SELENIUM AND TELLURIUM

By Robert D. Brown, Jr.

Primary selenium was produced domestically as a byproduct of copper refining in 1995; 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 4% in 1995, to 373 metric tons. The value of U.S. production was $4.0 million.

Apparent consumption of selenium decreased 2.5% in 1995 in response to a slackening of demand in the glass, chemical, and pigment industries, which used 23%, 14%, and 7% of the total, respectively. Other uses included electronics (photoreceptors), 21%; agricultural feed additives and other uses, 20%; and metallurgical applications, 15%. 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. Worldwide, about 250 tons of secondary selenium is produced annually. World refinery production increased 10%, to 2,070 tons; Canada, Japan, the United States, 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 estimated to have increased slightly in 1995. About 55% of consumption was for free-machining additives to steel. Other uses included catalysts, chemical uses, nonferrous alloys, photoreceptors, and thermoelectric devices.

Legislation and Government Programs

Selenium is generally regarded as a necessary nutrient for both humans and livestock. This, along with the apparent toxic nature of high doses has caused reversals in government policy. In 1987, Federal regulations established the amount of selenium allowed in animal feeds. In September 1993, the Food and Drug Administration (FDA) announced that selenium supplements were no longer allowed. This action was suspended until December 1995, by legislation passed in September 1994. The Federal Crop Insurance Reform Act of October 1994 further states that the FDA may not implement the no-selenium restrictions unless the FDA Commissioner can certify that selenium supplementation is not essential to maintain animal health, is not safe to animals consuming it or to humans consuming edible portions of selenium-supplemented animals, is not effective in promoting normal health, and that supplementation is not reasonably controlled by adherence to current good manufacturing practice.[1]

Production

Domestic data are collected by a voluntary survey of the domestic producers of selenium and tellurium. The selenium production canvass was sent to the three known producers and the tellurium canvass to the sole producer. All companies responded, but company proprietary data are not released.

Selenium was recovered from anode slimes generated in the electrolytic production of copper. Domestic production increased 4%. 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, 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. Detector-grade tellurium (99.99999% purity) was produced by Cabot Performance Metals, Revere, PA.

Consumption

Selenium demand by end use can be divided broadly into six categories: glass manufacturing, electronics (including photoconductor uses), agricultural and other uses, metallurgical applications, chemicals, and pigments. In glass manufacturing, selenium is used principally as a decolorant in container glass and other soda-lime silica glasses. The addition of selenium under weak oxidizing conditions adds a pink color to the glass that combines with the green color imparted by ferrous ions to create a neutral 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 23% of the selenium market in 1995.

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 21%. 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. Other electronic uses included rectifier and photoelectric applications.

Other uses, mainly agriculture, comprise 20% of the market. 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.

Metallurgical uses comprised 15% of the market. Selenium is added to steel, copper, and lead alloys to improve machinability and casting and forming properties. Several domestic producers of rolled steel bar produce both leaded and selenium-bearing free-machining rod. However, selenium-containing free-cutting steels are generally cost competitive only when used with high-speed automatic machine tools.

Selenium is also added to low-antimony lead alloys used in the support grids of lead-acid storage batteries. The addition of 0.02% selenium by weight as a grain refiner improves the casting and mechanical properties of the alloy. The quantity of selenium consumed in this application has been greatly affected by technological changes in battery grid manufacture. 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.

Chemical uses of selenium, including industrial and pharmaceutical applications, accounted for 14% of usage. Small quantities of selenium also are used as human food supplements; selenium has been recognized as a nutrient essential for human health. The principal pharmaceutical use of selenium is in antidandruff hair shampoos. Miscellaneous industrial chemical uses include lubricants, rubber compounding, and catalysts.

In pigment applications, selenium was used to produce color changes in cadmium sulfide-based pigments. With increasing substitution of selenium for sulfur, the yellow cadmium pigment becomes more red. Sulfoselenide red pigments have good heat stability and are used in ceramics and plastics, as well as in paint, inks, and enamels. Because of the relatively high cost and the toxicity of cadmium-based pigments, their use is generally restricted to applications requiring long life, brilliance, and high thermal stability and chemical resistance. Pigments were about 7% of the market.

Tellurium is used principally as an alloying element in the production of free-machining low-carbon steels, where additions of up to 0.1% tellurium, usually in conjunction with lead, greatly improve machinability. Similarly, the addition of tellurium to copper and other nonferrous alloys improves their machinability, strength, and corrosion resistance. Tellurium catalysts are used chiefly for the oxidation of organic compounds but are used also in hydrogenation, halogenation, and chlorination reactions. Tellurium chemicals are used as curing and accelerating agents in rubber compounding. Electronic semiconductor applications for high-purity tellurium include its use with selenium as a 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 some consumer applications. These devices consist of a series of couples of different semiconducting materials, which when connected to a direct current, cause one side of the thermoelement to cool while the other side evolves heat. The warm side is connected to a heat sink to dissipate the heat. Thermoelectric coolers are used for infrared detectors, integrated circuits, medical instrumentation, laser diodes, etc., more than for consumer products such as portable coolers.

