

# SELENIUM AND TELLURIUM

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Selenium and tellurium are byproduct metals usually associated with copper production. Primary selenium was produced domestically as a byproduct of copper refining in 2000; secondary (recycled) selenium was not produced. Five electrolytic copper refineries generated selenium-containing anode slimes. One of the refineries recovered commercial-grade selenium; one recovered a semirefined filter cake, which was shipped to Asia for further refining; and three exported anode slimes for refining. Domestic production increased in 2000.

Selenium use as a photoreceptor for plain-paper copiers has been decreasing in recent years and declined again in 2000 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 2000 are as follows: glass, 25%; metallurgical applications, 24%; miscellaneous chemical uses, 14%; photoreceptors, 10%; pigments, 8%; and other uses, including agricultural feed additives, 19%.

About 250 metric tons (t) of secondary selenium is produced every year worldwide. World refinery production of primary selenium (excluding U.S. production withheld to protect proprietary data) increased 4%, to 1,460 t; the largest producers, excluding the United States, in decreasing order of output, were Japan, Canada, Belgium, and Germany. These countries accounted for 86% of world refined selenium production in 2000.

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. Domestic consumption is believed to have increased in 2000. 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.

## 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

**Selenium.**—Selenium was recovered from anode slimes generated in the electrolytic production of copper. Because selenium is a byproduct of copper production, its output cannot be easily adjusted to meet market conditions. Therefore, the selenium market is subject to supply and price fluctuations. Domestic production was higher than that in 1999. Only one domestic copper refinery recovered selenium—ASARCO Inc., 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.

Hydromet Environmental Recovery Ltd. will accept waste material for the recovery of tin and selenium at its new plant scheduled to open during 2001 in Newman, IL. The plant expects to process selenium materials from both the copper refining and photocopy industries (American Metal Market, 2000b).

**Tellurium.**—Commercial-grade tellurium and tellurium dioxide were produced by Asarco, 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. Domestic tellurium production decreased in 2000, compared with that for 1999.

## Consumption

**Selenium.**—Selenium demand by end use can be divided broadly into the following categories: glass manufacturing, electronics (including photoreceptor uses), agricultural 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 2000.

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 2000.

The Copper Development Association has changed the name of its alloys introduced in 1995 as SeBiLOY (containing selenium and bismuth) to Envirobrass to highlight the significant environmental and health benefits to manufacturers and consumers. Envirobrass I and II contain a mixture of bismuth and selenium substituted for lead in red brasses used for water meters, valves, and plumbing fixtures. A new alloy, Envirobrass III is a lead-free yellow brass for permanent mold casting (Payne, 2000).

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 19% 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 10% 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 14% of usage. 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 verifies the apparent cancer-preventative properties of selenium, this application is increasing, but the low dosage requirement

precludes it 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. Pigments accounted for about 8% of the selenium market.

**Tellurium.**—World demand for tellurium increased in 2000. 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 slightly more than 10% of total use, and photoreceptor and thermoelectric applications accounted for slightly less than 10%. Other uses were about 5%.

As an alloying element in the production of free-machining low-carbon steels, additions of up to 0.1% tellurium, usually in conjunction with lead, greatly improve machinability. Similarly, the addition of tellurium to copper and other nonferrous alloys improves their machinability, strength, and corrosion resistance. Tellurium catalysts are used chiefly for the oxidation of organic compounds but are also used in hydrogenation, halogenation, and chlorination reactions. Tellurium dioxide is used as a curing and accelerating agent in rubber compounds.

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 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 electronic 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. New applications include a germanium-antimony-tellurium compound used for optical storage on digital video discs (Metal Bulletin Monthly, 2000).

## Prices

The domestic producer price for selenium averaged \$3.84 per pound in 2000. Beginning the year at \$2.78 per pound, the domestic producer price rose steadily to \$4.30 per pound in

early March, held firm for a month, and then retreated to \$4.25 during April and May. In June, the price fell to \$3.95 per pound and held steady for 4 months. During the last quarter of the year the price fell to \$3.85 per pound in October, then to \$3.25 per pound in mid-November where it remained for the rest of the year. The producer price for tellurium fell to \$14 per pound by yearend, averaging about \$14.50 for the year.

## Trade

International trade is important in U.S. selenium and tellurium markets. In 2000, imports of selenium increased significantly (46%), while exports decreased markedly (65%). The United States was a net importer of selenium by 390 t including the selenium content of selenium dioxide compared with only 93 t in 1999. Canada, the Philippines, and the Republic of Korea (in order of decreasing quantity) were the leading foreign suppliers of selenium. They accounted for 86% of the imports of selenium metal to the United States in 2000. Imports of tellurium increased by 38% during the year. The leading suppliers were the United Kingdom, the Philippines, Belgium, and Canada. Data for tellurium exports were not available.

