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PACIFIC NORTHWEST LABORATORY
MONTHLY REPORT
ON SPACE NUCLEAR SYSTEMS PROGRAM
FOR NOVEMBER 1974

Battelle

Pacific Northwest Laboratories
Richland, Washington 99352

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by
H. T. Fullam

December 1974

BATTELLE
PACIFIC NORTHWEST LABORATORIES
RICHLAND, WASHINGTON 99352

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STRONTIUM HEAT SOURCE DEVELOPMENT PROGRAM

At Hanford, strontium will be separated from the high-level waste, then 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). This 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 4400-hr 1000°C tests with high-purity SrF_2 , containing controlled levels of added impurities, have been completed and photomicrographs of the test specimens obtained. Analysis of selected couples by electron microprobe (EM) and scanning electron microscope (SEM) is now underway and will be completed in December. Estimates of metal attack for the 1500- and 4400-hr couples (based on the photomicrographs) are presented in Table 1. Attack of the superalloys by the various SrF_2 mixtures consisted almost entirely of changes in the microstructure (principally precipitate formation). There was little evidence of intergranular attack, subsurface void

TABLE 1. Preliminary Estimates of Metal Attack Found in Couples Containing High-Purity SrF_2 with Controlled Levels of Impurities Added - Tests Carried Out at 1000°C

Metal	Impurity Added	Depth of Metal Affected, mils**	
		1500 Hours	4400 Hours
TZM	NaF	<< 1*	<< 1
"	MnF ₂	<< 1*	< 1
"	PbF ₂	< 1	< 1
"	CuF ₂	2*	6
"	FeF ₃	2*	3
"	AlF ₃	<< 1	< 1
"	(Ca-Ba-Mg)F ₂	<< 1	<< 1
"	SrO	< 1	< 1
"	Sr(NO ₃) ₂	<< 1*	<< 1
"	H ₂ O	< 1	<< 1
Tungsten	NaF	<< 1	< 1
"	MnF ₂	< 1*	< 1
"	PbF ₂	0*	< 1
"	CuF ₂	2	< 1
"	FeF ₃	<< 1	< 1
"	AlF ₃	0*	< 1
"	(Ca-Ba-Mg)F ₂	<< 1	< 1
"	SrO	< 1	< 1
"	Sr(NO ₃) ₂	0*	< 1
"	H ₂ O	< 1*	0
Hastelloy-X	NaF	3	2
"	MnF ₂	4	5
"	PbF ₂	3*	4
"	CuF ₂	30*	12
"	FeF ₃	12	22
"	AlF ₃	4	3
"	(Ca-Ba-Mg)F ₂	3*	4
"	SrO	15*	10
"	Sr(NO ₃) ₂	5*	4
"	H ₂ O	4*	5

* Indicated specimens overheated to 1200°C for about 4 hours.

** Estimated from photomicrographs.

TABLE 1. (contd)

Metal	Impurity Added	Depth of Metal Affected, mils**	
		1500 Hours	4400 Hours
Hastelloy-N	NaF	4	6
"	MnF ₂	2	5
"	PbF ₂	3	3
"	CuF ₂	6	20
"	FeF ₃	12	15
"	AlF ₃	3	3
"	(Ca-Ba-Mg)F ₂	3	4
"	SrO	25	35
"	Sr(NO ₃) ₂	2*	15
"	H ₂ O	2*	5
Hastelloy C-276	NaF	3*	3
"	MnF ₂	3	4
"	PbF ₂	2*	3
"	CuF ₂	8	15
"	FeF ₃	3	8
"	AlF ₃	2*	4
"	(Ca+Ba+Mg)F ₂	3	3
"	SrO	12	10
"	Sr(NO ₃) ₂	4*	10
"	H ₂ O	6*	6
Inconel 600	NaF	1*	1
"	MnF ₂	5	3
"	PbF ₂	3	1
"	CuF ₂	3	8
"	FeF ₃	6*	8
"	AlF ₃	< 1	1
"	(Ca+Ba+Mg)F ₂	3	1
"	SrO	20	10
"	Sr(NO ₃) ₂	3*	2
"	H ₂ O	1*	1
Inconel 625	NaF	3	12
"	MnF ₂	8	10
"	PbF ₂	4*	6
"	CuF ₂	6*	12
"	FeF ₃	6*	13
"	AlF ₃	3	6
"	(Ca+Ba+Mg)F ₂	5*	10
"	SrO	10*	18
"	Sr(NO ₃) ₂	5*	10
"	H ₂ O	3	6

