# **BISMUTH**

By Robert D. Brown, Jr.

One domestic refinery in Nebraska produced bismuth as a byproduct of lead refining; however, most of the bismuth consumed in the United States was imported. Thirty-six companies, mostly in the Eastern United States, accounted for an estimated 80% of the bismuth consumed in 1996. About 56% of bismuth production was used in pharmaceuticals and chemicals, 27% in bismuth alloys, 15% as metallurgical additives, and 2% in other uses. After the anomalously high consumption of 1995, domestic demand fell nearly 30% in 1996, returning to a level more typical of recent years. Only a small amount of bismuth is obtained by recycling old scrap.

Several newly developed uses for bismuth providing nontoxic substitutes for lead have been introduced in recent years. These include the use of bismuth in fishing sinkers, brass plumbing fixtures, pigments, ceramic glazes, solders, lubricating greases, and crystalware. However, the only application showing a consistent, significant increase in demand through the lead replacement scenario is bismuth shot for waterfowl hunting.

In recent years, world production has remained steady. Sales from the National Defense Stockpile (NDS) also remained steady. Domestic production declined for 1996, as net imports rose. The New York dealer price for bismuth averaged \$3.65 per pound for 1996. This was the first decrease after 2 years of significant increases. The value of bismuth consumed domestically was more than \$12 million.

Bismuth is the leading candidate for replacing lead in applications that have an environmental impact. The U.S. Fish and Wildlife Service granted final approval for the use of bismuth shot for waterfowl hunting. The Safe Drinking Water Act Amendments of 1996 will eventually ban the use of lead in plumbing materials that contact drinking water.

The largest foreign producers (in decreasing order) of refined bismuth were Mexico, Peru, Belgium, and China.

# **Legislation and Government Programs**

The Defense Logistics Agency (DLA), which administers the NDS sold 122 metric tons of bismuth from the stockpile in 1996: 84 tons in September and 38 tons in November (American Metal Market, 1996a, b). The September sale, combined with 52.5 tons sold on November 15, 1995, represented slightly more than the 136 tons allocated for disposal in fiscal year 1996, which ended September 30, 1996. The DLA was authorized to dispose of another 136 tons of bismuth in fiscal year 1997. The NDS inventory on December 31, 1996, was 191.5 tons.

The U.S. Fish and Wildlife Service granted final approval of the use of 97% bismuth-3% tin shot for waterfowl hunting. This

approval was granted on the basis of further testing by the Bismuth Cartridge Council, which found that the shot was not toxic when ingested by waterfowl. The bismuth-tin shot is the leading alternative to steel shot, which replaced lead for waterfowl hunting several years ago (Fish and Wildlife Service, 1997).

The U. S. Congress passed, and the President signed, the Safe Drinking Water Act Amendments of 1996, (Public Law 104-182) which will eventually require all pipes, fixtures, solders, and fluxes used for the installation or repair of facilities providing water for human consumption to be lead-free.

#### **Production**

ASARCO Incorporated was the only domestic producer of primary bismuth. Production for 1996 decreased compared to that for 1995. To avoid disclosing company proprietary information, production data were not published. Some firms recovered bismuth from fusible alloy scrap, but secondary production data were not available. It is estimated that secondary production accounts for 5% or less of the domestic supply.

On April 15, 1996, many months after such a resolution had been foreseen by industry watchers, Asarco announced that it had reached agreement with the City of Omaha, NE, to cease all operations at its Omaha refinery by February 1, 1998, and to remediate the property for use as a park. It would have cost the company \$40 million in improvements to meet current and pending environmental standards. The company stopped lead refining at Omaha on June 1, 1996, but planned to continue processing other materials, including bismuth, at the plant until June 1997 (ASARCO Incorporated, 1997). By this step, the result of long discussions on emission controls, modernization, and cost-benefit analysis, the United States will lose its only domestic source of primary bismuth. Consumers' fears about supply seemed to have peaked before the announcement was made, and the long lead time before actual shutdown of the bismuth operations appeared to have softened such concerns.

### Consumption

Domestic consumption data are collected through a voluntary survey. Of the 45 firms that received the consumption survey form in 1996, 73% responded. The respondents accounted for an estimated 80% of the bismuth consumption in the United States. The amount used by the nonrespondents was estimated on the basis of reports from prior years or information from other sources.

Compared to the record- setting year of 1995, 1996 brought a significant decrease in domestic consumption. By weight, chemicals had the largest demand increase in 1995 and the largest decrease in 1996. Bismuth alloys had the largest percentage increase in 1995 and the second largest decrease in 1996.

