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STRONTIUM FLUORIDE FLOWSHEET DEVELOPMENT STUDIES
FOR THE WASTE PACKAGING PROGRAM

by

H. T. Fullam and L. A. Bray

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TABLE OF CONTENTS

	<u>Page</u>
1. INTRODUCTION	1
2. SUMMARY	1
3. THE MARTIN PROCESS FOR PREPARING SrF_2	2
4. FLOWSHEET DEVELOPMENT STUDIES	4
4.1 Feed Purification	6
4.2 Fluoride Precipitation and Filtration	11
4.3 Strontium Fluoride Firing	15
4.4 Product Purity	22
4.5 Hot Cell Studies	22
5. CONCLUSIONS	24
6. ACKNOWLEDGMENTS	25
7. REFERENCES	26

LIST OF FIGURES

	<u>Page</u>
FIGURE 1. MARTIN FLOWSHEET FOR PREPARING SrF_2	3
FIGURE 2. PROPOSED FLOWSHEET FOR SrF_2 PREPARATION	5
FIGURE 3. STRONTIUM LOST IN FEED PURIFICATION	8
FIGURE 4. FILTRATION CURVES FOR VARIOUS SrF_2 PRECIPITATES . .	13
FIGURE 5. EFFECT OF TEMPERATURE ON SrF_2 FILTRATION	14
FIGURE 6. THERMOGRAMS OF SrF_2 PREPARED BY PROPOSED FLOWSHEET	16
FIGURE 7. DIFFERENTIAL THERMAL ANALYSIS OF SrF_2	18
FIGURE 8. ALUMINA CRUCIBLE AFTER SEVERAL FIRING CYCLES . . .	20

LIST OF TABLES

	<u>Page</u>
TABLE I. TYPICAL DATA FROM FEED PURIFICATION	10
TABLE II. EFFECT OF pH ON FEED PURIFICATION	11
TABLE III. ANALYSIS OF SrF_2 PRODUCT	22
TABLE IV. ANALYSIS OF $^{90}\text{SrF}_2$ PRODUCT	23

STRONTIUM FLUORIDE FLOWSHEET DEVELOPMENT STUDIES
FOR THE WASTE PACKAGING PROGRAM

1. INTRODUCTION

The current waste management program at ARHCO calls for the isolation, packaging, and storage of cesium and strontium waste as individual compounds in small high integrity containers. Cesium chloride and strontium fluoride were selected for encapsulation.⁽¹⁾ The flowsheet for isolation of the strontium from Purex high level waste will utilize solvent extraction and sulfate precipitation. Conversion of the isolated strontium to the fluoride is to be accomplished by a modified version of the Martin process,^(2,3) which had been developed at the Quehanna facility of the Martin Company to prepare $^{90}\text{SrF}_2$ for use in SNAP devices.

This report summarizes the results of a series of laboratory studies to check out the various steps in the Martin process using both simulated and radioactive feed materials. The results of an engineering scale study of the process are presented in a separate report.⁽⁴⁾

2. SUMMARY

A modified version of the Martin flowsheet has been developed for preparing strontium fluoride for waste packaging. The flowsheet was evaluated using both simulated and radioactive strontium feed materials.

It was demonstrated, using the simulated Sr feed, that SrF_2 of

acceptable quality could be prepared by the proposed flowsheet.

Strontium losses in the process were acceptably low.

Tests of the flowsheet with a nonrepresentative radioactive strontium feed gave a satisfactory product, but the strontium losses were high in the feed purification step. When a representative ^{90}Sr feed is available, additional tests will be needed to show that the strontium losses can be reduced to an acceptable level.

3. THE MARTIN PROCESS FOR PREPARING SrF_2

The Martin process for preparing strontium fluoride is a chemically simple process involving precipitation of the fluoride from a nitrate medium with a metal fluoride. However, carrying out each step of the process requires careful operational control in order to maintain high strontium yields and adequate product quality.

The flowsheet developed by Martin is shown in Figure 1.⁽²⁾ Strontium-90 was received at Quehanna as the solid carbonate from the Hanford facility. The carbonate was converted to the nitrate by addition of nitric acid. The nitrate solution was then neutralized to pH 7 with sodium hydroxide and solid sodium fluoride added. The resulting slurry was digested for one hour, filtered, and the cake was washed with distilled water. The washed filter cake, after drying, was fired at 1100°C to remove any residual moisture. Fluoride prepared in this way contained greater than 96% strontium plus fluorine, and was suitable, after ball milling, for further processing to the required heat source shape. Considerable development effort was expended in optimizing each step of the process.

