SELENIUM AND TELLURIUM

By Robert D. Brown, Jr.

Primary selenium was produced domestically as a byproduct of copper refining in 1996; there was no production of secondary (recycled) selenium. 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, increased in 1996 to a level slightly higher than the previous high, obtained in 1995.

Domestic apparent consumption of selenium increased a small amount to a level higher than the recent apex, reached in 1994, but not as high as the levels of 1988 and 1989. Selenium use as a photoreceptor for plain paper copiers has been decreasing each year recently in favor of cheaper organic compounds. Otherwise, the distribution among end-use sectors remained nearly the same. Estimates of end-use demand in 1996 are as follows: glass, 25%; photoreceptors, 16%; metallurgical applications, 16%; miscellaneous chemical uses, 15%; pigments, 8%; and other uses, including agricultural feed additives, 20%.

All selenium-containing scrap generated was exported for reprocessing. Worldwide, about 250 metric tons of secondary selenium is produced annually. World refinery production of selenium increased 4%, to 2,150 metric tons; Japan, Canada, the United States, Belgium, and Germany were the largest producers in order of output. World production was slightly lower than the level achieved in 1994.

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. There was no domestic production of secondary tellurium, but some scrap was exported for recycling. Production data are company proprietary. Domestic consumption was believed to have increased in 1996. 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 tellurium to the sole producer. All companies responded, but company proprietary data are not released.

Legislation and Government Programs

Tellurium metal was removed from the Environmental Protection Agency's (EPA's) most hazardous list. Its placement on the list had been based on the properties of a tellurium compound that is quite soluble in water and was already on the list. When informed that the properties of tellurium metal are quite different, EPA removed tellurium metal from the list (Federal Register, 1996).

Production

Selenium was recovered from anode slimes generated in the electrolytic production of copper. Domestic production increased slightly to a new high. Three domestic copper refineries recover selenium: ASARCO Incorporated, Amarillo, TX; Phelps Dodge Refining Corp., El Paso, TX; and Kennecott Utah Copper Corp., 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 six 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. The addition of selenium under weak oxidizing conditions adds a pink color to the glass that combines with the green color imparted by ferrous ions to create a neutral gray 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 1996.

In electronics, a large end-use market, accounting for 16% 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 over the past decade. However selenium compounds 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.

Other uses, mainly agriculture, comprise about 20% of the market. Dietary supplements for livestock are the largest agricultural usage, although selenium also may be added to fertilizer, a practice that is more prevalent outside the United States.

Metallurgical uses comprised an estimated 16% of the market. Selenium is added to steel, copper, and lead alloys to improve machinability and casting and forming properties. Several domestic producers of rolled steel bar produce both leaded and selenium-bearing free-machining rod. However, selenium-containing free-cutting steels are generally cost competitive only when used with high-speed automatic machine tools. It is estimated that more than one-half of the metallurgical uses are for these applications. A smaller amount is used for batteries. A more detailed breakdown of this category is not available.

Selenium is 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 quantity of selenium consumed in this application has been greatly affected by technological changes in battery grid manufacture. The development of low-maintenance batteries in the early 1970's encouraged the use of low-antimony grid alloys requiring selenium. Since 1975, lead-calcium maintenance-free automotive batteries have captured a greater share of the automotive battery market, decreasing the demand for selenium in this application. But more recently, hybrid batteries, which employ low-antimony lead positive plates and lead-calcium negative plates, have been gaining in usage, again increasing the demand for selenium.

Chemical uses of selenium, including industrial and pharmaceutical applications, accounted for about 15% of usage. Small quantities of selenium also are used as human food supplements; selenium has been recognized as a nutrient essential for human health. 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 increased in 1996. The largest use for tellurium was as an additive to free-machining steel, about 50% of the market. Chemicals and catalyst usage was about 25% of the market. Additives to nonferrous alloys used about 10%, and photoreceptor and thermoelectric applications accounted for another 10%. Other uses were about 5%.

Tellurium is used principally as an alloying element in the production of free-machining low-carbon steels, where 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 used also 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 with selenium as a photoreceptor in plain paper copiers and in thermoelectric and photoelectric devices. 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 in 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. Thermoelectric coolers are still used to cool infrared detectors, integrated circuits, medical instrumentation, and laser diodes more than for consumer products, such as portable coolers.

Prices

The domestic producer price for selenium averaged $4.00 per pound in 1996. The price drifted downward from just below $5.00 at the beginning of the year to just above $3.00 per pound at yearend. The producer price for tellurium fell to $21 per pound by yearend, averaging about $22 for the year.

World Review

World production and consumption data for selenium and tellurium were limited. Apparently, the supply is adequate to meet demand. Supply and demand have been in fairly close balance for several years. Better productivity has increased the modest oversupply, putting downward pressure on prices.

