# **BISMUTH**

By Robert D. Brown, Jr.

Interest remains 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. Research sponsored by the American Foundrymen's Society and the U.S. Department of Commerce on combinations of bismuth and selenium to replace lead in brasses for plumbing component applications has been completed, with very encouraging results. 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.

Domestic consumption and production data are collected through a voluntary survey. Of the 45 firms that received the consumption survey form in 1995, 71% responded. The respondents accounted for an estimated three-fourths of the bismuth consumption for the United States. The amount used by the nonrespondents is estimated on the basis of reports from prior years or information from other sources.

## **Legislation and Government Programs**

The Defense Logistics Agency (DLA), which maintains the National Defense Stockpile Center (NDSC), sold 2,270 kilograms of bismuth from the Stockpile on March 8, 1995, and 137,000 kilograms on September 20, 1995. This represented slightly more than the amount allocated for disposal in fiscal year 1995, which ended September 30, 1995. The DLA was authorized to dispose of another 136,000 kilograms of bismuth in fiscal year 1996. At the first offering on November 15, 1995, 52,500 kilograms were sold. The Stockpile inventory on December 31, 1995, was 313,500 kilograms.

The U.S. Fish and Wildlife Service extended its approval of the use of 97% bismuth-3% tin shot for waterfowl hunting for the 1995-96 hunting season. This still "conditional approval," was granted on the basis of 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.<sup>1</sup>

#### **Production**

ASARCO Incorporated was the only domestic producer of primary bismuth. Production for 1995 was about the same as that for 1994. To avoid disclosing company proprietary information, production data are not published. Some firms recover bismuth from fusible alloy scrap, but secondary

production data were not available.

#### Consumption

Chemical and pharmaceutical uses account for more than one-half of the bismuth used domestically. Fusible alloys and metallurgical additives account for most of the remainder.

The best known chemical use is that of bismuth subsalicylate, the active ingredient in over-the-counter stomach remedies. Other bismuth pharmaceuticals were used to treat burns, stomach ulcers, intestinal disorders, and for veterinary applications. Other bismuth chemical and compound uses included widely varying applications, such as pearlescent pigments in cosmetics and paints, fire assaying, ceramic glazes, varistors, and superconductors.

Bismuth metal use is categorized into fusible 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 include holding lenses or other parts for machining or grinding, solders, fire sprinkler triggering mechanisms, and fuel tank safety plugs.

Bismuth is added to aluminum, copper, and steel to improve machinability. It is also added to malleable iron to prevent the formation of graphite flakes.

Numerical data on domestic consumption of bismuth in 1995 are undergoing extensive review by the U.S. Geological Survey and are not available at the time of publication. They will be published in a quarterly Mineral Industry Survey as soon as possible, and also in the 1996 Annual Report.

#### **Prices**

The domestic dealer price, published by Platt's Metals Week, averaged about \$3.85 per pound for the year, representing a moderate increase for 2 years in a row. The price was \$4.00 per pound at the beginning of the year, having been reduced from a 1994 high of \$4.10 per pound in July. The price declined gradually to a low of \$3.55 per pound in July 1995, and then gradually increased to \$4.20 per pound early in December where it held steady until the end of the year. The price trend for the year was influenced heavily by Chinese supply and pricing policies.

## Foreign Trade

Total imports fell 13% by weight in 1995, as imports from Canada, Kazakstan, Mexico, and Peru decreased significantly,

and were only partly offset by increases from Belgium and several other counries. Of 13 supplying countries, the 3 largest-Belgium, Mexico, and the United Kingdom--accounted for 84% of the total.

Exports rose 63% by weight and tripled in value in 1995, but still remained small compared to imports.

#### **World Review**

Usually bismuth is a byproduct of lead or tungsten production. The Tasna Mine in Bolivia is the world's only significant primary source of bismuth. It was closed in 1985. The owners have obtained promising results from studies of the feasibility of reopening the mine. Ore reserves of 700,000 metric tons, grading 1.7% bismuth, 0.6% copper, 0.3% tin, and 1.5 grams per ton of gold have been reported. Pilot studies on a new smelting process capable of processing a bulk concentrate of all the metals to be recovered could result in a 50% reduction in smelting costs.

