SELENIUM AND TELLURIUM

By Robert D. Brown, Jr.

Primary selenium was produced domestically as a byproduct of copper refining in 1994; there was no production of secondary (recycled) selenium. Five 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 27% in 1994, to 360 metric tons. The increase was attributed reportedly to improvements to one company's purification circuit and a greater concentration of selenium in the ores.[1] The value of U.S. production was $3.8 million.

Apparent consumption of selenium increased 15% in 1994 in response to increased demand in the chemical and glass industries. Other uses included electronics (including photoreceptors), agricultural feed additives, metallurgical applications, and catalysts. Selenium use as a photoreceptor for plain paper copiers has been decreasing in favor of organic compounds.

All selenium-containing scrap generated was exported for reprocessing. World secondary production was estimated at 250 tons of selenium. World refinery production increased 7%, to 1,880 tons; Japan, the United States, Canada, Belgium, and Germany were the largest producers in order of output.

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 apparent consumption was believed to have increased slightly in 1994, according to the Selenium-Tellurium Development Association (STDA). About 50% of consumption was for free-machining additives to steel. Other uses included catalysts, chemical uses, nonferrous alloys, photoreceptors, and thermoelectric devices.

World reserves and resources for selenium and tellurium are based on copper reserves and resources using the following factors; for selenium, 0.64 kg/mt copper for Canada and 0.215 kg/mt copper for the rest of the world. For tellurium, 0.065 kg/mt. World reserves for selenium are 70,000 tons and resources are 130,000 tons. For tellurium, world reserves are 20,000 tons and resources 38,000 tons. Chile, the United States, and Canada possess the largest reserves for both metals in order of magnitude.

Domestic Data Coverage

Domestic production, shipments, and stock 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 some company proprietary data were not released.

Production

Selenium was recovered from anode slimes generated in the electrolytic production of copper. Domestic production increased 27% from 1993 reportedly owing to one company improving its electrolyte purification facility and having a greater concentration of selenium in its ores.[2] Five domestic copper refineries generated selenium-containing slimes, but only three recovered selenium; ASARCO Incorporated at Amarillo, TX; Phelps Dodge Refining Corp. at El Paso, TX; and Rio Tinto Zinc at its Kennecott refinery in Magna, UT. One producer exported semirefined selenium (90% selenium content) for toll-refining in Asia. Selenium-containing slimes from the other two refineries were exported for processing.

Most domestic selenium was produced as commercial-grade materials, averaging a minimum of 99.5% selenium and available in various forms including shot, lumps, 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, mainly from copper anode slimes, 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 five categories; electronic (includes photoconductor uses), glass manufacturing, pigments and chemicals, and other, including agricultural and metallurgical uses. In electronics, a large end-use market, high-purity selenium compounds were used principally as photoconductors on the drums of plain paper copiers. Photoreceptors have been the largest application for selenium over the past decade. However, the percentage of total selenium used for photoreceptors has dropped to nearly 30% and is expected to drop 8%-10% per year until 1997, before leveling off. 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 rates. OPC's also are free of the environmental concerns associated with the disposal of selenium compounds.[3] Other electronic uses included rectifier and photoelectric applications.

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 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 30% of the selenium market in 1994.

In pigment applications, selenium is used to produce color changes in cadmium sulfide-based pigments. With increasing substitution of selenium for sulfur, the yellow cadmium pigment becomes redder. 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 toxicity of cadmium-based pigments, their use is generally restricted to applications requiring long life, brilliance, and high thermal stability and chemical resistance. Pigments were about 18% of the domestic market.

Chemical uses of selenium, including industrial, pharmaceutical, agricultural, and biological applications, accounted for 10% of domestic usage. Dietary supplements for livestock are the largest agricultural usage, though selenium also may be added to fertilizer,

a practice that is more prevalent outside the United States. Small quantities of selenium also may used as human food supplements; selenium has been recognized as an essential nutrient for human health. The principal pharmaceutical use of selenium is in antidandruff hair shampoos. Miscellaneous industrial chemical uses include lubricants, rubber compounding, and catalysts.

Metallurgical and miscellaneous uses comprised the remaining 12% 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. Selenium-containing free-cutting steels are generally cost competitive only when used with high-speed automatic machine tools.

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 nucleant 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. Development of low-maintenance batteries in the early 1970's encouraged the use of low-antimony grid alloys requiring selenium. Since 1975, lead-cadmium maintenance-free automotive batteries have captured a greater share of the automotive battery market. More recently, hybrid batteries, which employ low-antimony lead positive plates and lead-cadmium negative plates, have been gaining in usage.

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 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 photoconductor in plain paper copiers, in thermoelectric and photoelectric devices, and in optical disc storage systems. Mercury-cadmium-telluride (MCT) 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 consumer applications. Thermoelectric cooling 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 used for infrared detectors, integrated circuits, medical instrumentation, laser diodes, etc., as well as consumer products such as portable coolers.

