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BISMUTH

Introduction:

Several metals are outstanding in some particular characteristic which makes them extremely useful, even essential, in our daily life. Bismuth is such a metal. In normal times the supply is adequate and is more or less controlled by a few large companies, both domestic and foreign. They are able to balance supply and demand and it is reported, that because of ample supplies and close control, a lowering of price would not increase the use of the element.

Bismuth is a relatively uncommon metal known generally for its medicinal use; its metallurgical applications, though enhanced greatly because of the war, are not as well known. At the present time bismuth is one of the few metals placed by the War Production Board in Group I of "the most important materials essential to the war effort". Group I is defined as those materials, supply of which is insufficient to satisfy war plus essential industrial demands.

History:

According to early writers, bismuth may have been known to the ancients but was believed to be an undeveloped form of tin or lead. In 1530 Agricola described the metal under the name of "Bisemutum". Libarius wrote of the metal in his "Commentariorum Chymicorum" (1606) and stated that it was used to soften tin, but he confused bismuth and antimony. Other writers of this period had no clear ideas concerning bismuth as a true metal. J. H. Potts in 1739 first demonstrated characteristic reactions of bismuth, and these were further demonstrated by Geoffrey (1753) and by Bergmann (1780). How the medicinal qualities of bismuth salts were discovered is unknown, but this knowledge dates from the Middle Ages. Libarius discovered bismuth subnitrate and its efficacy in treatment of diseases of the intestinal tract for which medicinal use it is still applied. The use of the metal in industry is of relatively recent time.

Mineral Resources of the United States first mentions bismuth in the volume which reported on mineral production in 1882. After briefly describing occurrences in Colorado, Utah, and Arizona, the report states that production in the United States "has thus far been of no importance".

In the report for 1883-1884 mention is made of a little ore, "said to have carried 7 percent metal," which was shipped from the Bismuth mine in Beaver County, Utah, in 1871. It also states that supplies of bismuth came principally from mines in Saxony, Hungary, Baden, Cornwall, and Australia, and that total production was small. Market price was given as \$2.00 a pound. Domestic imports were listed beginning in 1868 (no weight given) valued at \$30,149. In 1882, 64,837 pounds valued at \$111,087 was imported.

In the Mineral Resources report for 1885 it is stated that one ton of bismuth was produced experimentally at Loveland, Colorado, during 1885 and that commercial production would probably start in 1886. It mentions that the uses of the metal "are limited".

Domestic consumption of bismuth increased progressively in the last part of the last century but there is a gap in the ^{bismuth} reports of Mineral Resources after 1885. In 1902 it was reported that, while there was no production in 1902, output for 1901 was 318.6 short tons of bismuth ore assaying from 4 to 12 percent bismuth and from 1 to 2 ounces of gold to the ton. All production was from Colorado. It mentioned that production and price of bismuth and its ores "continue under the control of Johnson, Mathey & Company, Limited, and the government of Saxony." Domestic imports in 1902 were reported as 190,837 pounds valued at \$213,704, compared with 165,182 pounds valued at \$239,061 in 1901.

In 1904 it was reported that "the price of the refined metal is kept so low by the combination controlling the business that profitable mining of our domestic ores is practically out of the question." Only 5,184 pounds of ore valued at \$314 was reported marketed in that year.

In 1905 the report states that the London price of the metal was reduced by the controlling combination from \$2.43 to \$1.22 a pound. Mention is made of resumption of work at the Ballard mine, Leadville, Colorado; of the large output in Saxony; of development in Tasmania of an enormous deposit of tin-bismuth-copper ore; of the important sources of supply in Bolivia and Mexico; of the extraordinary demand for medicinal and surgical purposes because of the Russo-Japanese war; and of marketing of 2,288 pounds of domestic metal valued at \$4,187.

The 1908 report first mentions recovery of bismuth in lead refining by two companies - the United States Metals Refining Co. and the Monsanto Chemical Co. Price of the metal was quoted at \$1.75 a pound in London, and it was stated that the price had been raised and maintained after the low price reported in 1906 had extinguished competition.