FIGURE 1. MARTIN FLOWSHEET FOR PREPARING SrF_2

4. FLWSHEET DEVELOPMENT STUDIES

The Martin process was selected as the best procedure available for preparing strontium fluoride for waste packaging. Although the process was well developed, it was decided that the various steps in the process should be checked out at PNL prior to design of the waste packaging plant. This involved two separate studies, a laboratory-scale program, reported below, using both simulated and radioactive strontium feeds; and a pilot-scale study using a simulated strontium feed.⁽⁴⁾

As a result of the laboratory studies, the flowsheet shown in Figure 2 was developed for preparing SrF_2 for packaging. It is a modified version of the Martin flowsheet in which the strontium feed is purified prior to the precipitation of the fluoride. Basically the proposed flowsheet breaks down into five major operations.

1. Purification of the strontium feed solution by adding sodium hydroxide to pH 10 and removing the precipitated solids, containing most of the impurities, by centrifugation.
2. Washing the precipitated solids with water to recover any occluded strontium carried down with the solids. The wash solution is combined with the strontium supernate solution.
3. Precipitation of the Sr as SrF_2 from the purified feed solution at pH 10 by the addition of solid sodium fluoride.
4. Filtration and washing of the SrF_2 .
5. Firing of the SrF_2 to remove residual water.

Each of the five operations is discussed in detail in the following sections.

FIGURE 2. PROPOSED FLOWSHEET FOR SrF_2 PREPARATION

(The laboratory studies described in this report were completed in 1969, and the proposed flowsheet for preparing SrF_2 was based on those studies. However, currently it is planned to use a sulfate precipitation process to purify the strontium solution. This may eliminate the need for the pH 10 precipitation step described in this report.)

4.1 Feed Purification

Operation of the fluoride process, as developed by Martin, is quite sensitive to feed composition. Many of the impurities in the feed are precipitated with the fluoride and end up in the final product. The presence of impurities in the fluoride increases the processing time required and the number of packages needed to contain the fluoride. More important, however, is the fact that the presence of these impurities in the fluoride can have a deleterious effect on the high temperature compatibility of the fluoride with materials of containment. This, in turn, can endanger the long term integrity of the strontium fluoride packages. Therefore, it is essential that the fluoride be as pure as possible when packaged.

When the flowsheet development studies were initiated, it was anticipated that the strontium feed solution from the solvent extraction process⁽⁵⁾ would have a nominal composition of:

	<u>M</u>	<u>Moles Cation/ Mole Sr</u>
Sr	0.4	1
Na	0.4	1
Fe	0.008	0.02
Al	0.008	0.02
Mg	0.12	0.3
Ca	0.04	0.1
HNO_3	0.5	

Strontium fluoride prepared from feed of the above composition, by the Martin flowsheet, would contain substantial amounts of impurities. It was decided, therefore, that the flowsheet should include a feed purification step. The process selected for feed purification was the caustic neutralization procedure developed by Bray⁽⁶⁾ for removing magnesium from strontium. Utilizing this process, the strontium feed solution is treated with sodium hydroxide solution to pH 10 and then centrifuged to remove the precipitated solids. The strontium-containing solution is collected for further processing. The solids are repulped with water to remove any occluded strontium and recentrifuged. The wash solution is combined with the original supernate, while the washed solids are discarded. The critical factors in the process are: (1) the degree of purification obtained, and (2) the amount of strontium lost with the discarded solids.

The purification process was evaluated using a simulated plant feed of the composition listed above. The amount of strontium lost in the purification operation depends on the effectiveness of the wash cycle. When the feed is taken to pH 10 with sodium hydroxide at 25°C, approximately 9-10% of the strontium is carried down with the precipitated solids. Up to 95% of this "loss" can be recovered in the wash cycle, with the amount of strontium recovered depending largely on the volume of wash water used. Figure 3 shows the strontium lost in the discarded solids as a function of the volume of wash water used. By using a large volume of wash water the strontium loss can be reduced to approximately 0.5% of the strontium in the feed solution.