## World Review

Overall, the world selenium market remained fairly well balanced, with a tendency toward excess supply replaced by steady production matched by strong increased demand from China (Metal Bulletin, 2000c). World production and consumption data for selenium and tellurium are limited. It is estimated that production of both selenium and tellurium, along with that of copper itself, increased in 2000 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, 2000b). Also, increased consumption of selenium in China, a net importer already, put upward pressure on prices for 2000 (Mining Journal, 2000a).

In the Philippines, the Philippine Associated Smelting and Refining Corp. announced plans for a substantial increase in copper production which will lead almost certainly to increases in selenium output (Mining Journal, 2001).

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 over supply (Roskill's Letter from Japan, 2000).

In Belgium, Savi Alloys, N.V., sold its selenium production operations and will concentrate on bismuth and tellurium (Metal Bulletin, 2000b).

## 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 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). The Prevention of Cancer by Intervention with Selenium (PRECISE) trial in Europe will involve 33,000 men in three countries, Denmark, Sweden, and the United Kingdom. The SELECT and PRECISE trials are attempts to replicate the encouraging results of the 1996 trial on a larger scale. When too much selenium is taken by humans, it becomes toxic. The maximum safe level has been determined by several expert panels to be 400 to 450 micrograms per day from all sources, including diet and supplementation (Rayman, 2000).

In China, research has shown that variations in human selenium levels affect the incidence rate of esophageal and gastric cardia cancers. There was strong statistical evidence that increased selenium levels lowered the incidence of these cancers. Selenium levels were measured in about 1,000 patients with these cancers and in 1,000 subjects who did not have these cancers (Mark, 2000).

A new solar cell, based on a copper/indium/selenium compound has been developed in Germany. Cis-Solartechnik, GmbH, partly owned by Norddeutsche Affinerie AG, will continue development work on the new product, which is made mostly by deposition through galvanic processes onto a flexible copper strip. The new cell, with greater than 10% efficiency, is light in weight and extremely tough (American Metal Market, 2000a).

Evidence mounts that tellurium is not as toxic as generally thought. An 18 month old boy ingested tellurium dioxide in a hydrogen chloride solution. Although his serum tellurium levels were six times normal, there was no clinical evidence of tellurium toxicity (Higgins and others, 1999).

## Outlook

Demand for selenium in photoreceptors, except where they are required for existing photocopiers, is likely to continue declining as the cost of substituting organic compounds decreases. 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.

As a byproduct of copper production, the outlook for selenium supply and price could be significantly affected by events in the copper industry (Metal Bulletin, 2001). When a copper plant closes or uses processes that do not generate anode slimes, the ultimate amount of selenium that can be produced is decreased (Platt's Metals Week, 2000). Thus, if current demand levels remain steady or increase, prices could continue to rise well above the lows that occurred in the past decade (Metal Bulletin, 2000a).

Chinese demand is still increasing, but there is no significant domestic production; consequently, China is dependent on imports, mostly from Japan. This growing import reliance suggests that Chinese producers may not be able to introduce low-cost supplies in the world selenium market when prices increase (Mining Journal, 2000b).

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 of it would be 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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## GENERAL SOURCES OF INFORMATION

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TABLE 1  
SALIENT SELENIUM AND TELLURIUM STATISTICS 1/

(Kilograms of contained metal, unless otherwise specified)

	1996	1997	1998	1999	2000
<b>Selenium:</b>					
United States:					
Production, primary refined	379,000 2/	W	W	W	W
Shipments to consumers	400,000	W	W	W	W
Exports, metal and waste and scrap	322,000	127,000	151,000	233,000	82,100
Imports for consumption 3/	428,000	346,000	339,000	326,000	476,000
Apparent consumption, metal 4/	564,000	W	W	W	W
Dealers' price, average per pound, commercial grade 5/	\$4.00	\$2.94	\$2.49	\$2.50	\$3.84
World, refinery production	2,250,000	1,710,000 r/	1,460,000	1,400,000 r/	1,460,000 e/
<b>Tellurium:</b>					
United States:					
Imports for consumption 6/	73,700	63,900	88,900	38,000	52,300
Producer price quote, yearend, commercial grade, per pound	\$21.00	\$19.00	\$18.00	\$15.00	\$14.00

