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The Solubility and Dissolution Behavior of $^{90}SrF_2$ in Aqueous Media

by
H. T. Fullam

November 1976

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ABSTRACT

The ERDA-sponsored Strontium Heat Source Development Program is currently underway at PNL to obtain the data needed to license radioactive $^{90}SrF_2$ for terrestrial heat source applications. One phase of the program involved the experimental determinations of the solubility and dissolution rate of $^{90}SrF_2$ and nonradioactive SrF_2 in aqueous media at various temperatures.

The solubility of strontium fluoride in demineralized water and seawater at 23°C was determined to be approximately 0.14 g/ℓ. The presence of soluble fluoride impurities in the SrF_2 caused a marked decrease in the solubility of SrF_2 in demineralized water, but had little effect on the solubility in seawater.

The data show the dissolution rate of nonradioactive SrF_2 in aqueous solution is affected by several properties of the fluoride including its surface area, impurity content and thermal history, as well as the nature and temperature of the aqueous solvent. In demineralized water at 24°C the dissolution rate varied from 32 to 1900 μg strontium dissolved/hr-g strontium initially present depending upon the properties of the SrF_2. The dissolution rate increased with increasing solvent temperature as expected. The $^{90}SrF_2$ dissolved up to 18 times faster than nonradioactive SrF_2 of similar composition and thermal history; and overall, the dissolution rate of strontium fluoride was about three times greater in demineralized water than in natural seawater.

Previous terrestrial applications of ^{90}Sr in heat sources used $SrTiO_3$ or Sr_2TiO_4 as the fuel form. Comparison of available data on radioactive and inert SrF_2, $SrTiO_3$ and Sr_2TiO_4 indicate that the relative dissolution rates in aqueous media are $Sr_2TiO_4 > SrF_2 > SrTiO_3$.

In assessing the dissolution behavior of $^{90}SrF_2$ it appears that the solubility and dissolution rate are sufficiently high that adequate containment must be assured to prevent contact of the $^{90}SrF_2$ fuel with water if a heat source is accidentally exposed to an aqueous environment.

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THE SOLUBILITY AND DISSOLUTION BEHAVIOR OF $^{90}SrF_2$ IN AQUEOUS MEDIA

1.0 INTRODUCTION

A significant fraction of the heat generated by the discharged fuel from nuclear reactors results from the radioactive decay of the fission product ^{90}Sr. Because of its relative abundance, moderately long half-life ($T_{1/2}$ = 28.6 yr), and heat output (0.93 watts/g) the ^{90}Sr is a candidate fuel for radioisotope power generation systems in terrestrial applications. To date, terrestrial applications for ^{90}Sr have used strontium titanate ($SrTiO_3$) or strontium orthotitanate (Sr_2TiO_4) as the fuel form.

At Hanford strontium is recovered from the high-level waste generated in the fuel reprocessing operation and consists of a mixture of the desired radioactive isotope ^{90}Sr and stable strontium isotopes. Freshly discharged reactor fuel also contains the radioactive isotopes ^{89}Sr ($T_{1/2}$ = 50.5 days) and ^{91}Sr ($T_{1/2}$ = 9.48 hr), but these isotopes have usually decayed to very low levels by the time the strontium is recovered from the fuel reprocessing wastes. The ^{90}Sr isotopic content of the strontium will depend on the age of the wastes from which the strontium is recovered. A typical isotopic analysis of strontium recovered from recent Hanford wastes is shown in Table 1.

TABLE 1. Typical Isotopic Analysis of Strontium Recovered from Hanford Wastes

Isotope	at.%[(a)]
^{90}Sr	55.1 ± 0.4
^{88}Sr	43.8 ± 0.4
^{87}Sr	0.398 ± 0.004
^{86}Sr	0.565 ± 0.006
^{84}Sr	0.103 ± 0.006

(a) at the 95% confidence level

In this report strontium recovered from the fuel reprocessing wastes will be referred to as ^{90}Sr even though the ^{90}Sr isotopic content is 55% or less. Similarly, compounds prepared from the recovered strontium will be referred to as ^{90}Sr compounds (i.e., $^{90}SrF_2$, $^{90}SrTiO_3$).

If the strontium is to be used as a heat source fuel, the ^{90}Sr content should be as high as possible to maximize the power density. Fuel-grade strontium compounds are generally considered to be materials having a ^{90}Sr isotopic content of 50% or higher at the time of encapsulation.

As part of the current waste management programs at Hanford, ^{90}Sr which is recovered from stored high-level fuel reprocessing waste, is purified and converted to strontium fluoride. The fluoride is doubly encapsulated in a Hastelloy C-276 inner capsule and 316L stainless steel outer capsule for subsequent storage underwater. The strontium recovery and purification take place in B-Plant, while the fluoride conversion, encapsulation and storage take place in the Waste Encapsulation and Storage Facility (WESF). Both facilities are operated for the Energy Research and Development Administration (ERDA) by the Atlantic Richfield Hanford Company (ARHCO).

The encapsulated $^{90}SrF_2$ produced at WESF represents a potentially economic heat source fuel for radioisotope power generation if it can be licensed by the necessary national and international agencies. The Strontium Heat Source Development Program is currently underway at the Pacific Northwest Laboratories (PNL) to develop the data needed to license $^{90}SrF_2$ for use in terrestrial applications, primarily as the fuel in heat sources for dynamic and static power conversion systems. Other potential applications include use of the $^{90}SrF_2$ sources as thermal conditioners in cold regions. The work at PNL is sponsored by ERDA's Division of Nuclear Research and Applications. The program was started in FY 1973 and will continue through FY 1980. The principal areas where additional data are needed include:

- $^{90}SrF_2$ chemical and physical properties,
- $^{90}SrF_2$-clad compatibility, and

- heat source capsule design, fabrication and qualification.

Efforts are proceeding concurrently at PNL in all three areas.

An important property of any proposed radioisotope heat source fuel, with regard to safety and licensing considerations, is its dissolution behavior and release of radioactivity if accidentally exposed to an aqueous environment. The solubility of the fuel form must also be considered, but this fundamental property is only of interest if it serves to limit the dissolution and dispersal of the radioisotope in the aqueous environment. Strontium-90 is an extremely toxic material; therefore, the release behavior of ^{90}Sr from the fuel form, should it be accidentally exposed to water, is a very important factor in evaluating the fuels potential applicability for terrestrial power generation systems.

Some work on the dissolution behavior of strontium fluoride was carried out a number of years ago by Gray(1) at the Martin Company, Nuclear Division but the studies were limited to nonradioactive SrF_2 spiked with low levels of ^{85}Sr tracer. Additional information was needed on the dissolution characteristics of strontium fluoride, especially the $^{90}SrF_2$ produced at WESF. This report summarizes the results of experimental studies at PNL to determine the dissolution behavior of $^{90}SrF_2$ in aqueous media. The dissolution behavior of $SrTiO_3$ and Sr_2TiO_4 was also studied briefly to permit a comparison of the dissolution behavior of the fluoride and titanates.

2.0 SUMMARY

The Strontium Heat Source Development Program is currently underway at PNL to obtain the data needed to license $^{90}SrF_2$ fueled heat sources for terrestrial applications. The work is sponsored by ERDA's Division of Nuclear Research and Applications.

One phase of the PNL program involves determining the dissolution behavior and solubility of $^{90}SrF_2$ in aqueous media with special emphasis on $^{90}SrF_2$ produced in the Hanford Waste Encapsulation and Storage Facility (WESF). The data is needed to evaluate the consequences of an accidental exposure of $^{90}SrF_2$ in a heat source to an aqueous environment. Because work with significant quantities of $^{90}SrF_2$ requires heavily shielded facilities and is inordinately expensive, most of the solubility and dissolution rate measurements were carried out using nonradioactive SrF_2.

The solubility of nonradioactive strontium fluoride in demineralized water and natural seawater was determined using two different procedures. The effect of impurities on the solubility of the SrF_2 was also determined. The results show that the solubility product for SrF_2 in demineralized water increased from 4.7×10^{-9} to 7.7×10^{-9} as the temperature was increased from 4 to 50°C. The equilibrium strontium concentration varied from 0.00106 $\underline{M}$ to 0.00126 $\underline{M}$ over the same temperature range. The presence of soluble fluoride impurities in the SrF_2 (similar to those found in WESF produced $^{90}SrF_2$) produced a marked decrease in the equilibrium strontium concentration in demineralized water, due to the common ion effect, and in the amount of SrF_2 which dissolved.

When high purity SrF_2 was equilibrated with seawater, the equilibrium strontium and fluoride concentrations were slightly higher than in demineralized water (0.00119 $\underline{M}$ versus 0.00107 $\underline{M}$ for strontium at 23°C), and the amount of SrF_2 which dissolved was somewhat greater (0.138 g/ℓ versus 0.135 g/ℓ at 23°C). The presence of soluble fluoride impurities in the SrF_2 appeared to have little effect on its solubility in seawater.

The dissolution rate of strontium fluoride in demineralized water, plant tap water, and natural and synthetic seawater was measured using both static and dynamic (flowing) systems. The accidental exposure of a $^{90}SrF_2$ to an aqueous environment, such as an ocean or river, would be more closely approximated by the dynamic system, and the bulk of the dissolution rate measurements were obtained using that technique. Both nonradioactive SrF_2 and $^{90}SrF_2$ were used for the tests. The nonradioactive SrF_2 was used in an attempt to identify the variables which affect the dissolution rate.

When SrF_2 granules were exposed to a flowing solvent the dissolution rate changed initially but reached a constant value after a few hours exposure. The dissolution rate remained constant even upon prolonged exposure to the flowing solvent. In no case were the SrF_2 granules observed to disintegrate to a fine powder as has been observed with some other isotopic fuels.

The results obtained show the dissolution behavior of SrF_2 in aqueous solutions is a complex phenomenon that is affected by several properties of the fluoride including its impurity content, surface area and thermal history as well as the nature and temperature of the dissolving medium. For a specific solvent and reaction temperature the dissolution rate of nonradioactive SrF_2 varied up to sixty-fold depending on its impurity content, surface area and thermal history. The maximum and minimum rates observed were as follows:

	Dissolution Rate at 24°C (μg Sr dissolved/hr-g Sr initially present)	
	Minimum	Maximum
Demineralized Water	32	1900
Natural Seawater	24	460

Even SrF_2 samples having the same impurity content and surface area had markedly different dissolution rates depending on the thermal treatment they had received. The dissolution rate of SrF_2 increased with temperature as expected, and at temperatures above 60°C the rate increased very rapidly making reliable measurements difficult to obtain.

Dissolution rate measurements with $^{90}SrF_2$ were limited to a few key experiments using demineralized water and natural seawater. The tests were carried out at 30°C using the dynamic system. The measured dissolution rates were as follows:

	Dissolution Rate at 30°C (μg Sr dissolved/hr-g Sr initially present)	
	Demineralized Water	Natural Seawater
WESF-produced $^{90}SrF_2$	440	300
WESF-grade $^{90}SrF_2$	1600	270

Comparison of the $^{90}SrF_2$ dissolution rates with those for nonradioactive SrF_2 are difficult because it was impossible to reproduce the exact composition and thermal history of the $^{90}SrF_2$ using nonradioactive SrF_2. However, for samples having approximately the same impurity content and thermal history the dissolution rate of the $^{90}SrF_2$ is up to 18 times greater than that of the nonradioactive SrF_2.

Evaluation of the dissolution rate data for strontium fluoride leads to the following general conclusions:

- The relative dissolution rates of SrF_2 in the test solutions are plant tap water > demineralized water > synthetic seawater > natural seawater. Although there are marked variations, the overall dissolution rate of SrF_2 in demineralized water is about three times as great as in natural seawater, while the rate in tap water is about 20% greater than the rate in demineralized water.
- The average dissolution rate of high purity nonradioactive SrF_2 is 1 1/2 to 2 times greater than that of nonradioactive SrF_2 containing impurities similar to those found in WESF-produced $^{90}SrF_2$.
- The higher the temperature at which the SrF_2 is fired and the longer it is held at temperature the lower will be its dissolution rate in aqueous media.

- The effect of thermal treatment on the dissolution rate of SrF_2 involves more than simply surface area effects. However, the scope of the program did not permit a detailed evaluation of the effects of thermal treatment on the dissolution behavior of SrF_2.

Comparison of available dissolution rate data for radioactive and inert SrF_2, $SrTiO_3$ and $SrTiO_4$ indicates that under similar conditions the dissolution rate of SrF_2 is greater than that of $SrTiO_3$ but somewhat less than that of Sr_2TiO_4 (exact comparisons of the dissolution behavior of the fluoride and titanates cannot be made because the dissolution rates of the titanates change continually with time).

The dissolution rate and solubility of $^{90}SrF_2$ in aqueous media are sufficiently high that rapid dispersal of ^{90}Sr would occur if the $^{90}SrF_2$ is accidentally exposed to an aqueous environment. Therefore, if $^{90}SrF_2$ is to be used as a heat source fuel for terrestrial applications, the fuel containment must be adequate to ensure the $^{90}SrF_2$ will not contact the water if the heat source is accidentally exposed to an aqueous environment.