Apparent domestic demand for tellurium, calculated from production, stock, and trade data, increased slightly in 1994. 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 and photoreceptor applications each used 20%. Other uses were about 5%.

Prices

The domestic producer price for selenium averaged $4.75 per pound in 1994. The producer price for tellurium was $27 per pound.

World Review

The Fifth International Symposium on the Uses of Selenium and Tellurium was held in May in Brussels, Belgium. The 3-day symposium featured 74 presentations on agriculture, chemical uses, environmental issues, metallurgy, and photoelectric applications. The proceedings are available from the STDA.[4]

World production and consumption data for tellurium were limited. According to STDA statistics, the supply increased at a faster rate than demand. STDA data reflect only shipments and inventories from companies that accounted from about 70% of the Western World supply. Supply and demand have been in balance for several years and each were estimated to have averaged 220 tons per year over the past 3 years. Production figures for many countries are withheld because of the need to conceal company proprietary data.

Current Research and Technology

Selenium has been tested as a free-machining additive to replace lead in plumbing brass. Two industry consortia are evaluating several different compositions that use varying contents of bismuth and other additives including selenium. One alloy containing 2% bismuth and 1% selenium showed machinability near that of leaded brass. However, the limited supply for bismuth and selenium must be taken into consideration in determining an alloy that would be commercially successful.[5]

Outlook

Selenium is dependent upon copper production; and in the past 5 years, the supply has exceeded demand. Because it is recovered as a byproduct, selenium output cannot be easily adjusted to meet market conditions and is subject to supply and price fluctuations. Although several new uses have been developed, they have not 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 only possible large increase in demand would come from use as an additive to plumbing brass, but this is still under development.

Tellurium supply and demand have remained in balance since 1990. This situation is likely to continue as there are no large increases foreseen in either consumption of production for the next 5 years. Demand for high purity tellurium may increase for solar cells, but would not have a major impact on demand. Little information is available on the selenium or tellurium content of new ore bodies.

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[1]ASARCO Company Annual Report 1994.

[2]Reference cited in footnote 1.

[3]Springett, B. F. Status of Selenium Alloys in Non-Impact Printers and Photocopiers. Paper in Proceedings of the 5th International Symposium on the Uses of Selenium and Tellurium (Brussels, Belgium, May 8-10, 1994). STDA, 1994, pp. 187-190.

[4]STDA, 301 Borgtstraat, B-1850, Grimbergen, Belgium, Tel. (322) 252-1490, Fax: (322) 252-2775

[5]The Bulletin of the Selenium-Tellurium Development Association. Selenium-Containing Pb-Free, Free-Cutting Copper Alloys for Plumbing Fixtures. Nov. 1994, p. 4.2

OTHER SOURCES OF INFORMATION

U.S. Bureau of Mines Publication

Selenium. Ch. in Mineral Commodity Summaries, annual.

Other Sources

Bulletin of the Selenium-Tellurium Development Association.
ABMS Nonferrous Metal Data.
American Metal Market.
Journal of Metals.
Metal Bulletin (London).
Platt's Metals Week.

TABLE 1
SALIENT SELENIUM AND TELLURIUM STATISTICS 1/

(Kilograms of contained metal unless otherwise specified)

	1990	1991	1992	1993	1994
SELENIUM					
United States:					
Production, primary refined	287,000	260,000	243,000 2/	283,000 2/	360,000 2/
Shipments to consumers	250,000	275,000	221,000	258,000	302,000
Exports, metal, waste and scrap	207,000	210,000	175,000	261,000	246,000
Imports for consumption 3/	381,000	344,000	371,000	382,000	411,000
Apparent consumption, metal 4/	530,000	510,000	490,000	460,000	530,000
Dealers' price, average per pound, commercial grade 5/	$5.82	$5.41	$5.13	$4.90	$4.75
World: Refinery production	1,770,000 r/	1,640,000 r/	1,770,000 r/	1,760,000 r/	1,880,000 e/
TELLURIUM					
United States:					
Imports for consumption 6/	34,000	29,300	48,400	45,000	27,400
Producer price quote, yearend, commercial grade, per pound	$31.00	$32.00	$35.00	$32.00	$26.00

e/Estimated. r/Revised.
1/Previously published and 1994 data are rounded by the U.S. Bureau of Mines to three significant digits.
2/Includes semi-refined 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: Platt's 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)

	1993		1994	
Country	Quantity	Value	Quantity	Value
Australia	5,120	$55,600	11,400	$36,100
Brazil	10,600	167,000	15,400	246,000
China	10,200	3,260	--	--
Hong Kong	39,500	342,000	--	--
Japan	29,700	272,000	4,600	58,100
Mexico	20,300	210,000	45,600	708,000
Netherlands	11,300	65,000	28,900	307,000
Philippines	58,700	412,000	115,000	488,000
Spain	11,300	6,250	--	--
United Kingdom	21,700	22,400	626	10,000
Venezuela	14,400	98,400	2,210	37,400
Other	28,600 r/ 2/	542,000 r/ 2/	21,400	386,000
Total	261,000	2,200,000	246,000	2,280,000

r/ Revised.
1/ Previously published and 1994 data are rounded by the U.S. Bureau of Mines to three significant digits; may not add to totals shown.
2/ Unspecified group of countries differs from that in the 1993 Annual Report.

