SELENIUM AND TELLURIUM

By Robert D. Brown, Jr.

Domestic survey data and tables were prepared by Lisa D. Miller, statistical assistant, and the world production tables were prepared by Ronald L. Hatch, international data coordinator.

Selenium and tellurium are byproduct metals usually associated with copper. Primary selenium was produced in the United States as a byproduct of copper refining in 1998; secondary (recycled) selenium was not produced. Five electrolytic copper refineries generated selenium-containing anode slimes. One of the refineries recovered commercial-grade selenium; one recovered a semirefined filter cake, which it shipped to Asia for further refining; and three exported anode slimes for refining. Domestic production, excluding exported anode slimes, was about the same as that of 1997.

Selenium use as a photoreceptor for plain-paper copiers has been decreasing each year in favor of cheaper organic compounds. The distribution among other end-use sectors remained nearly the same, except that metallurgical applications increased. U.S. Geological Survey estimates of end-use demand in 1998 were as follows: glass, 25%; metallurgical applications, 22%; miscellaneous chemical uses, 14%; photoreceptors, 12%; pigments, 8%; and other uses, including agricultural feed additives, 19%.

All selenium-containing scrap generated was exported for reprocessing. Worldwide, about 250 metric tons per year of secondary selenium is produced. World refinery production of selenium (not counting domestic production) decreased by 16%, to 1,450 metric tons; the largest producers, excluding the United States, in order of output, were Japan, Canada, Belgium, and Germany. World production was lower than it had been in more than 5 years (table 5).

World producers of tellurium were Canada, Japan, Peru, and the United States. Domestically, tellurium was recovered by one company from anode slimes generated in the electrolytic refining of copper and from soda slag skimmings generated in lead refining. Secondary tellurium was not produced domestically, but some scrap was exported for recycling. Production data are company proprietary. Domestic consumption increased in 1998. About 55% of the tellurium was used as free-machining additives to steel. Other uses included catalysts, chemical uses, nonferrous alloys, photoreceptors, and thermoelectric devices.

Production

Domestic data are collected through a voluntary survey of U.S. selenium and tellurium producers. The production survey was sent to the two known domestic producers of selenium and the sole domestic producer of tellurium. All the companies responded to the survey. To protect proprietary interests of the companies, however, survey data have been withheld from publication.

Selenium.—Selenium was recovered from anode slimes

generated in the electrolytic production of copper. Domestic production was about the same as that of 1997. Two domestic copper refineries—ASARCO Incorporated at Amarillo, TX, and Phelps Dodge Refining Corp. at El Paso, TX—recovered selenium. One producer exported semirefined selenium (90% selenium content) for toll refining in Asia.

Three other companies generated selenium-containing slimes, but did not produce selenium. The slimes from these refineries were exported for processing.

Most domestic selenium was produced as commercial-grade metal, averaging a minimum of 99.5% selenium and available in various forms, including lump, powder, or shot, or as pigment-grade powder having a minimum 99.8% selenium content.

Tellurium.—Commercial-grade tellurium and tellurium dioxide were produced by Asarco at Amarillo, mainly from copper anode slime but also from lead refinery skimmings. Asarco also produced high purity tellurium (99.999% purity) and selenium (99.999% purity) and other high-purity metals and compounds at its plant in Denver, CO.

Consumption

Selenium.—Selenium demand by end use in the United States can be divided broadly into the following categories, listed in decreasing order of selenium market share: glass manufacturing, metallurgical applications, agricultural uses, chemicals, electronics (including photoreceptor uses), and pigments.

In glass manufacturing, selenium is used principally as a decolorant in container glass and other soda-lime silica glasses. The addition of selenium produces a pink color in the glass that, combined with the green color imparted by ferrous ions, creates a neutral grey color that has low perceptibility to the human eye. Selenium is also used to reduce solar heat transmission in architectural plate glass and to add red color to glass, such as that used in traffic lights. Glass manufacturing accounted for about 25% of the selenium market in 1998.

