SELENIUM AND TELLURIUM

By Robert D. Brown, Jr.

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

Domestic apparent consumption of selenium increased by 11% to a level higher than the previous apex reached in 1988. 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. Estimates of end-use demand in 1997 are as follows: glass, 25%; metallurgical applications, 20%; miscellaneous chemical uses, 14%; photoreceptors, 14%; 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 decreased 12%, to 1,990 metric tons; the largest producers, in order of output, were Japan, Canada, the United States, Belgium, and Germany. World production was the lowest since 1993.

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 was believed to have decreased in 1997. 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.

Domestic Data Coverage

Domestic data are collected by a voluntary survey of the domestic producers of selenium and tellurium. The selenium production canvass was sent to the three known producers and the tellurium production canvass, to the sole producer. All but one company responded. Data for this company was estimated from previous reports received and published reports of that company's results for copper refining in 1997. Company proprietary data are not released.

Production

Selenium was recovered from anode slimes generated in the electrolytic production of copper. Domestic production decreased by nearly 7% but remained close to the levels achieved in the 3 previous years. Three domestic copper refineries recover selenium—ASARCO Incorporated at Amarillo, TX, Phelps Dodge Refining Corp. at El Paso, TX, and Kennecott Utah Copper Corp. at Magna, UT. One producer exported semirefined selenium (90% selenium content) for toll-refining in Asia.

Two other companies generated selenium-containing slimes, but did not produce selenium. Selenium-containing slimes from the other two 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 shot, lump, or powder or as pigment-grade powder having a minimum 99.8% selenium content.

Commercial-grade tellurium and tellurium dioxide were produced by Asarco at Amarillo, TX, 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. Detector-grade tellurium (99.99999% purity) was produced by Cabot Performance Metals, Revere, PA.

Consumption

Selenium demand by end use can be divided broadly into the following categories: glass manufacturing, electronics (including photoreceptor uses), agricultural and other uses, metallurgical applications, chemicals, and pigments.

In glass manufacturing, selenium is used principally as a decolorant in container glass and other soda-lime silica glasses. Under weak oxidizing conditions, the addition of selenium adds a pink color to the glass that combines with the green color imparted by ferrous ions to create 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 1997.

Metallurgical uses composed an estimated 20% of the market. It is estimated that more than one-half of the metallurgical selenium is used as an additive to steel, copper, and lead alloys to improve machinability and casting and forming properties. Several domestic producers of rolled steel bar produce 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. The use of selenium, along with bismuth, in free-machining red brasses for plumbing applications began to increase in 1997. Bismuth and selenium are replacing lead in this application, providing the same free-machining properties as lead without the negative environmental effects of lead (King and Li, 1997). A smaller amount of metallurgical selenium is used as an additive 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. Hybrid batteries, which employ low-antimony lead positive plates and lead-calcium negative plates, have been gaining in usage, thus increasing the demand for selenium.

Other uses, mainly agricultural, compose about 19% of the market. Dietary supplements for livestock are the largest agricultural use. Selenium also may be added to fertilizer, a practice that is more prevalent outside the United States.

In electronics, which is a decreasing end-use market accounting for 14% 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.

Chemical uses of selenium, including industrial and pharmaceutical applications, accounted for about 14% of usage. Small quantities of selenium also are used as human food supplements; selenium has been recognized as a nutrient essential for human health. More-extensive testing on the effectiveness of selenium as a cancer preventive for humans has been planned. The principal pharmaceutical use of selenium is in antidandruff hair shampoos. Miscellaneous industrial chemical uses include lubricants, rubber compounding, and catalysts.

In pigment applications, selenium was used to produce color changes in cadmium-sulfide-based pigments. With increasing substitution of selenium for sulfur, the yellow cadmium pigment becomes more red. Sulfoselenide red pigments have good heat stability and are used in ceramics and plastics, as well as in paints, inks, and enamels. Because of the relatively high cost and the toxicity of cadmium-based 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.