In 1910 production consisted of the by-product from the United States Metals Refining Company's Grasselli, Indiana, plant together with a few tons of bismuth-bearing gold ore from Leadville, Colorado. Domestic imports were 198,174 pounds valued at \$332,668. Price of the metal rose during the year from \$1.70 to \$2.15 a pound.

The 1912 report mentions the American Smelting and Refining Co. (in addition to the United States Metals Refining Co.) as a producer of bismuth from lead refining operations. The following is quoted to show the feelings of the trade at that time:

"Heretofore large buyers have claimed that they could not safely buy of American producers of bismuth, for should they do so and should the American producers be unable to continue supplies the agents of the foreign sellers would thereafter refuse to sell bismuth to them, and the lack of a constant supply has always been a possibility to be feared."

The 1911 report describes in considerable detail the European combination which fixed the price of bismuth and allotted the trade territory to kill competition. It is stated in the report that flue dust of the Anaconda Washoe smelter amounted to 76.8 tons and carried 1.15 percent bismuth trioxide equivalent to 1,580 pounds of bismuth a day, and that this amount was not considered worth saving. A table is given showing recoveries of bismuth from electrolytically refined blister copper at various copper smelters in the United States, Mexico, Peru, and Tasmania. The recoveries range from 0.33 to 27.3 pounds of bismuth to the ton of blister copper. The lowest recovery was at Steptoe, Nevada; the highest at Mountain City, California. Imports during 1911 were 117,747 pounds valued at \$213,257.

Conditions did not change materially between 1911 and the start of World War I. In 1915 domestic imports fell off sharply, dropping in that year to 44,362 pounds valued at \$108,288. It is stated in the 1915 report that the production in this country was in the hands of companies which were so strong and whose bismuth supplies were so certain that the control formerly exercised by the European combination had been considerably weakened.

In 1918 imports jumped to 135,700 pounds valued at \$277,273 compared with 69,250 pounds valued at \$142,300 in 1917.

After World War I control of prices apparently returned to the English firm of Johnson, Matthey & Co. Although production statistics were not published, it was estimated that domestic sales in 1921 did not exceed 232,000 pounds valued at \$396,000. In March 1921 the price dropped to \$1.50 a pound where it remained for the balance of the year. Imports were 94,085 pounds valued at \$114,891.

In 1922 price of the metal jumped to \$2.45 a pound. The 1922 Mineral Resources report states that in normal times bismuth ores and concentrates without other metals should contain at least 15 percent of metallic bismuth to be marketable. Bismuth purchased in the domestic market was estimated at 226,385 pounds (including some imported metal) at a cost to the consumer of \$2.26 a pound. Imports were estimated as 121,505 pounds valued at \$239,777.

The succeeding reports of Mineral Resources do not contain/production statistics, and the history of the domestic industry is generally brought up-to-date under the later heading of "Statistics and Prices."

Physical properties:

Bismuth is a soft, heavy, lustrous metal, silvery white in color with a reddish tinge and subject to tarnish. Its specific gravity is 9.8 in the solid state and 10.06 when liquid. The specific gravity of the liquid phase decreases to 9.6 with increase of temperature to 650°C. The metal is brittle and granular; the fracture is coarsely crystalline, and crystal habit is hexagonal rhombohedral. Melting point is 271°C (520°F); boiling point is from 1090° to 1450°C. Bismuth has the nearly unique property of expanding on solidification. Heat conductivity is the lowest of any metal except mercury; electrical conductivity is very low - only 1.19 percent that of silver at 13.8°C. Unlike most metals the electrical conductivity of bismuth is greater when melted than in the solid state. It is the most diamagnetic of any metal, that is, it is repelled instead of attracted by a magnet.

Chemical properties:

In the periodic table bismuth is grouped with antimony; many properties of the two metals are similar. Air at ordinary temperatures does not attack bismuth, but at higher temperatures the metal takes on a coating of dark-colored oxide. Bismuth decomposes steam slowly, liberating hydrogen; at room temperature water has little effect on the metal. Bismuth is easily dissolved by nitric acid; it is dissolved by hot concentrated sulphuric acid with emission of sulphur dioxide. Hot concentrated hydrochloric acid dissolves bismuth slowly. Chlorine, bromine, and iodine combine directly with bismuth to form the halides. Likewise sulphur combines with molten bismuth to form the sulphide (Bi_2S_3). Bismuth sulphide is precipitated from solution by hydrogen sulphide and all the soluble sulphides. Bismuth nitrate obtained from nitric acid solutions is the most important bismuth salt.

