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**Pacific Northwest Laboratory
Monthly Report to Space
Nuclear Systems Division
for April 1975**

by H. T. Fullam

May 1975

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ERRATA FOR APRIL PROGRESS REPORT (BNWL-1845-10)

1. Page 8 - Lines 11-13 should read "At the higher temperatures, the WESF-grade SrF_2 showed the highest diffusivity, the commercial-grade the lowest values, and the high-purity grade intermediate values."
2. Page 9 - Figure 3 - The scale on the ordinate is incorrect with the zero point (base line) displaced two units.
3. Page 12 - Line 2 - The definition for λ should read "where λ is the thermal conductivity in cal/cm-°C-sec".

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PACIFIC NORTHWEST LABORATORY MONTHLY REPORT
TO SPACE NUCLEAR SYSTEMS DIVISION FOR APRIL 1975

By
H. T. Fullam

May 1975

Battelle
Pacific Northwest Laboratories
Richland, Washington 99352

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PACIFIC NORTHWEST LABORATORY
MONTHLY REPORT
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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

Work continues on preparation of the topical report covering the short-term compatibility tests.

LONG-TERM COMPATIBILITY TESTS

All hardware and materials (except $^{90}\text{SrF}_2$) required for the long-term compatibility tests are being assembled. Startup of the tests is being delayed until the fall of 1975 when fuel-grade WESF $^{90}\text{SrF}_2$ will be available.

THERMAL PROPERTIES OF SrF_2 (G. B. Mellinger and J. L. Bates)

The thermal properties of SrF_2 are important in evaluating the thermal conditions of encapsulated, radioactive SrF_2 . The purpose of this study was to measure the specific heat, thermal expansion, and thermal diffusivity of strontium fluoride as a function of temperature. Since the radioactivity associated with $^{90}\text{SrF}_2$ does not affect these properties significantly, the measurements were made using nonradioactive SrF_2 .

Three grades of nonradioactive strontium fluoride were used in the measurements.

1. High-purity SrF_2 containing less than 1000 ppm total impurities.
2. Commercial SrF_2 containing approximately 0.5 wt% impurities (Na, Ca, Ba, and $\text{SO}_4^{=}$ were the principal impurities).
3. WESF-grade SrF_2 - A mixture of fluorides approximating the composition of WESF-produced $^{90}\text{SrF}_2$ (contains approximately 5% impurities).

Each grade of fluoride was fired at 1100°C for 16 hr in air and ball milled to -100 mesh prior to use.

Sample Preparation

The SrF_2 samples were prepared by pressing SrF_2 powder into discs and right cylinders with subsequent sintering in air. The powders were initially pressed at 4000, 12,000, and 20,000 psi and sintered at 800°C . Other samples were pressed at 43,700 psi and sintered at 1000°C . Discs, 0.635 cm in diameter and 0.050 cm thick, were used for thermal diffusivity and heat capacity measurements. Right cylinders, approximately 1.9 cm long and 0.635 cm in diameter, were used for measuring the thermal expansion.

Property measurements were complicated by sample changes which occurred during heating at the higher temperatures, and from laminations in the sample discs. In order to obtain consistent heat capacity results,

the SrF_2 discs were heated in air at 500°C for 2 hr. This eliminated the presence of unknown constituents thought to be water vapor or organic die lubricant (used in pressing the samples). Heat capacity measurements were made after heating and with minimum exposure to the atmosphere. The thermal diffusivity samples were laminated as fabricated and easily broke when hand-ground to the desired disc thicknesses. Ultimately, the new samples without lamination were fabricated by being pressed at 43,271 psi and sintered at 1000°C . Thermal diffusivity samples were coated with graphite to minimize penetration of the laser beam optical path from the detector beyond the sample surface into the solid.

Specific Heat

The specific heats of the SrF_2 were measured using a differential scanning calorimeter. A sample disc was subjected to a linear temperature increase with the heat flow into the sample and a reference being continuously measured. Under these conditions, the heat flow is proportional to the instantaneous specific heat of the sample. Two holders are mounted symmetrically inside an enclosure initially at room temperature. The temperature control system controls the average temperature of the two holders with platinum resistance thermometers and with resistance heating elements embedded in the holders. A secondary temperature control system measures the difference between the two holders and adjusts this difference to zero by controlling a differential component of the total heating power. This differential power is measured. Knowing the constants of the system and the temperature rate change, the specific heat can be calculated. The absolute determination of these parameters can be eliminated if a material of known specific heat is placed in the reference holder. This reference is then used to calibrate the instrument. A specific heat of $\alpha\text{-Al}_2\text{O}_3$ is known to five significant figures between 0° and 1200°K . For this study, an $\alpha\text{-Al}_2\text{O}_3$ single crystal was used to calibrate the calorimeter. The data indicate an error of less than 2%.