Chinese production had a major influence on the market in 1995. The average price was lowered during the first half of the year, while China continued to sell at low prices. The average price was raised in the second half because Chinese production was limited by a decrease in tungsten mining and the Chinese began to demand higher prices for their bismuth.<sup>2</sup>

## **Current Research and Technology**

Experimental measurements have been completed to determine the feasibility of replacing lead with a bismuth/selenium combination (at a 2:1 ratio) in red brass (copper, tin, zinc, lead) in order to reduce possible toxicity from plumbing components. This work was organized, administered, and conducted by the American Foundrymen's Society, based in Des Plaines, IL, in conjunction with the foundry industry and was supported by a grant from the Department of Commerce as well as contributions by the companies. In the experimental phase, environmental characteristics, as well as the foundry behavior, mechanical properties, and machinability characteristics were measured. The new alloys had slightly higher melting temperatures, making dross rates somewhat higher. The ductility of the experimental alloys was a little lower, but the tests indicated that they had the same or better properties in all other respects.

A phase II program of more detailed experiments further verified the ability of bismuth/selenium to replace lead in this application. Variations in properties from foundry to foundry were no higher than for the leaded alloys. The new alloys had the same or better corrosion resistance, the same free machining properties, and excellent leach test results.<sup>3</sup>

Medical researchers have determined that a combination treatment using bismuth subsalicylate and antibiotics reduces the recurrence rate for ulcers to only 12%, where it is as high as 80% within a year and nearly 100% for 2 years when the treatment is limited to stress reduction and diet adaptation. This is because most ulcers are actually caused by bacteria rather than by stomach acid.<sup>4</sup>

#### Outlook

The long range outlook for bismuth remains optimistic, especially as development activity increases in the area of nontoxic replacements for lead. Demand has increased slowly in recent years. Since bismuth is mainly a byproduct of lead, a rapid increase in supply is not likely, especially since the total consumption of lead remains somewhat flat. Some relief would be provided by the resumption of production at the Tasna Mine in Bolivia, the only significant primary source of bismuth. Significant increases in demand due to the new applications appear to be a few years off.

## OTHER SOURCES OF INFORMATION

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

Bismuth Ch. in Minerals Commodity Summaries, annual. Hasler, J.W., Miller, M. H., and Chapman, R.M., 1973, Bismuth, *in* Brobst, D.A., and Pratt, W.P., eds., United States Mineral Resources: U.S. Geological Survey Professional Paper 820, p. 95-98.

#### **Other Sources**

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

<sup>&</sup>lt;sup>1</sup>Brister, B. Bismuth Comes of Age: The Wait is Finally Over: Waterfowlers Now Have a Nontoxic Legal Alternative to Steel Shot. Field and Stream, v. 100, No. 7, Nov. 1995, p. 5.

<sup>&</sup>lt;sup>2</sup>Mining Journal. Minor Metals in July. V. 325, No. 8338, Aug. 4, 1995, p. 87.

<sup>&</sup>lt;sup>3</sup>Sahoo, M. Modified Red Brass with Bismuth/Selenium Phase II, Final Report, American Foundry men's Society, Des Plaines, IL, June 1996.

<sup>&</sup>lt;sup>4</sup>Schwade, S. Medical Care Update: Stamp Out Ulcers. Prevention, v. 47, No. 4, Apr. 1995, p. 83.

## TABLE 1 SALIENT BISMUTH STATISTICS 1/

## (Metric tons)

	1991	1992	1993	1994	1995
United States:					
Consumption	1,260	1,300	1,300	1,450 r/	(2/)
Exports 3/	75	90	70	160	261
Imports for consumption	1,410	1,620	1,330	1,660	1,450
Price, average, domestic dealer, per pound	\$3.00	\$2.66	\$2.50	\$3.25	\$3.85
Stocks, Dec. 31: Consumer	247	272	323	402 r/	390
World:					
Mine production (metal content) 4/	3,230	2,740	3,090	3,020	3,040 e/
Refinery production 4/	3,820 r/	3,670	4,240	4,100	4,320 e/

e/ Estimated. r/ Revised.

- 1/ Data are rounded to three significant digits.
- 2/ Data currently under review.
- 3/ Includes bismuth, bismuth alloys, and waste and scrap.
- 4/ Excludes the United States.

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

#### (Metric tons)

Use	1994	1995
Chemicals 2/	841	(3/)
Fusible alloys	276	(3/)
Metallurgical additives	306 r/	(3/)
Other 4/	26	(3/)
Total	1,450 r/	(3/)

r/ Revised

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

	1994		1995			
•	Quantity	Value	Quantity	Value (thousands)		
Country	(kilograms)	(thousands)	(kilograms)			
Belgium	54,900	\$98	157,000	\$1,200		
Brazil	113	4	32	4		
Canada	44,400	782	43,200	1,880		
China	20,400	36	30,300	39		
France			15,500	137		
Honduras	8,390	26				
Hong Kong	4,150	17	80	4		
India	247	3				
Ireland	309	3	414	12		
Japan	965	12				
Korea, Republic of	200	3				
Netherlands	18,800	17	307	8		
Singapore	495	7	2,320	23		
South Africa	2,000	7				
Taiwan			650	9		
Thailand	272	4				
United Kingdom	4,290	29	9,680	83		
Other	119	12	2,060	32		
Total	160,000	1,060	261,000	3,430		

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

Source: Bureau of the Census.