3.0 WESF PROCESS FOR THE PREPARATION AND ENCAPSULATION OF $^{90}SrF_2$

The dissolution behavior of strontium fluoride is significantly affected by its impurity content and thermal history. Therefore, the process used to prepare and encapsulate $^{90}SrF_2$ will have a marked effect on its dissolution behavior in aqueous media. At Hanford spent reactor fuel is reprocessed using the Purex process. The flowsheet used for recovery of strontium from the fuel reprocessing waste, conversion to the fluoride, and subsequent encapsulation of the fluoride, is shown in Figure 1. In the process the strontium is recovered from current Purex acid waste (CAW) or Purex acid sludge (PAS) by solvent extraction using di-2-ethyhexylphosphoric acid

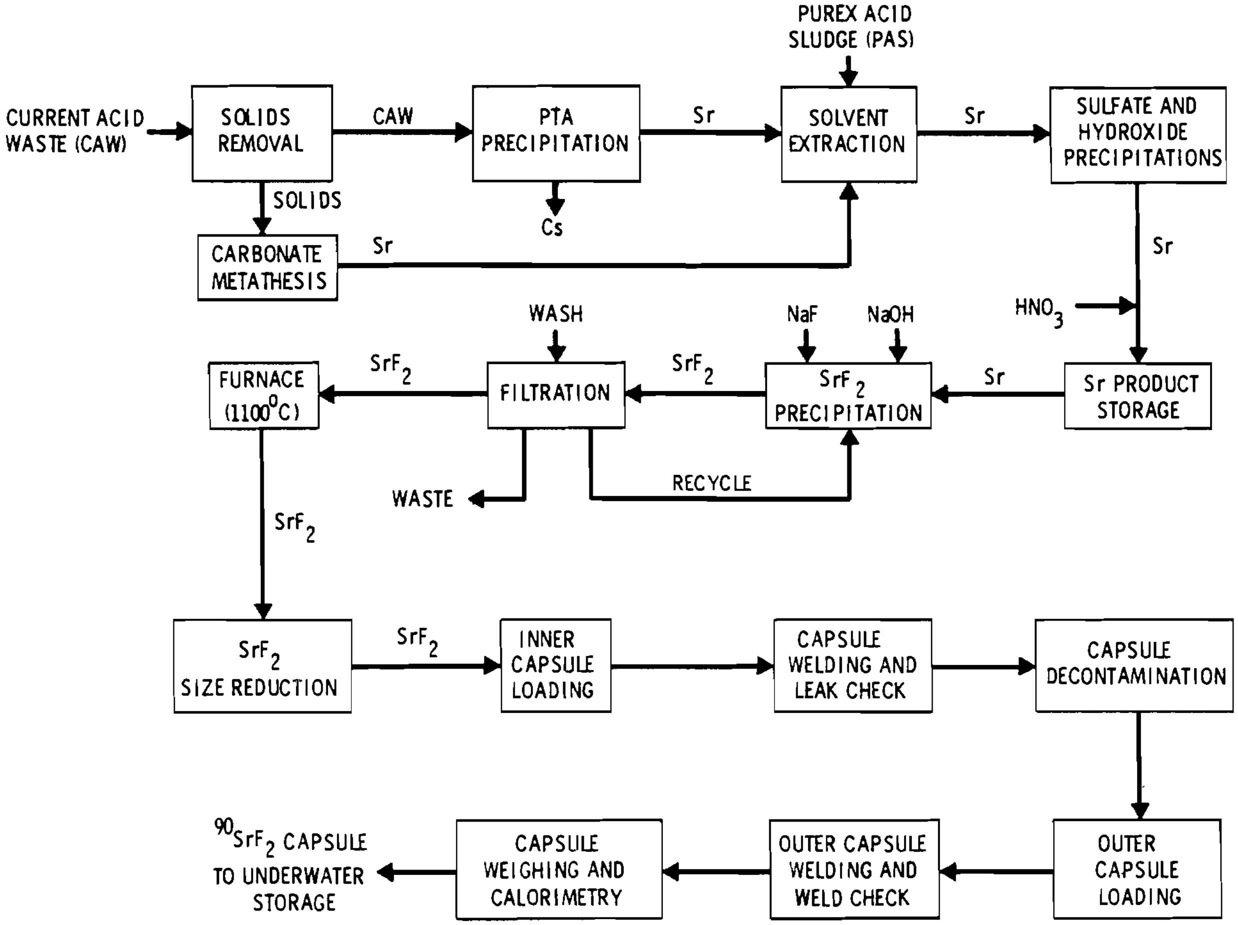

FIGURE 1. Simplified Flowsheet of the WESF Process for the Preparation and Encapsulation of $^{90}SrF_2$

(HDEHP), tributyl phosphate (TBP) and normal paraffin hydrocarbon (NPH). The strontium is stripped from the organic phase with dilute nitric acid and purified by a series of sulfate and hydroxide precipitation steps. The purified strontium is stored as strontium nitrate in dilute nitric acid. Strontium recovery and purification take place in B-Plant, and subsequent operations take place in the Waste Encapsulation and Storage Facility.

The purified strontium nitrate solution serves as the feed to the WESF process. All steps in the process are batch operations. A volume of feed solution containing 3 to 5 kg of strontium is neutralized to pH 8-9 with sodium hydroxide solution. Solid sodium fluoride is added to the solution to precipitate SrF_2. The resulting slurry is digested at about 80°C with air sparging and then filtered. The SrF_2 filter cake is washed with water, transferred to furnace boats, and fired at approximately 1100°C in an argon atmosphere for several hours. After cooling, the SrF_2 is removed from the boats and crushed to minus 1/2 in. granules. The pulverized fluoride is loaded into a Hastelloy C-276 inner capsule by impact consolidation, which is essentially a cold pressing operation. The capsule is sealed by tungsten inert gas (TIG) welding the lid in place, leak checked, and decontaminated. The cleaned capsule is placed in an outer capsule of 316L stainless steel(a) which is also sealed with a TIG weld. The integrity of the outer capsule weld is checked using ultrasonic techniques. The capsule is weighed and the heat output determined using a calorimeter, after which the capsule is stored under water. Pertinent data on the WESF capsule containing fuel grade $^{90}SrF_2$ ($\geq 50\%$ ^{90}Sr isotopic content) are given in Table 2.

Waste management planning calls for the long-term storage of the encapsulated $^{90}SrF_2$ at near-ambient temperatures until the ^{90}Sr decays to an innocuous level. The WESF capsule was designed to safely contain the $^{90}SrF_2$ during the required storage period, and is perfectly adequate

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(a) Hastelloy C-276 was used as the outer capsule material during the early stages of the WESF operation.

TABLE 2. Characteristics of a WESF Capsule Containing Fuel Grade $^{90}SrF_2$

Strontium Fluoride:

1. Amount ∿ 3 kg/capsule
2. Purity ∿ 95 wt%
3. ^{90}Sr Isotopic Content ≥ 50%
4. Bulk density ∿ 70% of theoretical density
5. Power density ∿ 1.1 W/cm^3
6. Loading ∿ 150,000 Ci
7. Power Output ∿ 1000 W

Capsule Data:	Inner	Outer
1. Material	Hastelloy C-276	316L Stainless Steel
2. Inner Diameter	2.010 in.	2.385 in.
3. Outer Diameter	2.250 in.	2.625 in.
4. Length	19.050 in.	20.100 in.

for that requirement. However the WESF $^{90}SrF_2$ capsule may not be adequate for heat source service and some modification of the capsule may be required if the $^{90}SrF_2$ is to be used in high temperature applications.

There are several facets of the WESF process which can affect the dissolution behavior of the $^{90}SrF_2$ produced.

- The impurity content of the strontium fluoride may vary between batches depending on the source of the feed material. Strontium recovered from different waste tanks can contain varying amounts of impurities. The process operations used to purify the feed solution are only partially effective, and some of the impurities in the feed will precipitate with the strontium fluoride. Typical impurities which may be present in the WESF produced $^{90}SrF_2$ and their probable forms and concentration ranges are shown in Table 3. After the $^{90}SrF_2$ has been fired at 1100°C it is possible that some of the impurity fluorides may be present as complex fluorides. The relatively soluble fluorides, such as NaF, appear to have a greater influence on the dissolution behavior of SrF_2 than do the less soluble fluorides such as CaF_2 and BaF_2.

TABLE 3. Typical Impurities Found in WESF Produced $^{90}SrF_2$

Impurity	Concentration Range, wt%	Probable Compound Form
Al	<0.5	AlF_3
Ba	0.1 - 2.0	BaF_2
Ca	0.1 - 2.0	CaF_2
Cd	<0.1	CdF_2
Cr	<0.2	CrF_3
Cu	<0.01	CuF_2
Fe	<0.1	FeF_3
H	<0.01	H_2O
K	<0.1	KF
Mg	0.05 - 0.5	MgF_2
Mn	<0.1	MnF_2
N	<0.01	NO_3^-
Na	1 - 4	NaF
Ni	<0.1	NiF_2
O	<0.05	H_2O and NO_3^-
Pb	<0.2	PbF_2
RE(a)	<2.0	REF_3
Si	<0.02	SiO_2 or $SiF_6^=$
Zr	Variable-decay product	ZrF_4 ?

(a) RE = Rare Earths

- Based on previous work with the strontium titanates one would expect the dissolution behavior of strontium fluoride to be affected by its ^{90}Sr isotopic content with a higher ^{90}Sr content resulting in an increased dissolution rate. The ^{90}Sr isotopic content of WESF produced SrF_2 can vary over a wide range depending on the age of the waste from which it is produced. Much of the high level fuel reprocessing waste at Hanford has been stored for many years. The ^{90}Sr isotopic content of strontium recovered from the older wastes can be as low as 25%, while that of strontium recovered from recent wastes can exceed 55%. Other factors being equal, fuel-grade $^{90}SrF_2$ should dissolve at a faster rate than fluoride having a lower ^{90}Sr content.

- For a heat source fuel, $^{90}SrF_2$ has a relatively low melting point of approximately 1425°C (versus >2000°C for $SrTiO_3$ and >1800°C for Sr_2TiO_4). When SrF_2 powder is heated above about 500°C sintering begins which leads to the agglomeration of fluoride particles and a reduction in surface area. The presence of impurities in the SrF_2 can lead to the formation of low melting phases which accelerates the sintering and reduction in surface area. In the WESF operation the $^{90}SrF_2$, after firing at 1100°C, is normally a partially sintered mass which must be crushed to minus 1/2 in. granules before it can be fed to the capsule loading equipment. The material is compacted into the inner capsule by impact consolidation. A small quantity of granules is placed into the capsule and compacted using a pneumatic hammer. Additional increments of fluoride are added and compacted until the capsule is filled to the desired level. Although the temperature of the fluoride and capsule are above the ambient cell temperature, due to heat from the ^{90}Sr, the loading process is essentially a cold pressing operation. Using this loading procedure the bulk density of the compacted $^{90}SrF_2$ is about 65 to 70% of the theoretical SrF_2 density. Since the bulk density of the $^{90}SrF_2$ is relatively low, additional sintering and agglomeration is possible, leading to a further reduction in surface area, if the WESF capsule is used in heat source applications at temperatures above about 500°C. This makes it difficult to obtain meaningful dissolution rate data for $^{90}SrF_2$ because the dissolution behavior will continue to change during heat source service as the fluoride continues to sinter and agglomerate. The time required for the fuel to reach a stable condition will depend on the fuel composition and temperature. This is not the case with the strontium titanates. In previous work with these compounds the normal procedure was to hot press or cold press and sinter the fuel into high density pellets prior to encapsulation. Because of the relatively high melting points of the titanates and the initial high densities of the pellets, very little change in titanate density or surface area occurs during heat source service.

An additional factor which must be considered, that is not directly related to the WESF process, is the effect of decay product buildup on the dissolution behavior of $^{90}SrF_2$. Strontium-90 decays to stable ^{90}Zr through a short-lived ^{90}Y intermediate

$$^{90}SrF_2 \rightarrow [^{90}Y \cdot F_2] \rightarrow {}^{90}Zr \cdot F_2 + 2e + Q.$$

The equilibrium concentration of ^{90}Y is very small, but the ^{90}Y probably has a significant effect on the dissolution behavior of the fluoride because of its intense, very high energy beta and related bremsstrahlung activity. Because of the short half life of the ^{90}Y, it is very difficult to measure experimentally its effect on the dissolution behavior of strontium fluoride.

Strontium-90 has a half life of about 28.6 yr. In fuel grade $^{90}SrF_2$ the Zr concentration will build up initially at a rate of slightly more than 1%/yr. The exact chemical form(s) of the decay product(s) has not been established. Zirconium difluoride (ZrF_2) has been reported in the literature(2) but is said to disproportionate at elevated temperatures according to the reaction

$$2ZrF_2 \rightarrow ZrF_4 + Zr.$$

Any ZrF_2 formed as a decay product in a $^{90}SrF_2$ heat source should disproportionate at source operating temperatures, but this has not been demonstrated experimentally. The possibility also exists that the ZrF_2 could react with other fluorides present to form a stable complex fluoride. Regardless of the nature of the zirconium decay product, it would be expected to have an effect on the dissolution behavior of the $^{90}SrF_2$.

4.0 EXPERIMENTAL PROCEDURES

Ideally all of the dissolution rate measurements should be carried out using fuel grade $^{90}SrF_2$. However, work with any significant quantities of ^{90}Sr compounds must be carried out in a heavily shielded facility such as a hot cell or lead cave because of the intense very high energy beta radiation and bremsstrahlung associated with the ^{90}Sr and its daughter product ^{90}Y. Such work is inordinately expensive where a large number of experiments are required. Work with ^{90}Sr compounds is further handicapped by a lack of facilities for the chemical and physical analysis of the compounds. For example, the surface area of nonradioactive SrF_2 is easily determined using the standard BET method, but shielded equipment is not available for measuring the surface area of the radioactive compound. This made it impossible to evaluate the effects of impurities and thermal history on the surface area of WESF-produced $^{90}SrF_2$. While it is difficult to reproduce the composition and thermal history of WESF $^{90}SrF_2$ using nonradioactive SrF_2, the more extensive problems of working with $^{90}SrF_2$ made it necessary to carry out most of the dissolution measurements using nonradioactive strontium fluoride. The tests with $^{90}SrF_2$ were limited to a few critical experiments.

Since $^{90}SrF_2$ is a possible replacement for ^{90}Sr titanatesin heat source applications, a comparison of the dissolution behavior of the fluoride and titanates is desirable. Some data were available in the literature on the dissolution behavior of radioactive and inert $SrTiO_3$ and Sr_2TiO_4. However, it was felt that a more valid comparison of dissolution behavior could be made if data for the titanates was obtained using the same procedures and equipment as was used with the fluoride. Therefore, a limited number of dissolution rate measurements were made on nonradioactive $SrTiO_3$ and Sr_2TiO_4.

4.1 MATERIALS

The strontium compounds used in the dissolution behavior studies were prepared under controlled conditions, and the impurity content of each determined by various procedures. The nonradioactive compounds were analyzed for anionic and cationic impurities by spark source mass spectroscopy, emission spectroscopy, neutron activation, atomic absorption, flame photometry and wet chemistry. Analysis of the $^{90}SrF_2$ was limited to cationic impurities using atomic absorption, flame photometry and emission spectroscopy. The thermal history of the various compounds was closely monitored and the surface area of the nonradioactive compounds determined as a function of thermal history using the BET method.