Source: Bureau of the Census.

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

(Kilograms, contained selenium)

Class and country	1993 Quantity	1993 Value	1994 Quantity	1994 Value
Unwrought and waste and scrap:				
Belgium	35,200	$1,470,000	40,000	$1,700,000
Canada	146,000	3,160,000	174,000	3,400,000
Finland	13,400	119,000	9,710	81,300
Germany	11,300	139,000	6,960	75,200
Japan	30,400	1,140,000	39,300	1,500,000
Philippines	108,000	597,000	103,000	511,000
Sweden	10,000	122,000	--	--
United Kingdom	1,790	34,200	17,500	135,000
Other	11,600	110,000	5,650	28,400
Total	367,000	6,880,000	396,000	7,420,000
Selenium dioxide: 2/				
Germany	7,010	62,200 r/	8,000	83,900
United Kingdom	5,770	75,800 r/	6,540	80,900
Other	1,740	19,600 r/	709	8,710
Total	14,500	158,000 r/	15,300	173,000
Grand total	382,000	7,040,000 r/	411,000	7,600,000

r/Revised.
1/Previously published and 1994 data are rounded by the U.S. Bureau of Mines to three significant digits; may not add to totals shown.
2/Figures adjusted by the U.S. Bureau of Mines.

Source: Bureau of the Census.

TABLE 4
U.S. IMPORTS FOR CONSUMPTION OF TELLURIUM 1/ 2/

(Kilograms, gross weight)

Class and country	1993 Quantity	1993 Value	1994 Quantity	1994 Value
Unwrought and waste and scrap:				
Belgium	14,500	$1,100,000	1,930	$164,000
Canada	5,150	393,000	3,400	239,000
France	356	4,550	1,080	21,400
Germany	5,780	453,000	294	57,600
Japan	7,250	592,000	9,530	658,000
Philippines	9,110	457,000	1,790	53,500
Russia	100	12,400	1,040	134,000
United Kingdom	2,230	101,000	7,420	205,000
Other	478	65,900	892	43,000
Total	45,000	3,180,000	27,400	1,570,000

1/Previously published and 1994 data are rounded by the U. S. Bureau of Mines to three significant digits; may not add to totals shown.
2/Listed as "tellurium" under the Harmonized Tariff System, and grouped together with boron. However, imports of boron are thought to be very small, relative to tellurium.

Source: Bureau of the Census.

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

(Kilograms, contained selenium)

Country3/	1990	1991	1992	1993	1994e/
Belgium e/	250,000	250,000	250,000	250,000	250,000
Canada 4/	342,000	207,000	294,000	295,000 e/	300,000
Chile	49,400	50,600	50,000 e/	49,500 e/	45,000
Finland	31,200	35,200 r/	30,000	30,400 r/	30,500
Germany e/	125,000	110,000	125,000	120,000	120,000
India e/	3,840 5/	4,000	9,700 r/	13,500 r/	14,000
Japan	495,000	537,000	573,000	541,000	595,000
Mexico	12,200	2,800	400	-- r/	--
Peru	8,910	12,400	14,400	14,400 e/	14,000
Philippines e/ 6/	55,600 r/	60,000	60,000	40,000	40,000
Serbia and Montenegro e/ 7/	XX	XX	57,800 r/	45,500 r/ e/	40,000
Sweden	29,000	23,000	32,000 r/	50,000 r/	50,000
United States	287,000	260,000	243,000 8/	283,000 8/	360,000 5/ 8/
Yugoslavia 7/ 9/	59,200	64,100 r/	XX	XX	XX
Zambia 10/	21,700	21,900	31,800	27,000 r/	25,000
Zimbabwe	2,300 e/	2,550	1,740	1,110 r/	1,000
Total	1,770,000	1,640,000	1,770,000	1,760,000	1,880,000

e/Estimated. r/Revised. XX Not applicable.

1/Previously published and 1994 data are rounded by the U.S. Bureau of Mines to three sigificant digits; data 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. 7, 1995.

3/In addition to the countries listed, Australia, and the former U.S.S.R. produced refined selenium, but output is not reported, and 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/Reported figure.

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

7/All production in Yugoslavia from 1990-91 came from Serbia and Montenegro.

8/Includes production of semi-refined selenium exported for further refining.

9/Dissolved in Apr. 1992.

10/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/	1990	1991	1992	1993	1994 e/
Canada 4/	9,860	12,400	21,800	24,000 r/ e/	27,000
Japan	49,700	57,200	57,200	46,800	48,000
Peru	7,840	13,400	18,600	18,600	18,600
United States	W	W	W	W	W

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

1/ Previously published and 1994 data are rounded by the U.S. Bureau of Mines 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. 14, 1995.

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.