As in several recent years, chemical uses accounted for more than one-half of the bismuth used domestically. The best known chemical use is that of bismuth subsalicylate, the active ingredient in over-the-counter stomach remedies. Other bismuth pharmaceuticals are used to treat burns, stomach ulcers, intestinal disorders, and for veterinary applications. Other bismuth chemical and compound uses include widely varying applications, ranging from pearlescent pigments in cosmetics and paints to superconductors.

The metallic uses of bismuth are categorized in table 2 into bismuth alloys, metallurgical additives, and other uses. Fusible (low-melting-point) alloys are combinations of bismuth and other metals such as cadmium, gallium, indium, lead, and tin. Applications for these alloys include holding lenses or other parts for machining or grinding, solders, fire sprinkler triggering mechanisms, and fuel tank safety plugs. Also included in bismuth alloys is the metal used to produce shot for waterfowl hunting.

Bismuth is added in relatively small percentage amounts to aluminum, copper, and steel alloys to improve machinability. It is also added to malleable iron to prevent the formation of graphite flakes.

Interest remained high in using bismuth as a nontoxic substitute for lead in several applications. Bismuth oxide replaces lead oxide in the fire assaying of precious metals. Bismuth replaces lead in ceramic glazes, and bismuth shotgun pellets are replacing the steel ones that replaced lead. Bismuth is the primary candidate for substitution when researchers seek to remove lead from products that traditionally have contained lead, such as plumbing fixtures and solders. Research and development continues on the use of bismuth (often in combination with selenium) to replace lead in plumbing brasses. Although this strategy appears to be the most promising metallurgical approach to meeting forthcoming more stringent tap water standards in the United States, bismuth consumption for this application has not yet increased significantly.

Since 1994, one area of large, steady increases has been the use of bismuth alloy cartridges for waterfowl hunting. The alloy used is 97% bismuth and 3% tin.

#### **Prices**

The domestic dealer price for commercially pure bismuth, published by Platt's Metals Week, averaged about \$3.65 per pound for the year, representing a 5% (\$0.20) decrease after increases of 30% (\$0.75) and 18% (\$0.60) in 1994 and 1995, respectively. The price was \$4.20 per pound at the beginning of 1996, having gradually increased from a low of \$3.55 per pound in July, 1995. The price declined gradually throughout 1996 to a low of \$3.15 per pound in early December and then

increased to \$3.30 per pound in mid-December, where it held steady until the end of the year.

# **Foreign Trade**

Total imports increased 3% by weight and 11% by value in 1995, even though imports from Belgium, the largest supplier, decreased. A small increase from Mexico and larger increases from the United Kingdom and China offset the decrease from Belgium. Of nine supplying countries, the four largest-Belgium, Mexico, the United Kingdom, and China--in descending order, accounted for 92% of the total.

Exports fell 42% by weight and 44% by value in 1996. Exports remained small (about 10% by weight and 17% by value) compared to imports.

#### **World Review**

China, Mexico, and Peru, had abundant bismuth to supply the world market at low prices (Mining Journal, 1966a, b). This apparent indicator of adequate supply kept prices down for the year in spite of the expected shutdown of the only U.S. bismuthproducing plant.

Usually, bismuth is recovered as a byproduct of lead or tungsten production. The Tasna Mine in Bolivia, which was closed in 1985, is the world's only significant potential source where bismuth would be the principal product. The new owners, Corriente Resources, Inc. of Vancouver, continued to obtain promising results from studies of the feasibility of reopening the mine. Corriente adjusted the mine's established reserves from 400,000 to 500,000 tons graded at 1.47% bismuth and 1.28% copper, with credits for gold, silver, and tungsten. Additionally, a new vein was discovered in a previously unworked area of the property with grades of 3% bismuth, 1.43% copper, 0.2% tungsten, and 4.21 grams of gold per ton. Other veins have been discovered, with less bismuth but higher gold content. The company purchased a nearby smelter that must be converted from zinc to bismuth-copper production, but the acquisition will eliminate costly exportation of concentrates for smelting. The company expects the mine to produce 900 to 1,000 tons of bismuth and 10,000 to 15,000 ounces of gold annually, but has projected the need for a steady price of \$4.00 per pound of bismuth to start up.

# **Current Research and Technology**

The most common soldering alloy for electronic applications, tin with 37% lead, has a melting point of 183° C and requires board temperatures of 205° C to 220° C to enable the alloy to form acceptable soldered joints. A newly developed replacement alloy of tin plus 42% lead and 8% bismuth allows a 10° C drop in processing temperature. The further addition of 0.5% silver allows another 5° C drop in temperature and provides higher strength and ductility in the soldered joint than in the original tin-lead alloy. This is a case where the properties of bismuth make the manufacturing process more efficient even

though lead is still present in the alloy (McCormack, and others, 1996).

