel composition, and lasting 1500 and 4400 hours. The four fuel compositions tested were:

1. High-purity nonradioactive SrF_2 containing less than 0.1% total impurities.
2. High-purity $^{90}\text{SrF}_2$ ($\sim 50\%$ ^{90}Sr isotopic content). The $^{90}\text{SrF}_2$ was prepared from $^{90}\text{Sr}(\text{NO}_3)_2$ solution obtained from the Atlantic Richfield Hanford Company (ARHCO). The ^{90}Sr solution was purified by Battelle, Pacific Northwest Laboratory (PNL) using ion exchange and converted to $^{90}\text{SrF}_2$ using the WESF flowsheet.
3. WESF grade $^{90}\text{SrF}_2$ ($\sim 50\%$ ^{90}Sr isotopic content). The $^{90}\text{SrF}_2$ was prepared from $^{90}\text{Sr}(\text{NO}_3)_2$ solution obtained from ARHCO by PNL using the WESF flowsheet.
4. High-purity nonradioactive SrF_2 ($< 0.1\%$ total impurities) containing controlled levels of added impurities.

The first three series of tests were carried out at 800, 1000 and 1100°C.

The last series of tests was carried out at 1000°C. Nine containment materials were evaluated in the tests. They were:

1. Hastelloy C-276	4. Haynes 25	7. Inconel 625
2. Hastelloy X	5. Haynes 188	8. TZM
3. Hastelloy N	6. Inconel 600	9. Tungsten

All of the tests have now been completed. The results of the tests with high-purity SrF_2 were presented in an earlier report. The couples from the $^{90}\text{SrF}_2$ tests are now being evaluated and should be completed in January. Evaluation of the couples containing SrF_2 with controlled levels of impurities has been completed and the results are discussed below.

Tests With SrF_2 Containing Added Impurities

The tests with high-purity nonradioactive SrF_2 (< 0.1% total impurities initially) containing controlled levels of added impurities have been completed and the test couples evaluated. The fuel compositions used in the tests are given in Table 1. Selection of the impurities to be tested was based on analysis of $^{90}\text{SrF}_2$ prepared by the WESF flowsheet. Each fuel composition was tested with each containment material for 1500 and 4400 hours at 1000°C, requiring a total of 180 test couples. In the tests involving water and nitrate, duplicate couples were tested for each set of conditions bringing the total number of couples required to 216.

The couples were evaluated by optical microscopy, scanning electron microscopy and electron microprobe. The metal attack observed in the various test couples can be divided into two general types.

1. Chemical attack of the metal surface by the fuel. Includes various types of attack such as surface dissolution, pitting, intergranular penetration and subsurface void formation.
2. Changes in metal microstructure, principally increased or decreased precipitation (both intragranular and at the grain boundaries) and changes in grain size.

TABLE 1
COMPOSITIONS OF SrF_2 - IMPURITY
MIXTURES USED IN SHORT-TERM COMPATIBILITY TESTS

<u>Mixture</u>	<u>Composition, wt%</u>
1. Sr^{+2} (as SrF_2)	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

The results of the tests are presented in Table 2. Both types of attack were observed in the bulk of the couples (except for the couples involving the refractory metals where little change in microstructure was observed). With the superalloys, the depth of metal affected by chemical attack was usually much less than that affected by changes in structural morphology. There was one exception to this. In the couples containing SrO, the depth of the chemical attack usually approached or exceeded the depth to which microstructure changes were apparent. Due to a furnace controller failure, some of the 1500 hour test couples were accidentally overheated to 1200°C for about 4 hours. This resulted in accelerated attack of the metal surface in some couples. The couples which were overheated are indicated by an asterisk in Table 2. Because of the overheating, some of the 1500 hour couples exhibited significantly more attack than the equivalent 4400 hour couples.

