# **STRONTIUM**

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Strontium occurs commonly in nature, averaging 0.04% of the Earth's crust, making it the 15th element in abundance (MacMillan and others, 1994). Only two minerals, celestite (strontium sulfate) and strontianite (strontium carbonate), however, contain strontium in sufficient quantities to make its recovery practical. Of the two, celestite occurs much more frequently in sedimentary deposits of sufficient enough size to make development of mining facilities attractive. Strontianite would be the more useful of the two common minerals because strontium is used most often in the carbonate form, but few deposits have been discovered that are suitable for development. A mine in China is believed to be the only developed strontianite deposit in the world (Hong, 1993).

Chemical Products Corp. (CPC) of Cartersville, GA, was the only U.S. producer of strontium compounds from celestite. CPC produced strontium carbonate from imported Mexican ore; no celestite mines were active in the United States.

#### **Legislation and Government Programs**

Government stockpiling of celestite began in 1942 to provide a secure supply for the production of strontium compounds required for defense applications during World War II. Celestite purchase specifications issued in 1960 for the National Defense Stockpile established quality requirements of greater than 95% strontium sulfate content with less than 1.5% calcium sulfate and less than 2% barium sulfate (U.S. Department of Defense, 1960).

In 1963, Congress determined that the celestite stockpile was unnecessary, and the General Services Administration began selling stockpiled material. All stockpile-grade celestite was sold by 1973. The remaining material graded less than 91% strontium sulfate and more than 4% calcium sulfate and some with more than 10% barium sulfate (Defense Logistics Agency, 1998, p. 30).

In 2001, the stockpile contained approximately 12,000 metric tons of celestite, all of which was authorized by Congress for disposal. The low quality of the material remaining in the stockpile made it undesirable as raw material for strontium carbonate production. Reports issued by the Defense National Stockpile Center of the Defense Logistics Agency, the agency now responsible for managing stockpile sales, listed the celestite as valueless.

#### **Production**

Although celestite mines have not been active in the United States since 1959, deposits have been identified nationwide. During World War II, celestite resources were mined in California and Texas; at that time, mines had been inactive since

World War I, and strontium minerals were imported to satisfy domestic demand.

The sole U.S. strontium carbonate producer voluntarily provided domestic production and sales data to the U.S. Geological Survey (USGS). Production and stock data, however, have been withheld from publication to avoid disclosing company proprietary data (table 1). CPC was the only domestic company that produced strontium carbonate from celestite; the company also produced strontium nitrate. All the celestite CPC used in 2001 was imported from Mexico; CPC owned and operated a second strontium carbonate plant in Reynosa, Tamaulipas, Mexico. The company used the black ash method of strontium carbonate production at both of its facilities.

The black ash and the soda ash methods are the two most common recovery techniques. The black ash method, known alternatively as the calcining method, produces chemical-grade strontium carbonate, which contains at least 98% strontium carbonate. The soda ash or direct conversion method produces technical-grade strontium carbonate, containing at least 97% strontium carbonate.

The first step in the black ash process involves mixing the crushed and screened celestite with powdered coal. The mixture is then heated to about 1,100° C, expelling oxygen in the form of carbon dioxide from the insoluble strontium sulfate to form water-soluble strontium sulfide. Strontium sulfide is dissolved in water, and the resulting solution is filtered. Then either carbon dioxide is passed through the solution or soda ash is added, forming and precipitating strontium carbonate from the solution. The precipitated strontium carbonate is filtered, dried, ground, and packaged. The byproduct sulfur from the process is recovered as elemental sulfur or other byproduct sulfur compounds (Mannsville Chemical Products Corp., 1993). The black ash method is the preferred means of strontium carbonate production because it yields a higher grade product; most new production facilities employ black ash technology.

In the soda ash method, ground celestite is washed and most of the water removed. The thickened mixture is combined with soda ash and treated with steam for 1 to 3 hours. During this time, celestite and soda ash react to form strontium carbonate and sodium sulfate. Sodium sulfate is water soluble, making it possible to separate the insoluble strontium carbonate by centrifuging.

Several U.S. companies produced strontium compounds from strontium carbonate. Mallinkrodt Chemical Inc. of St. Louis, MO, and Laporte Pigments Corp. of Beltsville, MD, produced strontium chloride and strontium chromate, respectively. A few other companies produced downstream strontium compounds on a limited scale.

