# **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 large enough size to make development of mining facilities attractive. Neither mineral is mined in the United States at present. Strontianite would be the more useful of the two 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). A company in Malawi was investigating the possibility of developing the Kangankunde strontianite/rareearths deposit in that country (Tassell, 2002). The majority of strontium consumption is in color television picture tube faceplate glass. Other important uses are in ferrite ceramic magnets and pyrotechnics and signals. Smaller uses include chemicals, electrolytic production of zinc, and pigments and fillers.

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.

#### **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 2002, the stockpile contained approximately 12,000 metric tons (t) of celestite, all of which was authorized by Congress for disposal. No bids were made on the material that was offered for sale. Celestite has been offered for sale from the stockpile every year since 1994; none has been purchased. The low quality of the material remaining in the stockpile makes 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, list the celestite as valueless.

#### **Production**

CPC 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 2002 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 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.

#### 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 2002, 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 is in pyrotechnic devices. Strontium burns with a brilliant red flame, and no other material is known to perform 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 to the electrolyte of strontium carbonate dissolved in sulfuric acid reduces the lead content of the electrolyte and of the zinc deposited on the cathode (Bratt and Smith, 1963).

Strontium chromate is used as an additive to corrosion-resistant 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 strontium additions 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 also 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 \$58 per metric ton, 8% lower than that of 2001. The average unit customs value of imported strontium carbonate was \$0.55 per kilogram, unchanged since 2000. In 2002, the corresponding value for strontium nitrate was \$2.66 per kilogram, the second consecutive year with a 13% decrease.

#### Foreign Trade

Exports of strontium compounds continued to decline, reaching only about one-third of the total quantity reported in 2001; exports were at the lowest level since 1993 (table 3). Imports of celestite from Mexico were 2,580 t, only about 20% those of 2001. Low imports of celestite could indicate decreased production of strontium carbonate or drawdown of stockpiled celestite.

Mexico continued to be the most important source for imported strontium compounds with 92% of the total, followed by Germany with 5% (table 4). Imports of strontium carbonate in 2002 were slightly lower than those of 2001. Imports from Mexico were 94% of total strontium carbonate imports. Imports of strontium nitrate, the second largest imported strontium compound, vary significantly from year to year but typically represent less than 2% of total strontium imports. In 2002, imports of strontium nitrate were 7% lower than those of 2001.

#### **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 raw 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 Tajikistan; 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 has 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, Germany, Japan, the Republic of Korea, Mexico, Poland, and the United States. In 2002, world strontium carbonate production was estimated to be between 350,000 and 400,000 t with capacity of nearly 420,000 metric tons per year (t/yr) (Mineral PriceWatch, 2002).

Canada.—The world's leading producer of strontium metal, Timminco Ltd., produced strontium metal in Ontario. The company also produced 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, and precise weight. Timminco sold strontium as crowns, sections, and turnings and in master alloys containing 90% strontium and 10% aluminum (Timminco Ltd., 2000§¹).

Germany.—Solvay Barium Strontium GmbH (a subsidiary of Belgium's Solvay S.A.) operated a 150,000-t/yr barium and strontium carbonate plant at Bad Hönningen. Solvay used imported Spanish celestite as the raw material for strontium carbonate production in Germany. Including its strontium carbonate plants in Italy, the Republic of Korea, and Mexico, Solvay is the world's largest strontium carbonate supplier (Houssa, 1999a).

Malawi.—Rift Valley Resource Development Ltd. was conducting a feasibility study on the development of the Kangankunde strontianite/rare-earths deposit. The Malawian Geological Survey reported that the deposit contains 11 million metric tons (Mt) of strontianite and monazite (a rare-earth mineral). Phase 1 of development would produce strontium carbonate for export and monazite concentrates that would be stockpiled for later phases of the project. Glass-grade strontium carbonate production was expected to be about 20,000 t/yr (Tassell, 2002). The European Investment Bank and the Development Bank of South Africa were funding the feasibility study (Saner, 2002).

*Mexico.*—The world's largest celestite producer 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 also the world's largest strontium carbonate producing country. The vast majority of all U.S. strontium imports, including minerals and compounds, came from Mexico. The largest Mexican celestite producer is Minas de Celestita S.A. de C.V., a company completely controlled by CPC. Minas de Celestita controls celestite reserves of between 6 Mt and 6.5 Mt of proven and inferred ore that is mined to supply its operations in Mexico and the United States. CPC operates a 50,000-t/yr strontium carbonate plant in Reynosa, Tamaulipas State (Moore, 2002, p. 30-31).