FIGURE 3. STRONTIUM LOST IN FEED PURIFICATION

This results, however, in the necessity of processing a large volume of solution in the fluoride precipitation step. The use of two wash cycles, instead of one, would be quite effective in reducing the strontium loss but would not reduce the volume of wash solution required and would needlessly complicate the process.

In an actual plant operation, effective washing of the centrifuged solids may be difficult. It may be desirable (or necessary) to redissolve the collected solids in nitric acid and then reprecipitate with sodium hydroxide at pH 10. This would allow recovery of most of the strontium lost with the first precipitate in an effective manner. Tests using the simulated strontium feed show that strontium losses can be reduced to <1% using this procedure. The solids dissolved very readily in a dilute nitric acid solution.

From a processing standpoint, the recovery of strontium through a wash cycle is the preferred operation. Redissolution and reprecipitation is only recommended if the wash cycle is ineffective in recovering the strontium.

The purification process is quite effective in removing most of the crucial impurities from the strontium feed solution. Essentially all of the iron and most of the magnesium are precipitated, while lesser amounts of aluminum and calcium are removed. Table I shows typical results obtained using the simulated feed and precipitating at pH 10. Based on the results shown, the purified feed should yield a fluoride product of better than 96% purity. When the wash solution is added to the purified feed the strontium concentration is

decreased, but the strontium-impurity ratios are not changed significantly.

TABLE I. TYPICAL DATA FROM FEED PURIFICATION

Cation	CONCENTRATION						DF Obtained
	Simulated Feed			Purified Feed			
	g/l	M	Cation/Sr	g/l	M	Cation/Sr	
Sr ⁺²	35	0.4	---	34.7	0.4	---	---
Ca ⁺²	1.6	0.04	0.1	1.51	0.37	0.093	1.08
Mg ⁺²	2.9	0.12	0.3	0.13	0.005	0.0125	24
Fe ⁺³	0.45	0.008	0.02	<0.01	<0.0002	<0.0005	>40
Al ^{+3*}	0.22	0.008	0.02	0.04	~0.0015	~0.0038	~ 5

* Based on analysis of fluoride product

The effectiveness of the purification step was evaluated over a range of pH values from 6 to 12. At the lower pH values (≤ 8) the purification obtained was decreased substantially. At higher pH values (> 11) strontium losses (after washing the precipitate) were excessive. Satisfactory operation is possible in the pH range of 9-11 and a value of 10 is recommended as optimum for plant operation. Data showing the effect of pH on feed purification are summarized in Table II.

TABLE II. EFFECT OF pH ON FEED PURIFICATION

pH of Precipitation	Sr in Purified Feed M	Decontamination Factors Obtained			
		Ca	Mg	Fe	Al*
6	0.41	0.98	1.1	>40	~1
8	0.38	0.98	1.9	>40	
10	0.39	1.08	24	>40	~5
11	0.37	1.06	>40	>40	
12	0.29	1.1	>300	>40	

*Based on analysis of SrF_2 product

4.2 Fluoride Precipitation and Filtration

In the proposed flowsheet the strontium is precipitated from the purified feed as the fluoride, at a pH of 10, by the addition of solid sodium fluoride. This differs from the Martin flowsheet in which the precipitation is carried out at pH 7. Except for the pH, all other conditions of precipitation are the same as used in the Martin flowsheet. As long as the solution pH is 6 or higher, pH appears to have little effect on the fluoride precipitation.

The precipitation is carried out between 60 and 90°C and the slurry is digested at temperature for one hour prior to filtration. A slight excess of sodium fluoride (5-10%) is used in the precipitation.

A number of precipitating agents were tested including solid and dissolved potassium fluoride, solid and dissolved sodium fluoride, solid and dissolved ammonium fluoride and hydrofluoric acid. All of

the precipitants, except solid sodium fluoride, gave a finely divided product which was difficult to filter and wash. Solid sodium fluoride gave a relatively coarse granular product which was easy to filter. Figure 4 shows a series of filtration curves for SrF_2 slurries prepared under identical conditions using different precipitants. In carrying out the tests, 500 ml of SrF_2 slurry were filtered through #42 Whatman filter paper under 20-in. Hg vacuum. The advantage of using solid sodium fluoride as the precipitant is readily apparent. Data for SrF_2 prepared using dissolved KF and HF are not shown because the precipitate was so fine it could not be filtered with the system used.