Specific heats were measured from 320° to 710°K for commercial-grade, WESF-grade and high-purity SrF₂ using specimens pressed at 2 and 10 tons.

The specific heats of the three grades of SrF₂ are shown in Figure 1. The specific heat of the samples pressed at 2 and 10 tons were the same within experimental error. All three compositions showed an increase in heat capacity with increasing temperature reaching a near-constant value above 500°K. The initial values at 320°K, constant heat capacity values, and the temperatures where C_p approaches a constant for each SrF₂ sample are tabulated in Table I. The final values were the same for all three SrF₂ samples within experimental errors. Scatter in the data was observed at higher temperatures. This is attributed to irregularities in the heating system which occurred after replacement of heating elements which had failed.

TABLE I. Specific Heat of Strontium Fluoride

Grade of SrF ₂	Initial C _p cal/g -°C	at T, °K	Final C _p cal/g -°C	at T, °K
Commercial	0.1330	320	0.1510 ± 0.0025	560
WESF-Grade	0.1395	320	0.1537 ± 0.0015	520
High-Purity	0.1340	320	0.1510 ± 0.0010	560

Thermal Expansion

The thermal expansion of the commercial-grade, WESF-grade, and high-purity SrF₂ were measured from near room temperature to 700°C. Each sample was measured twice, except for the high-purity which was measured three times.

Measurements were made using a quartz push rod dilatometer. The temperature was increased linearly with a proportional controller and programmer. The increase in length of the sample was measured with a transducer positioned at one end of the quartz push rod. The transducer signal can be recorded to ±0.017% (0.07% for 1.90 cm long sample).

The samples were 1.90 cm long and 0.64 cm in diameter. Each end of the sample was machined with a rounded end to maintain alignment. The width and length of each sample were measured before and after the thermal expansion tests.

FIGURE 1. Specific Heat of SrF_2

Data points were calculated at $\sim 50^\circ\text{C}$ intervals from the continuous sample length and temperature curves. Changes in sample composition, presumably due to fluoride or other vapor loss occurred above 750°C for all three compositions. This prevented measurements to higher temperatures and resulted in irregularities in expansion results.

The thermal expansion data is shown in Figure 2. The apparent decrease in expansion coefficient above 600°C in the commercial-grade is apparently due to composition changes. The greatest expansion is exhibited by the WESF-grade SrF_2 . The values for the linear thermal expansion coefficient are tabulated in Table II.

TABLE II. Thermal Expansion Coefficients of SrF_2

<u>Composition</u>	<u>Linear Thermal Expansion</u>	
	<u>Coefficient</u> <u>($\text{cm}/\text{cm}-^\circ\text{C} \times 10^5$)</u>	<u>T, $^\circ\text{C}$</u>
High-Purity	2.13	$50^\circ - 700^\circ\text{C}$
WESF-Grade	2.19	$50^\circ - 700^\circ\text{C}$
Commercial	1.83	$50^\circ - 700^\circ\text{C}$

Thermal Diffusivity and Thermal Conductivity

The thermal diffusivities of the three SrF_2 samples were measured using the pulsed laser technique. One surface of a thin sample disc, 0.064 cm thick was heated with a short 3-7 joule heat pulse from a ruby laser. A heat pulse produced on the sample surface passed through the sample, and the temperature transient on the back surface of the sample was measured. The temperature change was displayed on an oscilloscope recorded on a photograph. The thermal diffusivity was determined from the shape of the temperature-versus-time curve. The over-all accuracy for measuring the tracing from the photograph is estimated to be $\pm 2\%$.

The samples were heated in a resistance-heated furnace under 1 atmosphere of Argon. The temperature was measured with a W-5% Re versus W-26% Re thermocouple positioned on the adjacent sample holder and calibrated against a Pt-Pt 10% Rh thermocouple. The estimated accuracy of the temperature measurement was $\pm 3^\circ\text{C}$.

FIGURE 2. Thermal Expansion of SrF₂

The thermal diffusivities of the three grades of SrF_2 are shown in Figures 3, 4, and 5. The diffusivity values for the three samples at various temperatures are tabulated in Table III. Data are shown for WESF-grade and high-purity samples pressed at 45,271 psi and sintered at 1000°C , and a commercial-grade sample pressed at 4000 psi and sintered at 800°C . Data for a high-purity sample pressed at 12,000 psi and sintered at 800°C is also included. Inspection of this sample, however, showed extensive laminations which were not present in the other samples. All three unlaminated samples show the same general behavior. The thermal diffusivity decreased with increased temperature at the lower temperatures. This rate decreased as the temperature increased from 50 to 850°C . At the higher temperatures, the WESF-grade SrF_2 showed the highest diffusivity, the commercial-grade intermediate values, and the high-purity the lowest values. However, these differences between the three SrF_2 samples without lamination are small and could represent differences in fabrication as well as composition. For example, the laminated high-purity sample showed a consistently lower diffusivity than the unlaminated sample, with the values for both samples approaching each other at the higher temperatures. Thus, the thermal diffusivity of the SrF_2 in the projected heat source will probably be affected more by the laminations and voids present in the material than by differences in composition.