The test results show that certain impurities have a very deleterious effect on fluoride compatibility. The worst offenders are Fe^{+3} , Cu^{+2} and SrO. Fortunately, analysis of strontium fluoride produced by the WESF flowsheet indicates that the harmful impurities are present at very low levels.

It is interesting to compare the results given in Table 2 with those previously reported for couples containing only high-purity SrF_2 . The results obtained with high-purity SrF_2 are given in Table 3. A comparison of the two sets of results show that, in general, the additions of impurities to the SrF_2 increased the metal attack observed. There are, however, certain exceptions; the Hastelloy C-276 and Haynes 188 showed more attack by the high-purity SrF_2 than by fluoride containing impurities. Only fluoride containing SrO attacked the Hastelloy C-276 and Haynes 188 to a greater degree than the high-purity SrF_2 .

Tests With $^{90}\text{SrF}_2$

The two series of tests with $^{90}\text{SrF}_2$ have been completed and the couples are now being evaluated. To date, approximately 60% of the couples have been examined, and it is expected that the work will be completed in January. The results will be presented when all the data are available. To reduce the time required in examining the $^{90}\text{SrF}_2$ capsules, approximately 50% of the couple test specimens have been shipped to Oak Ridge National Laboratory (ORNL) for evaluation (to the Electron and Radiation Metallography Group).

TABLE 2
METAL ATTACK OBSERVED IN SrF_2 COUPLES CONTAINING
CONTROLLED LEVELS OF ADDED IMPURITIES - AT 1000°C

Material Tested	Impurity Added	Depth of Metal Affected, mils			
		Chemical Attack		Change in Microstructure	
		1500 Hr	4400 Hr	1500 Hr	4400 Hr
Hastelloy C-276	NaF	1*	1	3*	3
"	MnF ₂	2	1	3	4
"	PbF ₂	2*	1	2*	3
"	CuF ₂	1	2	8	15
"	FeF ₃	2	1	8	8
"	AlF ₃	< 1*	< 1	2*	4
"	(Ca-Ba-Mg)F ₂	1	1	3	3
"	SrO	12	10	12	10
"	Sr(NO ₃) ₂	1*	1	4*	10
"	H ₂ O	4*	1	6*	5
Hastelloy X	NaF	< 1	< 1	3	2
"	MnF ₂	4*	1	0*	5
"	PbF ₂	1*	1	3*	4
"	CuF ₂	30*	1	30*	12
"	FeF ₃	1	3	12	22
"	AlF ₃	< 1	1	4	3
"	(Ca-Ba-Mg)F ₂	< 1*	1	3*	4
"	SrO	15*	8	18*	10
"	Sr(NO ₃) ₂	5*	1	0*	4
"	H ₂ O	1*	1	4*	5
Hastelloy N	NaF	2	2	10	10
"	MnF ₂	2	3	2	5
"	PbF ₂	3	3	6	8
"	CuF ₂	3*	4	6*	20
"	FeF ₃	6*	8	12*	15
"	AlF ₃	< 1	1	3	10
"	(Ca-Ba-Mg)F ₂	< 1	1	3	4
"	SrO	25	35	28	35
"	Sr(NO ₃) ₂	2*	2	4*	15
"	H ₂ O	2	1	5	5
Haynes 25	NaF	< 1	1	3	2
"	MnF ₂	< 1*	< 1	3*	3
"	PbF ₂	< 1	1	4	3
"	CuF ₂	2*	1	12*	18
"	FeF ₃	2*	3	10*	20
"	AlF ₃	< 1	< 1	3	4
"	(Ca-Ba-Mg)F ₂	< 1	1	2	1
"	SrO	5	7	0	3
"	Sr(NO ₃) ₂	1*	2	5*	0
"	H ₂ O	1	1	0	0

Table 2 (Cont.)