Uses:

Normally the most important use of bismuth is in pharmaceutical preparations. A common use of its compounds is in X-ray examination of the digestive tract and in the treatment of digestive disorders.

The low melting point of bismuth forms the basis of a number of useful alloys. The property of expansion on solidification is also adapted to counteract shrinkage in certain applications. Bismuth combined with lead, tin, cadmium, and antimony forms alloys used in sprinkler and other fire-protection apparatus, solders, and electrical fuses, all of which require a low melting point. Alloys containing bismuth are used for bearing metals and die castings, and for taking impressions of wood cuts, coins, and various fragile objects where sharp delineation is required. A small percentage of bismuth added to certain metals and alloys improves machinability.

The following table* gives characteristics of various low-melting point alloys:

Fusible Bismuth Alloys.

Fusible below the boiling point of water, 212°F.

	Bismuth, melting point 520° F.	Lead, melting point 621.1°F.	Copper melting point 1981.5°F.	Tin, melting point 449.4°F.	Cadmium, melting point 609.6°F.	Mercury, melting point 37.7°F.	Antimony, melting point 1,166°F.	Melting point of alloy, °F.
Charpy's eutectic	8	5	---	2½	---	---	---	204°
Newton's metal	8	5	---	3	---	---	---	201°
D'Arcet's metal	8	4	---	4	---	---	---	199°
Rose's metal	8	8	---	3	---	---	---	174°
Onion's mercuric	8	5	---	3	---	1½	---	170°
Lipowitz's metal	8	5	---	2	1	---	---	150°
Lipowitz's mercuric	8	4	---	2	2	1	---	143°
Wood's metal	7½	4	---	2	2	---	---	140°
Guthrie's eutectic	8	3	---	3	2½	---	---	(1)
D'Arcet's mercuric	8	4	---	4	---	20	---	113°

(1) Very fusible.

Bismuth minerals:

The most important bismuth minerals are the native metal, the sulphide (bismuthinite), and bismuth-bearing lead sulphides. Oxidized minerals are bismite ($\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), bismutite ($\text{Bi}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$), and some combinations with arsenic. Textbooks on mineralogy also list rather rare bismuth minerals as follows: oxychloride, silicate, telluride, tellurate, selenide, uranate, and vanadate.

Native bismuth, usually in cube-like rhombohedrons having a brilliant metallic lustre, is found in crystalline rocks sometimes associated with silver, cobalt, lead and zinc ores.

Bismuthinite (Bi_2S_3), generally massive with a fibrous structure, has a lead-gray color and streak, sometimes inclining to lighter shades with a yellowish tarnish. It is associated sparsely with some other metallic minerals in various parts of the world.

Oxidized bismuth minerals have been found concentrated in the oxidized zone of some ore deposits, notably at Tintic, Utah, and at the Great Cobar copper mine, New South Wales. Like some other metals which are affected little if at all in the laboratory by water at ordinary temperatures, oxidation of the primary bismuth minerals may occur under natural conditions, and the resultant oxides are more or less concentrated in the oxidized zone of the deposit. Bismuth oxide minerals are commonly yellowish in color and powdery.

*Credited by Mineral Resources of the United States, 1917, to B. Dunstan, Queensland mineral deposits (bismuth); Queensland Gov. Min. Jour. January, 1917.

Sources:

Domestic bismuth is derived almost entirely from secondary refining operations at lead and copper smelters. No deposit of record in the United States is mined for bismuth alone, but, as stated, it is an accessory constituent of some lead and copper ores mainly in Utah, Nevada, Idaho, Montana, Colorado, New Mexico, and Arizona. In 1940 the Bunker Hill and Sullivan Company started a new refinery designed to produce both antimony and bismuth from the tetrahedrite ores of the Coeur d'Alene district, Idaho.

In Canada bismuth has been produced both from the silver-cobalt ores of the famous cobalt deposits in Ontario and from the ores treated at the Trail smelter in British Columbia.