The rate of filtration of the SrF_2 slurry is also dependent on the filtration temperature. Figure 5 shows the effect of temperature on the filtration of SrF_2 prepared using solid sodium fluoride. As one would expect, the rate increased with increased filtration temperature.

The strontium content of the filtrate depended primarily on the digestion temperature and time; the higher the temperature and the longer the time, the lower the strontium concentration in the filtrate. To obtain a minimum strontium loss a slight excess of NaF was required. A 10% excess appeared optimum. Amounts in excess of 10% failed to lower the Sr content of the filtrate. If the excess was less than 5%, the strontium loss increased rapidly. These results confirm those reported by the Martin Company.⁽²⁾

To reduce the strontium losses to a minimum the digestion

FIGURE 4. FILTRATION CURVES FOR VARIOUS SrF₂ PRECIPITATES

FIGURE 5. EFFECT OF TEMPERATURE ON SrF_2 FILTRATION

temperature should be at least 60°C and the digestion time at least one hour. Since increasing the filtration temperature did not increase the strontium loss significantly, a filtration temperature of at least 60°C is also recommended. Under these conditions, the strontium loss to the filtrate should not exceed 0.05%, and may be substantially less in a plant operation.

The strontium fluoride, after filtration, will contain substantial amounts of sodium fluoride. Most of the sodium fluoride can be removed by washing the filter cake with water. In most cases the sodium fluoride content of the SrF_2 can be reduced to 2% or less by washing with a volume of water equal to the volume of the filtrate. Strontium losses to the wash solution are negligible (<0.01%).

4.3 Strontium Fluoride Firing

The precipitated SrF_2 must be dried and then heated, to remove any traces of water, prior to encapsulation. In the Martin flowsheet, a temperature of 1100°C was used. Thermogravimetric analysis (TGA) of SrF_2 , prepared by the proposed flowsheet using simulated feed, shows that a temperature of at least 850-900°C is required to remove the last traces of water from the fluoride. Typical thermograms of SrF_2 prepared by the proposed flowsheet are shown in Figure 6.

In order to insure complete water removal from the SrF_2 a temperature of at least 1000°C is recommended for plant operation. If the furnace temperature is maintained at 1000°C, internal heating of the $^{90}\text{SrF}_2$ will raise the temperature of at least a part of the fluoride

FIGURE 6. THERMOGRAMS OF SrF_2 PREPARED BY PROPOSED FLOWSHEET

substantially above 1000°C. This will lead to the formation of agglomerates which may have to be broken up by milling prior to encapsulation. While formation of agglomerates is to be avoided, if possible, it is felt that the necessity of removing all traces of moisture from the fluorides makes the use of a furnace temperature of at least 1000°C mandatory.

At temperatures above 1100°C some volatilization of the fluoride product occurs. The volatilized species is mainly NaF, but some volatilization of SrF_2 will also occur if the temperature exceeds 1150°C. (Samples of pure SrF_2 heated to 1150°C showed a slow but steady weight loss.) This means that the temperature of the fluoride in the furnace should be maintained between 1000 and 1100°C. This requires that shallow layers of $^{90}\text{SrF}_2$ be fired to prevent excessive temperatures due to internal heating.

At 1000°C the fluoride product is at least partially molten. Differential thermal analysis of SrF_2 , prepared from simulated feed, indicates that melting starts at about 830°C. The exact melting characteristics of the SrF_2 will depend on its impurity content. Although pure SrF_2 melts at about 1400°C, the impurities present in the product fluoride result in the formation of a low melting eutectic which forms a liquid phase as low as 820-830°C. As the fluoride is heated above 830°C, melting continues until at about 1360°C all the material is molten (see Figure 7).

In the firing operation the strontium fluoride product reacts with most container materials. Only high purity fused alumina has been

FIGURE 7. DIFFERENTIAL THERMAL ANALYSIS OF SrF_2

found to be relatively stable to attack by the fluoride above 800°C, as well as resistant to oxidation. Other ceramics tested, such as magnesia, zirconia and quartz, were all attacked by the fluoride. Metals such as stainless steel and Inconel, while only slightly attacked by the SrF_2 , were not sufficiently oxidation resistant to be used in the firing operation. Platinum was a possible crucible material, but was ruled out because of the cost involved. Even platinum showed some attack by the fluoride and would have to be discarded after a few processing cycles.