Apparent domestic and world demand for tellurium decreased in 1997. The largest use for tellurium was as an additive to free-machining steel, about one-half of the market. Chemicals and catalyst usage composed about 25% of the market. Additives to nonferrous alloys used about 10% of the total, and photoreceptor and thermoelectric applications accounted for another 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, are finding wider application in electronic and some consumer applications. These devices consist of a series of couples of different semiconducting materials which, when connected to a direct current, cause one side of the thermoelement to cool while the other side evolves 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, has begun to increase.

Prices

The domestic producer price for selenium averaged $2.94 per pound in 1997. Beginning the year at $3.08 per pound, the price dropped to $2.88 per pound and then increased to $3.02 per pound before the end of January 1997. It then drifted downward to $2.82 per pound at yearend. The producer price for tellurium fell to $19 per pound by yearend, averaging about $20 for the year.

Foreign Trade

Trade is important in the selenium and tellurium markets. In 1997, imports and exports of selenium decreased, the latter by nearly 60%. More than one-half of this decrease was accounted for by the decrease in exports to the Philippines to 36 tons in 1997 from 147 tons in 1996. Decreases in exports to most of the other countries importing selenium from the United States were significant. Besides the Philippines, the leading importers of selenium from the United States were, in order of importance, Mexico, Germany, and India. These four accounted for 61% of U.S. exports in 1997. Imports of selenium metal decreased by 19% for the year, with the Philippines, Canada, Belgium, and Japan (in order of quantity) as the leading suppliers. They accounted for 80% of the imports to the United States in 1997. Imports of tellurium decreased by 13%. Data for tellurium exports were not available.

World Review

World production and consumption data for selenium and tellurium were limited. Apparently, the supply is 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. Production decreased in 1997.

Late in the year, selenium from the Philippines and the Republic of Korea was being sold at prices of less than $2.00 per pound (Metal Bulletin, 1997a).

In accordance with the U. N. Environmental Program's Basel Convention, 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 are selenium and tellurium waste and scrap. This is in spite of many cases where ACP countries are already importing scrap for their metal industries, and the materials are being processed and sold, not simply being disposed of (Metal Bulletin, 1997b).

Current Research and Technology

A recent study indicates that selenium supplementation provides significant reductions in the rate of occurrence of lung, prostate, and colorectal cancers for subjects living in selenium-poor regions. The treatment subjects in the double blind study received 200 micrograms per day of selenium. Compared with the placebo group, cancer incidence in the treatment group was 46% lower for lung cancer, 48% lower for colorectal cancer, and 63% lower for prostate cancer. The study also determined the safety of selenium supplementation at the 200-microgram-per-day dose (Clark, 1997).

A steady daily dosage of 120 micrograms of selenium will increase the blood levels of selenium of a person living in a selenium-poor region to just below that obtained naturally without supplementation by persons living in selenium-rich areas (Colditz, 1996). Researchers have also found that Brazil nuts from selenium-rich central Brazil contain 120 micrograms of selenium per nut (Yeykal, 1996).

A workshop was held at the Danish Cancer Society campus in Copenhagen to plan a large-scale international test to replicate the results already obtained. The new study will involve 52,000 subjects from Denmark, Finland, the Netherlands, Norway, Sweden, the United Kingdom, and the United States. Dosages will be placebo, 100, 200, and 300 micrograms per day (Clark, 1977).

A device using cadmium zinc telluride could replace the gamma ray detectors now used to monitor the deterioration of nuclear weapons and to diagnose cancers. This new application will allow a 1,500-kilogram gamma camera to be replaced by a 30-kilogram device that works at room temperature instead of liquid nitrogen temperatures. This could open these devices to numerous other applications. With medical and military applications prevailing, these are high-cost devices, but the small amount of tellurium per device limits the possible impact on total demand (Gross, 1997).

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. The largest likely increase in demand would come from its use as an additive to plumbing brasses, as part of the efforts to produce lead-free alloys for this sector.

Tellurium supply and demand have remained in close balance since 1990. Large increases are not foreseen in either consumption or production for the immediate future. Demand for high-purity tellurium for solar cells could increase, and this would have a major impact on demand. Little information is available on the selenium or tellurium content of new ore bodies.