Bismuth is found as an accessory mineral in many Mexican mines, and a large part of the Mexican production is exported to the United States in ore or lead bars.

The two South American countries, Peru and Bolivia, contain the largest known sources of bismuth. They have large reserves of bismuth minerals associated with other metallic ores. In normal times these two countries could supply world demand without difficulty. Occurrences of bismuth minerals are known in Argentina, Chile, and Brazil.

European sources are mainly in Spain. Both England and Germany formerly produced some bismuth. In recent years these countries have been dominant in the marketing of bismuth but through cartels and smelting facilities rather than through mine production.

In Africa bismuth occurs with the South African gold ores and has been reported at several places in Northern Rhodesia.

Asiatic production has been largely dormant because of the war. Formerly China exported a material amount. Japan produces the metal mainly as a by-product of smelting operations. Occurrences of bismuth minerals have been reported in Burma, Korea, Siberia, and the Dutch East Indies.

Occurrences of bismuth in association with other minerals are known in various parts of Australasia. The most important deposits are in New South Wales, Queensland, Victoria, South Australia, Tasmania, and New Zealand. A small to moderate production has been maintained for many years.

It is reported that the United Nations control 80 percent of the world supply of the metal.

Statistics and prices:

Domestic production statistics are not published. Mineral Industry reported that imports, mainly in the form of metal, into the United States in 1939 amounted to 182,832 pounds - double the amount in 1938. Exports during the first eight months of 1939 were estimated to have been about 314,000 pounds compared to 225,600 pounds for all of 1938.

World production of bismuth in 1938 was estimated by Mineral Industry at about 1,000 tons. This amount has been greatly increased because of the war. It was estimated that the apparent world consumption in 1939 was about 2,600,000 pounds, of which about 500,000 pounds was consumed in the United States and 2,000,000 pounds in Europe. Probably a part of the apparent consumption went into stocks in anticipation of restricted trade.

Before the war London quotations through the firm of Johnson, Matthey & Co. governed the world market price. The few large smelting companies which control production in the United States accepted London quotations as the basis of sales made for the most part entirely in the domestic market. Because of the war, rigid government control is now exercised.

Market price just prior to the war in Europe was about \$1.00 a pound. Late in 1939 the price advanced to \$1.25 a pound where it has remained unchanged. Quotations for the pharmaceutical trade are for 99.9 percent metal, free from arsenic. According to U. S. Bureau of Mines Information Circular 6466 a typical analysis is as follows:

Silver	0.05	percent
Lead	.005	"
Copper	.007	"
Iron	.005	"
Zinc	.01	"
Bismuth	99.923	"

Prices for bismuth during the early part of the present century were generally considerably higher than at present. Just before World War I, prices were about \$2.00 a pound. In 1916 the price was \$4.00 a pound; in 1917 the price was set at \$3.50 a pound and was unchanged until the end of the war. In the 1920's quotations were generally over \$2.00 a pound. The price declined in the depression years of the 1930's to below \$1.00 and showed signs of strength only late in that period when unsettled conditions in Europe caused the trade to accumulate supplies.

The present market quotation is for metal bars in ten lots.

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ANOTHER TALL TALE OF A SOURDOUGH

James H. Batcheller, Corvallis, whose reputation for veracity is as clean and spotless as the newly fallen snow of the North Country which he loves to talk about, told us the following story, and we unhesitatingly vouch for the truth of anything Jim tells us. (Ed.).

I was talking with a lonely prospector, in a low valley 'way north of the Arctic Circle. He was one of the misfits of the horde of gold rushers who did not find anything but, in spite of that, was so gripped by the vastness of the country, he had managed to hang on in a little dugout with just one lone window, facing south.

He thought it would cheer his loneliness if, in the long hot sunlit days, he could just grow a few of the hardy flowers from his homeland in the temperate zone. He sent for a variety of seeds and started them indoors in flats, early in the spring. As soon as danger of late frosts was over he set them out. He protected and nursed them along with surprising success, for in the constant warm sunlight they grew fast and many managed to bloom. He was greatly disappointed, however, in his sunflowers. They grew tall and strong, and developed splendid big buds, but as fast as they blossomed they developed weak stems! For, as the blossoms followed the sun around during the 24-hour days, they wrung their own necks!

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