CMV reported proven and estimated reserves of 5 Mt, enough to continue production well into the future (Cia. Minera La Valenciana S.A. de C.V., undated§). Other sources suggested that CMV's San Augustin Mine was nearing depletion after lifetime production of more than 1 Mt. The Belgian company Solvay also operates a 27,000-t/yr strontium carbonate plant near Monterrey using celestite mined by Minera La Roja, S.A. de C.V. (Moore, 2002, p. 31).

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.) owned a 22,000-t/yr strontium carbonate plant in Cartegena (Reguiro y Gonzáles-Barros and Sanz, 2000, p. 53-55).

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; progress on this project was unknown. 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 completed. 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, 1999b, p. 47).

#### Outlook

Sales of televisions and computer monitors in the United States will continue to influence U.S. strontium consumption significantly, although increased imports of faceplate glass and decreased growth in CRT demand will contribute to lower domestic consumption of strontium compounds. As long as CRTs are used in television and computer monitors, world consumption should continue, but at lower growth rates than have been experienced in recent years. Ferrite magnet markets are expected to be strong. Growth in other markets will probably continue at the current slower rate. Improved economic conditions worldwide could 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 the cost of the new technology has restricted growth. Flat panels, however, have begun to have an impact on the CRT

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

market, and the flat panel market is growing at a much higher rate than that of the CRT market. Improvements have increased the likelihood that the large flat screens that use 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. The market for LCD materials is expected to grow at a rate of 16.4% per year through 2005 (Markarian, 2002).

Worldwide, about 150 million CRTs per year are produced. In 2001, the last year for which such data were available, about 300,000 plasma displays were sold; by 2005, sales are expected to approach 4 million units, a 13-fold increase (Tremblay, 2002). Plasma technology is more common for large, high-definition televisions with screens 60 inches and wider (Tremblay, 1999). Neither LCD or plasma technology requires strontium carbonate in the glass, but both have been too expensive to make serious inroads in the domestic CRT market until now. In 2002, the value of the market for flat panels was expected to overtake that of CRTs for the first time (Markarian, 2002). In 2000, a 20-inch flat screen television in Japan cost around \$2,500, significantly more than a comparable device with a CRT. The costs of larger plasma screens (usually between 37 and 60 inches diagonally) were between \$10,000 and \$14,000 (Landers, 2000). In 2002, prices were reported to be between \$6,000 and \$10,000 for similar items, a significant decrease, but still quite expensive (Tremblay, 2002). Major retailers, however, were offering some plasma display systems at \$3,000 and below. As these new display systems become more economically attractive to the public, CRTs will become obsolete, and so will the major market for strontium carbonate.

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## $\label{eq:table1} \textbf{TABLE 1} \\ \textbf{SALIENT STRONTIUM STATISTICS}^{\textbf{I}}$

(Metric tons of contained strontium unless otherwise noted)<sup>2</sup>

	1998	1999	2000	2001	2002
United States:					
Production, strontium minerals					
Imports for consumption: <sup>3</sup>					
Strontium minerals	10,600	13,700	7,460	5,640	1,150
Strontium compounds	25,000	26,800	29,900	26,500	25,400
Exports (compounds) <sup>3</sup>	875	2,890	4,520	929 <sup>r</sup>	340
Shipments from Government stockpile excesses					
Apparent consumption <sup>4</sup>	34,700	37,600	36,400	31,200	26,500
Price, average value of mineral imports at port					
of exportation dollars per ton	60	73	62	63	60
World, production of celestite <sup>5</sup>	264,000	322,000	322,000 r	350,000 r	344,000 e

<sup>&</sup>lt;sup>e</sup>Estimated. <sup>r</sup>Revised. -- Zero.

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

(Percent)

End use	2001	2002
Electrolytic production of zinc	2	2
Ferrite ceramic magnets	9	9
Pigments and fillers	3	2
Pyrotechnics and signals	9	9
Television picture tubes	75	75
Other	2	3
Total	100	100

 $\label{eq:table 3} \textbf{U.S. EXPORTS OF STRONTIUM COMPOUNDS, BY COUNTRY}^1$ 

	2001		2002	
	Gross weight		Gross weight	
	(kilograms)	Value <sup>2</sup>	(kilograms)	Value <sup>2</sup>
Strontium carbonate precipitated:				
Brazil	5,460	\$7,530		
Canada	289,000	225,000	76,500	\$59,600
Germany	21,500	194,000	15,000	125,000
Hong Kong	17,400	19,800	16,400	28,900
Japan	108,000	97,100	3,840	3,590
Mexico	204	4,090		
United Kingdom	4,280	4,070	3,370	26,500
Total	446,000	551,000	115,000	244,000

See footnotes at end of table.

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

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

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

<sup>&</sup>lt;sup>4</sup>Production plus imports minus exports.

<sup>&</sup>lt;sup>5</sup>Excludes China and Tajikistan.