Metallurgical uses composed an estimated 22% of the market. Of that, more than one-half was estimated to have been used as an additive to steel, copper, and lead alloys to improve machinability and casting and forming properties. Several domestic manufacturers of rolled steel bar produced leaded and selenium-bearing free-machining rod. Selenium-containing free-cutting steels, however, are generally cost competitive only when used with high-speed automatic machine tools.

In 1998, potential selenium use was significantly affected by the Safe Drinking Water Act Amendments of 1996 (Public Law 104-182), which requires that all fixtures, fluxes, pipes, and solders used for the installation or repair of facilities providing water for human consumption contain no lead after August. Bismuth and selenium can replace lead in plumbing applications because they provide the same free-machining properties as lead without its negative environmental effects (King and Li, 1997). Boosted by the targets set by Public Law 104-182, selenium use in plumbing materials could eventually reach more than 500 tons annually (Pede, 1995).

Metallurgical selenium was also added to low-antimony lead alloys used in the support grids of lead-acid storage batteries. The addition of 0.02% selenium by weight as a grain refiner improves the casting and mechanical properties of the alloy. The use of hybrid batteries, which incorporate low-antimony lead positive plates and lead-calcium negative plates, has been increasing, thus increasing the demand for selenium.

Other uses, mainly agricultural, composed about 19% of the market. Dietary supplements for livestock are the largest agricultural use. Selenium also was added to fertilizer used in growing animal feed, a practice that is more prevalent outside the United States.

Chemical applications of selenium, including industrial and pharmaceutical, accounted for about 14% of usage. Selenium has been recognized as a nutrient essential for human health; small quantities of selenium are also used as human food supplements. More-extensive testing on the effectiveness of selenium as a cancer preventive for humans continued. The principal pharmaceutical use of selenium is in antidandruff hair shampoos. Miscellaneous industrial chemical uses include catalysts, lubricants, and rubber compounding. Electronics, which is a decreasing end-use market, accounted for 12% of selenium use. High-purity selenium compounds were used principally as photoreceptors on the drums of plain paper copiers. Photoreceptors have been the largest single application for selenium during the past decade. Selenium compounds, however, are being replaced by organic photoreceptor compounds (OPC), which reportedly offer better performance and lower cost at printing speeds under 80 pages per minute and comparable cost and performance at faster printing speeds. OPC's also are free of the environmental concerns associated with the disposal of selenium compounds. Other electronic uses included rectifier and photoelectric applications.

In pigment applications, selenium was used to increase the red tint in yellow cadmium sulfide-based pigments. Sulfoselenide red pigments have good heat stability and are used in ceramics and plastics, as well as in enamels, inks, and paints. Because of the high cost and the toxicity of cadmiumbased pigments, their use is generally restricted to applications requiring long life, brilliance, high thermal stability, and chemical resistance. Pigments were about 8% of the market.

Tellurium.—The largest use for tellurium, about one-half of the market, was as an additive to free-machining steel. Chemicals and catalyst usage made up about 25% of the market. Additives to nonferrous alloys were slightly more than 10% of the total, and photoreceptor and thermoelectric applications accounted for slightly less than 10%. Other uses were about 5%.

As an alloying element in the production of free-machining

low-carbon steels, additions of up to 0.1% tellurium, usually in conjunction with lead, greatly improve machinability. Similarly, the addition of tellurium to copper and other nonferrous alloys improves their machinability, strength, and corrosion resistance. Tellurium catalysts are used chiefly for the oxidation of organic compounds but are also used in hydrogenation, halogenation, and chlorination reactions. Tellurium chemicals are used as curing and accelerating agents in rubber compounding.

Electronic semiconductor applications for high-purity tellurium include its use in thermoelectric and photoelectric devices and with selenium as a photoreceptor in plain-paper copiers. Mercury cadmium telluride is used as a sensing material for thermal imaging devices. Thermoelectric cooling devices, based on bismuth telluride semiconducting materials, found wider application in electronic and some consumer applications. These devices consist of a series of couples of different semiconducting materials that, when connected to a direct current, cause one side of the thermoelement to cool while the other side generates heat. The warm side is connected to a heat sink to dissipate the heat. Although thermoelectric coolers are still used more in military and electronic applications, such as the cooling of infrared detectors, integrated circuits, medical instrumentation, and laser diodes, their use in consumer products, such as portable coolers, continued to increase.

