

SELENIUM AND TELLURIUM

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Selenium and tellurium are rare elements that occur widely in the earth's crust, but never in concentrations high enough to justify mining solely for the selenium and tellurium content. Instead, selenium and tellurium are recovered as byproducts, mostly from the electrolytic refining of copper. Copper anode slimes are a byproduct of the electrolytic refining process. An estimated 41,000 wet metric tons (t) of copper anode slimes is generated annually, with about 17% of these being produced at refineries without equipment for processing them. The sulfate-based electrolyte used in electrolytic refining is chosen not only for its capacity to absorb copper ions, but also for its ability to reject precious and base metals. The precious and base metals, along with refractory components accumulate at the bottom of the electrolytic cell. The base metals included are typically bismuth, lead, nickel, selenium, tellurium, and tin. The presence and concentration of these metals are dependent on their initial content in the anode material and therefore on the origin of the copper concentrate. Slimes resulting from primary metal refining can have an average selenium concentration of 10%, increasing to 40% in a few cases. Tellurium concentrations are generally lower, 5% being the maximum (Metal Bulletin Monthly, 2002).

In the United States, five electrolytic copper refineries generated selenium-containing anode slimes. One of the refineries recovered commercial-grade selenium, one recovered a semirefined filter cake, which was shipped to Asia for further refining, and three exported anode slimes for refining. Domestic production of selenium increased in 2001.

Selenium and tellurium are economically recoverable from industrial scrap and chemical process residues. For example, worn out and damaged photoreceptor drums are returned to manufacturers for recycling. The selenium-tellurium alloy is stripped off and shipped to refineries for recovery of selenium and tellurium. About 15% of refined selenium production comes from secondary sources (Selenium-Tellurium Development Association, 2002¹).

Selenium is chemically similar to sulfur but with some of the properties of metal. One of the most important uses of selenium is in the form of arsenic triselenide, which is used as a photoreceptor in xerography. Selenium is widely used in cadmium sulfoselenide pigments. In the glass industry, selenium is used as a decolorizing agent. In metallurgy, selenium is used as a microalloying element to improve the machinability, casting, and forming properties in steel, copper, and lead alloys.

The major uses of tellurium are as a trace additive in iron, steel, and copper to improve machining; as catalysts in the

chemical industry; and in the production of photoreceptors and photovoltaic devices.

Domestic Data Coverage

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. In order to protect proprietary interests of the companies, however, it is necessary to withhold the survey data from publication.

Production

About 250 t of secondary selenium is produced every year worldwide. World refinery production of primary selenium (excluding U.S. production) increased 9%, to 1,580 t (table 5). Japanese output, which accounted for about 40% of the world total, is reported to have increased by 21% to 739 t. Canada, Belgium, Japan, and the United States represent more than 80% of the total world mine production of selenium and tellurium. Much of the selenium mined in the United States comes from Texas and Utah (Roskill's Letters from Japan, 2002).

World producers of refined 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 reported to the U.S. Geological Survey are treated as company proprietary information.

Selenium.—Because selenium is a byproduct of copper production, its output cannot be easily determined. Only about 20 of the approximately 80 copper refineries in operation around the world report recovery of selenium and less than one-half of that number report tellurium refining (Selenium-Tellurium Development Association, Inc., 2002). Domestic production of selenium was estimated to have been higher in 2001 than production in 2000. In the United States, only one domestic copper refinery recovered selenium—ASARCO Incorporated, Amarillo, TX. 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. Selenium-containing 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 shot, lump, and powder or pigment-grade powder having a minimum 99.8% selenium content.

¹A reference that includes a section twist (§) is found in the Internet Reference Cited section.

Tellurium.—Data on the production of tellurium are not readily available. The world's leading producers, Asarco in the United States and the Union Minière BU in Belgium do not publish production figures. Commercial-grade tellurium and tellurium dioxide were produced by Asarco, in Amarillo, TX, 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. Domestic tellurium production was estimated to have decreased in 2001, compared with that for 2000.

Consumption

The average annual global consumption of selenium over the past 4 years is estimated to have been about 1,900 t. Estimates of end-use demand in 2001 are as follows: glass, 35%; chemicals and pigments, 20%; electronics, 12%; other uses, including agriculture and metallurgy, 33%. Domestic consumption is believed to have decreased in 2001 (Brown, 2002).

Metallurgical and chemical uses dominate tellurium demand, estimated at about 220 tons per year. About 55% of the tellurium was used as free-machining additives to steel. Other uses included catalysts, chemical uses, nonferrous alloys, photoreceptors, thermoelectric devices, and digital video discs.