4.1.1 Strontium Fluoride

Several grades of strontium fluoride were used in the studies to determine the effects of radiation and impurity content on the dissolution behavior of the fluoride. They included:

- WESF-produced $^{90}SrF_2$ which had an initial $^{90}SrF_2$ isotopic content of 51% and contained about 4.5 wt% cationic impurities. The material was part of the $^{90}SrF_2$ used in a long-term compatibility testing program. The composition of the fluoride is given in Table 4; it was approximately 6 months old at the time of use and the zirconium content was estimated to be about 0.6 wt%. As part of the WESF process the $^{90}SrF_2$ had been fired at approximately 1100°C for 8 hr and then crushed to -1/2-in. granules. At PNL the material was further crushed and a -1/4 + 1/8-in. size fraction used for the dissolution rate measurements.

- WESF-grade $^{90}SrF_2$ which was prepared by PNL using the WESF flowsheet and ^{90}Sr feed solution obtained from ARHCO. The composition of the fluoride is given in Table 4. The material was about 2 yr old at the time of use and had a ^{90}Sr isotopic content of 52.6%. The zirconium content was approximately 2.4 wt% due to decay of the ^{90}Sr.

TABLE 4. Composition of the $^{90}SrF_2$ Used in the Dissolution Rate Studies

Element	Concentration, wt%	
	WESF-Produced $^{90}SrF_2$	WESF-Grade[(a)] $^{90}SrF_2$
Sr	63.5(b)	∿62.5(b)
Al	0.30	<0.01
Ba	0.95	0.35
Ca	0.53	0.48
Cd	0.02	0.04
Co	ND(c)	ND
Cr	<0.03	<0.01
Cu	--	0.01
Fe	<0.09	0.03
K	ND	ND
Mg	0.06	0.20
Mn	0.01	<0.01
Na	2.2	2.0
Ni	0.02	<0.01
P	ND	ND
Pb	0.02	<0.015
RE(d)	--	1.7
Si	<0.01	<0.005
Sn	--	ND
Zn	--	ND
Zr (decay product)	∿0.6(b)	∿2.4(b)
^{90}Sr Isotopic content	50.5%(b)	52.6%(b)

(a) Prepared at PNL using the WESF flowsheet and ^{90}Sr solution obtained from ARHCO.

(b) At time of use

(c) ND - not detected (the detectable limit for most elements was ∿0.01%)

(d) RE - rare earths

The fluoride had been used in a short-term compatibility testing program during which it had been held at 800°C for 6 months. After removal from the test couple, the material was crushed and stored in an alumina crucible at approximately 100°C until used in the dissolution tests. A -1/4 +1/8 in. size fraction was used for the tests.

- High-purity nonradioactive SrF_2 containing less than 0.1 wt% total impurities (see Table 5). It was prepared from reagent-grade $Sr(NO_3)_2$ and NaF using the WESF flowsheet. The SrF_2 was washed very thoroughly to remove residual sodium fluoride, fired at 1100°C for several hours, and ground to -200 mesh prior to use.
- Commercially-obtained nonradioactive SrF_2 containing about 0.5 wt% impurities (see Table 5). The fluoride was fired at 1100°C and ground to -200 mesh.
- WESF grade nonradioactive SrF_2 containing impurities similar to those found in WESF produced $^{90}SrF_2$. The material was prepared by the WESF flowsheet, fired at 1100°C, and crushed to -200 mesh. The compositions of the SrF_2 is given in Table 5.
- High-purity nonradioactive SrF_2 with added NaF. Mixtures of high-purity nonradioactive SrF_2 (<0.1 wt% impurities) and NaF were fired at 1100°C and crushed to -200 mesh.

To evaluate the effect of thermal history on the dissolution behavior of SrF_2 the different grades of nonradioactive SrF_2 powder were fired at various temperatures for specified time periods. They were then crushed, and the surface area and dissolution behavior of the -1/4 + 1/8-in. size fractions were determined.

4.1.2 Strontium Titanates

Nonradioactive strontium titanate ($SrTiO_3$) and strontium orthotitanate (Sr_2TiO_4) were prepared by the reaction of reagent-grade strontium carbonate and titanium dioxide. The following procedure was used.

TABLE 5. Composition of the Nonradioactive SrF_2 Used in the Dissolution Behavior Studies

Component[(a)]	Concentration, wt% High-Purity SrF_2	Commercial SrF_2	WESF-Grade SrF_2
Sr	69.7	69.2	65.0
F	30.2	30.2	31.0
Al	0.007	0.01	0.21
Ba	0.002	0.14	0.63
Ca	0.022	0.01	0.25
Cd	ND	ND	0.01
Cr	0.003	0.03	0.05
Fe	0.008	0.1	0.01
Mg	0.001	<0.01	0.07
Mn	0.001	<0.01	0.01
Na	0.030	0.02	1.97
Ni	<0.001	<0.01	0.01
Pb	ND	ND	0.02
RE(b)	ND	ND	0.69
$SO_4^=$	ND	0.02	ND
NO_3^-	ND	<0.01	<0.01
H_2O	<0.01	<0.01	<0.01

(a) Elements not reported are less than detectable limit which is normally 0.001%.
(b) Rare earth - typically Neodymium
(c) ND - not detected (<0.001%)

The stoichiometric amounts of $SrCO_3$ and TiO_2 were mixed with demineralized water to form a thin slurry. The slurry was ball milled for several hours using a porcelain jar and Alundum balls. The milled slurry was filtered and the cake was washed with water. The washed cake was vacuum dried at 200°C and then fired at 1450°C for 4 or 8 hr in an alumina crucible. The fired product was then crushed and a -1/4 + 1/8-in. size fraction used for the dissolution rate measurements. Each product was analyzed by X-ray defraction. The $SrTiO_3$ contained less than 1% Sr_2TiO_4 while the Sr_2TiO_4 contained less than 1% $SrTiO_3$. The surface areas of the two titanates were determined using the BET method.

4.1.3 Test Solutions

Four different solvents were used in the dissolution rate studies.

- Demineralized water having a resistivity of 2 megohms. The water was prepared by ion exchange purification of distilled water using a Corning Model LD-5 water purifier.
- Plant tap water having a resistivity of 0.003 megohms (the resistivity was measured using a conductivity bridge).
- Synthetic seawater prepared according to the formulation of May and Alexander.(3) The solution contained 13.9 mg/ℓ strontium and 1.4 mg/ℓ fluoride and had a pH of 8.2.
- Natural seawater, taken from the Strait of Juan de Fuca at Sequim, WA: it contained 7.9 mg/ℓ strontium and 1.6 mg/ℓ fluoride; the pH was 8.0.

Only the demineralized water and natural seawater were used in the solubility studies.

4.2 DISSOLUTION RATE MEASUREMENTS

The bulk of the dissolution rate data on strontium fluoride (including $^{90}SrF_2$) and the strontium titanates were obtained using the dynamic (flowing) system shown in Figure 2. The tests were carried out in the following manner (using SrF_2 as an example).

A weighed amount of -1/4 +1/8-in. SrF_2 granules, usually about three grams, was placed in a vertical glass reaction column and supported on a fine pyrex frit. The SrF_2 was held in place using a plug of glass wool.

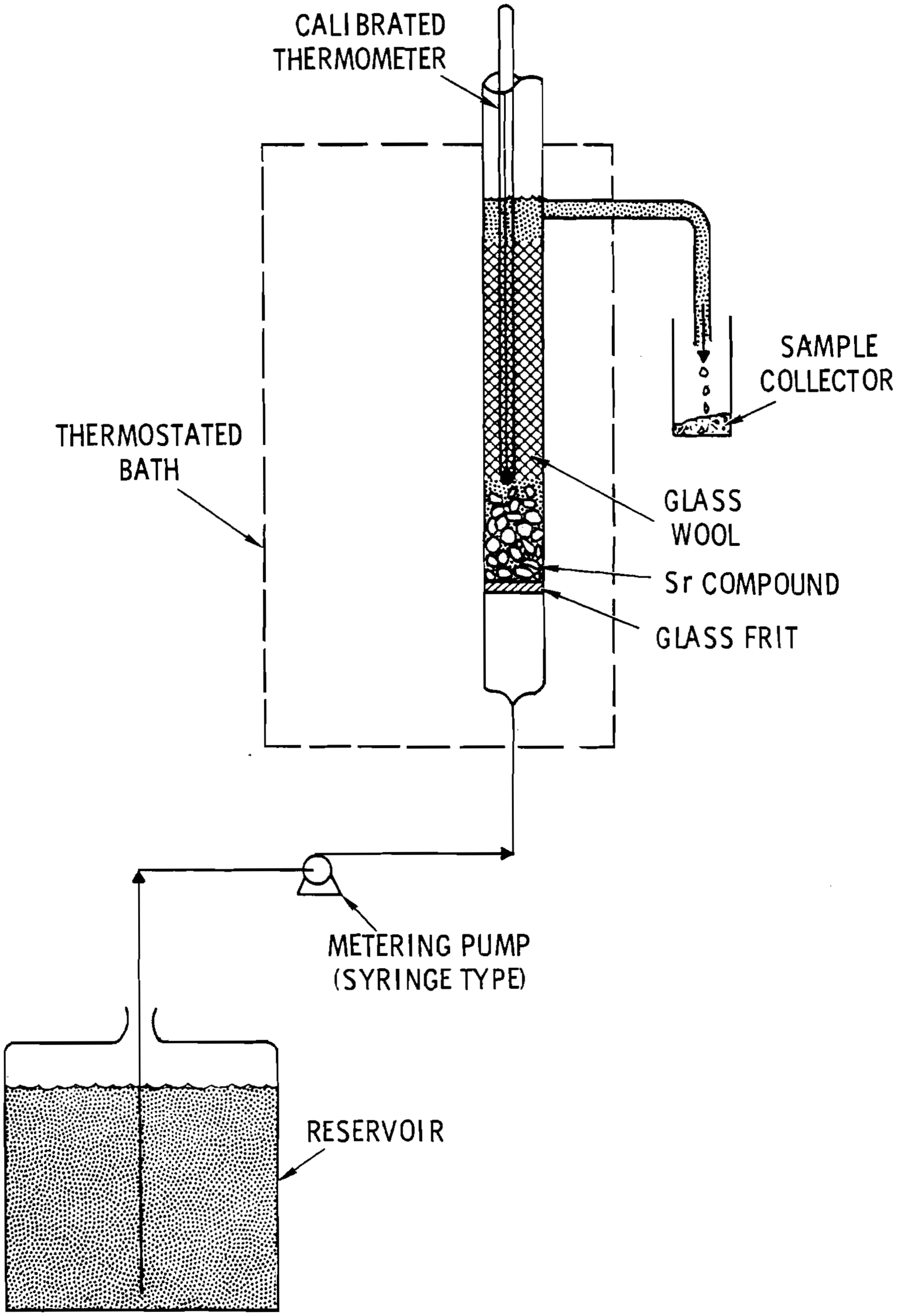

FIGURE 2. Dynamic (Flowing) System Used to Measure the Dissolution Rate of Strontium Compounds

A calibrated thermometer was inserted in the column above the SrF_2 to measure the solution temperature. Fresh solvent from the supply reservoir was flowed past the SrF_2 in an upward direction and overflowed the reaction column into a discharge vessel. Samples of the solution leaving the reaction column were taken on a periodic basis, filtered through 0.05 micron (μ) Millipore filters to remove particulates, and analyzed for strontium and fluoride.

The dissolution rate of the SrF_2 was calculated from the measured strontium content of the solution leaving the column and the known solvent flowrate.

Using a thermostated bath the solution temperature in the reaction column could be maintained within ±0.3°C over a range of 3 to 90°C. The test solution was metered to the reaction column using a calibrated continuous-flow syringe pump (Harvard Apparatus Model 954-4 channel pump). With the pump solution flow could be controlled within ±0.5% over a range of 1 to 40 mℓ/min for extended periods of time. The pump was capable of metering four streams concurrently, and it was standard practice to run four reaction columns at one time using one or more test solvents.

Determining the dissolution rate of strontium fluoride using the dynamic procedure would be representative of an accidental exposure of $^{90}SrF_2$ to an essentially infinite water reservoir such as the ocean or a flowing stream. Natural ocean or stream currents would disperse the dissolved strontium, and dissolution would occur at a strontium concentration only slightly above that of the water environment.

Some dissolution rate measurements were attempted using a static system in which strontium fluoride was contacted with a known volume of solvent and the increase in strontium concentration followed as a function of time. The procedure used was as follows:

A weighed amount of SrF_2 was added to a known volume of solvent in a 2-ℓ flat bottom polyethylene flask. The flask was sealed and the dissolution allowed to proceed. Shortly before a sample was to be taken, the solution was stirred using a magnetic stirrer to ensure adequate mixing. The stirrer was stopped, the solids allowed to settle, and a small sample taken. The sample was filtered through a 0.05 μ Millipore filter to remove particulates and analyzed for strontium and fluoride.

It was found that the static system could not be used to obtain a reliable measure of the dissolution rate of strontium fluoride. As the concentrations of strontium and fluoride in solution increased, the dissolution rate of the fluoride decreased. At high strontium and fluoride concentrations the limit of precision of the analytical procedures used to determine the concentrations made it difficult to obtain a reliable measure of the rate of change of concentration. Only a limited number of dissolution experiments were carried out using the static system; however, the static system was used for solubility measurements.

4.3 SOLUBILITY MEASUREMENTS

The solubility of strontium fluoride in demineralized water and natural seawater was measured using a static system similar to that used to measure the dissolution rate of SrF_2. A quantity of fluoride was added to the test solvent in a flat bottom polyethylene flask and the flask was then sealed. The resulting slurry was stirred using a magnetic stirrer. Periodically, the stirring was stopped and the solids were allowed to settle. A sample of the clear solution was taken, filtered through a 0.05 μ Millipore filter, and analyzed for strontium and fluoride. The test was continued until no changes in strontium and fluoride concentrations were observed. It usually required a period of several weeks to reach equilibrium.

The solubility of SrF_2 was also measured using a slightly different procedure. The SrF_2 was added to the test solvent in a flask equipped with a condenser and an inert gas purge. The slurry was heated for several hours, cooled to the desired temperature, and a sample was then taken. The samples were filtered and analyzed for strontium and fluoride. The entire operation was repeated several times until the strontium and fluoride concentrations reached constant values.

4.4 ANALYSIS OF TEST SOLUTIONS

The ^{90}Sr content of test samples was determined with a 2π gas flow proportional counter using methane as the counting gas. Determined precision of the procedure was ±3% and the accuracy was ±5%. To ensure that secular equilibrium had been established between the ^{90}Sr and ^{90}Y, the samples were aged at least 20 days before analysis. The strontium isotopic content of the strontium fluoride was determined by mass spectroscopy. The total strontium content of the test samples was calculated from the measured ^{90}Sr content and the isotopic analysis.