Apparent domestic and world demand for tellurium increased slightly in 1995. The largest use for tellurium was as an additive to free-machining steel, about 55% of the market. Chemicals and catalyst usage was about 25% of the market. Additives to nonferrous alloys and photoreceptor applications used 15%. Other uses were about 5%.

World production and consumption data for selenium and tellurium were limited. Apparently, the supply increased at a somewhat faster rate than demand. Supply and demand have been in balance for several years. Better productivity has increased the oversupply, putting downward pressure on prices.

Prices

The domestic producer price for selenium averaged $4.89 per pound in 1995. The producer price for tellurium fell to $23 per pound by yearend, averaging about $25 for the year.

Current Research and Technology

Selenium has been tested as a free-machining additive to replace lead in plumbing brass. Two industry consortia continue to evaluate 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.

According to results obtained at the National Renewable Energy Laboratory, cadmium telluride has good potential for use in photovoltaic cells to provide electricity to consumers in remote areas. Energy demand has quadrupled in developing countries since 1960, and it is expected to double again by 2010. The countries of greatest growth have been China, India, Bangladesh, Indonesia, and Pakistan. Cadmium telluride is particularly suitable for large area thin film applications that would be used in solar collectors. If large area solar cells become the preferred method for supplying electricity in remote areas, the demand for tellurium for solar cells could increase dramatically.

Researchers at the University of North Carolina have discovered that a selenium deficiency in mice can facilitate the mutation of a benign virus to a virulent one. The virus, coxsackievirus, infects more than 20 million people annually in the United States. Most of the viruses are benign, so only about 10,000 infected people actually get sick. Illnesses of those who do range from colds to a heart inflammation. If this and similar viruses become virulent when they infect undernourished people, it would help explain the steady emergence of new strains of influenza virus from China, where widespread areas of land are low in selenium.[2]

Workers at Xerox Corp. have developed commercial applications for a "dry film" process they discovered many years ago. The new product, called Verde, because it is "green technology," with no wastes to clean up, is made by placing four coatings on a clear plastic film. The first layer is aluminum thin enough to be transparent. Next is a plastic that softens when warmed, followed by a layer of selenium powder. Finally, a plastic backing seals the other layers in place. An image is created on the film in a machine called an image setter or scanner. The aluminum layer is charged up, and the selenium particles become light sensitive, collecting a charge when exposed. Then the film is warmed, and the charged particles migrate into the plastic, eventually creating the clear portions of the image. The uncharged particles remain on the surface, blocking out light; this becomes the dark portion of the image. Xerox is working with other manufacturers to develop machines that could expose both Verde and traditional film and to find ways to retrofit this technology to existing cameras or image processors.[3]

Outlook

Selenium supply is dependent upon copper production; and in the past 5 years, it has exceeded demand. Because it is recovered as a byproduct, selenium output cannot be easily adjusted to meet market conditions, resulting in supply and price fluctuations. Although several new uses have been developed, they have not impacted the overall demand for selenium. Demand for selenium in photoreceptors is likely to continue to decline as the cost of using organic compounds decreases. The largest possible increase in demand would come from use as an additive to plumbing brass, but this application is still under development.[4]

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 or production for the next several years. Demand for high purity tellurium may increase for solar cells, and it could have a major impact on demand. Little information is available on the selenium or tellurium content of new ore bodies.

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[1] Countryside and Small Stock Journal. Federal Regulations on Selenium Have Changed. V. 79, No. 2, 1995, p. 74.

[2] Adler, Tina. Diet Causes Viral Mutation in Mice (Selenium Deficiency). Science News, v. 147, No. 18, 1995, p. 276.

[3] The Economist. Based on an Original Lunch by …(New Film). V. 334, No. 7906, p. 80.

[4] The Bulletin of the Selenium-Tellurium Development Association. Selenium-Containing Lead-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)

	1991	1992	1993	1994	1995
Selenium:					
United States:					
Production, primary refined	260,000	243,000 2/	283,000 2/	360,000 2/	373,000 2/
Shipments to consumers	275,000	221,000	258,000	302,000	320,000
Exports, metal, waste and scrap	210,000	175,000	261,000	246,000	269,000
Imports for consumption 3/	344,000	371,000	382,000	411,000	324,000
Apparent consumption, metal 4/	510,000	490,000	460,000	530,000	517,000
Dealers' price, average per pound, commercial grade 5/	$5.41	$5.13	$4.90	$4.90 r/	$4.89
World: Refinery production	1,640,000	1,770,000	1,740,000 r/	2,160,000 r/	2,070,000 e/
Tellurium:					
United States:					
Imports for consumption 6/	29,300	48,400	45,000	27,400	45,800
Producer price quote, yearend, commercial grade, per pound	$32.00	$35.00	$32.00	$26.00	$23.00

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

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

(Kilograms, contained selenium)