Selenium.—In glass manufacturing, selenium is used principally as a decolorant in container glass and other soda-lime silica glasses. Selenium decolorizes the green tint caused by iron impurities in glass. Under weak oxidizing conditions, the addition of selenium adds a pink color to the glass that combines with the green color 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 35% of the selenium market in 2001.

Metallurgical uses comprised an estimated 24% of the selenium 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 selenium-bearing free-machining rod. Selenium-containing free-cutting steels, however, are generally cost competitive only when used with high-speed automatic machine tools.

Selenium (with bismuth) 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). The Safe Drinking Water Act Amendments of 1996 (Public Law 104-182) requires that all pipes, fixtures, solders, and fluxes used for the installation or repair of facilities providing water for human consumption contain no lead after August 1998. Boosted by the goal set by Public Law 104-182, selenium use in plumbing continued to increase in 2001.

A smaller amount of metallurgical selenium is used as an additive to low-antimony lead alloys forming 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 9% of the selenium market. Dietary supplements for livestock are the largest agricultural use. Selenium also may be added to fertilizer used in growing animal feed, a practice that is more prevalent outside the United States.

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 had been the largest single application for selenium during the 1970s and 1980s. 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. OPCs also are free of the environmental concerns associated with the disposal of selenium compounds. Other electronic uses of selenium included rectifier and photoelectric applications.

Chemical uses of selenium, including industrial and pharmaceutical applications, accounted for about 20% of use. Selenium is gaining greater recognition as a nutrient essential for human health; small but increasing quantities of selenium are used as human dietary supplements. As ongoing research attempts to verify the cancer-preventative properties of selenium, the use of selenium for the treatment of cancer is increasing. However, the low dosage requirement precludes selenium from becoming significant in terms of quantity consumed. The principal pharmaceutical use of selenium is in antidandruff shampoos. Miscellaneous industrial chemical uses include lubricants, rubber compounds, and catalysts.

In pigment applications, selenium is used to produce color changes in cadmium-sulfide-based pigments. Yellow cadmium pigment becomes more red as the selenium-to-sulfur ratio increases. 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 special applications requiring any combination of long life, brilliance, high thermal stability, or chemical resistance.

Tellurium.—World demand for tellurium is believed to have decreased in 2001. The largest use for tellurium was as an additive to free-machining steel, about one-half of the market. Chemicals and catalyst usage made up about 25% of the market. Additives to nonferrous alloys accounted for about 10% of total use, and photoreceptor and thermoelectric applications accounted for slightly about 10%. Other uses (as an ingredient in blasting caps and as a pigment to produce various colors in glass and ceramics) were about 5% of consumption (Selenium-Tellurium Development Association, 2002).

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 dioxide is used as a curing and accelerating agent in rubber compounds.

Electronics 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 electronics and for some consumer products. These devices consist of a series of couples composed of different semiconducting materials which, 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 electronics applications, such as the cooling of infrared detectors, integrated circuits, medical instrumentation, and laser diodes, their use in consumer products, such as portable food-and-beverage coolers, continued to increase.

Prices

Platts Metals Week's average New York dealer price for selenium in 2001 was \$3.90 per pound. Beginning the year at \$3.40 to \$3.95 per pound, the price held firm through August, and then increased to \$3.84 to \$4.30 in the first week of September. In November, the price increased to \$4.00 to \$4.50 per pound and held steady for the remainder of the year. The producer price for standard grade tellurium averaged about \$15.00 per pound in 2001 with higher grade materials selling for \$17 to \$18 per pound.

Trade

International trade is important in U.S. selenium and tellurium markets. In 2001, imports of selenium dioxide and unwrought waste and scrap increased by a little more than 1% to 483,000 kg valued at \$3.71 million (table 3). The United States was a net importer of selenium by 442 t including the selenium content of selenium dioxide compared with 390 t in 2000. Canada, the Philippines, and Belgium (in order of decreasing quantity) were the leading foreign suppliers of selenium. They accounted for 79% of the imports of selenium metal to the United States in 2001. Imports of tellurium decreased by 46% during the year (table 4). The leading suppliers were the Philippines, Belgium, and Canada. Data for tellurium exports were not available.

World Review

World production of selenium was estimated to have remained stable in 2001; a tendency toward excess supply was replaced by steady production matched by increased demand from China and Japan (Roskill's Letter from Japan, 2002). World production and consumption data for selenium and tellurium are limited. It is estimated that production of selenium and tellurium increased in 2001 despite various interruptions, cutbacks, and closures in the copper industry. World

production of the byproducts has been fairly steady over the past few years. Supply and demand have been in fairly close balance for several years. Better productivity has increased the possibility of oversupply, placing some downward pressure on prices. But cuts in copper production and the increased use of solvent extraction-electrowinning could shift the trend toward lower selenium and tellurium availability (Mining Journal, 2000). Also, increased consumption of selenium in China, a net importer already, put upward pressure on prices for 2001 (Roskill's Letter from Japan, 2002).