Prices

The domestic producer price for selenium averaged \$2.48 per pound in 1998. Beginning the year at \$2.82 per pound, the price dropped to \$2.48 per pound, increased to \$2.73 per pound in July, and then declined to \$2.15 per pound by yearend. The producer price for tellurium fell to \$18 per pound by yearend, averaging about \$18.50 for the year.

Foreign Trade

International trade is important in U.S. selenium and tellurium markets. The leading foreign suppliers of selenium, in order of quantity, were the Philippines, Canada, Belgium, and Japan. They accounted for 86% of the imports of selenium metal to the United States in 1998 (table 3). Imports of selenium decreased slightly while exports increased moderately (table 2). Imports of tellurium increased by nearly 40% during the year. The leading suppliers, in decreasing order, were Belgium, the United Kingdom, the Philippines, and Japan (table 4). Data for tellurium exports were not available.

World Review

World production and consumption data for selenium and tellurium were limited in 1998. Apparently, supply remained more than adequate to meet demand. Supply and demand have been in fairly close balance for several years. Better productivity has increased the probability of oversupply, putting downward pressure on prices. Compared with those of 1997, production of selenium decreased by 16%, and that of tellurium

increased by 5% (tables 5 and 6).

Producers claimed that supplies were limited and sought higher prices, but traders concluded sales in the low end of the reported price ranges; sales from the Far East were as low as \$1.50 per pound (Metal Bulletin, 1998; Mining Journal, 1998a, b).

In accordance with the United Nations Environmental Program's Basel Convention, the aim of which is to prevent the "dumping" of hazardous wastes in developing countries, the European Union's Council of Ministers banned the export of certain scrap from Europe to African, Caribbean, and Pacific (ACP) nations. Included in the ban were selenium and tellurium waste and scrap. The ban was instituted despite many cases in which ACP countries already have been importing scrap for their metal industries to be processed and sold, not simply "dumped" (Broad, 1998).

Current Research and Technology

A recent pioneering study indicated that selenium supplements provide significant reductions in the occurrence of lung, prostate, and colorectal cancers in selenium-poor regions. Patients treated in the ramdomized, double blind study received 200 micrograms per day of selenium. Compared with a placebo group, cancer incidence among the patients receiving selenium was 46% lower for lung cancer, 48% lower for colorectal cancer, and 63% lower for prostate cancer (Clark and others, 1996). This line of research continued and has been reported on extensively in medical and popular health journals.

Clinical and epidemiological evidence mounts as replication and other studies are being carried out. An increase in daily intake of selenium for men appears to lower the incidence of prostate cancer. For example, as the average intake of selenium has decreased during the past several decades in England (primarily because diets include European rather than North American wheat), the incidence of prostate cancer has increased (Giovannucci, 1998). It has been theorized that selenium may prevent several types of cancer by killing cancerous cells in premalignant lesions (Fremerman, 1998).

Further studies have shown that higher levels of selenium prevent clogged arteries and depression. Selenium is a component of an important enzyme that protects arteries and cell membranes from damage by free radicals, which could explain why selenium helps lower the incidence of heart disease as well as cancer. Researchers do not yet know the mechanism by which selenium affects mood (Fremerman, 1998).

Outlook

Demand for selenium in photoreceptors is likely to continue to decline as the cost of using organic compounds decreases. Although several new uses have been developed, they have not yet affected the overall demand for selenium. Selenium supply is dependent upon copper production. Because it is recovered as a byproduct, selenium output cannot be easily adjusted to meet market conditions, resulting in possible supply and price

fluctuations. Use as an additive to plumbing brasses, as part of the effort to produce lead-free alloys, affords the greatest possibility for significant increases in demand.