Material Tested	Impurity Added	Depth of Metal Affected, mils			
		Chemical Attack		Change in Microstructure	
		1500 Hr	4400 Hr	1500 Hr	4400 Hr
Haynes 188	NaF	< 1	1	0	3
"	MnF ₂	< 1*	1	6*	5
"	PbF ₂	1	2	5	4
"	CuF ₂	1*	2	12*	13
"	FeF ₃	2*	1	15*	7
"	AlF ₃	< 1	< 1	< 1	2
"	(Ca-Ba-Mg)F ₂	< 1	1	1	3
"	SrO	12	20	0	10
"	Sr(NO ₃) ₂	1*	< 1	4*	5
"	H ₂ O	< 1*	1	4*	2
Inconel 600	NaF	1*	1	7*	1
"	MnF ₂	2	1	5	3
"	PbF ₂	1	1	3	10
"	CuF ₂	1	3	3	8
"	FeF ₃	2*	4	8*	8
"	AlF ₃	1	1	0	1
"	(Ca-Ba-Mg)F ₂	1	1	3	1
"	SrO	20	10	0	0
"	Sr(NO ₃) ₂	3*	1	4*	12
"	H ₂ O	1*	1	1*	1
Inconel 625	NaF	1	1	4	12
"	MnF ₂	1	2	8	10
"	PbF ₂	1	1	6	6
"	CuF ₂	6*	2	12*	12
"	FeF ₃	2*	4	6*	13
"	AlF ₃	1	< 1	6	6
"	(Ca-Ba-Mg)F ₂	5*	1	5*	10
"	SrO	7*	10	10*	18
"	Sr(NO ₃) ₂	3*	1	5*	10
"	H ₂ O		2		5
Tungsten	NaF	<< 1	< 1	0	0
"	MnF ₂	< 1*	< 1	0*	0
"	PbF ₂	0*	< 1	0*	0
"	CuF ₂	2	1	0	0
"	FeF ₃	<< 1	< 1	0	0
"	AlF ₃	0*	< 1	0*	0
"	(Ca-Ba-Mg)F ₂	<< 1	< 1	0	0
"	SrO	< 1	< 1	0	0
"	Sr(NO ₃) ₂	0*	< 1	0*	0
"	H ₂ O	< 1*	0	0	0

Table 2 (Cont.)

Material Tested	Impurity Added	Depth of Metal Affected, mils			
		Chemical Attack		Change in Microstructure	
		1500 Hr	4400 Hr	1500 Hr	4400 Hr
TZM	NaF	<< 1*	<< 1	0*	0
"	MnF ₂	<< 1*	< 1	0*	0
"	PbF ₂	< 1	< 1	0	0
"	CuF ₂	2*	6	2*	6
"	FeF ₃	2*	3	2*	3
"	AlF ₃	<< 1	< 1	0	0
"	(Ca-Ba-Mg)F ₂	<< 1	<< 1	0	0
"	SrO	< 1	< 1	0	0
"	Sr(NO ₃) ₂	<< 1*	<< 1	0*	0
"	H ₂ O	< 1	<< 1	0	0

* Indicates couples accidentally overheated to 1200°C for about 4 hours.

TABLE 3
METAL ATTACK OBSERVED IN TESTS
WITH HIGH-PURITY NONRADIOACTIVE SrF₂

Material Tested	Test Temperature (°C)	Depth of Metal Affected, mils			
		Chemical Attack		Change in Microstructure	
		1500 Hr	4400 Hr	1500 Hr	4400 Hr
Hastelloy C-276	800	1	2	1	1
"	1000	4	7	1	2
"	1100	6	8	0	2
Hastelloy N	800	1	4	2	5
"	1000	3	3	5	5
"	1100	< 1	1	5	6
Hastelloy X	800	1	< 1	2	2
"	1000	1	1	2	1
"	1100	2	1	1	4
Haynes 25	800	<< 1	1	< 1	< 1
"	1000	<< 1	1	< 1	1
"	1100	<< 1	1	1	2
Haynes 188	800	2	1	2	2
"	1000	2	3	0	0
"	1100	2	4	1	1
Inconel 600	800	0	< 1	3	6
"	1000	< 1	< 1	5	7
"	1100	< 1	1	0	4
Inconel 625	800	1	1	1	2
"	1000	3	3	4	4
"	1100	2	3	0	0
TZM	800	0	0	0	0
"	1000	0	0	0	0
"	1100	0	0	0	0
Tungsten	800	0	0	0	< 1
"	1000	0	0	0	< 1
"	1100	0	0	0	< 1