TABLE 1. (contd)

Metal	Impurity Added	Depth of Metal Affected, mils**	
		1500 Hours	4400 Hours
Haynes 25	NaF	3	2
"	MnF ₂	3*	3
"	PbF ₂	4	3
"	CuF ₂	12*	18
"	FeF ₃	10*	20
"	AlF ₃	3	4
"	(Ca+Ba+Mg)F ₂	2	1
"	SrO	5	7
"	Sr(NO ₃) ₂	5*	2
"	H ₂ O	1	1
Haynes 188	NaF	< 1	3
"	MnF ₂	6*	5
"	PbF ₂	6	3
"	CuF ₂	12*	13
"	FeF ₃	12	7
"	AlF ₃	< 1	2
"	(Ca+Ba+Mg)F ₂	< 1	3
"	SrO	12	20
"	Sr(NO ₃) ₂	4*	5
"	H ₂ O	4*	2

formation or pitting, and only limited surface attack; except for the couples containing SrO. In every case the SrO-superalloy couples exhibited extensive intergranular attack.

Work is underway on the examination of the 51 ⁹⁰SrF₂ compatibility samples shipped to ORNL. By the end of November approximately 20 samples had been examined and the photomicrographs obtained. ORNL is doing an excellent job of analyzing the samples and the work should be completed in January.

STRONTIUM FLUORIDE DISSOLUTION RATE STUDIES

The dissolution rate studies with nonradioactive SrF_2 , SrTiO_3 and Sr_2TiO_4 have been completed. The materials tested, their method of preparation and surface areas are described in Table 2. The equilibrium dissolution rates for the various grades of SrF_2 are given in Table 3. The data for the titanates are given in Figures 1 through 4. All the dissolution rate data were obtained with the dynamic (flow) system.

The distrontium titanate sample (SR-6B) was unstable in demineralized water and after about 40 hours exposure the lumps of material began to disintegrate with a resulting increase in dissolution rate. This disintegration was not observed in seawater. None of the other titanate or fluoride samples exhibited such behavior; except for the SrF_2 sample SR-3E which contained a large amount of NaF. Cause of the disintegration of the Sr_2TiO_4 in demineralized water has not been determined.

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 tested varied about one order of magnitude. Even samples having about the same surface area showed a wide variation in dissolution rate indicating the effect of composition and thermal history on dissolution.

To determine the effect of thermal exposure on the surface area of SrF_2 , samples of WESF grade SrF_2 powder (-100 mesh) were fired at 1100°C for varying periods of time. Each sample was then crushed and the surface area of the $-1/4 +1/8$ in. fraction was determined. The results obtained are shown in Table 4. The surface area increased with increasing time at temperature up to about 20 hours, and then decreased upon further heating. The sample held for 96 hours had a completely different appearance from the sample heated for shorter periods. The 96-hr sample looked like solidified foam with little visual evidence of individual particles. The samples heated for shorter periods of time (≤ 24 hours) had the typical appearance of partially sintered powders. The reason for the difference between the samples has not been determined, but is under investigation.