Tellurium supply and demand have remained in fairly close balance since 1990. Large increases are not foreseen in either consumption or production for the immediate future. The demand for high-purity tellurium for solar cells, however, could increase, and this would have a major impact on tellurium consumption.

The most exciting area of development is that of selenium in cancer prevention. This could have profound worldwide public health implications, but it will not result in a large increase in demand because of the small dosage requirements.

References Cited

Broad, Alex, 1998, The ins and outs of transborder "waste" shipments: Metal Bulletin Monthly, May, p. 59-65.

Clark, L.C., and others, 1996, Effect of selenium supplementation for cancer prevention: Journal of the American Medical Association, v. 276, no. 24, December 26, p. 1957-1963.

Fremerman, Sarah, 1998, Selenium—This mineral may help protect you from heart disease and cancer: Natural Health, v. 27, no. 6, November-December, p. 141.

Giovannucci, Edward, 1998, Selenium and risk of prostate cancer: Lancet, v. 352, no. 9130, September 5, p. 755.

King, M.G., and Li, Taie, 1997, Method for making machinable lead-free copper alloys with additive: U.S. Patent 5,614,038, March 25, 4 p.

Metal Bulletin, 1998, Cobalt market continues to come under fire: Metal Bulletin, no. 8294, July 13, p. 7.

Mining Journal, 1998a, Minor metals in July: Mining Journal, v. 331, no. 8492, August 7, p. 111.

———1998b, Minor metals in November: Mining Journal, v. 331, no. 8509, December 4, p. 457.

Pede, M.E., 1995, The future outlook for selenium market, *in* Minor Metals Conference, 10th, Proceedings: Metal Bulletin, Brussels, June 11-13, 18 p.

SOURCES OF INFORMATION

U.S. Geological Survey Publications

Selenium. Ch. in Mineral Commodity Summaries, annual. Selenium. Ch. in United States mineral resources, U.S.

Geological Survey Professional Paper 820, 1973.

Tellurium. Ch. in Mineral Commodity Summaries, annual. Tellurium. Ch. in United States mineral resources, U.S. Geological Survey Professional Paper 820, 1973.

Other

American Bureau of Metal Statistics; Nonferrous Metal Data. American Metal Market.

JOM (formerly Journal of Metals).

Mining Journal (London).

Platt's Metals Week.

Selenium. Ch. in Mineral facts and problems, U.S. Bureau of Mines Bulletin 675, 1985.

Tellurium. Ch. in Mineral facts and problems, U.S. Bureau of Mines Bulletin 675, 1985.

¹Prior to January 1996, Published by the U.S. Bureau of Mines.

TABLE 1 SALIENT SELENIUM AND TELLURIUM STATISTICS 1/

(Kilograms of contained metal, unless otherwise specified)

	1994	1995	1996	1997	1998
Selenium:					
United States:					
Production, primary refined	360,000 2/	373,000 2/	379,000 2/	W r/	W
Shipments to consumers	302,000	320,000	400,000	W	W
Exports, metal, waste and scrap	246,000	270,000	322,000	127,000	151,000
Imports for consumption 3/	441,000	324,000	428,000	346,000 r/	339,000
Apparent consumption, metal 4/	530,000	517,000	564,000	W	W
Dealers' price, average per pound, commercial grade 5/	\$4.90	\$4.89	\$4.00	\$2.94	\$2.49
World: Refinery production	2,160,000	2,070,000	2,250,000	1,720,000 r/	1,450,000 e/
Tellurium:					
United States:					
Imports for consumption 6/	27,400	45,800	73,700	63,900	88,900
Producer price quote, yearend, commercial grade, per pound	\$26.00	\$23.00	\$21.00	\$19.00	\$18.00

e/ Estimated. r/ Revised. W Withheld to avoid disclosing company proprietary data.