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#### Consumption

The USGS estimated the distribution of strontium compounds by end use. Of the six operations to which a survey request was sent, five responded. The information collected from this survey and the information provided by the U.S. Census Bureau on strontium trade were the bases for the end-use estimates listed in table 2.

In 2001, almost 85% of all strontium was consumed in ceramics and glass manufacture, primarily in television faceplate glass and secondarily in ceramic ferrite magnets and other ceramic and glass applications. Since 1970, production of faceplate glass for color television picture tubes had been the major use of strontium.

All color televisions and other devices containing color cathode-ray tubes (CRTs) sold in the United States were required by law to contain strontium in the faceplate glass of the picture tube to block x ray emissions. Major manufacturers of television picture tube glass incorporated, by weight, about 8% strontium oxide in their glass faceplate material. Added to the glass melt in the form of strontium carbonate, it was converted to strontium oxide. In addition to blocking x rays, strontium improves the appearance of the glass and the quality of the picture and increases the brilliance (Wagner, 1986).

Permanent ceramic magnets were another large end use for strontium compounds in the form of strontium ferrite. These magnets were used extensively in small direct current motors for automobile windshield wipers, loudspeakers, other electronic equipment, toys, and magnetically attached decorative items. Strontium ferrite magnets have high coercive force and high thermal and electrical resistivities and are chemically inert. They retain their magnetism well, are not adversely affected by electrical currents or high temperatures, do not react with most chemical solvents, and have a low density (Haberberger, 1971).

One of the most consistent and continuing applications for strontium was in pyrotechnic devices. Strontium burns with a brilliant red flame, and no other material was known to be better in this application. The compound used most frequently in these devices was strontium nitrate. Although strontium carbonate, strontium oxalate, strontium sulfate, and strontium chlorate could also be used, strontium nitrate was used in significantly larger quantities. Pyrotechnic devices were used in military and nonmilitary applications. Military pyrotechnic applications included tracer ammunition, military flares, and marine distress signals. Nonmilitary applications included warning devices and fireworks (Conkling, 1981).

Strontium can be used to remove lead impurities during the electrolytic production of zinc. The addition of strontium carbonate dissolved in sulfuric acid to the electrolyte reduces the lead content of the electrolyte and of the zinc deposited on the cathode (Bratt and Smith, 1963).

Strontium chromate also was used as an additive to corrosionresistant paint to effectively coat aluminum, most notably on aircraft fuselages and ships. These paints were used, to some degree, on aluminum packaging to prevent corrosion (Roskill Information Services Ltd., 1992, p. 76).

Strontium metal had a very limited part in total strontium consumption. Small amounts of strontium added to molten

aluminum improve the castability of the metal, making it more suitable for casting items that had been made traditionally from steel. The addition of strontium to the melt improved the machinability of the casting. The use of cast aluminum parts had become common in the automotive industry because of the reduced weight and improved gas mileage achieved from the use of cast aluminum parts instead of steel (Lidman, 1984).

Other end uses consumed only small amounts of strontium and strontium compounds. As mentioned above, the presence of strontium in glass applications improves the brilliance of the glass. It also improves the quality of certain ceramic glazes and eliminates the toxicity that may be present in glazes containing lead or barium. Strontium titanate was sometimes used as substrate material for semiconductors and in some optical and piezoelectric applications. Strontium chloride was used in toothpaste for temperature-sensitive teeth. For this application, impurities must be strictly controlled; some limits are in the parts-per-million range. Strontium phosphate was used in the manufacture of fluorescent lights, and the entire range of strontium chemicals was used in analytical chemistry laboratories.

#### **Prices**

Based on data published by the U.S. Census Bureau, the average customs value for celestite imported from Mexico was about \$63 per metric ton, the same as that of 2000. The average unit customs value of imported strontium carbonate was \$0.55 per kilogram, virtually the same as in 2000. The corresponding value for strontium nitrate was \$3.07 per kilogram, a decrease of about 13% from that of 2000.

#### Foreign Trade

Exports of strontium compounds were only about 20% of the levels reported in 2000 as a result of dramatically lower exports of strontium carbonate, especially to Asia (table 3). Exports in 2001 were more in line with export totals prior to 1999. Exports were exceptionally high in 1999 and 2000. Imports of celestite from Mexico were 12,800 t, a decrease of nearly 25% from those of 2000. Celestite imports have decreased significantly for the past 2 years, with 2001 imports only 41% of what they were in 1999.