The strontium content of nonradioactive test samples was determined by flame photometry. Precision of the procedure was ±5% with no significant bias. The fluoride content of the samples was determined using an Orion Model 94-09 fluoride electrode. Precision of the procedure was ±5% with no significant bias.

In some SrF_2 dissolution experiments, a ^{85}Sr tracer was used to analyze for strontium in the test samples. The strontium fluoride was prepared from a strontium nitrate solution of known strontium content and ^{85}Sr activity. Calibration standards were prepared from the nitrate solution. The ^{85}Sr activity of test samples was determined by gamma counting, and the strontium concentration determined by comparison with the calibration standards. Precision of the procedure was poor (±25) because of low counting levels, and only a few experiments were carried out using the ^{85}Sr tracer.

5.0 RESULTS AND DISCUSSION

5.1 STRONTIUM FLUORIDE SOLUBILITY

The solubility of strontium fluoride in water is of interest insofar as it determines the maximum possible strontium concentration when SrF_2 is exposed to a stagnant or limited water reservoir. Impurities in the SrF_2, especially soluble fluorides, will affect the equilibrium strontium concentration and must be considered when measuring SrF_2 solubility. In seawater the equilibrium strontium concentration may be controlled by ionic species other than F^-. All solubility measurements were made using nonradioactive SrF_2.

5.1.1 Solubility of SrF_2 in Demineralized Water

The solubility of nonradioactive strontium fluoride in demineralized water was determined using the two procedures described in Section 4.3. When the solubility was determined by equilibrating SrF_2 and water at a given temperature it required up to 6 weeks for equilibrium to be established, but several of the tests lasted for 12 to 15 months to ensure equilibrium had been reached. Figure 3 shows the data for a typical solubility experiment. The solubility of high purity SrF_2 (having the composition given in Table 5) in demineralized water was measured over a temperature range of 4 to 50°C, and the results obtained are summarized in Table 6. The solubility data are slightly higher than those reported by Kohlrausch(4) and much lower than the single value reported by Carter(5) (see Figure 4). Neither Kohlrausch or Carter discussed the impurity content of the SrF_2 they used for the solubility measurements; and differences in composition could account for the difference between the three sets of data. In addition, Carter did not attempt to analyze the saturated solution to determine the equilibrium strontium and fluoride concentrations. Instead he filtered the saturated solution, evaporated the filtrate to dryness and fired the residue. He then assumed the residue corresponded to the SrF_2 content of the solution at saturation; a procedure which could be badly in error if the SrF_2 contained any soluble impurities.

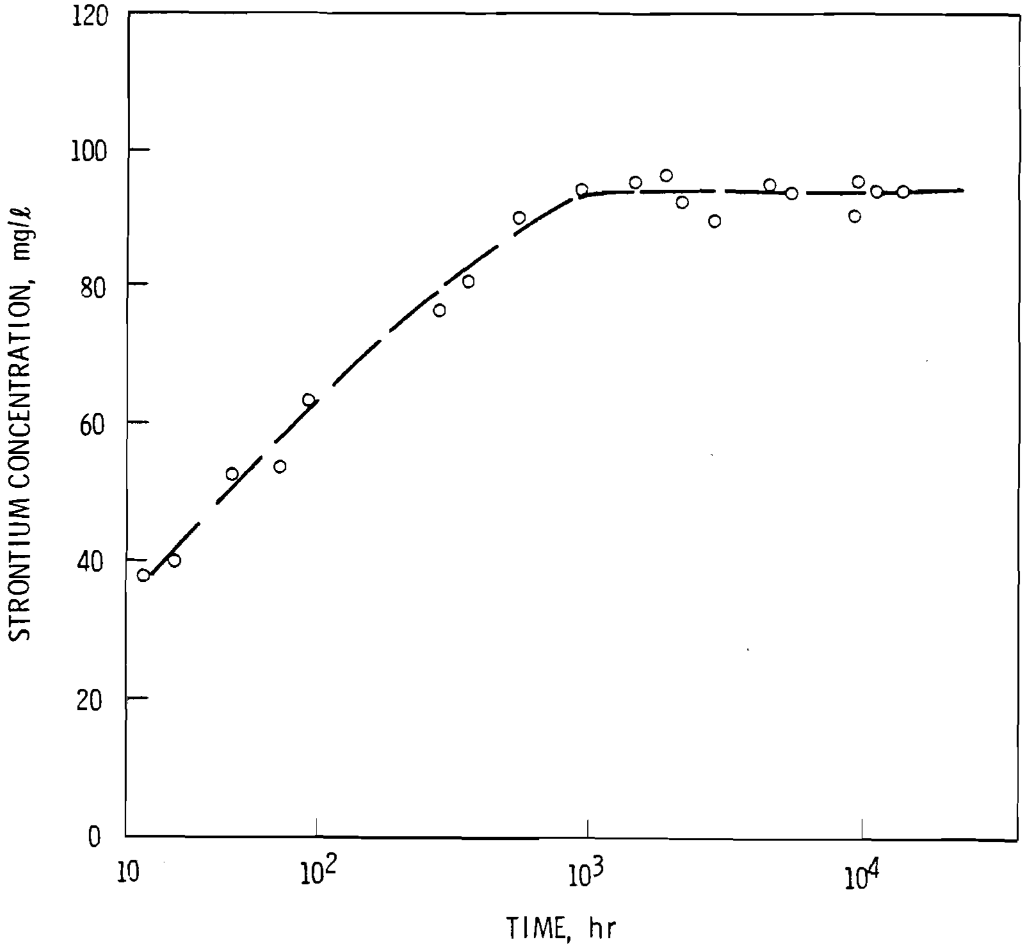

FIGURE 3. Dissolution Behavior of High Purity Nonradioactive Strontium Fluoride in Demineralized Water at 23°C

TABLE 6. Solubility of High Purity SrF_2 in Demineralized Water

Temperature, °C	Strontium Concentration, M	Fluoride Concentration, M	SrF_2 Solubility, g/ℓ	Solubility Product, K_{sp}
4	0.00106	0.00217	0.133	4.7×10^{-9}
23	0.00107	0.00219	0.135	5.1×10^{-9}
35	0.00114	0.00225	0.143	5.8×10^{-9}
50	0.00126	0.00247	0.157	7.7×10^{-9}

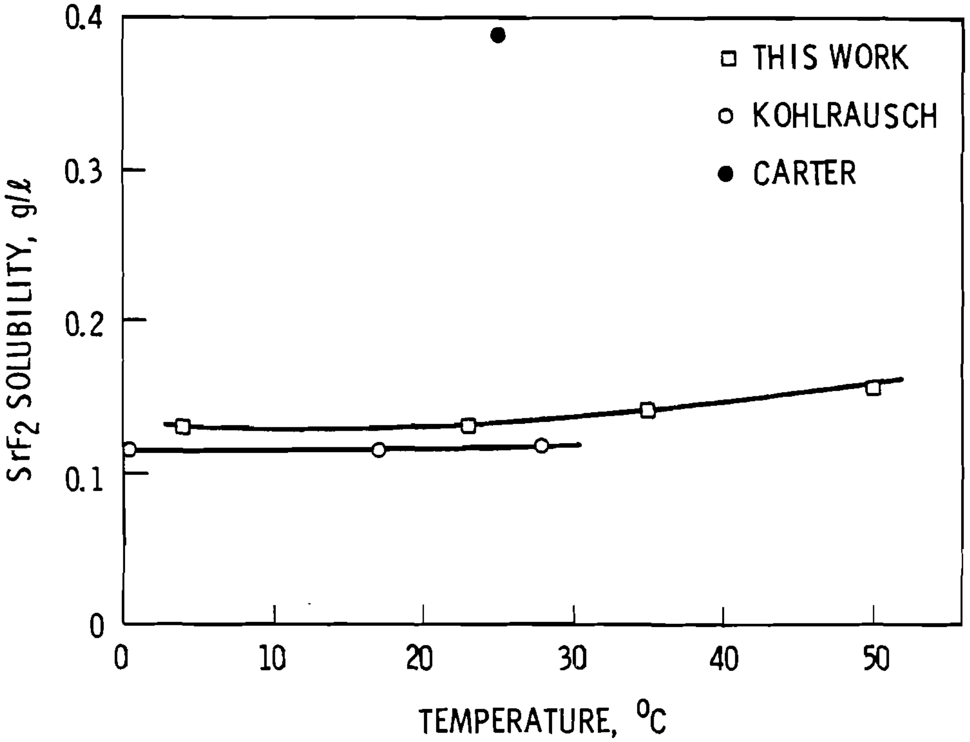

FIGURE 4. The Solubility of Strontium Fluoride in Water

Impurities in the SrF_2 can have a significant effect on the solubility of SrF_2 in demineralized water, both by the common ion effect and by their effect on the ionic strength of the solution. This is shown by the solubility data obtained using the commercial SrF_2 and WESF-grade SrF_2 whose compositions are given in Table 5. In each case a mixture containing 15 g of fluoride per liter of demineralized water was reacted until the solution was saturated. The results obtained are shown in Table 7 together with results obtained with the high purity SrF_2. The increased fluoride concentration, resulting from dissolution of soluble fluoride impurities in the SrF_2, produced a corresponding decrease in the equilibrium strontium concentration and the solubility of SrF_2.

The effect of impurities on SrF_2 solubility varies as the ratio of solid SrF_2 to water in the test mixture varies. As the quantity of SrF_2

is increased the dissolution of soluble fluoride impurities increases, producing a corresponding decrease in SrF_2 solubility. The data given in Table 8 show the change in SrF_2 solubility when varying amounts of WESF-grade SrF_2 were equilibrated with a constant volume of demineralized water.

TABLE 7. The Effect of Impurities on the Solubility of SrF_2 in Demineralized Water at 23°C(a)

Material	Equilibrium Sr Concentration, M	Equilibrium F Concentration, M	SrF_2 Dissolved,(b) g/ℓ
High-Purity SrF_2	0.00107	0.00219	0.135
Commercial SrF_2	0.000596	0.00462	0.0749
WESF-Grade SrF_2	0.000110	0.0130	0.0138

(a) 15 g of solid SrF_2 added per liter of water.
(b) Calculated from the Sr concentration.

TABLE 8. The Effect of the WESF-Grade SrF_2 - Water Ratio on the Solubility of SrF_2 in Demineralized Water at 23°C

Grams of WESF-Grade SrF_2 Added/ℓ of Water	Equilibrium Sr Concentration, M	Equilibrium F Concentration, M	SrF_2 Dissolved,(a) g/ℓ
1	0.0010	0.0028	0.13
5	0.00069	0.0047	0.087
15	0.00011	0.013	0.0138
25	0.000051	0.021	0.0064

(a) Calculated from the Sr Concentration.

5.1.2 Solubility of SrF_2 in Seawater

The solubility of high-purity nonradioactive SrF_2 in natural seawater was determined over a temperature range of 4 to 50°C using the procedures that were used with demineralized water. The results obtained are presented in Table 9. The data show that the strontium and fluoride concentrations at saturation are about 10% higher in seawater than in demineralized water. After correcting for the initial strontium and fluoride concentrations of the seawater, the data also show that the solubility of SrF_2 is slightly higher in seawater than in demineralized water.

TABLE 9. Solubility of High-Purity Nonradioactive SrF_2 in Natural Seawater

Temperature, °C	Equilibrium Sr Concentration, M	Equilibrium F Concentration, M	SrF_2 Dissolved,(a) g/ℓ
4	0.00115	0.00227	0.114
23	0.00119	0.00255	0.149
35	0.00129	0.00243	0.150
50	0.00139	0.00268	0.163

(a) Calculated from the strontium and fluoride concentrations after correcting for the initial strontium and fluoride content of the seawater.

The solubility data show that the impurities in the commercial and WESF-grades of SrF_2 have minimal effect on the solubility of SrF_2 in seawater (see Table 10). The equilibrium strontium and fluoride concentrations in seawater for the three grades of SrF_2 used in the tests were approximately the same. This differs drastically from the tests with demineralized water where the solubilities of the impure fluorides were much lower than that of the high-purity SrF_2.

TABLE 10. Solubility of Various Grades of SrF_2 in Natural Seawater at 23°C

Material	Equilibrium Sr Concentration, M	Equilibrium F Concentration, M	SrF_2 Dissolved, g/ℓ
High-Purity SrF_2	0.00119	0.00255	0.149
Commercial SrF_2	0.00124	0.00311	0.144(a)
WESF-Grade SrF_2	0.00121	0.00269	0.141(a)

(a) Calculated from the strontium concentration after correcting for the initial strontium concentration of the seawater.

The activity solubility product (K_s) for SrF_2 is given by the equation

$$K_s = (a_{Sr^{++}})(a_{F^-})^2. \tag{1}$$

The activities can be written as the product of the respective concentrations and activity coefficients so that

$$K_s = (C_{Sr}\gamma_{Sr})(C_F\gamma_F)^2. \tag{2}$$

In demineralized water with no other electrolytes present the activity coefficients for a slightly soluble salt such as SrF_2 can be taken as unity so that

$$K_s \cong (C_{Sr})(C_F)^2 \cong 5.1 \times 10^{-9} \text{ (at 23°C)}. \tag{3}$$

The activity coefficients for strontium and fluoride in seawater have not been published, but based on available data for other divalent and monovalent ions in seawater it is reasonable to assume that $\gamma_{Sr} \cong 0.12$ and $\gamma_F \cong 0.7$. Using these values, and assuming that none of the strontium and fluoride are complexed, it is possible to calculate the equilibrium strontium and fluoride concentrations for SrF_2 in contact with seawater. At 23°C the calculated saturation values are $C_{Sr} \cong 0.0028$ $\underline{M}$ and $C_F \cong 0.0055$ $\underline{M}$. Since the calculated values are over twice the measured values (see Table 9) it indicates that some mechanism other than the activity solubility product for SrF_2 probably limits the solubility of SrF_2 in seawater. This controlling mechanism was not determined experimentally, but calculations indicate that the solubility product for $SrSO_4$ and the high concentration of $SO_4^=$ in seawater probably limit the solubility of SrF_2 in seawater. If this is true it would explain why soluble fluoride impurities in the SrF_2 have no appreciable effect on the solubility of the SrF_2 in seawater.