	1994		1995	
Country	Quantity	Value	Quantity	Value
Australia	11,400	36,100	--	--
Austria	--	--	401	6,200
Belgium	--	--	46,700	309,000
Brazil	15,400	246,000	14,600	220,000
Canada	--	--	1,090	29,900
Denmark	--	--	1,730	41,500
El Salvador	--	--	3,710	57,500
France	--	--	23,600	119,000
Germany	--	--	1,040	28,300
India	--	--	15,500	247,000
Israel	--	--	1,000	11,200
Japan	4,600	58,100	4,700	25,900
Korea, Republic of	--	--	4,620	80,300
Mexico	45,600	708,000	30,700	520,000
Netherlands	28,900	307,000	32,300	237,000
Philippines	115,000	488,000	80,900	253,000
Poland	--	--	182	2,910
South Africa	--	--	370	5,910
Syria	--	--	952	27,200
Taiwan	--	--	1,430	22,900
United Kingdom	626	10,000	332	2,690
Venezuela	2,210	37,400	4,050	43,000
Other	21,400	386,000	--	--
Total	246,000	2,280,000	269,000	2,260,000

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

Source: Bureau of the Census.

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

(Kilograms, contained selenium)

Class and country	1994 Quantity	1994 Value	1995 Quantity	1995 Value
Unwrought and waste and scrap:				
Australia	--	--	5,540	$44,600
Barbados	--	--	80	2,400
Belgium	40,000	$1,700,000	45,900	1,980,000
Canada	174,000	3,400,000	128,000	2,220,000
China	--	--	528	18,000
Finland	9,710	81,300	3,600	28,800
Germany	6,960	75,200	4,200	96,700
Japan	39,300	1,500,000	32,800	993,000
Philippines	103,000	511,000	67,500	462,000
Russia	--	--	8,110	74,900
Spain	--	--	1,000	8,400
United Kingdom	17,500	135,000	13,600	110,000
Other	5,650	28,400	--	--
Total	396,000	7,420,000	311,000	6,050,000
Selenium dioxide: 2/				
France	--	--	53	1,730
Germany	8,000	83,900	4,320	59,800
Japan	--	--	816	22,500
Spain	--	--	710	8,260
United Kingdom	6,540	80,900	6,890	88,400
Other	709	8,710	--	--
Total	15,300	173,000	12,800	181,000
Grand total	411,000	7,600,000	324,000	6,230,000

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

Source: Bureau of the Census.

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

(Kilograms, gross weight)

Class and country	1994 Quantity	1994 Value	1995 Quantity	1995 Value
Unwrought and waste and scrap:				
Belgium	1,930	164,000	4,550	262,000
Canada	3,400	239,000	9,410	659,000
China	--		604	82,100
France	1,080	21,400	200	5,730
Germany	294	57,600	1	1,270
Japan	9,530	658,000	6,850	546,000
Philippines	1,790	53,500	6,800	240,000
Peru	--	--	1,060	29,500
Russia	1,040	134,000	71	5,250
Switzerland	--	--	135	10,900
United Kingdom	7,420	205,000	16,100	593,000
Other	892	43,000	--	--
Total	27,400	1,570,000	45,800	2,430,000

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

Source: Bureau of the Census.

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

(Kilograms, contained selenium)

Country 3/	1991	1992	1993	1994	1995 e/
Belgium e/	250,000	250,000	250,000	250,000	250,000
Canada 4/	207,286	294,057	295,000 e/	566,000 r/	553,000 5/
Chile e/	50,600 5/	50,000	49,500	45,000	46,000
Finland	35,210	30,040	30,400	30,000 r/ e/	30,000
Germany e/	110,000	125,000	120,000	120,000	115,000
India e/	4,000	9,700	13,500	14,000	15,000
Japan	537,295	572,998	540,943	614,134 r/	551,000
Mexico	2,800	400	--	--	--
Peru	12,422	14,396	14,400 e/	14,000 e/	14,000
Philippines e/ 6/	60,000	60,000	40,000	40,000	40,000
Serbia and Montenegro 7/	XX	57,800	27,677 r/	30,000 r/ e/	30,000
Sweden	23,000	32,000	50,000 e/	50,000 e/	30,000
United States	260,000	243,000 8/	283,000 8/	360,000 8/	373,000 5/ 8/
Yugoslavia 7/ 9/	64,140	XX	XX	XX	XX
Zambia 10/	21,858	31,785	26,967	25,000 e/	25,000
Zimbabwe	2,549	1,736	1,113	2,009 r/	2,000
Total	1,640,000	1,770,000	1,740,000 r/	2,160,000 r/	2,070,000

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

1/ World totals, U.S. data, and estimated data are rounded to three sigificant 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 10, 1996.

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 intermediate exported for refining.

5/ Reported figure.

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

7/ All production in Yugoslavia for 1991 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/	1991	1992	1993	1994	1995 e/
Canada 4/	12,374	21,776	24,000 e/	42,000 r/	45,000
Japan	57,178	57,178	46,768	47,256 r/	44,500
Peru	13,355	18,631	18,600 e/	18,600 e/	18,600
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 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 May 10, 1996.

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.