Mexico continued to be the most important source for imported strontium compounds followed by Germany (table 4). Imports of strontium carbonate in 2001 were 12% lower than those of 2000. Imports from Mexico were 91% of total carbonate imports. Imports of strontium nitrate were 21% higher than those of 2000. Strontium nitrate imports have varied significantly from one year to the next but represented less than 2% of total strontium imports.

#### **World Review**

In most instances, celestite deposits occur in remote, undeveloped locations far from population centers in areas where inexpensive labor is available for mining. Huge deposits of high-grade celestite have been discovered throughout the world. Strontium commonly occurs along with barium and

calcium, two elements with chemical properties very similar to strontium, thus making separation difficult. Because removing many impurities from celestite is difficult and energy-intensive, strontium chemical producers require that material contain at least 90% strontium sulfate. Most operating celestite facilities can produce sufficient supplies with only minimal processing necessary to achieve acceptable specifications. Hand sorting and some washing are all that are necessary at many strontium mines; a few operations use gravity separation, froth flotation, or other methods to beneficiate ore.

The leading celestite producing countries were, in decreasing order of importance, Mexico, Spain, and Turkey. Significant quantities of celestite were produced in China and the former Soviet Union (FSU); not enough information was available, however, to make any estimates on the location, number, or size of mines. Celestite was produced in smaller quantities in Argentina, Iran, and Pakistan.

Detailed information on most world resources was not readily available because very little information on exploration results had been published. Other deposits may be well identified but are in countries from which specific minerals information was not easily obtained (table 5). Production facilities for strontium compounds and metal were located in Canada, China, the FSU, Germany, Japan, the Republic of Korea, Mexico, Poland, and the United States.

Canada.—The world's leading producer of strontium metal Timminco Ltd. produces strontium metal in Ontario. The company also produces strontium-aluminum master alloys, which were advertised as the highest quality in the world, referring to their purity, low gas content, fast dissolution rate, low porosity, precise weight, and highest and most consistent strontium recovery. Timminco sells strontium as crowns, sections, and turnings and in master alloys containing 90% strontium and 10% aluminum (Timminco Ltd., [undated]§¹).

*Germany.*—Solvay Barium Strontium GmbH (a subsidiary of Belgium's Solvay S.A.) operated a 150,000-ton-per-year (t/yr) barium and strontium carbonate plant at Bad Hönningen. Solvay used imported Spanish celestite as the raw material for strontium carbonate production. The company had other strontium carbonate plants in Italy, the Republic of Korea, and Mexico (Houssa, 1999b).

Mexico.—With three strontium carbonate plants operated by CPC, Cia. Minera La Valenciana S.A. de C.V. (CMV), and Solvay Química y Minera, S.A. de C.V., Mexico was the world's largest producer of strontium carbonate. The vast majority of all U.S. strontium imports came from Mexico. CPC met its celestite requirements for its Georgia and Mexican plants from mines that were completely controlled by CPC (Ceramics and Industrial Minerals, [undated]§). CMV had proven and estimated reserves of 5 million metric tons, enough to continue production well into the future (Cia. Minera La Valenciana S.A. de C.V., [undated]§).

*Spain.*—Two companies operated celestite mines in Spain, the last remaining celestite producing country in Europe. Solvay mined the Escuzar deposit to supply its German strontium carbonate operation. Canteras Industriales SL (a

subsidiary of Bruno S.A.) produced celestite from the Montevives deposit. Quimico Estroncio (a joint venture of Minas de Almadadén y Arrayanes, S.A., Fertiberia S.A., and Erkimia S.A.) completed a new 22,000-t/yr strontium carbonate plant in Cartegena early in 2000. The plant produced strontium carbonate from Spanish celestite (Reguiro y Gonzáles-Barros and Sanz, 2000, p. 53-55). No production details from the new plant were available.

Turkey.—A long-time celestite producer for the export market, Barit Maden Turk AS sold most of its production to the Republic of Korea and China. The company was building its own strontium carbonate plant in 2001. In preparation for its expansion into carbonate production, Barit Maden built a carbon dioxide plant that was profitable for the company even before the strontium carbonate facilities were complete. Its high-quality celestite resources and the in-house carbon dioxide supply contributed to Barit Maden's confidence that its strontium carbonate would be high-quality and cost competitive with other producers (Houssa, 1999a, p. 47).

