

STRONTIUM

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Strontium occurs commonly in nature, averaging 0.034% of all igneous rock; 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).

In 2000, the stockpile contained approximately 12,000 metric tons (t) 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

Strontium in the 20th Century

In 1900, no strontium minerals or chemicals were produced in the United States. Domestic production of celestite, a strontium sulfate ore, did not take place until 1916 when 250 metric tons containing approximately 100 tons of strontium were produced. Domestic and imported ores were used to produce strontium carbonate and strontium nitrate for use in fireworks, signal flares, refrigeration, steelmaking, and sugar beet processing. World War I created a demand for strontium nitrate for such military uses as tracer bullets and various types of flares. At the end of the war, demand decreased significantly. Domestic mining was inactive until the beginning of World War II, when military activities increased demand at the same time supply of imported ores from overseas was disrupted. Domestic production from California and Texas, with additional supplies from Mexico, were used to meet the demand with the few shipments that were available from the United Kingdom. During this time, celestite from Texas was used in drilling mud, substituting for barite, which was in short supply because of increased requirements for the war effort. The end of hostilities brought the collapse of the domestic celestite industry. The use of celestite in drilling muds ended at about the same time.

In the strontium chemical industry, domestic celestite could not compete in quality or price with imports from Mexico, Spain, and the United Kingdom. Domestic mining was minimal and sporadic until 1959 when it ceased completely. Uses for strontium chemicals for corrosion inhibitors, depilatories, greases, luminous paints, medicines, metallurgy, optics, and plastics increased slightly. In 1967, strontium ferrite ceramic magnets were developed. In 1969, strontium replaced barium in color television faceplate glass to block x-ray emissions, causing tremendous growth in the demand for strontium carbonate. By 1971, television glass was the largest end use for any strontium chemical and remained so through the end of the century, with its share of the strontium market increasing. Other uses were developed for strontium, but all were dwarfed by the chemical's consumption in television glass.

In 2000, U.S. apparent consumption was about 36,000 tons of contained strontium, about 77% of which was used in television glass and 10% in ferrite magnets. Pyrotechnic uses remained significant, accounting for an estimated 9% of total consumption. Other uses included the electrolytic production of zinc and applications in pigments and fillers.

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 2000 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 (Chemical Products Synopsis, 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 2000, more than 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 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 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 ton, 12.5% lower than that of 1999. The average unit customs value of imported strontium carbonate was \$0.56 per kilogram, slightly lower than in 1999. The corresponding value for strontium nitrate was \$3.53 per kilogram, a decrease of about 9% from that of 1999.

Foreign Trade

Exports of strontium compounds were 52% higher than the levels reported in 1999 (table 3). This increase in exports was a result of increased strontium carbonate exports to Asia. In 1998, U.S. strontium carbonate exports to Asian countries were 24 t; in 1999 exports to Japan, Singapore, Taiwan, and Thailand totaled 3,500 t. The growth continued in 2000, with exports to Japan, the Republic of Korea, Singapore, and Taiwan totaling 5,680 t. This astounding increase was due to decreased production in Japan that resulted from plant closures in 1998 and high demand for strontium carbonate at television glass operations in Asia.

Imports of celestite from Mexico were 17,000 t, a decrease of nearly 46% from those of 1999. Although celestite import figures have varied significantly from year to year, the decrease appeared to be attributable to a 2-year cycle of celestite imports. During the past 5 years, annual celestite imports averaged about 27,300 t (12,000 t contained strontium).

Mexico continued to be the most important source for imported strontium compounds, followed by Germany (table 4). Imports of strontium carbonate in 2000 were 12% higher than those of 1999. Imports from Mexico were 94% of total carbonate imports. Imports of strontium nitrate were 16% higher than those of 1999. Strontium nitrate imports have varied significantly from one year to the next but represented only about 1% 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 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 well be identified but are in countries from which specific minerals information is 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], Strontium products, accessed May 25, 2001, at URL <http://www.timminco.com/products/strontium.html>).

Germany.—Solvay Barium Strontium GmbH, a subsidiary of Belgium's Solvay S.A., operates 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 has other strontium carbonate plants in Italy, the Republic of Korea, and Mexico (Industrial Minerals, 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 plants in Georgia and Mexico from mines that were completely controlled by CPC (Chemical Products Corp., [undated], Profile of Chemical Products Corporation, accessed May 25, 2001, at URL <http://www.ceramics.com/cpc/cpc.html>). 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], Our future and our plans to remain the best, accessed May 25, 2001, at URL http://www.cmvlavalciana.com.mx/our_future_and_plans_to_remain_the_best.htm).

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 the year. The plant will produce strontium carbonate from Spanish celestite (Reguero y González-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 2000. 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, 1999, 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. Consumption for glass and ceramic applications for strontium carbonate is expected to grow at 3% to 5% per year for the near future (Industrial Minerals, 1999a). 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. Improvements have increased the likelihood that the large flat screens using either liquid crystal displays (LCDs) 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 of these developing technologies requires strontium carbonate in the glass, but both are currently too expensive to make serious inroads in the domestic CRT market. The first common applications of flat screens should occur in Japan, where many homes are small and space is at a premium. A 20-inch flat screen television in Japan can cost around \$2,500, significantly more than a comparable device with a CRT. Larger plasma screens (usually between 37 and 60 inches diagonally) cost between \$10,000 and \$14,000 (Landers, 2000).