5.1.3 Comparison of SrF_2, $SrTiO_3$ and Sr_2TiO_4 Solubility Data

Only a limited amount of data has been published on the solubility of $SrTiO_3$ and Sr_2TiO_4 in aqueous media. J. Neace(6) of the Martin Company, Nuclear Division, measured the solubility of nonradioactive $SrTiO_3$ and Sr_2TiO_4 in demineralized water at approximately 25°C. No information was provided on the impurity content of the titanates used, or on the procedures used in determining the solubilities of the titanates.

Table 11 provides a comparison of the PNL solubility data for SrF_2 with that reported by Neace for the titanates. It is difficult to explain the extremely high values reported by Neace for the solubility of Sr_2TiO_4 in aqueous solutions, especially in seawater. Other equilibria should serve to hold the solubility of Sr_2TiO_4 in seawater much below the reported value.

TABLE 11. A Comparison of the Solubilities of SrF_2, $SrTiO_3$ and Sr_2TiO_4 in Demineralized Water and Natural Seawater

		Solubility, mg/ℓ	
Material	Temperature, °C	Demineralized Water	Natural Seawater
SrF_2	23	135	149
$SrTiO_3$	25	32(6)	43(6)
Sr_2TiO_4	25	8,700(6)	9,600(6)

5.2 DISSOLUTION BEHAVIOR OF STRONTIUM COMPOUNDS

When strontium fluoride is contacted with water in a static system the dissolution rate continually decreases as the strontium and fluoride concentrations of the solution increase. Figure 5 shows a typical dissolution curve obtained using the static system. The dissolution rate is very high initially, but gradually decreases to zero as the solubility limit is reached. The scatter in the data makes it difficult to obtain a reliable measure of the differential dissolution rate; but the static system can be used to obtain an estimate of the dissolution rate as a function of solution strontium and fluoride concentrations.

When strontium fluoride is exposed to water in a dynamic (flowing) system the dissolution rate initially changes with time until a constant dissolution rate is attained. Figure 6 shows a typical dissolution rate curve obtained using the dynamic system. The time required for the dissolution rate to reach a steady-state value depends on several factors:

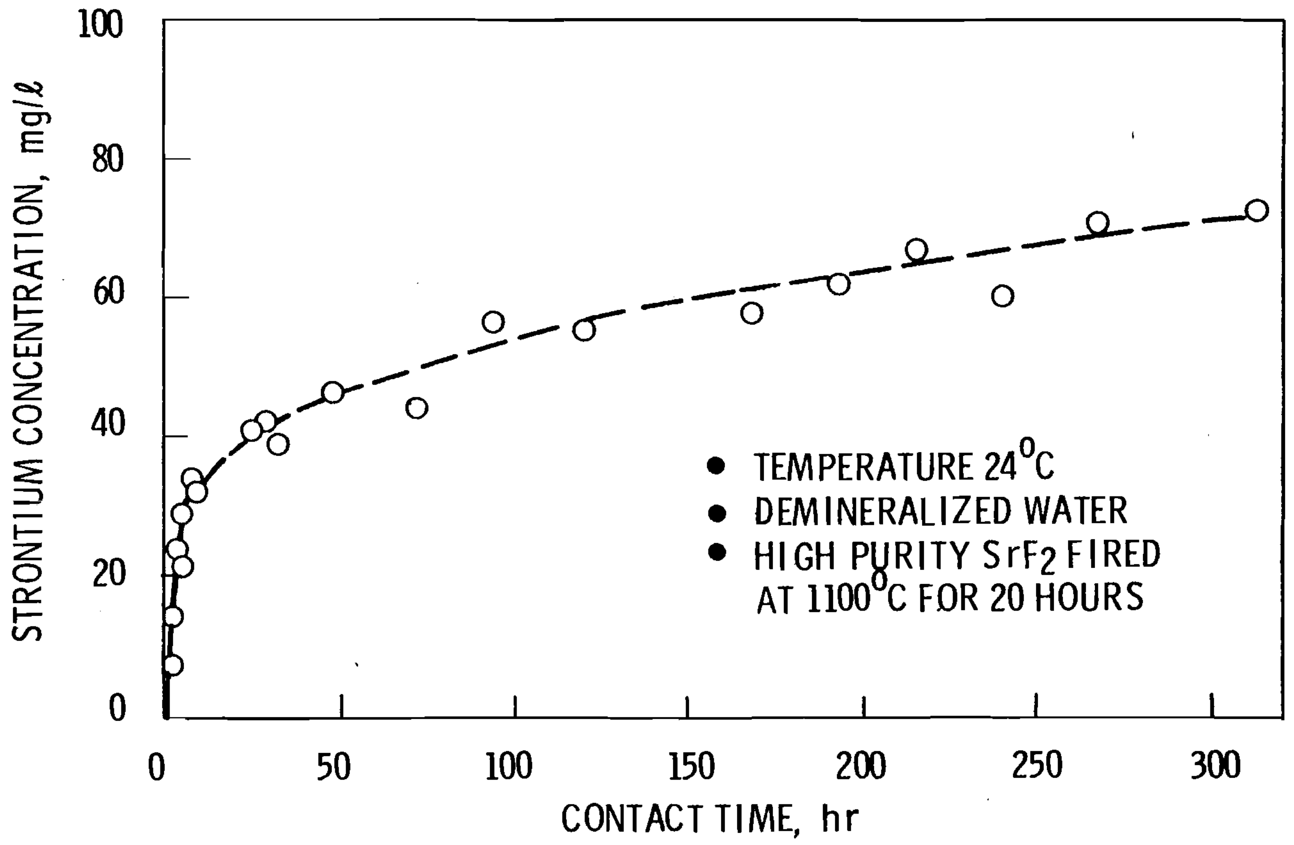

FIGURE 5. Typical Dissolution Behavior of SrF_2 in a Static System

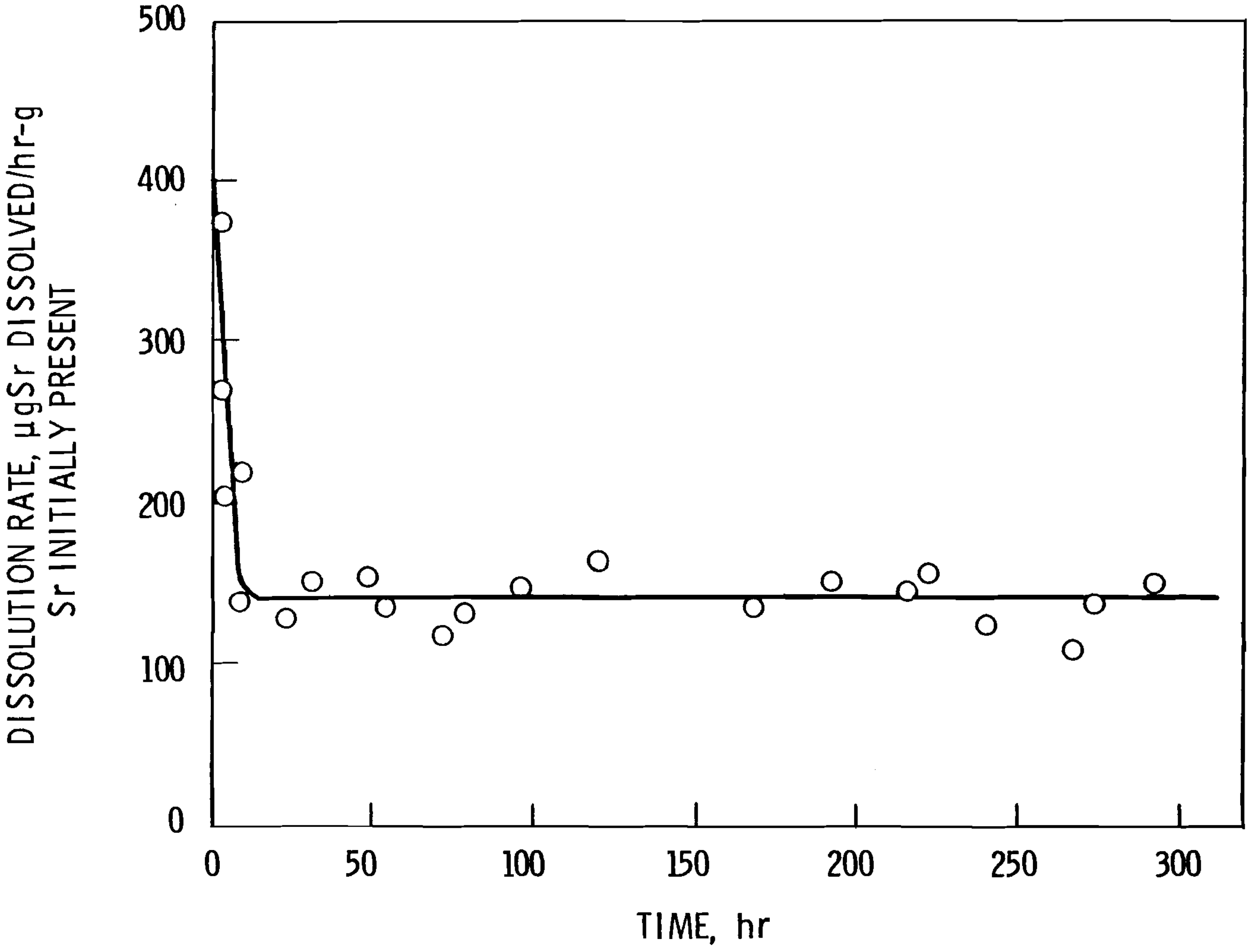

FIGURE 6. Typical Dissolution Rate Curve Obtained Using the Dynamic System

it is usually less than 6 hr but may be as long as 24 hr. The initial dissolution rate is usually higher than the steady-state rate, but may be lower if the SrF_2 contains a high concentration of readily soluble fluoride impurities such as NaF. The quantity of strontium fluoride which dissolves before steady state is reached is usually much less than 1% of the fluoride initially present. As can be seen from Figure 6 there is a considerable scatter in the data even after steady state is reached, and it is necessary to analyze a number of samples over a considerable time span to ensure a reliable measure of the steady-state dissolution rate is obtained. The reproducibility of the dissolution rate data obtained with the dynamic system is estimated to be ±15%.

It was found the solvent flow could be varied over a wide range without affecting the steady-state dissolution rate to any significant degree. For example, in tests with demineralized water and high-purity nonradioactive SrF_2 at 24°C the water flow was varied from 1.2 to 13.0 mℓ/min. The results obtained are presented in Table 12: they indicate that there was no significant change in the steady-state dissolution rate over the range of flow rates used, even though the strontium and fluoride concentrations varied by an order of magnitude.

TABLE 12. The Effect of Flow Rate on the Steady-State Dissolution Rate of High Purity Nonradioactive SrF_2[(a)] in Demineralized Water at 24°C

Water Flow (mℓ/min)	Steady State Solution Concentrations: Sr Concentration (mg/ℓ)	(M)	F Concentration (mg/ℓ)	(M)	Steady State Dissolution Rate (µg Sr Dissolved/hr-g Sr Initially Present)
1.2	8.7	9.9×10^{-5}	3.8	2.0×10^{-4}	290 ± 40
3.7	3.1	3.5×10^{-5}	1.3	6.8×10^{-5}	320 ± 60
6.4	1.6	1.8×10^{-5}	0.68	3.6×10^{-5}	310 ± 74
13.0	0.84	9.6×10^{-6}	0.38	2.0×10^{-5}	320 ± 52

(a) The SrF_2 was fired at 1100°C for 96 hr, after cooling the SrF_2 was crushed and a -1/4 +1/8-in. size fraction used for the dissolution tests. The surface area of the material was 440 cm^2/g.

Theoretically the dissolution rate of SrF_2 should be proportional to the difference between the saturation and actual solution strontium concentrations

$$\frac{dC_{Sr}}{dt} \propto (C_{Sr})_s - (C_{Sr})_a . \qquad (4)$$

For demineralized water at 24°C saturated with SrF_2 the strontium saturation concentration $(C_{Sr})_s$ is approximately 95 mg/ℓ. Referring to Table 12 it is seen that over the range of flow rates used the maximum solution strontium concentrations are only a small fraction of the saturation concentration (<10%). Therefore, the change in the driving force for dissolution $[(C_{Sr})_s - (C_{Sr})_a]$ is <10% as the flow is varied from 1.2 to 13.0 mℓ/min. Since the precision of the experimental procedure used was about ±15%, the procedure was not capable of detecting significant changes in the dissolution rate over the range of flows used.

The accidental exposure of a ^{90}Sr compound to a natural water environment is most closely approximated using the dynamic system. Natural currents in the water would serve to disperse the dissolved strontium and dissolution would occur at a strontium concentration only slightly above that of the water environment. Therefore, most dissolution rate measurements were obtained using the dynamic system; and, unless otherwise noted, all dissolution rate data presented in the following sections were so obtained. Also, all dynamic system rate data presented are the steady state values.

The dissolution rate data obtained using nonradioactive strontium fluoride are expressed in two different sets of units:

- grams of strontium dissolved per unit time per unit of initial exposed surface, and
- grams of strontium dissolved per unit time per gram of strontium initially present.

The two sets of units are used to permit a more valid comparison of the dissolution behavior of SrF_2 and the titanates. Unfortunately, it was not possible to measure the surface areas of $^{90}SrF_2$ samples, and the dissolution rates of the $^{90}SrF_2$ samples are expressed on a contained strontium basis only.

5.2.1 Nonradioactive Strontium Fluoride

The dissolution behavior of nonradioactive strontium fluoride in aqueous solutions was studied in an attempt to identify the factors which influence the dissolution rate. The three grades of nonradioactive SrF_2 and four test solvents described in Sections 4.1.1 and 4.1.3 were used for the dissolution rate measurements. Samples of the three grades of SrF_2 were given various thermal treatments and the dissolution rates of the treated samples determined using the dynamic system. A large number of samples were evaluated at 24°C and the dissolution results obtained are presented in Tables 13 through 15. The data show that the dissolution behavior of nonradioactive strontium fluoride is a complex phenomenon that is influenced by several properties of the SrF_2, such as impurity content, surface area and thermal history, as well as the nature and temperature of the dissolving medium. The thermal treatment and surface area of the strontium fluoride are interrelated and the relationship is highly dependent on the impurity content of the fluoride.

Referring to Tables 13 through 15 it can be seen that for a specific solvent (i.e., demineralized water) and constant test temperature (24°C) the measured dissolution rates varied up to sixty-fold depending on the characteristics of the SrF_2. Even fluoride samples having the same impurity content and surface area had markedly different dissolution rates depending on the thermal treatment they had received, differences that could not be accounted for by the lack of precision of the experimental procedures.

