SELENIUM AND TELLURIUM

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Selenium and tellurium are byproduct metals usually associated with copper. Primary selenium was produced domestically as a byproduct of copper refining in 1999; secondary (recycled) selenium was not produced. Five electrolytic copper refineries generated selenium-containing anode slimes. One of the refineries recovered commercialgrade selenium; one recovered a semirefined filter cake, which was shipped to Asia for further refining; and three exported anode slimes for refining. Domestic production, excluding (unreported) exported anode slimes, decreased in 1999 (Mining Journal, 2000).

Selenium use as a photoreceptor for plain-paper copiers has been decreasing in recent years and declined again in 1999 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 1999 are as follows: glass, 25%; metallurgical applications, 23%; miscellaneous chemical uses, 14%; photoreceptors, 11%; pigments, 8%; and other uses, including agricultural feed additives, 19%.

All selenium-containing scrap generated in 1999 was exported for reprocessing. About 250 metric tons of secondary selenium is produced every year worldwide. World refinery production of selenium (excluding U.S. production) increased 1%, to 1,480 metric tons; the largest producers, excluding the United States, in decreasing order of output, were Japan, Canada, Belgium, and Germany. These countries accounted for 87% of world selenium production in 1999.

World producers of tellurium were Canada, Japan, Peru, and the United States. Domestically, tellurium was recovered by one company from anode slimes generated in the electrolytic refining of copper and from soda slag skimmings generated in lead refining. Secondary tellurium was not produced domestically, but some scrap was exported for recycling. Production data reported to the U.S. Geological Survey are treated as company proprietary information. Domestic consumption is believed to have decreased in 1999. 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 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 lower than that in 1998. Only one domestic copper refinery recovered selenium—ASARCO Incorporated at 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.

Tellurium.—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 (99.9999% purity) was produced by Cabot Performance Materials Corp., Revere, PA.

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 1999.

Metallurgical uses comprised an estimated 23% 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 1999.

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 11% of selenium use. High-purity selenium compounds were used principally as photoreceptors on the drums of plainpaper copiers. Photoreceptors had been the largest single application for selenium during the 1970's and 1980's. Selenium compounds, however, are being replaced by organic photoreceptor compounds (OPC), which reportedly offer better performance and lower cost at printing speeds under 80 pages per minute and comparable cost and performance at faster printing speeds. OPC's also are free of the environmental concerns associated with the disposal of selenium compounds. Other electronic uses 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 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 hair shampoos. Miscellaneous industrial chemical uses include lubricants, rubber compounds, and catalysts.

In pigment applications, selenium is used to produce color

Tellurium.—World demand for tellurium increased slightly in 1999. 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 chemicals are used as curing and accelerating agents 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 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-andbeverage coolers, continued to increase.

Prices

The domestic producer price for selenium averaged \$2.50 per pound in 1999. Increasing from \$2.15 per pound to \$2.25 per pound during the last 2 weeks of 1998, the price held steady until March 1999, when it dropped back to \$2.15 per pound. The price fell further to \$2.00 per pound during the first week of April and then began a steady and fairly rapid increase to \$2.78 per pound by yearend, reaching \$3.35 per pound during the first week of 2000. The producer price for tellurium fell to \$15 per pound by yearend, averaging about \$16.50 for the year.

Foreign Trade

International trade is important in U.S. selenium and tellurium markets. In 1999, imports of selenium decreased slightly (4%), while exports increased significantly (54%). The United States was a net importer of selenium by 93 tons including the selenium content of selenium dioxide. The Philippines, Canada, Belgium, and the United Kingdom (in order of decreasing quantity) were the leading foreign suppliers of selenium. They accounted for 92% of the imports of selenium metal to the United States in 1999. Imports of tellurium decreased by 57% during the year. The leading suppliers were the Philippines, Canada, the United Kingdom, and Belgium. Data for tellurium exports were not available.

World Review

World production and consumption data for selenium and tellurium are limited. It is estimated that production of both selenium and tellurium increased slightly in 1999 despite some interruptions and closures in the copper industry. 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. Conversely, supplies of byproduct selenium also can be limited by reductions in copper production (Ryan's Notes, 1999). In 1999, for example, a strike at the Pasar, S.A. copper refinery in the Philippines (Metal Bulletin, 1999c) and a force majeure declared at the Kidd Creek plant of Falconbridge, Ltd. in Canada reduced selenium output (Mining Journal, 1999b). Another important factor in the world selenium market is that China is a net importer. Thus, Chinese producers have not responded to rising prices by marketing more selenium, as they have been able to do in recent years for other "minor" metals (Mining Journal, 1999a).