Fused alumina proved to be the only satisfactory container material for firing the fluoride in an air atmosphere. It is slowly attacked by the fluoride, but each container can be used for several cycles before being replaced. Figure 8 shows an alumina crucible after several heating cycles. The attack by the fluoride is readily apparent. In the laboratory tests the fluoride was fired in small impervious alumina crucibles. The crucibles used were quite resistant to thermal shock and could be rapidly heated to 1100°C and then rapidly cooled without cracking. Even after several firings cracking was not a problem. However, attack of the crucible by the fluoride, upon repeated firings, reduced the mechanical strength of the crucibles and they became quite fragile.

If the strontium fluoride is fired in an inert atmosphere a number of metals could be used to contain the fluoride. Various metals were heated to 1100°C, in contact with SrF_2 , under an argon atmosphere. The tests lasted for 24 hours. After cooling, the metal samples were

FIGURE 8. ALUMINA CRUCIBLE AFTER SEVERAL FIRING CYCLES

sectioned and the extent of fluoride attack determined by metallographic techniques. The results of the tests are summarized below.

<u>Metal Tested</u>	<u>Depth of Metal Affected (mils)</u>
316L SS	5
Hastelloy C	4
Haynes 25	2
Inconel 600	1
18-18-2 Alloy	2
Platinum	2
TZM	1
Tantalum	1
Ta - 10% W	3
Tungsten	0

Tungsten was the best of the metals tested and showed no evidence of fluoride attack. Inconel 600 was the best of the more common alloys tested, and showed only slight attack by the fluoride. Considering material cost and ease of fabrication, Inconel 600 is recommended over tungsten as the container material for firing SrF_2 in an inert atmosphere.

As mentioned previously, when the strontium fluoride is fired some agglomeration occurs (due to sintering and partial melting). Agglomerate size will depend on the firing temperature and time at temperature. When strontium fluoride, prepared from the simulated feed, was fired at 1000°C for sixteen hours the bulk of the fluoride was 20 mesh or larger. The material was easily reduced to minus 200 mesh by ball milling for 30-60 minutes using Alundum balls. Strontium fluoride fired at 1100°C formed more stable agglomerates, but could be reduced to a minus 100 mesh size by ball milling for one hour.

4.4 Product Purity

Several batches of SrF_2 were produced from the simulated feed solution by the proposed flowsheet. Each batch was analyzed for metallic impurities by emission spectroscopy. The results obtained are summarized in Table III. A product containing 96+% SrF_2 was produced routinely with Na and Ca being the major impurities.

TABLE III. ANALYSIS OF SrF_2 PRODUCT

Metallic Impurities	Concentration - Wt%		
	Typical	Range	Average*
Ca	1.0	0.5 - 2.0	1.0
Na	2.0	0.05- 3.0	2.0
Fe	0.01	<0.01- 0.02	<0.01
Al	0.03	0.01- 0.05	0.02
Mg	0.3	0.1 - 0.5	0.3

* Average for 5 batches of SrF_2

4.5 Hot Cell Studies

The various operations in the proposed flowsheet were evaluated in a hot cell using a radioactive strontium feed material obtained from ARHCO. Unfortunately the only feed available at the time the studies were started was not representative of the expected feed to the packaging plant. However, time considerations, especially the need to supply $^{90}\text{SrF}_2$ for the compatibility studies,⁽⁷⁾ dictated the use of the non-representative feed. The approximate analysis of the ^{90}Sr feed used is given below:

<u>Plant Feed</u>	<u>Cation/Sr</u>
Sr $\sim 0.094\text{M}$	1
Mg $\sim 0.014\text{M}$	0.15
Ca $\sim 0.004\text{M}$	0.043
Fe $\sim 0.002\text{M}$	0.021
Pb $\sim 0.001\text{M}$	0.011
Ba $\sim 0.001\text{M}$	0.011

The feed was concentrated by evaporation to 0.25M Sr prior to use.

It was found that excellent decontamination was obtained in the purification step by using the ^{90}Sr feed, and a fluoride product of approximately 96% purity was obtained. The emission spectrographic analysis of the SrF_2 product is given in Table IV.