The effect of temperature on the dissolution of nonradioactive strontium fluoride was studied over a range of 3 to 90°C using the dynamic system. The tests were limited to demineralized water and natural seawater using several different SrF_2 samples. The results obtained are presented in Table 16 and show that the dissolution rate increases with increasing solvent temperature as expected. At temperatures above 60°C the dissolution rate increased very rapidly, making it difficult to obtain a reliable measure of the rates at the higher temperatures. The effect of temperature on the dissolution rate was approximately the same for all of the SrF_2 samples tested.

TABLE 13. The Steady-State Dissolution Rate of High-Purity Nonradioactive SrF_2 in Aqueous Solutions at 24°C

			Dissolution Rate[b]							
			μg Sr Dissolved/hr-g Sr Initially Present				μg Sr Dissolved/hr-cm^2 of Initial Surface			
Sample No.	Thermal Treatment[a]	Surface Area cm^2/g	Demineralized Water	Tap Water	Synthetic Seawater	Natural Seawater	Demineralized Water	Tap Water	Synthetic Seawater	Natural Seawater
1-A	Fired at 1100°C for 20 hr	510	880 ± 190			290 ± 64	1.2 ± 0.26			0.40 ± 0.09
1-B	Fired at 1100°C for 96 hr	440	320 ± 60	450 ± 105	170 ± 45	120 ± 36	0.51 ± 0.10	0.71 ± 0.17	0.27 ± 0.07	0.19 ± 0.06
1-C	Fired at 900°C for 96 hr	500	680 ± 130	720 ± 68	310 ± 72	210 ± 36	0.95 ± 0.18	1.0 ± 0.10	0.43 ± 0.10	0.29 ± 0.05
1-D	Fired at 800°C for 240 hr	510	660 ± 140			290 ± 82	0.91 ± 0.19			0.40 ± 0.11
1-E	Fired at 1000°C for 1 hr	500	1200 ± 270			390 ± 75	1.70 ± 0.39			0.54 ± 0.11
1-F	Fused at 1500°C	620	170 ± 30	220 ± 30	90 ± 22	83 ± 4	0.19 ± 0.03	0.24 ± 0.03	0.10 ± 0.02	0.094 ± 0.005
1-G	Pellets pressed to 70% of TD, fired at 1100°C for 4 hr	910	350 ± 40	240 ± 26	130 ± 40	120 ± 17	0.27 ± 0.03	0.18 ± 0.02	0.10 ± 0.03	0.092 ± 0.01
1-H	Pellets pressed to 70% of TD, fired at 1100°C for 20 hr	390	120 ± 11			52 ± 30	0.21 ± 0.04			0.092 ± 0.05
1-I	SrF_2 + 10 wt% NaF fired at 1100°C for 4 hr	660	1800 ± 370			360 ± 130	1.80 ± 0.35			0.44 ± 0.12
1-J	SrF_2 + 10 wt% NaF fired at 1100°C for 20 hr	520	1200 ± 140		430 ± 100	280 ± 66	1.5 ± 0.19		0.53 ± 0.13	0.33 ± 0.09
1-K	SrF_2 + 10 wt% NaF fused at 1450°C	480	970 ± 150			220 ± 62	1.30 ± 0.20			0.35 ± 0.08

(a) After firing the SrF_2 was crushed and a -1/4 +1/8-in. size fraction used for the dissolution tests.
(b) At the 95% confidence level.

TABLE 14. The Steady-State Dissolution Rate of Commercial SrF_2 in Aqueous Solutions at 24°C

			Dissolution Rate[b]							
			μg Sr Dissolved/hr-g Sr Initially Present				μg Sr Dissolved/hr-cm^2 of Initial Surface			
Sample No.	Thermal Treatment[a]	Surface Area cm^2/g	Demineralized Water	Tap Water	Synthetic Seawater	Natural Seawater	Demineralized Water	Tap Water	Synthetic Seawater	Natural Seawater
2-A	Fired at 1100°C for 4 hr	560	1200 ± 220			360 ± 73	1.40 ± 0.27			0.45 ± 0.09
2-B	Fired at 1100°C for 20 hr	370	620 ± 40	680 ± 80	140 ± 47	110 ± 16	1.2 ± 0.07	1.3 ± 0.15	0.26 ± 0.09	0.21 ± 0.03
2-C	Fired at 1100°C for 48 hr	250	235 ± 17	330 ± 200	210 ± 35	150 ± 47	0.64 ± 0.05	0.92 ± 0.56	0.59 ± 0.10	0.48 ± 0.13
2-D	Fired at 900°C for 20 hr	580	980 ± 120	1200 ± 240	210 ± 43	350 ± 24	1.2 ± 0.15	1.4 ± 0.28	0.25 ± 0.05	0.42 ± 0.02
2-E	Fired at 900°C for 96 hr	430	610 ± 46			150 ± 16	0.99 ± 0.07			0.24 ± 0.03
2-F	Fused at 1500°C	510	290 ± 47			92 ± 17	0.40 ± 0.06			0.13 ± 0.02

(a) After firing the SrF_2 was crushed and a -1/4 + 1/8-in. size fraction used for the dissolution experiments.
(b) At the 95% confidence level.

TABLE 15. The Steady-State Dissolution Rate of WESF-Grade Nonradioactive SrF_2 in Aqueous Solutions at 24°C

			Dissolution Rate(b)							
			μg Sr Dissolved/hr-g Sr Initially Present				μg Sr Dissolved/hr-cm^2 of Initial Surface			
Sample No.	Thermal Treatment(a)	Surface Area cm^2/g	Demineralized Water	Tap Water	Synthetic Seawater	Natural Seawater	Demineralized Water	Tap Water	Synthetic Seawater	Natural Seawater
3-A	Fired at 1100°C for 0.5 hr	380	670 ± 72			120 ± 20	1.1 ± 0.10			0.20 ± 0.03
3-B	Fired at 1100°C for 1 hr	440	130 ± 24			75 ± 12	0.19 ± 0.04			0.11 ± 0.02
3-C	Fired at 1100°C for 1 hr	330	67 ± 34			30 ± 13	0.16 ± 0.08			0.07 ± 0.03
3-D	Fired at 1100°C for 4 hr	380	100 ± 42			74 ± 8	0.17 ± 0.03			0.13 ± 0.01
3-E	Fired at 1100°C for 4 hr (-140 +200 mesh fractions)	2400	650 ± 230			350 ± 120	0.18 ± 0.06			0.09 ± 0.03
3-F	Fired at 1100°C for 16 hr	820	200 ± 38			93 ± 19	0.16 ± 0.03			0.073 ± 0.02
3-G	Fired at 1100°C for 20 hr	660	140 ± 24	170 ± 29	76 ± 27	58 ± 20	0.15 ± 0.03	0.18 ± 0.03	0.08 ± 0.03	0.062 ± 0.02
3-H	Fired at 1100°C for 24 hr	600	140 ± 20			96 ± 14	0.17 ± 0.02			0.11 ± 0.02
3-I	Fired at 1100°C for 96 hr	200	120 ± 53			60 ± 14	0.40 ± 0.17			0.20 ± 0.05
3-J	Fired at 1100°C for 240 hr	140	32 ± 7			24 ± 6	0.15 ± 0.03			0.12 ± 0.03
3-K	Fired at 900°C for 96 hr	340	290 ± 42			66 ± 11	0.55 ± 0.08			0.13 ± 0.02
3-L	Fired at 800°C for 0.5 hr	820	1300 ± 210			460 ± 78	1.1 ± 0.17			0.36 ± 0.06
3-M	Fired at 800°C for 4 hr	1030	800 ± 73			160 ± 22	0.50 ± 0.05			0.10 ± 0.01
3-N	Fired at 800°C for 240 hr	510	360 ± 28	420 ± 56	130 ± 24	130 ± 12	0.46 ± 0.04	0.54 ± 0.07	0.17 ± 0.03	0.17 ± 0.02
3-O	Fired at 800°C for 4400 hr	290	62 ± 7			36 ± 4	0.14 ± 0.02			0.09 ± 0.01
3-P	Fused at 1550°C	480	150 ± 16	200 ± 42	110 ± 21	72 ± 7	0.21 ± 0.02	0.27 ± 0.06	0.15 ± 0.03	0.10 ± 0.01

(a) After firing the SrF_2 was crushed and, unless otherwise noted, a -1/4 +1/8-in. size fraction used for the dissolution measurements.
(b) At the 95% confidence level.

TABLE 16. The Effect of Temperature on the Dissolution Rate of Nonradioactive Strontium Fluoride

Solution Temperature, °C	Dissolution Rate, g Sr Dissolved/hr-g Sr Initially Present											
	Sample No. 1-F High-Purity SrF$_2$ Fused at 1500°C		Sample No. 1-B High-Purity SrF$_2$ Fired at 1100°C for 96 hr		Sample No. 2-G Commercial SrF$_2$ Fired at 1100°C for 48 hr		Sample No. 3-B WESF-Grade SrF$_2$ Fired at 1100°C for 1 hr		Sample No. 3-F WESF-Grade SrF$_2$ Fired at 1100°C for 16 hr		Sample No. 3-P WESF-Grade SrF$_2$ Fused at 1550°C	
	Demineral. Water	Natural Seawater	Demineral. Water	Natural Seawater	Demineral. Water	Natural Seawater	Demineral. Water	Natural Seawater	Demineral. Water	Natural Seawater	Demineral. Water	Natural Seawater
3	83	41	140	48	120	63	73	32	93	39	74	31
9	99	47	150	54	130	76	76	44	96	51	77	36
24	170	83	320	120	240	150	130	75	200	53	150	72
34	300						250		330		240	
35		110		150		220		100		120		89
42	380	140	640	230	490	270	300	130	490	150	310	120
58	700											
61	760		1100		770		680		740		680	
81	2500		3000		2500		1900		2400		2000	
90	3200						2600		3100		2500	

Although there are some obvious exceptions, evaluation of the dissolution rate data identifies several important factors regarding the dissolution behavior of nonradioactive SrF_2.

- The dissolution behavior of nonradioactive high-purity SrF_2 is similar to that of commercial SrF_2, and they both dissolve at a much faster rate than the WESF-grade SrF_2. The overall relative dissolution rates for the high purity, commercial and WESF-grade SrF_2 in demineralized water are estimated to be 1:1:0.5; although there are many instances where much greater differences were observed. In natural seawater the overall relative dissolution rates are estimated to be 1:1:0.7. The slower dissolution rate of the WESF-grade SrF_2 can be attributed to the impurities present in the fluoride. How the impurities serve to reduce the dissolution rate was not determined, but may result from the effects they have on the sintering characteristics of the SrF_2 or from the formation of complex phases. It should be noted, however, that when a large amount of a readily soluble fluoride (10 wt% NaF) was added to high-purity SrF_2 and samples of the mixture fired at high temperature, the dissolution rates of the treated samples in demineralized water were much higher than those of high-purity SrF_2 which had received the same thermal treatment. Thus it appears that different impurities can have greatly different effects on the dissolution behavior of SrF_2.
- The thermal treatment the strontium fluoride receives has a pronounced effect on its dissolution behavior. In general the higher the temperature at which the SrF_2 is fired the lower its dissolution rate. However, time at temperature also affects the dissolution rate; and it is possible for SrF_2 held at a relatively low temperature for a long period of time to have a lower dissolution rate than SrF_2 held at a higher temperature for a shorter period of time. Much of the influence of the thermal treatment on the dissolution rate can be attributed to its effect on the surface area of the SrF_2. The relationship is more complex than simply one of surface area, however, as witness the several experiments in which fluoride samples having the same

composition and surface area but different thermal treatment had markedly different dissolution rates (i.e., Table 15, Samples 3-A and 3-D; Table 13, Samples 1-C and 1-E). Unfortunately a detailed study to determine how the thermal treatment influences the dissolution rate, other than by its effect on surface area, was beyond the scope of this program. One apparent anomaly regarding the thermal treatment and surface area of SrF_2 should be noted. When SrF_2 powder is heated above the temperature where sintering begins, one would expect the surface area of the fluoride to decrease with time at temperature, and this is generally the case. It was found, however, that when WESF-grade SrF_2 powder was heated at 800°C and above the surface area did not decrease continuously with time at temperature (see Table 17). Instead, when the SrF_2 was held at a constant temperature of 800°C or higher the surface area decreased very rapidly at first, then increased somewhat and finally decreased to a minimum value. The cause of this unexpected temperature-time-surface area relationship was not determined, but it was observed in several experiments. The phenomenon was not observed with a similar number of SrF_2 samples heated at temperatures below 800°C. In these cases the surface area decreased continuously with time at temperature as expected.

- The dissolution rate of nonradioactive strontium fluoride depends on the composition of the aqueous solvent. For the three grades of SrF_2 used in the tests the dissolution rates were lowest in the natural seawater, slightly higher in the synthetic seawater, much higher in demineralized water and highest in plant tap water. Although the results from individual experiments varied over a considerable range, the overall average dissolution rate of nonradioactive SrF_2 in demineralized water was approximately three times as great as in the natural seawater. The reasons for the low dissolution rate of SrF_2 in seawater were not determined. However, it was shown that the initial strontium and fluoride concentrations of the synthetic and natural seawater were not high enough to cause the observed decreases in the dissolution rates. This was demonstrated experimentally by

TABLE 17. The Surface Area of WESF-Grade SrF_2 as a Function of Thermal Treatment

Time at Temperature, hr	600°C	700°C	800°C	900°C	1100°C	
0	2700	2700	2700	2700	2700	2700
0.5	2280	1340	820	460		380
1	2000	1120	970	640	300	460
2	1850	970		680		520
4	1740	910	1030	510	400	380
8	1650	860	950	470	500	380
20					660	
24	1530	780	830	440	600	370
72	1410	770	540	400		230
96					200	
240	1230	720	510	380	150	140
1500			470			
4400			480			

adding strontium nitrate and sodium fluoride to demineralized water to give Sr^{++} and F^- concentrations equivalent to those found in natural seawater, and measuring the dissolution rate of SrF_2 in the resulting solution. The dissolution rates so obtained were less than those obtained with the same SrF_2 in demineralized water, but were much higher than those observed in natural seawater (see Table 18).