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TABLE 1
SALIENT SELENIUM AND TELLURIUM STATISTICS 1/

(Kilograms of contained metal unless otherwise specified)

	1993	1994	1995	1996	1997
Selenium:					
United States:					
Production, primary refined 2/	283,000	360,000	373,000	379,000	353,000
Shipments to consumers	258,000	302,000	320,000	400,000	395,000
Exports, metal, waste and scrap	261,000	246,000	270,000	322,000	127,000
Imports for consumption 3/	382,000	441,000	324,000	428,000	352,000
Apparent consumption, metal 4/	460,000	530,000	517,000	564,000 r/	627,000
Dealers' price, average per pound, commercial grade 5/	$4.90	$4.90	$4.89	$4.00	$2.94
World: Refinery produuction	1,740,000	2,160,000	2,070,000	2,250,000 r/	1,990,000
Tellurium:					
United States:					
Imports for consumption 6/	45,000	27,400	45,800	73,700	63,900
Producer price quote, yearend, commercial grade, per pound	$32.00	$26.00	$23.00	$21.00	$19.00

r/ Revised.
1/ Data are rounded to three significant digits.
2/ Includes semirefined selenium produced 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: Metals Week. Calculated from plublished price ranges.
6/ Includes only wrought and waste and scrap.

TABLE 2
U.S. EXPORTS OF SELENIUM METAL, WASTE, AND SCRAP 1/

(Kilograms, contained selenium)

	1996		1997	
Country	Quantity	Value	Quantity	Value
Argentina	3,430	$32,100	--	--
Armenia	--	--	869	$5,520
Australia	317	7,090	1,180	18,300
Belgium	18,100	64,100	4,910	76,000
Brazil	23,700	368,000	4,040	65,400
Canada	1,140	31,300	3,720	107,000
China	13,200	205,000	--	--
Colombia	--	--	232	2,880
El Salvador	--	--	810	7,310
France	19,100	68,600	72	3,420
Georgia	--	--	869	7,560
Germany	208	2,930	18,100	87,200
Hong Kong	--	--	2,580	25,800
India	14,100	222,000	10,100	109,000
Israel	40	3,290	--	--
Japan	470	7,280	487	11,200
Korea, Republic of	7,980	123,000	194	2,990
Mexico	30,800	414,000	23,900	322,000
Netherlands	36,600	307,000	--	--
Panama	--	--	318	3,060
Philippines	147,000	738,000	35,700	233,000
Singapore	--	--	133	2,900
South Africa	--	--	3,970	10,200
Taiwan	211	3,260	--	--
Thailand	--	--	5,230	29,700
United Kingdom	311	4,820	794	12,200
Venezuela	3,090	31,400	7,220	47,600
Other	2,180	36,100	1,550	26,400
Total	322,000	2,670,000	127,000	1,220,000

1/ Data may not add to totals shown because of independent rounding.

Source: Bureau of the Census.

TABLE 3
U.S. IMPORTS FOR CONSUMPTION OF SELENIUM 1/

(Kilograms, contained selenium)

Class and country	1996 Quantity	1996 Value	1997 Quantity	1997 Value
Unwrought waste and scrap:				
Australia	--	--	18,000	$86,200
Belgium	55,300	$1,490,000	46,500	1,710,000
Canada	133,000	2,120,000	95,300	1,880,000
Chile	14,300	106,000	--	--
China	5,000	36,900	--	--
Finland	7,650	46,600	4,200	26,100
France	1,450	9,310	2,370	12,600
Germany	475	15,700	250	9,590
Japan	32,800	836,000	26,700	645,000
Korea, Republic of	248	17,000	3,590	133,000
Netherlands	14,800	124,000	500	15,000
Peru	5,000	28,200	14,000	97,600
Philippines	131,000	589,000	100,000	478,000
Russia	2,010	12,400	1,590	7,010
United Kingdom	9,690	72,200	19,500	117,000
Total	412,000	5,500,000	333,000	5,220,000
Selenium dioxide: 2/				
Belgium	--	--	1	9,330
Germany	7,640	96,700	15,400	176,000
Japan	1,550	18,800	2,640	28,300
Spain	--	--	225	6,380
United Kingdom	6,290	119,000	1,000	18,800
Total	15,500	234,000	19,300	239,000
Grand total	428,000	5,730,000	352,000	5,460,000

1/ Data may not add to totals shown because of independent rounding.
2/ Totals revised to 71% of original quantities and values.