 $\label{thm:continued} \textbf{U.S. EXPORTS OF STRONTIUM COMPOUNDS, BY COUNTRY}^1$ 

	2001		2002	
	Gross weight		Gross weight	
	(kilograms)	Value <sup>2</sup>	(kilograms)	Value <sup>2</sup>
Strontium oxide, hydroxide, peroxide:				
Australia	8,810	4,850	11,600	18,200
Canada	263,000	144,000	20,400	11,200
Colombia	548	3,160		
Germany	14,400	22,500		
Japan	9,010	4,950		
India	34,100	18,800		
Italy	18,900	10,400		
Korea, Republic of	548,000	301,000	63,900	35,100
Mexico	3,210	4,960	189,000	104,000
Norway			34,400	18,900
Portugal	6,780	3,730		
Sweden			57,200	31,500
Switzerland	7,090	3,900		
United Kingdom	9,440	5,190		
Total	923,000	528,000	377,000	219,000

<sup>--</sup> Zero.

Source: U.S. Census Bureau.

 $\label{table 4} \textbf{U.S. IMPORTS FOR CONSUMPTION OF STRONTIUM COMPOUNDS, BY COUNTRY}^1$ 

	200	2001		2002	
	Gross weight		Gross weight		
	(kilograms)	Value <sup>2</sup>	(kilograms)	Value <sup>2</sup>	
Strontium carbonate:					
Belgium	73,700	\$44,100	142,000	\$64,400	
China	931,000	355,000	392,000	164,000	
Germany	2,680,000	1,320,000	1,970,000	917,000	
France			79,400	46,400	
Italy	4,000	15,700	10,800	31,900	
Japan	1,260	20,300	3,700	45,900	
Mexico	39,800,000	22,300,000	39,400,000	21,900,000	
Russia	20,000	7,250			
Spain			19,400	9,480	
United Kingdom	13	3,370	10	2,560	
Total	43,500,000	24,100,000	42,000,000	23,200,000	
Strontium metal:					
Canada	48,600	385,000	30,500	193,000	
China	76,000	190,000	48,700	102,000	
France	11,000	66,900	10,000	68,500	
Germany	15,000	157,000			
Japan	119,000	410,000	62,400	245,000	
United Kingdom			4,000	5,420	
Total	270,000	1,210,000	156,000	615,000	

See footnotes at end of table.

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

<sup>&</sup>lt;sup>2</sup>Free alongside ship value.

 ${\it TABLE~4--} Continued\\ {\it U.S.~IMPORTS~FOR~CONSUMPTION~OF~STRONTIUM~COMPOUNDS,~BY~COUNTRY}^1$ 

	2001		2002	
	Gross weight		Gross weight	
	(kilograms)	Value <sup>2</sup>	(kilograms)	Value <sup>2</sup>
Strontium nitrate:				
Canada			20,000	15,400
China	352,000	277,000	399,000	321,000
France	221,000	1,300,000	70,000	433,000
Japan	118,000	857,000	160,000	1,190,000
Mexico	140,000	116,000	123,000	92,800
Total	831,000	2,550,000	771,000	2,050,000
Strontium oxide, hydroxide, peroxide:				
Australia			1,050	2,730
China	35,100	35,300	72,000	49,000
Germany			9	13,500
Japan	29,000	47,100	303	8,750
Total	64,100	82,300	73,400	74,000

<sup>--</sup> Zero.

Source: U.S. Census Bureau.

 ${\bf TABLE~5}$  CELESTITE: WORLD PRODUCTION, BY COUNTRY  $^{1,\,2}$ 

#### (Metric tons)

Country <sup>3</sup>	1998	1999	2000	2001	2002 <sup>e</sup>
Argentina	2,416	2,141	2,200 e	1,734 <sup>r</sup>	1,474 <sup>p</sup>
Iran <sup>e, 4</sup>	2,000	1,650 5	2,000	2,000	2,000
Mexico	118,230	164,682	157,420	145,789 <sup>r</sup>	140,000
Morocco			3,700 <sup>e</sup>	3,700 <sup>e</sup>	4,000
Pakistan	598	634	1,918	2,000 e	2,000
Spain <sup>e</sup>	111,000	128,000 5	130,000	130,000	125,000
Turkey <sup>e</sup>	30,000	25,000	25,000	65,000 <sup>r</sup>	70,000
Total	264,000	322,000	322,000 r	350,000 r	344,000

<sup>&</sup>lt;sup>e</sup>Estimated. <sup>p</sup>Preliminary. <sup>r</sup>Revised. -- Zero.

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

<sup>&</sup>lt;sup>2</sup>Free alongside ship value.

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

<sup>&</sup>lt;sup>2</sup>Table includes data available through May 20, 2003.

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

<sup>&</sup>lt;sup>5</sup>Reported figure.