TABLE 18. The Dissolution Rate of WESF-Grade SrF_2 in Various Solutions at 24°C

	Dissolution Rate, µg Sr Dissolved/hr g Sr Initially Present		
SrF_2 Used	Demineralized Water	Demineralized Water Spiked with Sr^{++} and F^-(a)	Natural Seawater
Sample 3-G, fired at 1100°C for 20 hr	140 ± 24	110 ± 19	58 ± 20
Sample 3-N, fired at 800°C for 240 hr	360 ± 28	290 ± 34	130 ± 12

(a) Sr and F were added to the water to give concentrations equal to those found in natural seawater.

One important additional fact should be mentioned regarding the dissolution behavior of nonradioactive strontium fluoride. The bulk of the tests were carried out using -1/4 +1/8-in. granules of SrF_2 which had been fired at 800°C or higher. In none of the tests were any of the SrF_2 granules observed to disintegrate to a powder, even after prolonged exposure to the flowing solvent. This is an important consideration in evaluating the use of strontium fluoride heat sources for terrestrial applications.

5.2.2 Radioactive Strontium Fluoride

The dissolution rate of $^{90}SrF_2$ in demineralized water and natural seawater was measured using the dynamic system. The two grades of $^{90}SrF_2$ described in Section 4.1.1 were used for the tests. The measurements were carried out at the ambient temperature of the hot cell and solvent temperatures were approximately 30°C. The results obtained are presented in Table 19. The high dissolution rate observed with the WESF-grade $^{90}SrF_2$ (Sample No. 4-B) in demineralized water is difficult to explain, since a similar high rate was not observed in seawater. Unfortunately, there was not sufficient WESF-grade $^{90}SrF_2$ having the same thermal history available to repeat the experiments. The dissolution rates for the $^{90}SrF_2$ are higher than those obtained with similar nonradioactive SrF_2 samples. Exact comparisons cannot be made because the surface areas of the $^{90}SrF_2$ samples are unknown and it is impossible to prepare nonradioactive SrF_2 having the same impurity content and thermal history as the $^{90}SrF_2$. However, Table 20 shows a comparison of radioactive and nonradioactive samples having approximately the same initial composition and thermal history (in preparing the nonradioactive SrF_2 no attempt was made to simulate decay product buildup). The data show that the dissolution rates for the radioactive $^{90}SrF_2$ samples are from 2 to 18 times as great as those for similar nonradioactive samples. However, the $^{90}SrF_2$ samples were similar to the nonradioactive samples in that the radioactive granules did not disintegrate to a powder even after prolonged exposure to the flowing solvent.

TABLE 19. The Dissolution Rate of $^{90}SrF_2$ in Aqueous Solutions at 30°C

Sample No.	Material	Dissolution Rate,(c) μg Sr Dissolved/hr-g Sr Initially Present: Demineralized Water	Natural Seawater
4-A	WESF-Produced Fuel(a) Grade $^{90}SrF_2$	442 ± 48	298 ± 25
4-B	WESF-Grade $^{90}SrF_2$(b)	1630 ± 260	270 ± 50

(a) Fired at 1100°C for ∿8 hr, -1/4 +1/8-in. size fraction used, approximately 6 months old at time of test.
(b) Fired at 1100°C for ∿8 hr, then held at 800°C for 4400 hr, -1/4 + 1/8-in. size fraction used, approximately 2 years old at time of use.
(c) Obtained from duplicate experiments.

TABLE 20. Comparison of the Dissolution Rates of SrF_2 and $^{90}SrF_2$ at 30°C

Material	Sample No.	Dissolution Rate, μg Sr Dissolved/hr-g Sr Initially Present: Demineralized Water	Natural Seawater
WESF-Produced $^{90}SrF_2$	4-A	442	298
WESF-Grade SrF_2	3-E	230(a)	150(a)
WESF-Grade $^{90}SrF_2$	4-B	1630	270
WESF-Grade SrF_2	3-0	90(a)	40(a)

(a) Estimated values for 30°C.

5.2.3 Nonradioactive Strontium Titanates

The dissolution behavior of nonradioactive strontium titanates in demineralized water and natural seawater was also studied using the dynamic system. The $SrTiO_3$ and $SrTiO_4$ used in the tests are described in Section 4.1.2. The thermal treatment given the titanate sample is described in Table 21. Unlike SrF_2, the dissolution rates of the titanates continued to decrease with time and failed to reach constant values even after several hundred hours exposure to the flowing solvent. The dissolution rate data for the titanates are shown in Figures 7 through 10. The data show that Sr_2TiO_4 dissolves at a much more rapid rate than $SrTiO_3$; and as was the case with SrF_2, the titanates dissolve several times faster in demineralized water than in natural seawater.

Because the dissolution rates of the titanates continually decrease with time, it is difficult to compare their dissolution rates with those of $^{90}SrF_2$ and SrF_2. The wide variations in dissolution rate of SrF_2, depending on impurity content, surface area and thermal treatment, make the comparison even more difficult. In Table 22 the maximum and minimum dissolution rates observed for SrF_2 and $^{90}SrF_2$ are compared with the dissolution rates of the titanates after 50-hr exposure. If the dissolution rates are compared on a surface area basis it is apparent that SrF_2 dissolves many times faster than $SrTiO_3$ and substantially faster than the Sr_2TiO_4. On the basis of contained strontium, however, the SrF_2 and $^{90}SrF_2$ dissolve at a slower rate than the Sr_2TiO_4 but several times faster than $SrTiO_3$. For an operating heat source of a given heat output, the number of curies (and grams) of ^{90}Sr required will be about the same regardless of the compound used. Therefore, in evaluating source safety it appears the most reasonable procedure is to compare the fluoride and the titanates on a basis of contained strontium.

TABLE 21. Thermal Treatment of Strontium Titanate Samples Used in the Dissolution Tests

Sample No.	Material	Thermal Treatment	Surface Area cm^2/g
4-A	$SrTiO_3$	Fired at 1450°C for 4 hr, crushed and -1/4 +1/8-in. size fraction used for tests.	15,000
4-B	$SrTiO_3$	Fired at 1450°C for 8 hr, crushed and -1/4 +1/8-in. size fraction used for tests.	1,000
4-C	Sr_2TiO_4	Fired at 1450°C for 4 hr, crushed and -1/4 + 1/8-in. size fraction used for tests.	12,000
4-D	Sr_2TiO_4	Fired at 1450°C for 8 hr, crushed and -1/4 + 1/8-in. size fraction used for tests.	2,300

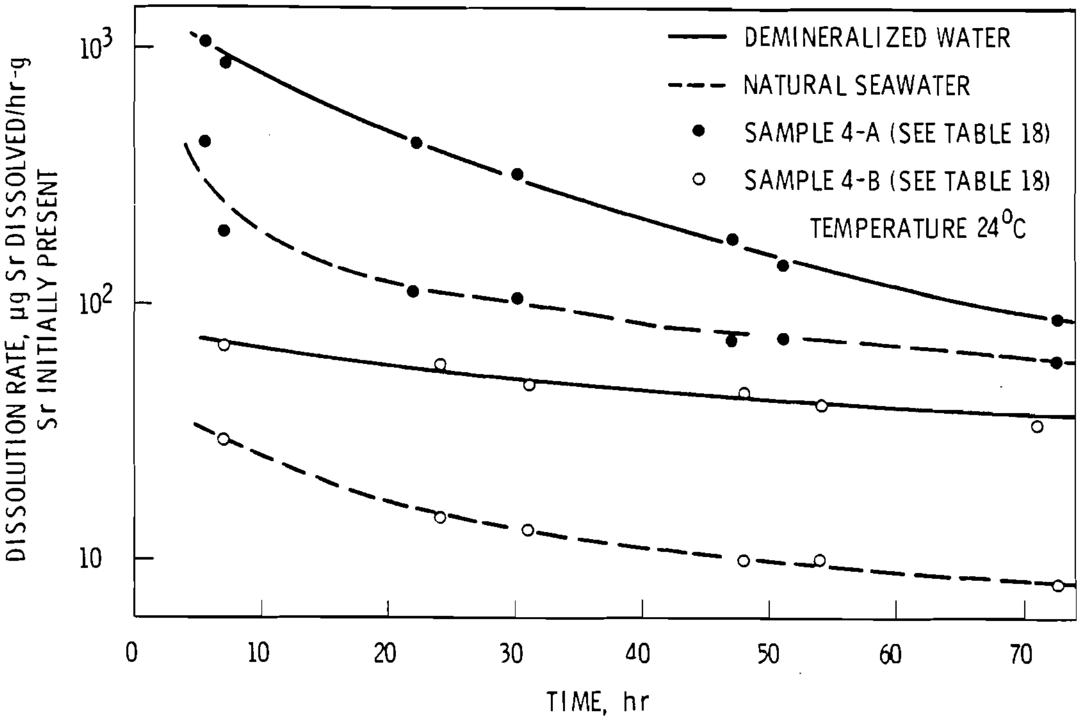

FIGURE 7. Dissolution Rate of $SrTiO_3$ in Demineralized Water and Natural Seawater at 24°C (in µg Sr dissolved/hr-g Sr initially present)

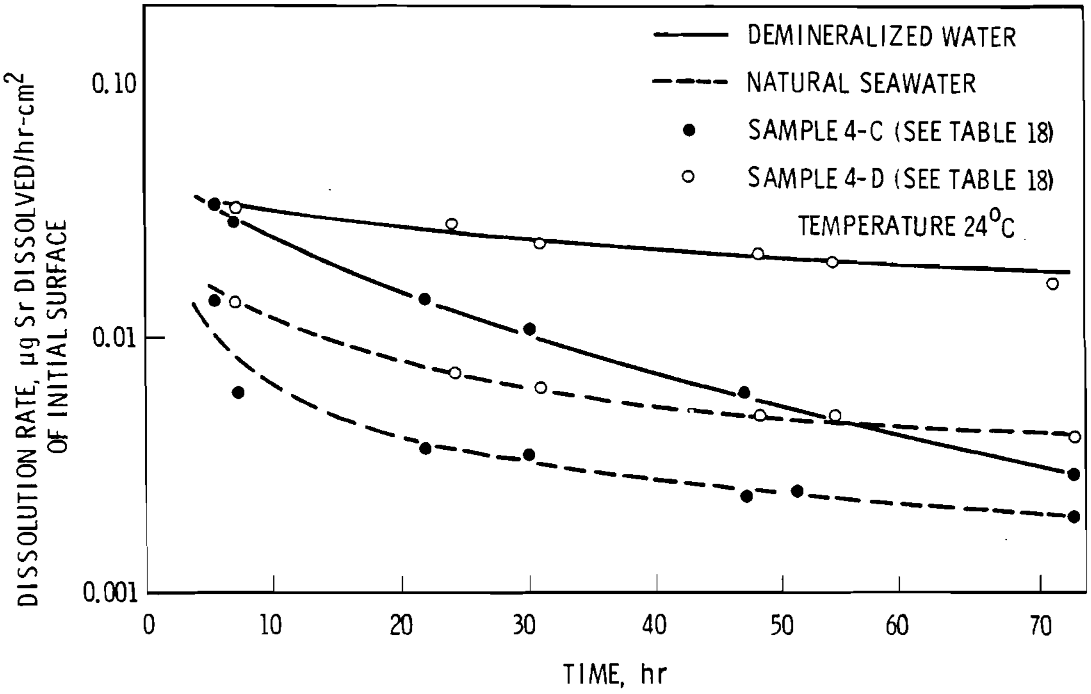

FIGURE 8. Dissolution Rate of $SrTiO_3$ in Demineralized Water and Natural Seawater at 24°C (in µg Sr dissolved/hr-cm^2 of initial surface)

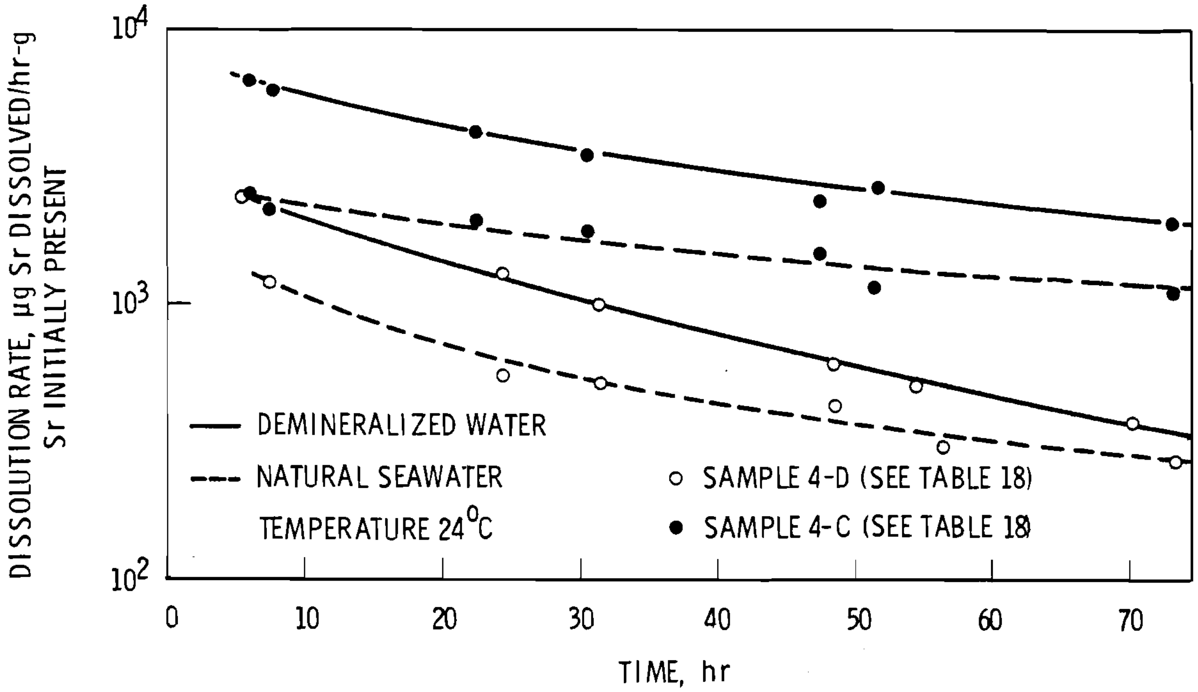

FIGURE 9. Dissolution Rate of Sr_2TiO_4 in Demineralized Water and Natural Seawater at 24°C (in μg Sr dissolved/hr-g Sr initially present)