In Japan, seleniun demand dropped 25% to 134 metric tons (t) in 1998 mainly because of lower consumption for photocopiers; consumption probably did not recover in 1999. As the world's largest selenium supplier, Japan focuses on selenium export markets. Japanese selenium exports were 553 t in 1998 and probably rose to more than 600 t in 1999. Exports for the first quarter of 1999 were 162 t; most of the exports were shipped to China, directly or through Hong Kong (Roskill's Letter from Japan, 1999).

In Canada, Noranda, Inc. sold its medical detectors and pure metals businesses, including high-purity selenium and tellurium, to the Analogic Corp. of Peabody, Massachusetts. The new subsidiary of Analogic Corp. was named ANRAD; it is located in St. Laurent, Quebec. ANRAD's objective is to develop and manufacture selenium-based flat panel x-ray detectors for the medical and industrial markets (Metal Bulletin, 1999a).

Current Research and Technology

Until recently, selenium was one of the least celebrated nutrients because human selenium deficiencies were rare (in the United States) and its toxicity was a risk. In the past few years, however, research has revealed that selenium supplementation could 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, 1996). Further testing and research is continuing and has been reported on extensively in medical and popular health journals during 1999 (Kidd, 1999).

Moreover, a 12-year study on 148 men found that the 52 men who developed prostate cancer had the lowest levels of selenium. A safe supplementation rate reportedly is 200 micrograms per day (Men's Health, 1999). In any case, research indicates that total intake including diet and all supplementation should not exceed 800 micrograms per day (Hughes, 1999). Additional studies have shown that selenium supplementation increases the effectiveness of influenza vaccine in elderly patients (Girodon, 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. Although a number of new uses have been developed, they have not yet affected 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. In addition to interruptions in output at copper plants in the Philippines and Canada during 1999, U.S. plants closed by Phelps Dodge Corp. and BHP Copper Corp. during the year decreased the ultimate amount of selenium that could be produced worldwide. Thus, if current demand levels remain steady or increase, prices could rise well above the lows that occurred in the last decade (Metal Bulletin, 1999b, 2000).

Chinese demand is increasing, but still there is no significant domestic production; consequently, China is dependent on imports, mostly from Japan. This growing import reliance bodes well for selenium producers because it suggests that Chinese producers cannot introduce low-cost supplies in the world selenium market when prices increase (Mining Journal, 1999a, 2000).

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.

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.

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¹Prior to January 1996, Published by the U.S. Bureau of Mines.

TABLE 1 SALIENT SELENIUM AND TELLURIUM STATISTICS 1/

(Kilograms of contained metal, unless otherwise specified)

	1995	1996	1997	1998	1999
Selenium:					
United States:					
Production, primary refined	373,000 2/	379,000 2/	W	W	W
Shipments to consumers	320,000	400,000	W	W	W
Exports, metal, waste and scrap	270,000	322,000	127,000	151,000	233,000
Imports for consumption 3/	324,000	428,000	346,000	339,000	326,000
Apparent consumption, metal 4/	517,000	564,000	W	W	W
Dealers' price, average per pound, commercial grade 5/	\$4.89	\$4.00	\$2.94	\$2.49	\$2.50
World, Refinery production	2,070,000	2,250,000	1,720,000	1,460,000 r/	1,480,000 e/
Tellurium:					
United States:					
Imports for consumption 6/	45,800	73,700	63,900	88,900	38,000
Producer price quote, yearend, commercial grade, per pound	\$23.00	\$21.00	\$19.00	\$18.00	\$15.00
United States: Imports for consumption 6/ Producer price quote, yearend, commercial grade, per pound	45,800 \$23.00	73,700 \$21.00	63,900 \$19.00	88,900 \$18.00	38,000 \$15.00

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

 $1/\operatorname{Data}$ 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 and waste and scrap and selenium dioxide.

4/ Calculated by using reported shipments, imports of selenium metal, and estimated exports of selenium metal, excluding scrap.

5/ Source: Metals Week. Calculated from published price ranges.

6/ Includes only wrought and waste and scrap.