LONG-TERM COMPATIBILITY TESTS

When all of the short-term test data have been evaluated, three of the nine materials tested will be selected for long-term compatibility testing. The long-term tests will be carried out for periods up to 4 years at temperatures of 800, 1000 and 1100°C. WESF produced $^{90}\text{SrF}_2$, as well as nonradioactive SrF_2 produced by the WESF flowsheet, will be used in the tests. The tests are designed to provide mechanical property data, as well as compatibility data, and are scheduled to begin in April 1975.

STRONTIUM FLUORIDE DISSOLUTION RATE STUDIES

Efforts are under way to measure the dissolution rate of $^{90}\text{SrF}_2$ in aqueous media. The measurements will be carried out using a dynamic (flow) system in which the test solution is flowed past $^{90}\text{SrF}_2$ granules and the exiting solution analyzed for its strontium content. The experimental procedure has been checked out using nonradioactive SrF_2 , SrTiO_3 and Sr_2TiO_4 . The tests with the nonradioactive compounds were carried out at $\sim 24^\circ\text{C}$ using demineralized water, plant tap water, synthetic seawater and natural seawater.

Several grades of nonradioactive SrF_2 , prepared by various methods, were evaluated in the tests. The materials tested are described in Table 4. The titanates used in the tests are also described in Table 4. The results obtained with the various fluorides are given in Table 5. With SrF_2 , the dissolution rate decreases initially with time and then reaches a constant level. The time required to reach a constant dissolution rate varied with the various samples tested, but never exceeded 24 hours. The rate data presented in Table 5 represent the equilibrium (constant) rates.

Nonradioactive SrF_2 shows a considerable variation in dissolution rate depending on surface area, composition, and thermal history. For a given solution, the dissolution rates for the various fluoride samples varied about one order of magnitude. Samples having approximately the same surface area (i.e., SR-1B, SR-3B and SR-3E) had substantially different dissolution rates indicating the effect of composition and thermal history on the dissolution rate.

TABLE 4
COMPOUNDS EVALUATED IN DISSOLUTION TESTS

Identification Number	Description of Material	Surface Area (cm ² /gram of compound)
SR-1A	SrF ₂ powder containing 0.5% impurities; fired at 1100°C for 20 hours; crushed to -1/4 in. +1/8 in. lumps.	370
SR-1B	SrF ₂ powder containing 0.5% impurities; fired at 900°C for 20 hours; crushed to -1/4 in. +1/8 in. lumps.	580
SR-2	Commercial SrF ₂ powder (99.5%); fired at 1100°C for 48 hours; crushed to -1/4 in. +1/8 in. lumps.	250
SR-3A	High-purity SrF ₂ powder (>99.9%); fired at 1100°C for 20 hours; crushed to -1/4 in. +1/8 in. lumps.	510
SR-3B	High-purity SrF ₂ powder (>99.9%); fused at 1500°C; crushed to -1/4 in. +1/8 in. lumps.	620
SR-3C	High-purity SrF ₂ powder (>99.9%); pressed into pellets at 70% TD; fired at 1100°C for 4 hours; crushed to -1/4 in. +1/8 in. lumps.	910
SR-3D	High-purity SrF ₂ powder (>99.9%); pressed to pellets at 70% TD; fired at 1100°C for 20 hours; crushed to -1/4 in. +1/8 in. lumps.	390
SR-3E	High-purity SrF ₂ powder (>99.9%) +10 wt% NaF; fired at 1100°C for 20 hours; crushed to -1/4 in. +1/8 in. lumps.	520
SR-4A	WESF-grade SrF ₂ powder; fired at 1100°C for 20 hours; crushed to -1/4 in. +1/8 in. lumps.	660
SR-4B	WESF-grade SrF ₂ powder; fired at 1100°C for 1 hour; crushed to -1/4 in. +1/8 in. lumps.	300

Table 4 (Cont.)