 ${\bf TABLE~2} \\ {\bf U.S.~EXPORTS~OF~SELENIUM~METAL,~WASTE,~AND~SCRAP~1/}$

(Kilograms, contained selenium)

	1997		1998		
Country	Quantity	Value	Quantity	Value	
Armenia	869	\$5,520			
Australia	1,180	18,300	1,120	\$17,400	
Belgium	4,910	76,000	7,630	118,000	
Brazil	4,040	65,400			
Canada	3,720	107,000	3,640	108,000	
Colombia		2,880	401	6,200	
Ecuador	1,090	19,300			
El Salvador	810	7,310			
France		3,420	843	13,100	
Georgia	869	7,560			
Germany	18,100	87,200	646	10,000	
Hong Kong	2,580	25,800			
India	10,100	109,000	1,350	13,700	
Japan	487	11,200	7,610	119,000	
Korea, Republic of		2,990			
Mexico	23,900	322,000	39,700	375,000	
New Zealand	460	7,130			
Panama	318	3,060	227	2,580	
Philippines	35,700	233,000	80,300	1,250,000	
Singapore		2,900	1,540	27,800	
South Africa	3,970	10,200			
Thailand	5,230	29,700			
United Kingdom	794	12,200	3,180	49,800	
Venezuela	7,220	47,600	2,570	19,800	
Total	127,000	1,220,000	151,000	2,130,000	

^{1/} Data are rounded to three significant digits; may not add to totals shown.

Source: Bureau of the Census.

 $^{1/\,\}mbox{Data}$ are rounded to three significant digits.

^{2/} Includes semirefined selenium produced by one company and exported for refining.

^{3/} Include unwrought and waste and scrap and selenium dioxide.

^{4/} Calculated by using reported shipments, imports of selenium metal, and estimated exports of selenium metal, excluding scrap.

^{5/} Source: Platt's Metals Week. Calculated from published price ranges.

^{6/} Includes only wrought and waste and scrap.

${\bf TABLE~3} \\ {\bf U.S.~IMPORTS~FOR~CONSUMPTION~OF~SELENIUM~1/}$

(Kilograms, contained selenium)

	1997		1998		
Class and country	Quantity	Value	Quantity	Value	
Unwrought waste and scrap:			-		
Australia	18,000	\$86,200			
Belgium	46,500	1,710,000	43,300	\$1,550,000	
Canada	95,300	1,880,000	100,000	1,550,000	
Finland	4,200	26,100	12,800	48,200	
France	2,370	12,600	10,700	53,100	
Germany	250	9,590	2,040	65,200	
Japan	2,740	645,000	19,100	320,000	
Korea, Republic of	3,590	133,000	1,000	3,530	
Netherlands	500	15,000	999	4,410	
Peru	14,000	97,600			
Philippines	100,000	478,000	116,000	597,000	
Russia	1,590	7,010	2	2,740	
United Kingdom	19,500	117,000	18,500	102,000	
Total	333,000	5,220,000	325,000	4,290,000	
Selenium dioxide: 2/					
Belgium	1	6,620 r/	1,410	79,100	
China			1,350	76,600	
Germany	10,900 r/	125,000 r/	9,350	103,000	
Japan	1,870 r/	20,100 r/	2,160	23,900	
Spain	160 r/	4,530 r/	178	2,870	
United Kingdom	710 r/	13,400 r/			
Total	13,700 r/	169,000 r/	14,400	285,000	
Grand total	346,000 r/	5,390,000 r/	339,000	4,580,000	

r/ Revised.

Source: Bureau of the Census.

 $\label{eq:table 4} \textbf{U.S. IMPORTS FOR CONSUMPTION OF TELLURIUM } 1/$

(Kilograms, gross weight)

	1997	1	1998	
Class and country	Quantity	Value	Quantity	Value
Unwrought and waste and scrap:				
Australia	1,200	\$43,000	6,800	\$183,000
Belgium	10,200	271,000	21,900	385,000
Canada	6,410	503,000	7,810	645,000
China	21	5,460	24	17,000
France	1,060	19,800		
Japan	2,330	245,000	13,200	540,000
Mexico	154	2,110	173	2,370
Philippines	19,600	635,000	17,800	325,000
Russia			4	13,400
United Kingdom	22,900	383,000	21,200	317,000
Total	63,900	2,110,000	88,900	2,430,000

^{1/} Data are rounded to three significant digits; may not add to totals shown.