#### Outlook

Sales of televisions and computer monitors in the United States will continue at a high rate and will continue to influence U.S. strontium consumption significantly. Sales of CRTs are expected to grow at about 6.3% per year through 2006, creating a corresponding demand for strontium carbonate in that end use (Business Communications Co., Inc., 2002§). As long as CRTs are the preferred display type for televisions and computers. trends should remain steady with some small increases. Growth in television sales is expected to continue, and larger screens are increasing in popularity. Likewise, the market for personal computers is expanding, and the average size of monitors is increasing. These factors are driving increased demand for strontium carbonate for CRTs. Ferrite magnet markets are expected to be strong. Growth in other markets will probably continue at the current slower rate. Improved economic conditions worldwide will spur growth in demand for strontium carbonate.

Flat screen display systems for televisions and computer monitors have threatened to replace CRTs for many years, but low-cost technology has been elusive. Flat panels, however, have begun to have an impact on the CRT market, and the flat panel market is growing at a much higher rate that of CRTs, with an estimated growth of 17.6% per year (Business Communications Co., Inc., 2002§). Improvements have increased the likelihood that the large flat screens using either liquid crystal displays (LCD) or plasma technology will replace bulkier CRTs. LCDs, which are smaller and use less energy than plasma display systems, seem to be filling the market for relatively small flat displays such as those required for portable computers. This market has experienced remarkable growth since 1997, and this trend is expected to continue. Plasma technology is more common for large, high-definition televisions with screens up to 60 inches wide. Significant growth is expected also in this area (Tremblay, 1999). Neither technology requires strontium carbonate in the glass, but both have been too expensive to make serious inroads in the domestic CRT market. The first common applications of flat

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<sup>&</sup>lt;sup>1</sup>References that include a section twist (§) are found in the Internet References Cited section.

screens should occur in Japan, where many homes are small and space is at a premium. In 2000, a 20-inch flat screen television in Japan cost around \$2,500, significantly more than a comparable device with a CRT. The cost of larger plasma screens (usually between 37 and 60 inches diagonally) was between \$10,000 and \$14,000 (Landers, 2000).

Most of these devices were more commonly available in Japan but are finding increased acceptance in the United States, especially as the technology matures and prices go down. When these new display systems become more economically attractive to the general public, CRTs will become obsolete, and so will the major market for strontium carbonate.

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## TABLE 1 SALIENT STRONTIUM STATISTICS 1/

(Metric tons, of contained strontium, unless otherwise noted) 2/

	1997	1998	1999	2000	2001
United States:					
Production, strontium minerals					
Imports for consumption: 3/					
Strontium minerals	12,500	10,600	13,700	7,460 r/	5,640
Strontium compounds	26,000	25,000	26,800	29,900	26,500
Exports (compounds) 3/	599	875	2,890	4,520	941
Shipments from Government stockpile excesses					
Apparent consumption 4/	37,900	34,700	37,600	36,400	31,200
Price, average value of dollars per metric ton	\$72	\$60	\$73	\$62	\$63
mineral imports at port of exportation					
World, production (celestite) 5/	264,000 r/	264,000 r/	322,000 r/	319,000 r/	321,000 e/

e/ Estimated. r/ Revised. -- Zero.

TABLE 2
U.S. ESTIMATED DISTRIBUTION OF PRIMARY
STRONTIUM COMPOUNDS, BY END USE

#### (Percent)

End use	2000	2001
Electrolytic production of zinc	2	2
Ferrite ceramic magnets	8	9
Pigments and fillers	2	3
Pyrotechnics and signals	9	9
Television picture tubes	77	75
Other	2	2
Total	100	100

<sup>1/</sup> Data are rounded to no more than three significant digits.

<sup>2/</sup> The strontium content of celestite is 43.88%, which was used to convert units to celestite.

<sup>3/</sup> Source: U.S. Census Bureau.

<sup>4/</sup> Production plus imports minus exports.

<sup>5/</sup> Excludes China and the former Soviet Union.