Identification Number	Description of Material	Surface Area (cm ² /gram of compound)
SR-4C	WESF-grade SrF ₂ powder; fired at 1100°C for 24 hours; crushed to -1/4 in. +1/8 in. lumps.	600
SR-4D	WESF-grade SrF ₂ powder; fired at 1100°C for 96 hours; crushed to -1/4 in. +1/8 in. lumps.	200
SR-5A	SrTiO ₃ powder; fired at 1450°C for 4 hours; crushed to -1/4 in. +1/8 in. lumps.	15,000
SR-5B	SrTiO ₃ powder; fired at 1450°C for 8 hours; crushed to -1/4 in. +1/8 in. lumps.	1,000
SR-6A	Sr ₂ TiO ₄ powder; fired at 1450°C for 4 hours; crushed to -1/4 in. +1/8 in. lumps.	12,000
SR-6B	Sr ₂ TiO ₄ powder; fired at 1450°C for 8 hours; crushed to -1/4 in. +1/8 in. lumps.	2,300
SR-7	SrF ₂ containing 2% Na, 0.63% Ba, 0.22% Ca and 0.14% Mg; fired at 1100°C for 16 hours; crushed to -1/4 in. +1/8 in. lumps.	400

TABLE 5

EQUILIBRIUM DISSOLUTION RATES OF SrF_2 IN AQUEOUS MEDIA AT 24°C*

SrF ₂ Sample Tested	μg Sr Dissolved/hr-g Sr Present				μg Sr Dissolved/hr-cm ² Of Surface			
	Demineralized Water	Tap Water	Synthetic Seawater	Natural Seawater	Demineralized Water	Tap Water	Synthetic Seawater	Natural Seawater
SR-1A	620	680	140	110	1.2	1.3	0.26	0.21
SR-1B	980	1200	210	350	1.2	1.4	0.25	0.42
SR-2	240	330	210**	150	0.64	0.92	0.59**	0.48
SR-3A	880			290	1.2			0.40
SR-3B	170	220	90	83	0.19	0.24	0.10	0.094
SR-3C	350	240	130	110**	0.27	0.18	0.080	0.086**
SR-3D	120			70**	0.21			0.13**
SR-3E	1200	430		280	1.5	0.58		0.38
SR-4A	140	170	76	60**	0.15	0.18	0.080	0.62**
SR-4B	67			30	0.16			0.070
SR-4C	140			96	0.17			0.11
SR-4D	120			60	0.42			0.21
SR-7	600**			150**	1.1**			0.25**

* Obtained using a dynamic (flow) system.

** Average of two experiments.

The dissolution rates of the strontium titanates tested decreased continuously with time throughout the tests, and failed to reach an equilibrium (constant) level even after several days exposure. The results obtained with the titanates are shown in Figures 1-4. One sample of Sr_2TiO_4 (SR-6B) in demineralized water showed an increase in the dissolution rate after about 40 hours exposure. Examination of the sample showed that the granules of material had begun to disintegrate to a fine powder with a resulting increase in surface area. Only the one sample exhibited such behavior.

Comparing the dissolution rates for the three nonradioactive compounds is difficult for two reasons: 1) the wide variations in dissolution rates for each compound depending on its composition, surface area and thermal history; and 2) the dissolution rates of the titanates change continuously with time. In Table 6, the maximum and minimum equilibrium dissolution rates measured with the various fluoride samples are compared with the instantaneous rates for the titanates after 20 hours exposure. The data show that, on a surface area basis, the dissolution rates for SrF_2 are much higher than those of SrTiO_3 , and about the same as those for Sr_2TiO_4 . On a contained strontium basis, the dissolution rates for the fluorides are somewhat higher than those for SrTiO_3 and substantially lower than those for Sr_2TiO_4 .