Source: Bureau of the Census.

^{1/} Data are rounded to three significant digits; may not add to totals shown.

^{2/} Totals revised to 71% of original quantities and values.

TABLE 5 SELENIUM: WORLD REFINERY PRODUCTION, BY COUNTRY 1/2/

(Kilograms, contained selenium)

Country 3/	1994	1995	1996	1997	1998 e/
Belgium e/	250,000	250,000	250,000	250,000	200,000
Canada 4/	566,000	553,000	694,000	592,000 r/	384,000
Chile e/	43,000 5/	51,000	50,000	49,500 r/	49,000
Finland e/	29,690 5/	29,000	28,000	28,000	26,000
Germany e/	120,000	115,000	115,000	115,000	100,000
India 5/	11,582	11,449	11,500 e/	11,500 e/	11,500
Japan	614,134	547,731	588,186	546,372 r/	551,000 6/
Peru e/	21,000 6/	21,000	21,000	21,000	21,000
Philippines e/	40,000	40,000	40,000	40,000	40,000
Serbia and Montenegro e/	30,000	30,000	30,000	30,000	30,000
Sweden e/	50,000	30,000	26,000	20,000	20,000
United States 7/	360,000	373,000	379,000	W r/	W
Zambia 8/	21,290	18,550	15,161 r/	20,165 r/	15,000
Zimbabwe	2,009	2,000 e/	2,000 e/	r/	
Total	2,160,000	2,070,000	2,250,000	1,720,000 r/	1,450,000

- e/ Estimated. r/ Revised. W Withheld to avoid disclosing company proprietary data; not included in "Total."
- 1/ World totals, U.S. data, and estimated data are rounded to three significant digits; may not add to totals shown.
- 2/ Insofar as possible, data relate to refinery output only; thus, countries that produced selenium contained in copper ores, copper concentrates, blister copper and/or refinery residues, but did not recover refined selenium from these materials indigenously were excluded to avoid double counting. Table includes data available through June 3, 1999.
- 3/ In addition to the countries listed, Australia produced refined selenium, but output is not reported; available information is inadequate for formulation of reliable estimates of output levels. Australia is known to produce selenium in intermediate metallurgical products and has facilities to produce elemental selenium. In addition to having facilities for processing imported anode slimes for the recovery of selenium and precious metals, the United Kingdom has facilities for processing selenium scrap.
- 4/ Excludes selenium intermediates exported for refining.
- 5/ Data are for Indian fiscal year beginning April 1 of year stated.
- 6/ Reported figure.
- 7/ Includes production of semirefined selenium exported for further refining.
- 8/ Data are for year beginning April 1 of year stated. Gross weight, purity unknown.

TABLE 6
TELLURIUM: WORLD REFINERY PRODUCTION, BY COUNTRY 1/2/

(Kilograms, contained tellurium)

Country 3/	1994	1995	1996	1997	1998 e/
Canada 4/	42,000	102,000	59,000	59,000 r/	57,000
Japan	47,256	43,129	37,945	25,260 r/	33,000
Peru	28,000	30,087	25,102	25,100 e/	25,100
United States	W	W	W	W	W

- e/ Estimated. r/ Revised. W Withheld to avoid disclosing company proprietary data.
- 1/ Estimated data are rounded to three significant digits.
- 2/ Insofar as possible, data relate to refinery output only; thus, countries that produced tellurium contained in copper ores, copper concentrates, blisster copper and/or refinery residues, but did not recover refined tellurium are excluded to avoid double counting. Table is not totaled because of exclusion of data from major world producers, notably the former U.S.S.R. and the United States. Table includes data available through June 3, 1999.
- 3/ In addition to the countries listed, Australia, Belgium, Chile, Germany, the Philippines, and the former U.S.S.R. are known to produce refined tellurium, but output is not reported; available information is inadequate for formulation of reliable estimates of output levels.
- 4/ Excludes tellurium intermediates exported for refining.