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

(Kilograms, contained selenium)

	19	998	1999		
Country	Quantity	Value	Quantity	Value	
Australia	1,120	\$17,400			
Belgium	7,630	118,000			
Canada	3,640	108,000	3,740	\$107,000	
Colombia	401	6,200	757	11,800	
Costa Rica			363	3,020	
Denmark			342	5,300	
France	843	13,100	7,080	110,000	
Germany	646	10,000			
Honduras			2,990	19,700	
India	1,350	13,700			
Italy			1,790	21,000	
Japan	7,610	119,000	27,100	426,000	
Mexico	39,700	375,000	33,500	212,000	
Panama	227	2,580	681	7,530	
Philippines	80,300	1,250,000	122,000	561,000	
Portugal			261	3,830	
Singapore	1,540	27,800			
Taiwan			16,900	261,000	
United Kingdom	3,180	49,800	11,300	107,000	
Venezuela	2,570	19,800	4,110	44,100	
Total	151,000	2,130,000	233,000	1,900,000	

-- 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)

	1998		19	99
Class and country	Quantity	Value	Quantity	Value
Unwrought waste and scrap:	-		-	
Belgium	43,300	\$1,550,000	29,100	\$1,160,000
Canada	100,000	1,550,000	99,000	833,000
Finland	12,800	48,200	5,240	19,200
France	10,700	53,100		
Germany	2,040	65,200	1,950	55,800
Japan	19,100	320,000	7,510	116,000
Korea, Republic of	1,000	3,530	6,950	30,900
Netherlands	999	4,410		
New Zealand			25	9,260
Philippines	116,000	597,000	140,000	762,000
Russia	2	2,740	904	27,100
United Kingdom	18,500	102,000	19,500	96,300
Total	325,000	4,290,000	311,000	3,110,000
Selenium dioxide: 2/				
Belgium	1,410	79,100		
China	1,350	76,600		
Germany	9,350	103,000	15,700	157,000
Japan	2,160	23,900		
Spain	178	2,870		
United Kingdom			8	2,780
Total	14,400	285,000	15,700	160,000
Grand total	339,000	4,580,000	326,000	3,270,000

-- 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)

	199	98	1999	
Class and country	Quantity	Value	Quantity	Value
Unwrought and waste and scrap:				
Australia	6,800	\$183,000		
Belgium	21,900	385,000	5,110	\$121,000
Canada	7,810	645,000	9,390	592,000
China	24	17,000	17	33,800
Japan	13,200	540,000	521	105,000
Mexico	173	2,370		
Peru			1,990	17,200
Philippines	17,800	325,000	14,000	468,000
Russia	4	13,400	1	5,000
Ukraine			4	6,770
United Kingdom	21,200	317,000	6,940	95,200
Total	88,900	2,430,000	38,000	1,440,000

-- Zero.

 $1/\operatorname{Data}$ are rounded to no more than three significant digits; may not add to totals shown.

Source: U.S. Census Bureau.

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

(Kilograms, contained selenium)

Country 3/	1995	1996	1997	1998	1999 e/
Belgium e/	250,000	250,000	250,000	200,000	200,000
Canada 4/	553,000	694,000	592,000	398,000 r/	438,000 p/
Chile e/	51,000	50,000	49,500	49,000	49,000
Finland e/	29,000	28,000	28,000	26,000	26,000
Germany e/	115,000	115,000	115,000	100,000	100,000
India e/ 5/	11,449 6/	11,500	11,500	11,500	11,500
Japan	547,731	588,186	546,372	549,615 r/	548,000
Peru e/	21,000	21,000	21,000	21,000	21,000
Philippines e/	40,000	40,000	40,000	40,000	40,000
Serbia and Montenegro e/	30,000	30,000	30,000	30,000	10,000
Sweden e/	30,000	26,000	20,000	20,000	20,000
United States 7/	373,000	379,000	W	W	W
Zambia 8/	18,550	20,165 r/	15,161 r/	14,670 r/	13,000
Zimbabwe	2,000 e/	2,000 e/	1,000 r/ e/	500 r/ e/	500
Total	2,070,000	2,250,000	1,720,000	1,460,000 r/	1,480,000

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, 2000.

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 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/	1995	1996	1997	1998	1999 e/
Canada 4/	102000	59000	59000	62000 r/	67000 p/
Japan	43129	37945	25260	39000 r/	35000 5/
Peru	30087	25089 r/	24754 r/	21680 r/	21682 5/
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 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 U.S.S.R. and the United States. Table includes data available through June 9, 2000.

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

4/ Excludes selenium intermediates exported for refining.

5/ Reported figure.