In Japan, total selenium demand is increasing in spite of lower consumption for photocopiers. Consumption is growing for glass, paint, pharmaceuticals, and shampoos. As the world's largest selenium supplier, Japan focuses on selenium export markets. Even so, as consumption increases, Japanese selenium exports have been dropping slightly every year since 1997. Considering the various worldwide production cutbacks, there is some concern about selenium and tellurium supply (Roskill's Letter from Japan, 2002).

Current Research and Technology

Until recently, selenium has been one of the least celebrated human nutrients because selenium deficiencies are rare (in the United States) and its toxicity is a risk. The toxicity risk overshadowed the use of selenium as a human food supplement, although the necessity of providing selenium in the diet of farm animals has been well established for years. In the past few years, research has revealed that human selenium supplementation may provide significant reductions in the occurrence rate of lung, prostate, and colorectal cancers. Medical tests have shown that, 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).

Further testing and research is continuing and was reported on extensively in medical and popular health journals during 2000. The U.S. National Cancer Institute is funding the 12-year Selenium and Vitamin E Cancer Prevention Trial (SELECT) in the United States. The trial will seek to enroll more than 32,000 men to test the effect of selenium and vitamin E on the incidence rate of prostate cancer (Tracey, 2001).

Outlook

The supply of selenium is directly affected by the supply of its coproducts, mainly copper, but also cobalt and nickel. The price of selenium is frequently inversely related to the supply and demand of its coproducts. For example, as a byproduct of copper refining, selenium prices fall during periods of high copper production. A key event in the copper market at the close of 2001 was the announcement of large-scale production cuts at mines in Asia, the United States, and Latin America (Edelstein, 2002). When a copper plant closes or converts to processes that do not generate anode slimes, the ultimate amount of selenium that can be produced is decreased (Platt's Metals Week, 2000). In line with the expected drop in copper output, production of selenium and tellurium is expected to fall in the short term. In 2002, copper prices have largely managed to hold their own and indeed increased slightly in the second

quarter. Metal Bulletin Research predicts that, led by economic recovery in the United States and lower refined output, the copper market will move into deficit during the 4th quarter of 2002. Demand for copper is also expected to increase, which could lead to the reactivation of idled capacity and indirectly increase the production of selenium.

Demand for selenium in photoreceptors is likely to continue declining as the cost of substituting organic compounds decreases. Once a major consumer of selenium and tellurium, use in photoreceptors has reached the replacement-only stage as selenium has been supplanted by newer materials in currently manufactured copiers. A number of new uses have been developed, and they are beginning to affect the overall demand for selenium. Use as an additive to plumbing brasses, as part of the effort to use lead-free alloys, affords the greatest possibility for significant increases in demand.

Further use of selenium in cancer prevention may eventually lead to profound public health benefits. However, this important application for selenium will not induce a large increase in demand for the metal because only small dosages are necessary for effective therapy.

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

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TABLE 1
SALIENT SELENIUM AND TELLURIUM STATISTICS 1/

(Kilograms of contained metal, unless otherwise specified)

	1997	1998	1999	2000	2001
Selenium:					
United States:					
Production, primary refined	W 2/	W	W	W	W
Shipments to consumers	W	W	W	W	W
Exports, metal and waste and scrap	127,000	151,000	233,000	82,100	41,200
Imports for consumption 3/	346,000	339,000	326,000	476,000	483,000
Apparent consumption, metal 4/	W	W	W	W	W
Dealers' price, average per pound, commercial grade 5/	\$2.94	\$2.49	\$2.50	\$3.84	\$3.80
World, refinery production	1,720,000 r/	1,470,000 r/	1,410,000 r/	1,450,000 r/	1,580,000 e/
Tellurium:					
United States:					
Imports for consumption 6/	63,900	88,900	38,000	52,300	28,000
Producer price quote, yearend, commercial grade, per pound	\$19.00	\$18.00	\$15.00	\$14.00	\$13.00

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

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

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

3/ Include unwrought 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: Platts Metals Week. Calculated from published price ranges.

6/ Includes only wrought and waste and scrap.

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

(Kilograms, contained selenium)

Country	2000		2001	
	Quantity	Value	Quantity	Value
Belgium	--	--	233	\$3,600
Canada	1,350	\$37,100	2,640	74,500
Colombia	166	2,570	--	--
Costa Rica	935	8,090	334	2,760
Egypt	--	--	38	3,080
Germany	--	--	50	3,250
Hong Kong	2,320	36,000	--	--
Guatemala	--	--	625	9,930
India	4,210	28,900	998	8,800
Italy	--	--	543	6,740
Japan	3,170	49,100	3,540	54,800
Korea, Republic of	1,000	12,000	820	11,600
Mexico	41,600	248,000	23,200	169,000
Panama	1,150	6,790	--	--
Philippines	11,400	29,700	--	--
Singapore	--	--	1,120	11,800
Sweden	--	--	244	3,000
Taiwan	--	--	351	5,440
United Kingdom	14,800	124,000	6,440	43,100
Total	82,100	583,000	41,200	411,000

-- Zero.