TABLE 2. 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 2. (contd)

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 3. Equilibrium Dissolution Rate^(a) of SrF_2 in Aqueous Media at 24°C

SrF ₂ Tested	Dissolution Rate							
	μg Sr Dissolved/hr - g Sr				μg Sr Dissolved/hr - cm ²			
	Demineral. Water	Tap Water	Synthetic Seawater	Natural Seawater	Demineral. Water	Tap Water	Synthetic Seawater	Natural Seawater
SR-1A	620 ± 40	680 ± 80	140 ± 47	110 ± 16	1.2 ± 0.07	1.3 ± 0.15	0.26 ± 0.09	0.21 ± 0.03
SR-1B	980 ± 120	1160 ± 240	210 ± 43	350 ± 240	1.2 ± 0.15	1.4 ± 0.28	0.25 ± 0.05	0.42 ± 0.02
SR-2	235 ± 17	330 ± 200	220 ± 27 200 ± 42	150 ± 47	0.64 ± 0.05	0.92 ± 0.56	0.61 ± 0.08 0.56 ± 0.12	0.48 ± 0.13
SR-3A	880 ± 190			290 ± 64	1.20 ± 0.26			0.40 ± 0.088
SR-3B	170 ± 30	220 ± 30	90 ± 22	83 ± 4	0.19 ± 0.03	0.24 ± 0.03	0.10 ± 0.02	0.094 ± 0.005
SR-3C	350 ± 40	240 ± 26	130 ± 40	120 ± 17 100 ± 15	0.27 ± 0.03	0.18 ± 0.02	0.080 ± 0.03	0.092 ± 0.01 0.080 ± 0.01
SR-3D	120 ± 21			52 ± 30 89 ± 24	0.21 ± 0.038			0.092 ± 0.05 0.160 ± 0.09
SR-3E	1200 ± 140	430 ± 100		280 ± 66	1.5 ± 0.19	0.58 ± 0.13		0.38 ± 0.088
SR-4A	140 ± 24	170 ± 29	76 ± 27	50 ± 14 67 ± 26	0.15 ± 0.03	0.18 ± 0.03	0.080 ± 0.03	0.053 ± 0.01 0.071 ± 0.027
SR-4B	67 ± 34			30 ± 13	0.16 ± 0.079			0.070 ± 0.030
SR-4C	140 ± 20			96 ± 14	0.17 ± 0.023			0.11 ± 0.017
SR-4D	120 ± 53			60 ± 14	0.42 ± 0.18			0.21 ± 0.049
SR-7	910 ± 280 300 ± 42			150 ± 40 140 ± 20	1.59 ± 0.49 0.52 ± 0.07			0.26 ± 0.070 0.24 ± 0.034

(a) Obtained using a dynamic (flow) system.

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 $\mu\text{g Sr}^{2+}$ dissolved/hr-cm² of surface)

TABLE 4. The Surface Area of WESF Grade SrF_2

As A Function Of Time At Held At 1100°C

Time at 1100°C (hours)	Particle Size	Surface Area - cm^2/g
1	-1/4" + 1/8"	300
4	-1/4" + 1/8"	400
8	-1/4" + 1/8"	500
20	-1/4" + 1/8"	660
24	-1/4" + 1/8"	600
96	-1/4" + 1/8"	200

The sample of WESF grade SrF_2 which has been fired at 1100°C for 4 hours was crushed and the surface area of various size fractions determined. The results obtained are presented in Table 5. The surface area generally increased with decreasing particle size as expected.

TABLE 5. Surface Area of WESF Grade SrF_2 Fired at 1100°C for 4 Hours as a Function of Particle Size

Particle Size	Surface Area - cm^2/g
-1/4" + 1/8"	400
-1/8" + 40 mesh	300
-40 + 70	800
-70 + 140	800
-140 + 200	2400
-200	2100

Comparing the dissolution rates of SrF_2 , SrTiO_3 and Sr_2TiO_4 is difficult for two reasons: 1) the wide variations in dissolution rates for each compound depending on its method of preparation, surface area, and thermal history; and 2) the dissolution rates of the titanates change continually with time. In Table 6 the maximum and minimum dissolution rates observed for SrF_2 are compared with the differential dissolution rates for the titanates after 20 hours exposure. The data show that on the basis of contained strontium the dissolution rates for SrF_2 are somewhat higher than those of SrTiO_3 and substantially lower than those of Sr_2TiO_4 . 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 .

PROGRAM PLAN

SNS has reviewed the initial draft of the program plan and returned it to BNW for minor additions and changes. Preparation of the final draft is now underway and will be completed in December.

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.

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