 ${\bf TABLE~3} \\ {\bf U.S.~EXPORTS~OF~STRONTIUM~COMPOUNDS,~BY~COUNTRY~1/}$ 

	2000		2001	
	Gross weight		Gross weight	
	(kilograms)	Value 2/	(kilograms)	Value 2/
Strontium carbonate precipitated:				
Australia	67,800	\$175,000		
Brazil			5,460	\$7,530
Canada	138,000	120,000	289,000	225,000
Germany	4,610	38,800	21,500	194,000
Hong Kong			17,400	19,800
Japan	5,170,000	3,400,000	108,000	97,100
Korea, Republic of	82,000	92,700		
Mexico	417,000	179,000	204	4,090
Singapore	307,000	164,000		
Taiwan	119,000	64,300		
United Kingdom	1,620	8,390	4,280	4,070
Venezuela	10,000	9,530		
Total	6,320,000	4,250,000	446,000	551,000
Strontium oxide, hydroxide, peroxide:				
Australia	14,900	8,200	8,810	4,850
Brazil	26,700	14,700		
Canada	432,000	238,000	263,000	144,000
Colombia			548	3,160
Germany	99,200	47,100	14,400	22,500
Japan	74,000	40,700	9,010	4,950
India			34,100	18,800
Italy			18,900	10,400
Korea, Republic of	161,000	88,300	548,000	301,000
Mexico			3,210	4,960
Norway	44,200	24,300		
Portugal	10,200	5,600	6,780	3,730
Switzerland			7,090	3,900
United Kingdom			9,440	5,190
Total	862,000	466,000	923,000	528,000

<sup>--</sup> Zero

Source: U.S. Census Bureau.

<sup>1/</sup> Data are rounded to no more than three significant digits; may not add to totals shown.

<sup>2/</sup> F.a.s. (free alongside ship) value.

TABLE 4
U.S. IMPORTS FOR CONSUMPTION OF STRONTIUM COMPOUNDS, BY COUNTRY 1/

	2000	0	2001		
	Gross weight		Gross weight		
	(kilograms)	Value 2/	(kilograms)	Value 2/	
Strontium carbonate:					
Belgium			73,700	\$44,100	
China	270,000	\$116,000	931,000	355,000	
Germany	2,510,000	1,240,000	2,680,000	1,320,000	
Italy	6,000	20,200	4,000	15,700	
Japan	280	7,210	1,260	20,300	
Mexico	46,500,000	26,200,000	39,800,000	22,300,000	
Russia			20,000	7,250	
United Kingdom			13	3,370	
Total	49,300,000	27,600,000	43,500,000	24,100,000	
Strontium metal:					
Canada	90,700	721,000	48,600	385,000	
China	211,000	542,000	76,000	190,000	
France	5,810	47,300	11,000	66,900	
Germany			15,000	157,000	
Japan			119,000	410,000	
Mexico	281	2,690			
Total	308,000 r/	1,310,000	270,000	1,210,000	
Strontium nitrate:	-				
China	234,000	254,000	352,000	277,000	
Finland	57,700	137,000			
France	209,000	1,190,000	221,000	1,300,000	
Germany	150	6,020			
Japan	107,000	698,000	118,000	857,000	
Mexico	79,000	63,800	140,000	116,000	
Total	687,000	2,350,000	831,000	2,550,000	
Strontium oxide, hydroxide, peroxide:					
China	71,000	54,900	35,100	35,300	
Germany	3,600	15,500			
Japan	117,000	396,000	29,000	47,100	
Total	192,000	466,000	64,100	82,300	

r/ Revised. -- Zero.

Source: U.S. Census Bureau.

TABLE 5
CELESTITE: WORLD PRODUCTION, BY COUNTRY 1/2/

#### (Metric tons)

Country 3/	1997	1998	1999	2000	2001 e/
Argentina	1,905 r/	2,416 r/	2,141 r/	2,200 r/e/	2,200
Iran e/ 4/	2,000	2,000	1,650 5/	2,000	2,000
Mexico	134,707	118,230	164,682	157,420	160,000
Pakistan	3,000 e/	598	634	1,918 r/	2,000
Spain e/	92,000	111,000	128,000 5/	130,000	130,000
Turkey e/	30,000	30,000	25,000	25,000	25,000
Total	264,000 r/	264,000 r/	322,000 r/	319,000 r/	321,000

e/ Estimated. r/ Revised.

<sup>1/</sup> Data rounded to no more than three significant digits; may not add to totals shown.

<sup>2/</sup> F.a.s. (free alongside ship) value.

<sup>1/</sup> World totals and estimated data are rounded to no more than three significant digits; may not add to totals shown

<sup>2/</sup> Table includes data available through May 20, 2002.

<sup>3/</sup> In addition to the countries listed, China and the former Soviet Union produce strontium materials, but output is not reported quantitatively, and available information is inadequate to make reliable estimates of output levels.

<sup>4/</sup> Data are for year beginning March 21 of that stated.

<sup>5/</sup> Reported figure.