Researchers from many academic and industrial laboratories followed various approaches to obtain lead-free solders for electronics applications. Studies included the tin-bismuth, tin-zinc-bismuth, tin-silver-bismuth, tin-bismuth-indium, and tin-bismuth-antimony systems. The research done by industrial laboratories included potential applications in communications and transportation (Journal of Metals, 1996).

#### Outlook

The long-range outlook for bismuth indicates that demand should increase, especially as development activity continues in the area of nontoxic replacements for lead. Demand has increased fairly slowly in recent years, with a big increase in 1995. Because bismuth is most often a byproduct of lead, a rapid increase in supply is unlikely, especially because the total consumption of lead remains fairly flat, with a large fraction of lead demand satisfied by recycling. Some relief would be provided by the resumption of production at the Tasna Mine in Bolivia, the world's only mine where the principal product would be bismuth. Furthermore, changes at Cominco's Trail, British Columbia, smelter to make its bismuth recovery process "continuous" rather than "campaign" should increase production.

Significant increases in demand for new applications, except for shot for waterfowl hunting, still appear to be a few years away. In summary, the big changes in supply and demand are not occurring as rapidly as earlier anticipated. This has stabilized the bismuth market for the near future.

#### **References Cited**

American Metal Market, 1996a, DLA sells bismuth: American Metal Market,

- v. 104, no. 222, November 14, p. 14.
- ———1996b, DLA sells final bismuth of year: American Metal Market, v. 104, no. 187, September 26, p. 12.
- ASARCO Incorporated, 1997, Annual Report 1996: New York, 45 p.
- Fish and Wildlife Service, 1997, Approval of bismuth-tin shot as non-toxic for waterfowl and coots hunting: Federal Register, v. 62, no. 12, January 31, p. 4873-4876.
- Journal of Metals, 1996, Design and reliability of lead-free solders and solder interconnects [abs]: Journal of Metals, v. 48, no. 11, p. 88-89.
- McCormack, M.T., Degani, Y., Chen, H.S. and Gesick, W.R., 1996, A lower-melting-point solder alloy for surface mounts: Journal of Metals, v. 48, no. 5, p. 54-56.
- Mining Journal, 1996a, Minor metals in July: Mining Journal, v. 327, no. 8390, August 9, p. 113.
- ———1966b, Minor metals in September: Mining Journal, v. 327, no. 8398, October 4, p. 274.

#### SOURCES OF INFORMATION

#### **U.S. Geological Survey Publications**

Bismuth. Ch. in Minerals Commodity Summaries, annual. Bismuth. Ch. in Minerals Yearbook, annual. 1

Bismuth. Ch. in United States Mineral Resources, U.S. Geological Survey Professional Paper 820.

Bismuth. Mineral Industry Surveys, quarterly.<sup>1</sup>

#### Other

Bismuth. Ch. in Mineral Facts and Problems, U.S. Bureau of Mines, Bulletin 675, 1985.

<sup>&</sup>lt;sup>1</sup>Prior to January 1996, published by the U.S. Bureau of Mines.

# TABLE 1 SALIENT BISMUTH STATISTICS 1/

# (Metric tons)

	1992	1993	1994	1995	1996
United States:					
Consumption	1,300	1,300	1,490 r/	2,150	1,520
Exports 2/	90	70	160	261	151
Imports for consumption	1,620	1,330	1,660	1,450	1,490
Price, average, domestic dealer, per pound	\$2.66	\$2.50	\$3.25	\$3.85	\$3.65
Stocks, Dec. 31: Consumer	272	323	402	390	122
World:					
Mine production (metal content) 3/	2,870 r/	3,220 r/	3,060 r/	3,490 r/	3,440 e/
Refinery production 3/	3,710 r/	4,360 r/	4,070 r/	4,260 r/	4,230 e/

e/ Estimated. r/ Revised.

 ${\bf TABLE~2}\\ {\bf BISMUTH~METAL~CONSUMED~IN~THE~UNITED~STATES,~BY~USE~1/}$ 

#### (Metric tons)

Use	1995	1996
Chemicals 2/	1,320	855
Bismuth alloys	544	401
Metallurgical additives	257	231
Other	27	35
Total	2,150	1,520

 $<sup>1/\,\</sup>mbox{Data}$  are rounded to three significant digits; may not add to totals shown.

 $<sup>1/\,\</sup>mbox{Data}$  are rounded to three significant digits.

 $<sup>2/ \,</sup> Comprises$  bismuth metal  $\,$  and the bismuth content of alloys and waste and scrap.

<sup>3/</sup> Excludes the United States.

<sup>2/</sup> Includes industrial and laboratory chemicals, cosmetics, and pharmaceuticals.