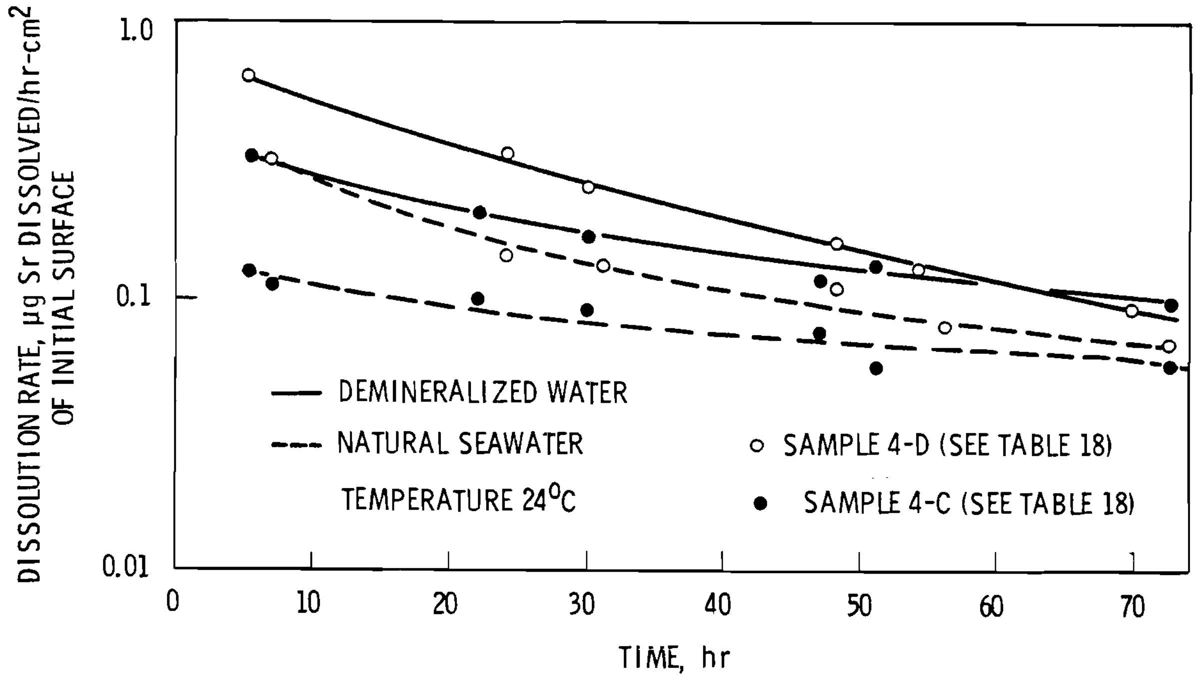

FIGURE 10. Dissolution Rate of Sr_2TiO_4 in Demineralized Water and Natural Seawater at 24°C (in μg Sr dissolved/hr-cm^2 of initial surface)

TABLE 22. Comparison of the Dissolution Rates of SrF_2, $^{90}SrF_2$, $SrTiO_3$ and Sr_2TiO_4 at 24°C[(a)]

Material	Dissolution Rate: μg Sr Dissolved/hr-g Sr Initially Present, Demineralized Water	Dissolution Rate: μg Sr Dissolved/hr-g Sr Initially Present, Natural Seawater	Dissolution Rate: μg Sr Dissolved/hr-cm^2 of Initial Surface, Demineralized Water	Dissolution Rate: μg Sr Dissolved/hr-cm^2 of Initial Surface, Natural Seawater
SrF_2 (minimum rate)(b)	32	24	0.14	0.062
SrF_2 (maximum rate)(b)	1900	460	1.8	0.54
$^{90}SrF_2$ (minimum rate)(c)	440	270		
$^{90}SrF_2$ (maximum rate)(c)	1630	298		
$SrTiO_3$ (minimum rate)(d)	48	11	0.0053	0.0024
$SrTiO_3$ (maximum rate)(d)	170	76	0.021	0.0050
Sr_2TiO_4 (minimum rate)(e)	600	440	0.13	0.07
Sr_2TiO_4 (maximum rate)(e)	3200	1400	0.16	0.095

(a) $^{90}SrF_2$ data are for 30°C.
(b) Minimum and maximum equilibrium dissolution rates observed with any nonradioactive SrF_2 sample.
(c) Minimum and maximum equilibrium dissolution rates observed with any $^{90}SrF_2$ sample.
(d) Minimum and maximum dissolution rates observed with any $SrTiO_3$ sample after 50-hr exposure.
(e) Minimum and maximum dissolution rates observed with any Sr_2TiO_4 sample after 50-hr exposure.

The above comparison does not take into account the apparent continual decrease in dissolution rate of the titanates with time. If the dissolution rate of the Sr_2TiO_4 continues to decrease with time then it is possible that the rate may decrease to the point where it is less than that of SrF_2.

No previous work has been reported on the dissolution behavior of radioactive strontium fluoride. However, a number of years ago Gray(1) studied the dissolution behavior of nonradioactive SrF_2 in deionized water, natural and synthetic seawater, and hydrochloric acid solutions. The strontium fluoride used for the tests was spiked with a low level of ^{85}Sr tracer for analytical purposes. Unfortunately no information was provided on the impurity content of the strontium fluoride used in the studies. The tests were carried out at 25°C and 66°C using both static and dynamic systems. The data were reported on a surface area basis, but sufficient information was provided to allow conversion of the data to a contained strontium basis. Gray also investigated the dissolution behavior of nonradioactive $SrTiO_3$ and Sr_2TiO_4 under similar conditions. Again, however, no data were provided on the purity of the two compounds.

Direct comparison of the PNL and Gray data is difficult because of differences in the thermal treatment and probable differences in impurity content of the compounds used for the two studies. Table 23 shows both sets of data for SrF_2, $SrTiO_3$, and Sr_2TiO_4 samples that had the greatest similarity in thermal treatment. It should be noted, however, that the surface areas of the compounds used by Gray were much less than those of the corresponding PNL compounds. Overall, there are substantial differences in the measured dissolution rates for each compound, especially when compared on a surface area basis. This is not unexpected, however, considering the differences in thermal treatment and surface areas of the various samples. Evaluation of the results does show several areas of agreement between the two sets of data including:

- The dissolution rate of SrF_2 in a dynamic system changes initially, but reaches a constant value after several hours exposure.
- The dissolution rates of the titanates in a dynamic system apparently decrease continually with time.
- The dissolution rates of the titanates are lower in natural and synthetic seawater than in demineralized or deionized water.
- Gray's data show the relative dissolution rates in all test solutions were $Sr_2TiO_4 > SrF_2 > SrTiO_3$. The PNL data are in agreement on a contained strontium basis; but on a surface area basis the dissolution rate is higher for SrF_2 than for Sr_2TiO_4.

One significant area of disagreement was that the PNL data show the dissolution rate of SrF_2 is higher in demineralized water than in seawater (same as the titanates), while Gray's data showed the opposite effect.

Other data have been reported in the literature on the dissolution behavior of nonradioactive $SrTiO_3$ and Sr_2TiO_4. All of the data were obtained using static systems, however, and are difficult to compare with the PNL data which were obtained with the dynamic system.

TABLE 23. Comparison of a PNL and Gray(1) Dissolution Rate Data Obtained with a Dynamic System

			Dissolution Rate(a)			
			µg Sr Dissolved/hr-g Sr Initially Present		µg Sr Dissolved/hr-cm^2 of Initial Surface	
Material	Surface Area cm^2/g	Temperature °C	Demineralized Water	Natural Seawater	Demineralized Water	Natural Seawater
PNL SrF_2(b)	660	24	140	58	0.14	0.06
Gray SrF_2(c)	93	25	340	480	2.4	3.7
PNL $SrTiO_3$(d)	1000	24	58	17	0.028	0.0082
Gray $SrTiO_3$(e)	62	25	19	9	0.15	0.069
PNL Sr_2TiO_4(f)	2300	24	1400	700	0.37	0.09
Gray Sr_2TiO_4(g)	65	25	1200	500	11.0	4.7

(a) The SrF_2 rates are the steady state dissolution rates, the titanate rates are the differential dissolution rates after 20 hr exposure.
(b) Sample 3-G WESF-grade SrF_2 fired at 1100°C for 20 hr.
(c) SrF_2 prepared by flowsheet similar to the WESF flowsheet. The SrF_2 was fired at 1200°C for 7 hr and then crushed. A -60 +80 mesh fraction was used for the tests.
(d) Sample 4-B fired at 1450°C for 8 hr.
(e) Material fired at 1400°C for 12 hr. A -60 +80 mesh fraction was used for the tests.
(f) Sample 4-D fired at 1450°C for 8 hr.
(g) Material fired at 1450°C for 12 hr. A -60 +80 mesh fraction was used for the tests.

Some data are available in the literature on the dissolution behavior of $^{90}SrTiO_3$.(7-9) All of the data reported were obtained using static systems. The $^{90}SrTiO_3$ used for the tests was in the form of hot pressed or cold pressed and sintered pellets; and the dissolution rate data were reported on the basis of pellet geometric surface area. Most of the tests used stoichiometric $SrTiO_3$ pellets, but pellets which contained an excess or deficiency of TiO_2 were also tested. Data on the impurity content of the titanate pellets was limited to the other alkaline earth elements Ca, Ba, and Mg. Comparison of the $^{90}SrTiO_3$ dissolution rate data with that for $^{90}SrF_2$ is difficult because they were obtained using different systems (static versus dynamic) and because of differences in impurity content and thermal history. To get a relative measure of the dissolution rates the average dissolution rate of $^{90}SrTiO_3$ for the first ten days exposure to a solvent was calculated from the reported data and compared with the PNL determined dissolution rates for $^{90}SrF_2$. The results so obtained are presented in Table 24; they show that the dissolution rate for $^{90}SrTiO_3$, on a contained strontium basis, is much less than that of $^{90}SrF_2$. It must be remembered, however, that the dissolution rate of $^{90}SrTiO_3$ in a flow system may be significantly different from its dissolution rate in a static system.

TABLE 24. Comparison of $^{90}SrF_2$ and $^{90}SrTiO_3$ Dissolution Rates

Material	Dissolution Rate, µg Sr Dissolved/hr-g Sr Initially Present Natural Seawater	 Demineralized Water
WESF $^{90}SrF_2$	298	442
WESF-Grade $^{90}SrF_2$	270	1630
$^{90}SrTiO_3$	150(7)(a)	30(8,9)(a)

(a) Average rate for first ten days in a static system.

5.3 ASSESSMENT OF $^{90}SrF_2$ DISSOLUTION BEHAVIOR DATA

The solubility and dissolution rate of $^{90}SrF_2$ in fresh water and seawater are relatively high and if $^{90}SrF_2$ is accidentally exposed to a water environment the consequences may be quite serious. Assessing the hazards associated with such an exposure is very difficult, however, because of the many variables involved. A number of theoretical analyses have been carried out by different investigators on the consequences of a release of radioactivity (i.e., $^{90}SrTiO_3$, $^{238}PuO_2$) to an ocean environment, and a similar study is planned for $^{90}SrF_2$ using the experimental data developed in this study. Such a study will allow a more realistic comparison of $^{90}SrF_2$ and $^{90}SrTiO_3$ as heat source fuels for terrestrial applications.

Some idea of the potential problems involved in using $^{90}SrF_2$ as a heat source fuel can be gained by considering the basic solubility and dissolution rate data. The maximum permissible concentration (mpc) for ^{90}Sr in water in an uncontrolled environment is 3×10^{-7} µCi/mℓ. The solubility of strontium fluoride in seawater at ocean temperatures is in the range of 0.13 to 0.14 g/ℓ. For $^{90}SrF_2$ having a ^{90}Sr isotopic content of 50% this corresponds to a ^{90}Sr concentration of about 6×10^{-3} Ci/mℓ which is about

2×10^{10} times the mpc level. Since a WESF capsule filled with fuel grade $^{90}SrF_2$ contains about 150,000 Ci of ^{90}Sr when freshly loaded, the potential exists for contaminating a large volume of water if the source is accidentally exposed to an aqueous environment.

Based on the measured dissolution rate for $^{90}SrF_2$ in seawater, it should require about 135 days for the $^{90}SrF_2$ contained in a WESF capsule to dissolve if exposed in the ocean. In actuality the time required would be much longer since several factors would serve to reduce the dissolution rate. Even so, the rate of dissolution would be much greater than the rate of decay of the ^{90}Sr and a large volume of water would be contaminated to a very high level with ^{90}Sr. The theoretical analyses mentioned above will be needed to define the extent to which the water surrounding the capsule would be contaminated and the consequences of the exposure.

6.0 CONCLUSIONS

Evaluation of the experimental data obtained in this study and that reported by previous investigators leads to several conclusions regarding the dissolution behavior of strontium fluoride and the strontium titanates when exposed to aqueous media.

- The dissolution rates of the radioactive strontium compounds in aqueous media are much greater than those of the nonradioactive compounds. This is most likely due to the intense beta and bremsstrahlung activity associated with ^{90}Sr-^{90}Y decay, but this has not been proven experimentally. For $^{90}SrF_2$ the measured dissolution rates in seawater and demineralized water are up to 18 times greater than the dissolution rates of nonradioactive SrF_2 of similar composition and thermal history.
- The presence of soluble fluoride impurities in the strontium fluoride, such as those normally found in WESF produced $^{90}SrF_2$, appears to decrease the dissolution rate in aqueous media. The impurities also decrease the solubility of SrF_2 in demineralized water, but have little effect on its solubility in seawater. The effect of decay product buildup on the dissolution rate and solubility of strontium fluoride was not determined.
- In general, the longer strontium fluoride is held at a high temperature (≥500°C) the lower will be its dissolution rate in aqueous media.
- The dissolution rates of the fluoride and titanates are much lower in seawater than in fresh or demineralized water. The overall average dissolution rate for all of the strontium fluoride samples studied was approximately three times greater in demineralized water than in seawater.
- Direct comparison of the dissolution of strontium fluoride and the strontium titanates is difficult because the dissolution rates of the titanates appear to decrease continually with time. However,

evaluation of all the data available for both nonradioactive and radioactive compounds indicate that SrF_2 dissolves in aqueous media at a faster rate than $SrTiO_3$ but at a slower rate than Sr_2TiO_4.

Both the dissolution rate and solubility of $^{90}SrF_2$ in aqueous media are relatively high. If $^{90}SrF_2$ is accidentally exposed to an aqueous environment, such as the ocean, rapid dispersal of the ^{90}Sr would result and the consequences could be quite serious. Therefore, if $^{90}SrF_2$ is to be used as a heat source fuel, the fuel containment must be adequate to ensure the $^{90}SrF_2$ will not be in contact with the water if the source is accidentally exposed to an aqueous environment.

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