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: 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	1999		2000	
	Quantity	Value	Quantity	Value
Canada	3,740	\$107,000	1,350	\$37,100
Colombia	757	11,800	166	2,570
Costa Rica	363	3,020	935	8,090
Denmark	342	5,300	--	--
France	7,080	110,000	--	--
Hong Kong	--	--	2,320	36,000
Honduras	2,990	19,700	--	--
India	--	--	4,210	28,900
Italy	1,790	21,000	--	--
Japan	27,100	426,000	3,170	49,100
Korea, Republic of	--	--	1,000	12,000
Mexico	33,500	212,000	41,600	248,000
Panama	681	7,530	1,150	6,790
Philippines	122,000	561,000	11,400	29,700
Portugal	261	3,830	--	--
Taiwan	16,900	261,000	--	--
United Kingdom	11,300	107,000	14,800	124,000
Venezuela	4,110	44,100	--	--
Total	233,000	1,900,000	82,100	583,000

-- 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	1999		2000	
	Quantity	Value	Quantity	Value
Unwrought waste and scrap:				
Australia	--	--	21,700	\$86,200
Belgium	29,100	\$1,160,000	14,800	388,000
Canada	99,000	833,000	237,000	783,000
Finland	5,240	19,200	1,110	4,740
Germany	1,950	55,800	3,680	118,000
Hong Kong	--	--	5,810	35,400
Japan	7,510	116,000	5,950	69,400
Korea, Republic of	6,950	30,900	29,100	183,000
Mexico	--	--	69	2,060
Netherlands	--	--	500	17,500
New Zealand	25	9,260	--	--
Philippines	140,000	762,000	121,000	914,000
Russia	904	27,100	1,300	9,750
United Kingdom	19,500	96,300	9,230	59,300
Total	311,000	3,110,000	452,000	2,670,000
Selenium dioxide: 2/				
Germany	15,700	157,000	23,600	180,000
Japan	--	--	709	6,250
United Kingdom	8	2,780	--	--
Total	15,700	160,000	24,300	186,000
Grand total	326,000	3,270,000	476,000	2,860,000

-- 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	1999		2000	
	Quantity	Value	Quantity	Value
Unwrought and waste and scrap:				
Belgium	5,110	\$121,000	7,210	\$143,000
Canada	9,390	592,000	5,140	630,000
China	17	33,800	1,240	71,200
Czech Republic	--	--	336	10,000
Ireland	--	--	316	14,600
Japan	521	105,000	9	8,100
Peru	1,990	17,200	4,030	29,100
Philippines	14,000	468,000	16,700	719,000
Russia	1	5,000	--	--
Ukraine	4	6,770	2	3,720
United Kingdom	6,940	95,200	17,200	170,000
Total	38,000	1,440,000	52,300	1,800,000

-- 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/	1996	1997	1998	1999	2000 e/
Belgium e/	250,000	250,000	200,000	200,000	200,000
Canada 4/	694,000	592,000	398,000	359,000 r/	350,000
Chile e/	50,000	49,500	49,000	49,000	49,000
Finland e/	42,000 r/	28,000	28,000 r/	26,000	26,000
Germany e/	115,000	115,000	100,000	100,000	100,000
India e/ 5/	11,500	11,500	11,500	11,500	11,500
Japan	588,186	546,372	549,615	546,292 r/	612,000 6/
Peru	12,602 r/	12,678 r/	18,006 r/	23,060 r/	23,000 p/
Philippines e/	40,000	40,000	40,000	40,000	40,000
Serbia and Montenegro e/	30,000	30,000	30,000	10,000	15,000
Sweden e/	20,000 r/	20,000	20,000	20,000	20,000
United States 7/	379,000	W	W	W	W
Zambia 8/	20,165	15,161	14,670	10,170 r/	9,820
Zimbabwe e/	2,000	1,000	400 r/	400 r/	415
Total	2,250,000	1,710,000 r/	1,460,000	1,400,000 r/	1,460,000

e/ Estimated. p/ Preliminary. r/ Revised. W Withheld to avoid disclosing company proprietary data; not included in "Total."

1/ World totals, U.S. data, and estimated data are rounded to no more than 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 9, 2001.

3/ In addition to the countries listed, Australia produced refined selenium, but output was not reported; available information is inadequate to formulate reliable estimate of output levels. Australia is known to produce selenium in intermediate metallurgical products and has facilities to produce elemental selenium. In addition to having facilities for processing imported anode slimes for the recovery of selenium and precious metals, the United Kingdom has facilities for processing selenium scrap.

4/ Excludes selenium intermediates exported for refining.

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

6/ Reported figure.

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

8/ Data are for year beginning April 1 of year stated. Gross weight, purity unknown.

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

(Kilograms, contained tellurium)

Country 3/	1996	1997	1998	1999	2000 e/
Canada 4/	59,000	59,000	62,000	64,000 r/	80,000
Japan	37,945	25,260	38,977 r/	35,272 r/	36,000
Peru	25,089	24,754	21,682 r/	16,610 r/	22,000
United States	W	W	W	W	W

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

1/ Estimated data are rounded to 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 June 9, 2001.

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 selenium intermediates exported for refining.