TABLE IV. ANALYSIS* OF $^{90}\text{SrF}_2$ PRODUCT

Element	Wt%	Element	Wt%
Al	0.015	Mg	0.05
Ca	0.60	Mn	0.002
Cu	0.01	Na	3
Fe	0.01	Si	0.01
K	<0.01	Zr	0.35

* Average of two emission spectrographic analyses

It was found in the course of the hot cell studies that a large percentage ($\sim 25\%$) of the strontium was carried down with the precipitate in the feed purification step. Attempts to recover the Sr by washing were unsuccessful. Only a small amount of the strontium was recovered when the solids were washed with water. When the precipitate was treated with nitric acid only a portion of the solids dissolved.

As a result, a substantial portion of the Sr was lost with the undissolved solids. The overall loss of strontium in the purification step amounted, therefore, to an unacceptable 10-15% of that present in the original feed solution. It was not determined why a portion of the solids were insoluble in nitric acid. In similar tests with the simulated feed all of the solids dissolved. Impurities present in the radioactive feed, but not in the simulated feed, were probably responsible for the insolubles.

When a representative radioactive feed is available, the purification tests should be repeated to make sure that the strontium losses can be reduced to an acceptable level, while maintaining the necessary product purity.

The other steps in the flowsheet (fluoride precipitation, filtration, calcination) were carried out without difficulty. It was decided, however, to use a 25% excess of NaF to ensure adequate precipitation of the SrF_2 . The large excess of NaF was used because of the relative uncertainty of cation concentrations in the radioactive feed compared to the synthetic feed.

5. CONCLUSIONS

It was demonstrated that the proposed flowsheet can produce SrF_2 of acceptable quality using a simulated feed of the same composition as the anticipated packaging plant feed. By careful control of operating conditions, strontium losses in the process can be reduced to an acceptable level.

Using a nonrepresentative radioactive feed (which contained impurities not present in the simulated feed) high strontium losses were encountered in the feed purification step, although the purification obtained was excellent. The other steps in the process presented no difficulties. Additional tests of the feed purification step will be necessary when a representative feed is available to ensure that strontium losses can be reduced to an acceptable level.

The proposed flowsheet differs from the Martin flowsheet in that a feed purification step is used in the proposed process. All the remaining steps in the process are essentially identical and the data and recommendations reported in the Martin publications appear applicable to the proposed process. Based on the results of this study (and including data published by the Martin Company), a detailed flowsheet with recommended operating conditions is given in the appendix.

6. ACKNOWLEDGMENTS

The authors wish to thank Mr. C. L. Nelson who performed most of the experimental studies with the simulated feeds, and Mr. G. N. Buck who carried out the hot cell studies.

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APPENDIX

RECOMMENDED OPERATING CONDITIONS
FOR PREPARING STRONTIUM FLUORIDE

Using the flowsheet shown in Figure 2, the following conditions are recommended for preparing SrF_2 for packaging.

A. Feed Purification

The strontium nitrate feed solution from the solvent extraction process is taken to pH 10, at 25°C, with 50% sodium hydroxide solution. The resulting slurry is stirred for 15-30 minutes. The slurry is then centrifuged and the supernate is saved.

The centrifuged solids are washed with a volume of water equal to the volume of the supernate. The wash solution is combined with the supernate for further processing. The washed solids, containing <1% of the original strontium, are discarded.

B. Fluoride Precipitation

The purified strontium solution is heated to 70°C and a ten percent excess of solid sodium fluoride is added. The slurry is digested for one hour at 70°C with stirring. After digestion, the slurry is filtered at 70°C and the filtrate is discarded. The filter cake is washed with a volume of water equal to the volume of the filtrate. The wash solution is discarded.

C. Fluoride Firing

The filter cake is allowed to dry, for four hours, due to

self-heating. The dried cake is then fired at 1050°C in a fused alumina tray for eight hours. The layer of SrF_2 should be no more than 2 inches deep in the alumina container. If the fluoride is fired in an inert atmosphere then Inconel 600 can be used to contain the fluoride.

D. Milling

The strontium fluoride particles agglomerate when the material is fired. Size reduction of the SrF_2 prior to packaging may or may not be required. If size reduction is required, then ball milling using Alundum balls is recommended. A milling time of one hour is sufficient.