STRONTIUM FLUORIDE PHYSICAL PROPERTY MEASUREMENTS

Work is under way to measure the thermal expansion, heat capacity and thermal diffusivity of SrF_2 . The thermal conductivity will be calculated from the heat capacity and thermal diffusivity data. Three grades of nonradioactive SrF_2 are being tested:

1. High-purity SrF_2 (< 0.1 wt% total impurities).
2. Commercial SrF_2 (~ 0.5 wt% total impurities).
3. Simulated WESF SrF_2 containing ~ 4 wt% impurities (composition based on analysis of $^{90}\text{SrF}_2$ produced by the WESF flowsheet using ^{90}Sr solution obtained from ARHCO).

TABLE 6

A COMPARISON OF THE DISSOLUTION RATES OF SrF_2 , SrTiO_3 , AND Sr_2TiO_4 AT 24°C

Material	Dissolution Rate			
	Demineralized Water		Seawater	
	$\mu\text{g Sr/hr-g Sr}$	$\mu\text{g Sr/hr-cm}^2$	$\mu\text{g Sr/hr-g Sr}$	$\mu\text{g Sr/hr-cm}^2$
SrF_2 (minimum rate)*	67	0.15	30	0.05
SrF_2 (maximum rate)*	1200	1.59	350	0.48
SrTiO_3 (minimum rate)**	56	0.03	15	0.008
SrTiO_3 (maximum rate)**	510	0.16	110	0.036
Sr_2TiO_4 (minimum rate)**	850	0.23	670	0.12
Sr_2TiO_4 (maximum rate)**	4300	0.25	2000	0.18

* Represents the minimum and maximum dissolution rates (at equilibrium) observed with any of the SrF_2 samples.

** Differential dissolution rate after 20 hours exposure.

FIGURE 1. Dissolution Rate of SrTiO_3 in Demineralized Water and Seawater (in $\mu\text{g Sr}$ dissolved/hr-g Sr present)

FIGURE 2. Dissolution Rate of SrTiO_3 in Demineralized Water and Seawater (in $\mu\text{g Sr dissolved/hr-cm}^2$ of surface)

FIGURE 3. Dissolution Rate of Sr_2TiO_4 in Demineralized Water and Seawater (in $\mu\text{g Sr}$ dissolved/hr-g Sr present)

FIGURE 4. Dissolution Rate of Sr_2TiO_4 in Demineralized Water and Seawater (in $\mu\text{g Sr}$ dissolved/hr-cm² of surface)

The thermal expansion and heat capacity measurements have been completed and the data are now being evaluated. The results will be presented in the next report.

Problems have been encountered in the thermal diffusivity measurements. The procedure being used requires the use of thin fluoride pellets (~ 50 mils thick). It has been impossible to obtain reproducible results because of laminations in the test pellets. Work is now under way to prepare suitable pellets.

THERMODYNAMIC ANALYSIS OF $^{90}\text{SrF}_2$ COMPATIBILITY

Work is under way on a thermodynamic analysis of the compatibility of $^{90}\text{SrF}_2$ with various containment materials. The first system analyzed was $^{90}\text{SrF}_2$ -tungsten. Because of the large number of constituents in the system ($^{90}\text{SrF}_2$, decay products, contained impurities and tungsten), a rigorous analysis of the system would involve literally hundreds of reactions. Such an analysis is hampered by a lack of thermochemical data for most of the complex compounds which might be present in the system. In carrying out the analysis, certain simplifying assumptions were made in order to reduce the number of reactions to be considered to a manageable level:

1. The impurities and decay products in the $^{90}\text{SrF}_2$ are present as individual compounds and not as complex compounds or solid solutions with $^{90}\text{SrF}_2$ on each other.
2. The reaction products do not form complex compounds or solid solutions with the $^{90}\text{SrF}_2$, its decay products, contained impurities or each other.