 ${\bf TABLE~3} \\ {\bf U.S.~EXPORTS~OF~BISMUTH~METAL,~ALLOYS,~AND~WASTE~AND~SCRAP,~BY~COUNTRY~1/}$ 

	199	5	1990	<del></del> 5
	Quantity		Quantity	
	(kilograms,		(kilograms,	
	metal	Value	metal	Value
Country	content)	(thousands)	content)	(thousands)
Argentina			137	\$11
Australia			197	5
Belgium	157,000	\$1,200	65,500	220
Brazil	32	4	50	6
Canada	43,200	1,880	59,500	1,410
Chile	54	3		
China	30,300	39		
Dominican Republic	112	4	1,150	35
Finland			472	4
France	15,500	137	5,380	77
Germany			497	38
Guatemala			14,200	16
Hong Kong	80	4		
Ireland	414	12	227	9
Korea, Republic of			63	18
Mexico	363	13	51	4
Netherlands	307	8	209	7
Norway	58	5		
Saudi Arabia	1,480	7		
Singapore	2,320	23	144	8
Switzerland			2,220	20
Taiwan	650	9		
Thailand			45	4
United Kingdom	9,680	83	596	44
Total	261,000	3,430	151,000	1,930

Total 261,000 3,430

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

Source: Bureau of the Census.

 ${\bf TABLE~4} \\ {\bf U.S.~IMPORTS~FOR~CONSUMPTION~OF~METALLIC~BISMUTH,~BY~COUNTRY~1/}$ 

	199	5	1996		
	Quantity	Value	Quantity	Value (thousands)	
Country	(kilograms)	(thousands)	(kilograms)		
Belgium	636,000	\$4,850	584,000	\$4,690	
Bolivia	28,300	146			
Canada	83,900	367	80,800	675	
China	82,600	605	151,000	1,180	
Germany	1,360	189	498	104	
Hong Kong	21,500	174	15,800	128	
Japan	1,350	30	1,680	90	
Korea, Republic of	10,000	75			
Mexico	444,000	3,220	453,000	3,380	
Peru	10,900	94	19,500	164	
United Kingdom	131,000	663	189,000	1,090	
Other	265	9			
Total	1,450,000	10,400	1,490,000	11,500	

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

Source: Bureau of the Census.

# ${\tt TABLE~5}$ BISMUTH: WORLD MINE AND REFINERY PRODUCTION, BY COUNTRY 1/2/

#### (Metric tons)

		Mine				Refinery				
Country	1992	1993	1994	1995	1996 e/	1992	1993	1994	1995	1996 e/
Belgium e/						800	950	900	800	800
Bolivia				121 r/	125	30 r/	7 r/	36	19 r/	20
Bulgaria e/	40	40	40	40	40	40	40	40	40	40
Canada 3/	224	144	129	187 r/	185					
China e/	820	740	610 r/	740 r/	700	1,060	1,050	850 r/	800 r/	800
Italy			e/	e/		20		5 e/	5 e/	5
Japan 4/	159 e/	149 e/	152 e/	177 e/	169	530	497	505	591	563 5/
Kazakstan e/	160 r/	160 r/	160 r/	155 r/	155	170 r/ 5/	170 r/	170 r/	166 r/ 5/	160
Korea, Republic of 4/	9 e/	5 e/	e/	e/		9	5	e/	e/	
Mexico 6/	807	908	900 e/	995 r/	1,000	550 e/	650 e/	650 e/	924 r/	925
Peru	550 e/	1,000 e/	1,000 e/	1,000 e/	1,000	419	937	871	870 e/	870
Romania e/	50	40	40	40	40	50	35	35	35	35
Russia e/	5	4	4	4	4	10	9	9	10	10
Serbia and Montenegro	10	5	5 e/	5 e/	5	20	10	(7/)	(7/)	(7/)
Tajikistan e/	20	16	12	11	5					
United Kingdom e/						r/				
United States	W	W	W	W	W	W	W	W	W	W
Uzbekistan e/	15	10	10	10	11					
Total	2,870 r/	3,220 r/	3,060 r/	3,490 r/	3,440	3,710 r/	4,360 r/	4,070 r/	4,260 r/	4,230

e/ Estimated. r/ Revised. W Withheld to avoid disclosing company proprietary data; excluded from "Total."

<sup>1/</sup>World totals and estimated data are rounded to three significant digits; may not add to totals shown.

<sup>2/</sup> Table includes data available through May 20, 1997. Bismuth is produced primarily as a byproduct of other metals, mostly lead; Bolivia is the sole producer of primary bismuth.

<sup>3/</sup> Figures listed under mine output are the metal content of concentrates produced.

<sup>4/</sup> Mine output figures have been estimated based on reported metal output figures.

<sup>5/</sup> Reported figure.

<sup>6/</sup> Refined metal includes Bi content of imported smelter products.

<sup>7/</sup> Less than 500 kilograms. Production in kilograms: 1994--88; 1995--86; and 1996--100 (estimated).