Source: Bureau of the Census.

TABLE 4
U.S. IMPORTS FOR CONSUMPTION OF TELLURIUM 1/

(Kilograms, gross weight)

Class and country	1996 Quantity	1996 Value	1997 Quantity	1997 Value
Unwrought and waste and scrap:				
Australia		--	1,200	$43,000
Belgium	6,860	$303,000	10,200	271,000
Canada	14,300	885,000	6,410	503,000
China	916	69,200	21	5,460
France	301	12,200	1,060	19,800
Germany	100	2,430		--
Japan	5,880	501,000	2,330	245,000
Mexico	961	13,100	154	2,110
Peru	24,600	848,000		--
Philippines	987	27,300	19,600	635,000
United Kingdom	18,800	525,000	22,900	383,000
Total	73,700	3,190,000	63,900	2,110,000

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

Source: Bureau of the Census.

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

(Kilograms, contained selenium)

Country 3/	1993	1994	1995	1996	1997 e/
Belgium e/	250,000	250,000	250,000	250,000	250,000
Canada 4/	295,000 e/	566,000	553,000	694,000 r/	509,000 p/
Chile e/	49,500	43,000 r/ 5/	51,000 r/	50,000 r/	50,000
Finland	30,400	29,690	29,000 e/	28,000 r/ e/	28,000
Germany e/	120,000	120,000	115,000	115,000 r/	115,000
India 6/	11,116	11,582	11,449	11,500 e/	11,500
Japan	540,943	614,134	547,731	588,186 r/	540,000
Peru	17,100	21,000	21,000 e/	21,000 e/	21,000
Philippines e/	40,000	40,000	40,000	40,000	40,000
Serbia and Montenegro e/	27,677 5/	30,000	30,000	30,000	30,000
Sweden e/	50,000	50,000	30,000	26,000 r/	20,000
United States 7/	283,000	360,000	373,000	379,000	353,000 5/
Zambia 8/	26,967	21,290	18,550 r/	20,400 r/ e/	20,200
Zimbabwe	1,113	2,009	2,000 e/	2,000 e/	2,000
Total	1,740,000	2,160,000	2,070,000	2,250,000 r/	1,990,000

e/ Estimated. p/ Preliminary. r/ Revised.
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, 1998.
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. Selenium is also produced in some countries of the former U.S.S.R., including probably Kazakstan and Russia, but information is not available for deriving production estimates.
4/ Excludes selenium intermediates exported for refining.
5/ Reported figure.
6/ Data are for Indian fiscal year beginning April 1 of year stated.
7/ Includes production of semi-refined 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/	1993	1994	1995	1996	1997 e/
Canada 4/	24000 e/	42000	102000	59000 r/	40000 p/
Japan	46,768	47256	43129	37945 r/	23500
Peru	17400 e/	28000	30087 r/	25102 r/	25100
United States	W	W	W	W	W

e/ Estimated. p/ Preliminary. 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, blister copper, and/or refinery residues, but did not recover refined tellurium, are excluded to avoid double counting. Table is not totaled because of the exclusion of data from major world producers, notably countries of the former U.S.S.R. and the United States. Table includes data available through June 3, 1998.
3/ In addition to the countries listed, Australia, Belgium, Chile, Germany, the Philippines, and countries of the former U.S.S.R. are known to produce refined tellurium, but output is not reported, and available information is inadequate for formulation of reliable estimates of output levels.
4/ Excludes tellurium intermediates exported for refining.