Current Research and Technology

In a study released early in 1996, the National Cancer Institute found that women having high blood levels of selenium were five times less likely to develop ovarian cancer than women with the lowest levels. While further testing to verify this effect is indicated, researchers believe that 70 to 120 micrograms of selenium daily as a human dietary supplement is also indicated. This amount is well below the threshold amount for toxic effects (thought to be higher than 1,000 micrograms.) 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 of the United States to just below that obtained naturally without supplementation by persons living in selenium rich areas (Colditz, 1996). Researchers have also found that Brazil nuts with shells, from selenium-rich central Brazil, contain 120 micrograms of selenium per nut (Yeykal, 1996).

Late in the year, the Journal of the American Medical Association (JAMA) announced the results of a study thought at first to be a "failure"—because a hoped for reduction in the recurrence of skin cancer with selenium therapy was not obtained. But the data revealed significant reductions in the rate of occurrence for lung, prostate, colon, and rectal cancers. The subjects receiving selenium instead of a placebo received 200 micrograms per day. The study was conducted in a selenium-poor region of the country. These results, approaching the "too-good-to-be-true" level, caused much excitement; but the JAMA editors have concluded that "for now it is premature to change individual behavior, to market specific selenium supplements, or to modify public health recommendations based on the results of this one randomized trial" (Clark, 1996).

Outlook

Selenium supply is dependent upon copper production; and in the past several years, it has exceeded demand. Because it is recovered as a byproduct, selenium output cannot be easily adjusted to meet market conditions, resulting in supply and price fluctuations. Although several new uses have been developed, they have not yet impacted the overall demand for selenium. Demand for selenium in photoreceptors is likely to continue to decline as the cost of using organic compounds decreases. The largest possible increase in demand would come from use as an additive to plumbing brass, as part of the efforts to produce lead-free alloys for this sector.

Tellurium supply and demand have remained in close balance since 1990. This situation is likely to continue as there are no large increases foreseen in either consumption or production for the immediate future. Demand for high purity tellurium may increase for solar cells, and this could 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)

	1992	1993	1994	1995	1996
Selenium:					
United States:					
Production, primary refined	243,000 2/	283,000 2/	360,000 2/	373,000 2/	379,000
Shipments to consumers	221,000	258,000	302,000	320,000	400,000
Exports, metal, waste and scrap	175,000	261,000	246,000	270,000 r/	322,000
Imports for consumption 3/	371,000	382,000	441,000	324,000	434,000
Apparent consumption, metal 4/	490,000	460,000	530,000	517,000	543,000
Dealers' price, average per pound, commercial grade 5/	$5.13	$4.90	$4.90	$4.89	$4.00
World: Refinery production	1,770,000	1,740,000 r/	2,160,000 r/	2,070,000	2,150,000
Tellurium:					
United States:					
Imports for consumption 6/	48,400	45,000	27,400	45,800	73,700
Producer price quote, yearend, commercial grade, per pound	$35.00	$32.00	$26.00	$23.00	$21.00

r/ Revised.
1/ Data are rounded to three significant digits.
2/ Includes semirefined selenium produced by one company and exported for refining.
3/ Includes unwrought and waste and scrap and selenium dioxide.
4/ Calculated using reported shipments, imports of selenium metal, and estimated exports of selenium metal, excluding scrap.
5/ Source: Metals Week. Calculated from published price ranges.
6/ Includes only unwrought and waste and scrap.

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

(Kilograms, contained selenium)

	1995		1996	
	Quantity	Value	Quantity	Value
Argentina	--	--	3,430	$32,100
Australia	--	--	317	7,090
Austria	401	$6,200	--	--
Belgium	46,700	309,000	18,100	64,100
Brazil	14,600	220,000	23,700	368,000
Canada	1,090	29,900	1,140	31,300
China	--	--	13,200	205,000
Denmark	1,730	41,500	--	--
El Salvador	3,710	57,500	--	--
France	23,600	119,000	19,100	68,600
Germany	1,040	28,300	208	2,930
India	15,500	247,000	14,100	222,000
Israel	1,000	11,200	40	3,290
Japan	4,700	25,900	470	7,280
Korea, Republic of	4,620	80,300	7,980	123,000
Mexico	30,700	520,000	30,800	414,000
Netherlands	32,300	237,000	36,600	307,000
Philippines	80,900	253,000	147,000	738,000
Poland	182	2,910	--	--
South Africa	370	5,910	--	--
Syria	952	27,200	--	--
Taiwan	1,430	22,900	211	3,260
United Kingdom	332	2,690	311	4,820
Venezuela	4,050	43,000	3,090	31,400
Other	--	--	2,180	36,100
Total	270,000 r/	2,290,000 r/	322,000	2,670,000

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

Source: Bureau of the Census.