Most of these devices were only available in Japan in 2000 but will eventually find 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/

	1996	1997	1998	1999	2000
United States:					
Production, strontium minerals	--	--	--	--	--
Imports for consumption: 3/					
Strontium minerals	11,600	12,500	10,600	13,700	11,000
Strontium compounds	20,500	26,000	25,000	26,800	29,900
Exports (compounds) 3/	712	599	875	2,890	4,520
Shipments from Government stockpile excesses	--	--	--	--	--
Price, average value of mineral imports at port of exportation, dollars per ton	\$67	\$72	\$60	\$73	\$62
World production (celestite) 4/	297,000 r/	265,000 r/	265,000 r/	323,000 r/	318,000 e/

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

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

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

3/ Source: U.S. Census Bureau.

4/ Excludes China and the former Soviet Union.

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

(Percent)

End use	1999	2000
Electrolytic production of zinc	2	2
Ferrite ceramic magnets	10	8
Pigments and fillers	3	2
Pyrotechnics and signals	6	9
Television picture tubes	75	77
Other	4	2
Total	100	100

TABLE 3
U.S. EXPORTS OF STRONTIUM COMPOUNDS, BY COUNTRY 1/

	1999		2000	
	Gross weight (kilograms)	Value 2/	Gross weight (kilograms)	Value 2/
Strontium carbonate precipitated:				
Australia	--	--	67,800	\$175,000
Canada	254,000	\$220,000	138,000	120,000
Germany	10,800	89,300	4,610	38,800
Japan	2,480,000	1,470,000	5,170,000	3,400,000
Korea, Republic of	--	--	82,000	92,700
Mexico	51,200	44,900	417,000	179,000
Singapore	577,000	342,000	307,000	164,000
South Africa	38,800	34,300	--	--
Taiwan	228,000	134,000	119,000	64,300
Thailand	213,000	129,000	--	--
United Kingdom	907	3,200	1,620	8,390
Venezuela	--	--	10,000	9,530
Total	3,860,000	2,470,000	6,320,000	4,250,000
Strontium oxide, hydroxide, peroxide:				
Australia	--	--	14,900	8,200
Brazil	124,000	48,300	26,700	14,700
Canada	272,000	150,000	432,000	238,000
Germany	19,600	9,500	99,200	47,100
Japan	176,000	96,900	74,000	40,700

See footnotes at end of table.

TABLE 3--Continued
U.S. EXPORTS OF STRONTIUM COMPOUNDS, BY COUNTRY 1/

	1999		2000	
	Gross weight (kilograms)	Value 2/	Gross weight (kilograms)	Value 2/
<u>Strontium oxide, hydroxide, peroxide--Continued:</u>				
Korea, Republic of	82,800	51,000	161,000	88,300
Malasia	21,600	11,900	--	--
Mexico	127,000	85,500	--	--
Norway	20,100	11,100	44,200	24,300
Portugal	--	--	10,200	5,600
United Kingdom	10,600	5,840	--	--
Total	854,000	470,000	862,000	466,000

-- Zero.

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

2/ Customs value.

Source: U.S. Census Bureau.

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

	1999		2000	
	Gross weight (kilograms)	Value 2/	Gross weight (kilograms)	Value 2/
<u>Strontium carbonate:</u>				
China	425,000	\$191,000	270,000	\$116,000
Germany	2,380,000	1,260,000	2,510,000	1,240,000
Italy	6,000	24,000	6,000	20,200
Japan	100	2,060	280	7,210
Mexico	41,100,000	24,200,000	46,500,000	26,200,000
United Kingdom	35	8,090	--	--
Total	44,000,000	25,700,000	49,300,000	27,600,000
<u>Strontium metal:</u>				
Canada	88,400	882,000	90,700	721,000
China	123,000	662,000	211,000	542,000
France	--	--	5,810	47,300
Germany	10	2,050	--	--
Japan	104,000	227,000	--	--
Mexico	--	--	281	2,690
Total	315,000	1,770,000	307,000	1,310,000
<u>Strontium nitrate:</u>				
China	195,000	256,000	234,000	254,000
Finland	--	--	57,700	137,000
France	174,000	1,150,000	209,000	1,190,000
Germany	--	--	150	6,020
Japan	98,700	771,000	107,000	698,000
Mexico	122,000	114,000	79,000	63,800
Switzerland	50	2,370	--	--
Total	590,000	2,290,000	687,000	2,350,000
<u>Strontium oxide, hydroxide, peroxide:</u>				
China	66,700	52,300	71,000	54,900
Germany	60,000	54,300	3,600	15,500
Japan	90,500	421,000	117,000	396,000
Mexico	30,300	57,300	--	--
Switzerland	20,000	15,600	--	--
Total	267,000	600,000	192,000	466,000

-- Zero.

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

2/ Customs value.

Source: U.S. Census Bureau.

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

(Metric tons)

Country 3/	1996	1997	1998	1999	2000 e/
Algeria e/	-- r/	-- r/	-- r/	-- r/	--
Argentina	3,775	3,049	3,100 e/	3,000 e/	3,000 4/
Iran e/ 5/	2,000 r/	2,000 r/	2,000 r/	1,650 r/ 4/	2,000
Mexico	143,892	134,707	118,230	164,682 r/	157,420 p/
Pakistan	2,500 e/	3,000 e/	598	634 r/	600
Spain e/	114,829 4/	92,000	111,000 r/	128,000 r/ 4/	130,000
Turkey e/	30,000	30,000	30,000	25,000	25,000
Total	297,000 r/	265,000 r/	265,000 r/	323,000 r/	318,000

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

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

2/ Table includes data available through May 18, 2001.

3/ 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.

4/ Reported figure.

5/ Data are for year beginning March 21 of that stated.