TABLE III. Thermal Diffusivity of SrF_2

T, $^\circ\text{C}$	Thermal Diffusivity (α) $\times 10^3$, $\text{cm}^2/^\circ\text{C}$		
	Commercial-Grade	WESF-Grade	High-Purity
100	19.4	20.0	21.0
350	9.7	11.2	11.0
600	6.4	7.8	7.0
850	4.6	5.9	4.9

The thermal conductivity of a material was calculated from the product of the thermal diffusivity, heat capacity, and density.

FIGURE 3. Thermal Diffusivity versus Temperature for Commercial-Grade SrF_2

$$\lambda = \alpha \cdot C_p \cdot \rho$$

where λ is the thermal conductivity in watts/cm-°C,
 α is the thermal diffusivity in cm²/sec,
 C_p is the heat capacity in cal/g-°C, and
 ρ is the density in g/cm³

The values for C_p were obtained from the previously measured C_p . It was assumed that the C_p remained constant at the higher temperature above 500°C.

The density for thermal expansion was obtained from sample geometric measurements and sample weights. The following expression for density was used to calculate the thermal conductivity:

$$\rho_T = \frac{\rho_o}{\left(1 + \frac{\Delta l}{l_o}\right)^3}$$

where ρ_T (g/cm³) is the density at temperature T,
 ρ_o (g/cm³) is the density at room temperature, and
 $\frac{\Delta l}{l_o}$ is the linear expansion at temperature T.

The calculated thermal conductivities are shown in Figure 6 as $1/\lambda$ versus T (where $1/\lambda$ is the thermal resistivity). The equation for the thermal conductivity versus temperature was expressed as $1/\lambda = A + BT$, where A and B are constants. The WESF-grade and commercial-grade showed linear behavior within experimental error over the entire temperature range. The high-purity sample, however, exhibited a break in the $1/\lambda$ versus T curve near 400°C. Two linear relationships were given to these regions. The constants A,B for the unlaminated SrF₂ are shown in Table IV and appear accurate to about 7%.

TABLE IV. Values of Constants for Equations of Thermal Resistivity Plots ($1/\lambda = A + BT$)

<u>Composition</u>	<u>A</u>	<u>B</u>	<u>Temperature Range</u>
Commercial	9.8	0.098	50° - 850°C
WESF-Grade	13.3	0.069	50° - 850°C
High-Purity	15.4	0.067	150° - 400°C
	0.6	0.104	400° - 850°C

FIGURE 6. Thermal Resistivity as a Function of Temperature for Various Grades of SrF_2

DISSOLUTION RATE STUDIES

The effect of temperature on the dissolution rate of nonradioactive SrF_2 in demineralized water and seawater is being determined using the dynamic procedure described previously (BNWL-1845-3). Two grades of SrF_2 are being studied. The compositions and thermal history of the fluoride samples are described in Table V.

TABLE V. Strontium Fluoride Used in Dissolution Studies

Identification Number	Description of Material	Surface Area $\text{cm}^2/\text{g SrF}_2$
SR-3B	High-purity SrF_2 (<0.1% total impurities) fused at 1550°C , crushed to $-1/4"$ $+1/8"$ granules.	620
SR-8A	WESF-grade SrF_2 powder* fused at 1550°C crushed to $-1/4"$ $+1/8"$ granules.	NA
SR-8B	WESF-grade SrF_2 powder* fired at 1100°C for 1 hr, crushed to $-1/4"$ $+1/8"$ granules.	440
SR-8C	WESF-grade SrF_2 powder* fired at 1100°C for 16 hr, crushed to $-1/4"$ $+1/8"$ granules.	NA

*Composition corresponds to expected composition of WESF-produced $^{90}\text{SrF}_2$ ($\sim 95.5\%$ purity).

NA - Not Yet Available

The tests in demineralized water are being carried out at temperatures from 3 to 81°C , while the tests in seawater range from 3 to 24°C . Results obtained to date are presented in Table VI. As expected, the dissolution rate increased as the temperature increased. The precision of the data was relatively poor and several of the experiments will be repeated.

TABLE VI. Effect of Temperature on the Dissolution Rate of Nonradioactive Strontium Fluoride

Temp. (°C)	Dissolution Rate, $\mu\text{g Sr/hr-g Sr Present}$							
	Demineralized Water				Seawater			
	SR-3B	Sr-8A	SR-8B	SR-8C	SR-3B	SR-8A	SR-8B	SR-8C
3	83	74	73	93	--	--	--	--
9	99	77	76	96	47	36	44	51
24	170	--	100	--	83	--	--	--
35	401	360	300	500	--	--	--	--
61	760	680	680	740	--	--	--	--
81	2460	1960	1920	2420				

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