These assumptions preclude the presence of complex fluorides, oxyfluorides, complex oxides and tungstates in the reaction system; and limit the reactions to be considered to those involving the simple fluorides, oxides and the corresponding metals.

Table 7 lists the impurities which will probably be present in WESF $^{90}\text{SrF}_2$ (and their expected concentration ranges). Since some oxygen is present in the $^{90}\text{SrF}_2$, it is possible that some of the cationic impurities could also be

TABLE 7
PROBABLE IMPURITIES IN WESF $^{90}\text{SrF}_2$

<u>Impurity</u>	<u>Probable Form</u>	<u>Concentration Range (wt%)</u>
Na	NaF	1 - 4
Ca	CaF_2	0.1 - 1.0
Ba	BaF_2	0.1 - 1.0
Mg	MgF_2	0.05 - 0.5
Mn	MnF_2	< 0.1
Fe	FeF_3	< 0.2
Pb	PbF_2	< 0.2
Cu	CuF_2	< 0.01
Al	AlF_3	< 0.5
Cr	CrF_3	< 0.2
Cd	CdF_2	< 0.1
Ni	NiF_2	< 0.1
K	KF	< 0.1
O_2	H_2O	< 0.05
H_2	H_2O	< 0.01
NO_3	$\text{Sr}(\text{NO}_3)_2$	< 0.05
Si	SiO_2	< 0.02
R*	RF_3	< 2.0

* Rare Earth

present as oxides. The $^{90}\text{SrF}_2$ -W system could also contain ZrF_4 , ZrF_2 , and Zr as decay products of $^{90}\text{SrF}_2$. Possible tungsten compounds in the system are WF_4 , WF_5 , WF_6 , WO_2 and WO_3 (the W-O system contains many intermediate oxide phases depending on temperature, but these are not considered). Therefore, the $^{90}\text{SrF}_2$ -W system could contain more than 20 elemental constituents and more than 40 simple fluoride and oxide compounds.

Free energy of formation data for the fluorides and oxides of interest are given in Tables 8-9. A comparison of the data in the two tables shows the tungsten should react with only a few of the fluorides or oxides which might be present in the system over the temperature range of interest (25-1200°C). Fluoride reactions which could theoretically proceed to an appreciable degree in a closed system, are limited to those involving the polyvalent ions (iron, copper and manganese). Any nickel, cadmium, lead or chromium fluorides present could react to a limited degree at higher temperatures. The tungsten could also react with the oxides of some of the cations tested if they are present in the $^{90}\text{SrF}_2$ (i.e., Cd, Cu, Fe, Mn, Ni and Pb). Fortunately, analytical data show that oxygen is present in the SrF_2 at low concentrations and is there primarily as water. The concentration of metal oxides in the fluoride, therefore, should be very low.

Thermodynamic calculations show that, if ZrF_2 or zirconium metal are present in the $^{90}\text{SrF}_2$ as decay products, they could reduce many of the impurity fluorides or oxides to the corresponding metals. The metals thus formed could alloy with the tungsten to form solid solutions or intermetallic compounds. The zirconium metal could also react directly with the tungsten to form ZrW_2 .

A more detailed discussion of the $^{90}\text{SrF}_2$ -W system and the related thermodynamic calculations are given in the October 1974 progress report.

PROGRAM PLAN

Space Nuclear Systems has reviewed the initial draft of the program plan and returned it to PNL for minor additions and changes. The program plan has been revised to accommodate these changes, and the final version of the plan has been submitted to SNS.