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

(Kilograms, contained selenium)

Class and country	1995 Quantity	1995 Value	1996 Quantity	1996 Value
Unwrought and waste and scrap:				
Australia	5,540	$44,600	--	--
Barbados	80	2,400	--	--
Belgium	45,900	1,980,000	55,300	$1,490,000
Canada	128,000	2,220,000	133,000	2,120,000
Chile	--	--	14,300	106,000
China	528	18,000	5,000	36,900
Finland	3,600	28,800	7,650	46,600
Germany	4,200	96,700	475	15,700
Korea, Republic of	--	--	248	17,000
Japan	32,800	993,000	32,800	836,000
Netherlands	--	--	14,800	124,000
Peru	--	--	5,000	28,200
Philippines	67,500	462,000	131,000	589,000
Russia	8,110	74,900	2,010	12,400
Spain	1,000	8,400	--	--
United Kingdom	13,600	110,000	9,690	72,200
Other	--	--	1,450	9,310
Total	311,000	6,050,000	412,000	5,500,000
Selenium dioxide: 2/				
France	53	1,730	--	--
Germany	4,320	59,800	10,800	136,000
Japan	816	22,500	2,190	26,400
Spain	710	8,260	--	--
United Kingdom	6,890	88,400	8,850	167,000
Total	12,800	181,000	21,800	330,000
Grand total	324,000	6,230,000	434,000	5,830,000

1/ Data are rounded to three significant digits; may not add to totals shown.
2/ Figure adjusted by the U.S. Geological Survey.

Source: Bureau of the Census.

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

(Kilograms, gross weight)

Class and country	1995 Quantity	1995 Value	1996 Quantity	1996 Value
Unwrought and waste and scrap:				
Belgium	4,550	$262,000	6,860	$303,000
Canada	9,410	659,000	14,300	885,000
China	604	82,100	916	69,200
France	200	5,730	301	12,200
Germany	1	1,270	100	2,430
Japan	6,850	546,000	5,880	501,000
Mexico	--	--	961	13,100
Philippines	6,800	240,000	24,600	848,000
Peru	1,060	29,500	987	27,300
Russia	71	5,250	--	--
Switzerland	135	10,900	--	--
United Kingdom	16,100	593,000	18,800	525,000
Total	45,800	2,430,000	73,700	3,190,000

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/	1992	1993	1994	1995	1996 e/
Belgium e/	250,000	250,000	250,000	250,000	250,000
Canada 4/	294,057	295,000 e/	566,000	553,000	561,000
Chile e/	50,000	49,500	45,000	46,000	46,000
Finland	30,040	30,400	29,690 r/	29,000 r/ e/	30,000
Germany e/	125,000	120,000	120,000	115,000	120,000
India 5/	9,628 r/	11,116 r/	11,582 r/	11,449 r/	11,500
Japan	572,998	540,943	614,134	547,731 r/	610,000
Mexico	400	--	--	--	--
Peru	14,396	17,100 r/	21,000 r/	21,000 r/ e/	21,000
Philippines e/ 6/	60,000	40,000	40,000	40,000	40,000
Serbia and Montenegro	57,800	27,677	30,000 e/	30,000 e/	30,000
Sweden e/	32,000 7/	50,000	50,000	30,000	30,000
United States 8/	243,000	283,000	360,000	373,000	379,000 7/
Zambia 9/	31,785	26,967	21,290 r/	20,000 r/	20,000
Zimbabwe	1,736	1,113	2,009	2,000 e/	2,000
Total	1,770,000	1,740,000	2,160,000	2,070,000	2,150,000

e/ Estimated. 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 Apr. 9, 1997.

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 Apr. 1 of year stated.

6/ Incomplete; data shown are for primary production at Philippine Associated Smelting and Refining Corp.

7/ Reported figure.

8/ Includes production of semirefined selenium exported for further refining.

9/ Data are for year beginning Apr. 1 of year stated. Gross weight, purity unknown.

TABLE 6

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

(Kilograms, contained tellurium)

Country 3/	1992	1993	1994	1995	1996 e/
Canada 4/	21,776	24,000 e/	42,000	102,000 r/	62,000 p/
Japan	57,178	46,768	47,256	43,129 r/	39,300
Peru e/	18,631 5/	17,400 r/	28,000 r/	28,000 r/	28,000
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 the former U.S.S.R. and the United States. Table includes data available through Apr. 9, 1997.

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, and available information is inadequate for formulation of reliable estimates of output levels.

4/ Excludes tellurium intermediates exported for refining.

5/ Reported figure.