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

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

<sup>3/</sup> Data currently under review.

<sup>4/</sup> Includes other alloys and experimental uses.

TABLE 4
U.S. IMPORTS FOR CONSUMPTION OF METALLIC BISMUTH, BY COUNTRY 1/

	1994		1995		
	Quantity	Value	Quantity	Value (thousands)	
Country	(kilograms)	(thousands)	(kilograms)		
Belgium	512,000	\$3,150	636,000	\$4,850	
Bolivia	<del></del>		28,300	146	
Canada	145,000	743	83,900	367	
China	80,100	543	82,600	605	
Germany	5,890	78	1,360	189	
Hong Kong			21,500	174	
Japan	1,670	81	1,350	30	
Kazakstan	38,500	128			
Korea, Republic of			10,000	75	
Mexico	665,000	3,850	444,000	3,220	
Morocco	158	3			
Peru	115,000	637	10,900	94	
Russia			15	6	
Spain	3,010	36	250	3	
United Kingdom	95,200	368	131,000	663	
Other		32			
Total	1,660,000	9,650	1,450,000	10,400	

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

Source: Bureau of the Census.

TABLE 5 BISMUTH: WORLD MINE AND REFINERY PRODUCTION, BY COUNTRY 1/2/

#### (Metric tons)

	Mine				Refinery					
Country	1991	1992	1993	1994	1995 e/	1991	1992	1993	1994	1995 e/
Australia e/	400									
Belgium e/						800	800	950	900	800
Bolivia							17	16	36 r/	121 3/
Bulgaria e/	40	40	40	40	40	40	40	40	40	40
Canada 4/	65	224	144	129 r/	126 3/				e/	
China e/	1,040	820	740	700	700	1,260	1,060	1,050	1,000	1,100
France e/	50									
Italy				e/		45	20	r/	5 e/	5
Japan 5/	138	159	149	152 r/	177	461	530	497	505 r/	591 3/
Kazakstan e/ 6/	XX	35	30	25	25		45	40	35	35
Korea, Republic of 5/	42	9	5	e/		42	9	5	e/	
Mexico 7/	651	807	908	900 e/	900	500 e/	550 e/	650 e/	650 e/	700
Peru	610 e/	550 e/	1,000 e/	1,000 e/	1,000	377 r/	419 r/	937	871 r/	870
Romania e/	55	50	40	40	40	50	50	35	35	35
Russia e/ 6/	XX	5	4	4	4		10	9	9	10
Serbia and Montenegro 8/	XX	10	5	5 e/	5	XX	20	10	10 e/	10
Tajikistan e/ 6/	XX	20	16 r/	12 r/	11	XX				
U.S.S.R. e/ 9/	70	XX	XX	XX	XX	70	XX	XX	XX	XX
United Kingdom e/						100	100			
United States	W	W	W	W	W	W	W	W	W	W
Uzbekistan e/ 6/	XX	15	10	10	10					
Yugoslavia 10/	70	XX	XX	XX	XX	70	XX	XX	XX	XX
Total	3,230	2,740	3,090	3,020	3,040	3,820 r/	3,670	4,240	4,100	4,320

e/ Estimated. r/ Revised. W Withheld to avoid disclosing company proprietary data; excluded from "Total." XX Not applicable.

<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 June 21, 1996. Bismuth is produced primarily as a byproduct of other metals, mostly lead; Bolivia is the sole producer of primary bismuth.

<sup>3/</sup> Reported figure.

<sup>4/</sup> Figures listed under mine output are the metal content of concentrates produced.

<sup>5/</sup> Mine output figures have been estimated based on reported metal output figures.

<sup>6/</sup>Formerly part of the U.S.S.R.; data were not reported separately until 1992.

 $<sup>7/\,</sup>Refined\ metal\ includes\ Bi\ content\ of\ imported\ smelter\ products.$ 

<sup>6/</sup>Formerly part of the Yugoslavia; data were not reported separately until 1992.

<sup>9/</sup> Dissolved in Dec. 1991.