TABLE 8
FREE ENERGY OF FORMATION OF METAL FLUORIDES

Compound	$-\Delta G_f^\circ$, kilocalories/g-atom of fluorine					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
SrF ₂	138.0	127.2	122.5	119.0	117.5	115.5
ZrF ₂	109.0	99.0	95.5	92	90	88.5
ZrF ₄	108.0	97.0	93.3	91.0	90.0	89.0
AlF ₃	113.0	101.3	97.3	93.3	91.3	89.3
BaF ₂	137.0	125.0	122.0	118.5	117.0	115.5
CaF ₂	140.0	128.5	124.5	121.0	119.0	117.0
CdF ₂	76.5	66.0	62.5	56.0	53.0	50.0
CrF ₂	86.0	77.0	73.5	70.0	68.5	67.5
CrF ₃	83.3	73.3	70.0	67.0	65.0	63.7
CuF	56	48	45	43	43	42
CuF ₂	59.0	50.0	47.0	44.5	43.5	42.5
FeF ₂	79.0	69.5	66.5	63.5	62.0	60.5
FeF ₃	73.0	63.0	60.0	56.7	55.0	53.7
KF	129	114	109	102	99	95
MgF ₂	127.5	116.0	112.0	107.5	105.5	102.5
MnF ₂	90.0	80.5	77.5	75.5	74.5	73.5
MnF ₃	74.3	64.0	61.0	58.0	57.0	56.0
NaF	129	115	110	104	101	97
NiF ₂	73.5	64.0	61.0	58.0	56.5	55.0
PbF ₂	73.5	62.0	58.5	55.0	54.0	52.5
WF ₄	57.5	48.25	46.7	45.25	44.5	43.7
WF ₅	52.0	47.2	46.4	45.4	44.6	43.8
WF ₆	46.8	41.0	38.8	36.7	35.7	34.7
RF ₃ *	130.7	120	117.0	113.2	111.0	109.1
HF	65	65.3	65.9	66.2	66.5	67

* RF₃ Rare earth fluoride - typically NdF₃

TABLE 9
FREE ENERGY OF FORMATION OF METAL OXIDES

Compound	$-\Delta G_f^\circ$, kilocalories/g-atom of oxygen					
	25°C	600°C	800°C	1000°C	1100°C	1200°C
SrO	134	121	116	111	103	106
ZrO ₂	123.0	110.0	105.0	101.0	99.0	97.0
Al ₂ O ₃	126.0	112.0	106.0	101.0	99.0	96.0
BaO	129	116	111	105	103	100
CaO	144	131	126	121	118	116
CdO	54	41	36	25	20	16
Cr ₂ O ₃	83.0	71.0	67.0	63.0	61.0	59.0
Cu ₂ O	35.0	24.0	21.0	18.0	16.0	14.0
CuO	30	19	15	11	9	7
FeO	58	49	46	43	42	40
Fe ₃ O ₄	59.7	49.0	45.3	41.3	39.3	37.5
Fe ₂ O ₃	59.0	48.0	43.0	39.0	37.0	35.0
K ₂ O	76.0	58.0	52.0	44.0	40.0	36.0
MgO	137	122	117	112	109	104
MnO	87	77	73	70	68	66
Mn ₃ O ₄	77.0	64.0	60.0	56.0	53.0	52.0
Mn ₂ O ₃	72.0	59.0	55.0	51.0	49.0	47.0
Na ₂ O	90.0	70.0	64.0	51.0	46.0	40.0
NiO	52	38	33	29	26	24
PbO	45	31	26	23	21	19
SiO ₂	102.0	90.0	86.0	81.0	79.0	77.0
WO ₂	63.5	53.5	49.5	46.0	44.0	42.0
WO ₃	60.7	49.3	45.7	42.0	40.0	38.0
R ₂ O ₃ *	137.0	125.0	121.0	117.0	115.0	113.0
H ₂ O	55.0	48.0	45.0	42.0	41.0	39.0

* R₂O₃ Rare earth oxide - typically Nd₂O₃

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