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

Source: U.S. Census Bureau.

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

(Kilograms, contained selenium)

Class and country	2000		2001	
	Quantity	Value	Quantity	Value
Unwrought waste and scrap:				
Australia	21,700	\$86,200	22,000	\$131,000
Belgium	14,800	388,000	30,100	498,000
Canada	237,000	783,000	261,000	1,560,000
Finland	1,110	4,740	3,310	24,800
Germany	3,680	118,000	8,050	124,000
Hong Kong	5,810	35,400	--	--
India	--	--	24,000	62,800
Japan	5,950	69,400	1,070	51,400
Korea, Republic of	29,100	183,000	366	3,750
Mexico	69	2,060	68	2,030
Netherlands	500	17,500	--	--
Peru	--	--	7,000	46,800
Philippines	121,000	914,000	92,100	861,000
Russia	1,300	9,750	8,500	50,200
United Kingdom	9,230	59,300	10,900	79,900
Total	452,000	2,670,000	468,000	3,490,000
Selenium dioxide: 2/				
France	--	--	114	3,680
Germany	23,600	180,000	12,600	181,000
India	--	--	1,420	17,000
Japan	709	6,250	354	4,230
Spain	--	--	142	3,790
Ukraine	--	--	1	5,410
Total	24,300	186,000	14,600	216,000
Grand total	476,000	2,860,000	483,000	3,710,000

-- Zero.

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

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

Source: U.S. Census Bureau.

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

(Kilograms, gross weight)

Class and country	2000		2001	
	Quantity	Value	Quantity	Value
Unwrought and waste and scrap:				
Belgium	7,210	\$143,000	3,790	\$55,600
Canada	5,140	630,000	2,210	722,000
China	1,240	71,200	616	41,200
Czech Republic	336	10,000	469	13,900
Germany	--	--	1,320	52,900
Ireland	316	14,600	--	--
Japan	9	8,100	36	36,600
Peru	4,030	29,100	--	--
Philippines	16,700	719,000	19,100	637,000
Russia	--	--	7	10,900
Ukraine	2	3,720	87	41,800
United Kingdom	17,200	170,000	346	16,000
Total	52,300	1,800,000	28,000	1,630,000

-- Zero.

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

Source: U.S. Census Bureau.

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

(Kilograms, contained selenium)

Country 3/	1997	1998	1999	2000	2001 e/
Belgium e/	250,000	200,000	200,000	200,000	200,000
Canada 4/	592,000	398,000	359,000	350,000	350,000
Chile e/	49,500	49,000	49,000	40,000 r/	45,000
Finland e/	28,000 5/	28,000	26,000	26,000	25,000
Germany e/	115,000	100,000	100,000	100,000	100,000
India e/ 6/	11,500	11,500	11,500	11,500 r/	11,500
Japan	546,372	549,615	546,292	612,316	739,415 5/
Peru	12,678	18,006	23,008 r/	23,110 r/	23,000
Philippines e/	40,000	40,000	40,000	40,000 e/	40,000
Serbia and Montenegro	38,000 r/ e/	40,866 r/	20,080 r/	20,000 r/ e/	20,000
Sweden e/	20,000	20,000	20,000	20,000	20,000
United States 7/	W	W	W	W	W
Zambia 8/	15,161	14,670	10,170	9,820	9,100
Zimbabwe e/	1,000	500 r/	500 r/	415	300
Total	1,720,000 r/	1,470,000 r/	1,410,000 r/	1,450,000 r/	1,580,000

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 have been 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 May 27, 2002.

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/ Reported figure.

6/ Data are for Indian fiscal year beginning April 1 of year stated.

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/	1997	1998	1999	2000	2001 e/
Canada 4/	59,000	62,000	64,000	80,000	80,000
Japan	25,260	38,977	35,272	35,687 r/	39,008 5/
Peru	24,754	21,682	17,110 r/	22,000	22,000
United States	W	W	W	W	W

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

1/ World totals and estimated data are rounded to no more than 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 exclusion of data from major world producers, notably the former Soviet Union and the United States. Table includes data available through May 9, 2002.

3/ In addition to the countries listed, Australia, Belgium, Chile, Germany, the Philippines, and the former Soviet Union 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.

5/ Reported figure.