



2009 Minerals Yearbook

ARSENIC

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By William E. Brooks

Domestic tables were prepared by Elsie D. Isaac, statistical assistant, and the world production table was prepared by Lisa D. Miller, international data coordinator.

In 2009, the United States produced no arsenic and relied mostly on Morocco and China, the leading and second ranked import sources, respectively, for arsenic trioxide and on China and Japan, the leading and second ranked import sources, respectively, for arsenic metal. There has been no domestic production of arsenic trioxide or arsenic metal since 1985 following the closure of the ASARCO Inc. copper smelter in Tacoma, WA. Arsenic trioxide has been used mainly for the production of chromated copper arsenate (CCA), a pesticide and preservative used to pressure treat some wood products, and for production of agricultural chemicals. Arsenic metal was used for electronics applications and in nonferrous alloys. The United States remained the world's leading consumer of arsenic trioxide and arsenic metal.

Legislation and Government Programs

In 1975, the Safe Drinking Water Act mandated that the U.S. Environmental Protection Agency (EPA) identify and regulate drinking water contaminants, such as arsenic, that may have adverse effects on human health. The maximum contaminant level for arsenic was established at 0.05 microgram per liter ($\mu\text{g/L}$), and in 2001, was revised to 0.01 $\mu\text{g/L}$. At the end of 2009, arsenic removal technology had been tested at sites in California, Minnesota, Nevada, New Hampshire, and Wisconsin. For example, at the Stewart, MN, site, source water contained from 31.4 to 56.4 $\mu\text{g/L}$ arsenic and after treatment, approximately 60% total arsenic was removed. (Williams and others, 2009).

Environmental and Human Health Issues

Arsenic is a naturally occurring element that may be present in drinking water as a result of weathering of arsenic-containing minerals exposed by natural processes or disturbed by mining or other anthropogenic activities; as runoff from arsenic-containing pesticides used in orchards; in wastewater runoff from glass and electronics production; or arsenic released by coal burning. In humans, some of the noncancerous effects of arsenic exposure include blindness, diarrhea, discoloration and thickening of the skin, nausea, stomach pain, and vomiting. Prolonged arsenic exposure has been linked to cancer of the bladder, kidney, lungs, liver, and prostate (Agency for Toxic Substances and Disease Registry, 2007).

As the result of a 4-year bankruptcy case, Asarco LLC, now owned by Grupo Mexico S.A. de C.V. (Mexico, Distrito Federal, Mexico) will make \$3.5 billion in payments to settle claims in 16 States that involve liability for pollution at mining and smelting sites once owned by ASARCO. The case was the largest settlement of environmental class in U.S. bankruptcy court history (Metal-Pages, 2009d).

According to university medical research scientists, the ability to have an immune response to H1N1 (Swine Flu) infection was compromised by low levels of arsenic exposure through drinking contaminated well water. Researchers noted that Mexico has areas of very high arsenic in well water that include locations where H1N1 first appeared, and researchers followed up with laboratory experiments on mice. They found that the immune response to exposure to H1N1 in lab animals that had ingested 100 parts per billion (ppb) of arsenic for 5 weeks was weak. Morbidity for arsenic-exposed mice was significantly higher than for lab mice similarly exposed to H1N1. The researchers concluded that arsenic exposure not only disrupts the immune system but also the endocrine system, which results in broad hormonal disruption (Kozul and others, 2009).

In Bangladesh, groundwater was widely used for irrigation of rice paddies; however, the groundwater may contain potentially high concentrations of arsenic. Researchers have found that in seasonally flooded fields, the arsenic concentrations decrease during the monsoon season. They concluded that monsoon floodwater removes from 13% to 62% of the arsenic that is added to the rice paddy from groundwater irrigation and that nonflooded fields were at risk of arsenic accumulation (Roberts and others, 2010).

Nanotechnology may help alleviate water pollution problems by removing contaminants such as arsenic, bacteria, mercury, and pesticides. Researchers at Rice University have used "nanorust" (nanoparticles of iron oxide) to remove arsenic from drinking water. The large surface area of nanorust and the magnetic interaction between the nanoparticles means that 100 times more arsenic can be captured using nanorust than with filtration systems using larger particles. The team is developing nanorust from inexpensive household items, which would reduce production costs and make nanorust a feasible product for widespread use (Science News, 2006).

A chemical-free method to remove arsenic from well water was working in India. The method was developed by European and Indian scientists and tested at Kasimpore, a village in West Bengal State, India, one of the most arsenic-contaminated sites in the world. Wells may have 50 $\mu\text{g/L}$ of arsenic in comparison to World Health Organization guidelines of 10 $\mu\text{g/L}$. The treatment plants contain a nozzle that sprays oxygen into water pumped from aquifers. The oxygen-rich water oxidizes Fe^{II} that was adsorbed from the groundwater onto the soil into ferric hydroxide, which removes arsenic as a coprecipitation product (Sen Gupta and others, 2009).

Electronic waste (e-waste) may contain arsenic, beryllium, cadmium, copper, gold, lead, mercury, and silver that may be recycled. However, the small-scale recovery of the metals may pose an environmental hazard and risk to human health (Schmit, 2008).

Consumption

Arsenic is one of the components of CCA, a widely used wood preservative used in pressure-treated wood. The major domestic consumers of arsenic, as CCA, include Arch Wood Protection, Inc., Norwalk, CT; Osmose Wood Preserving, Inc., Buffalo, NY; and Viance, a joint venture between Rohm and Haas Co. and Chemical Specialties, Inc., Charlotte, NC. In response to concerns about the effects of arsenic exposure on human health, domestic manufacturers of wood preservatives voluntarily reduced their use of CCA in 2003. The phaseout applied to wood used for boardwalks, decks, fencing, gazebos, picnic tables, and play structures. However, wood treated with CCA prior to December 31, 2003, could still be used, and glue-laminated beams, marine timbers, plywood flooring and roofing, and utility poles could still be treated with CCA (PR Newswire, 2002). In 2004, global arsenic consumption and domestic imports of arsenic declined significantly in response to this voluntary phaseout.

The United States remained the world's leading consumer of arsenic, mainly for the production of CCA. Apparent domestic consumption for arsenic was about 4,740 metric tons (t) in 2009, a 15% increase from about 4,130 t in 2008. The estimated value of arsenic compounds and metal consumed domestically in 2009 was approximately \$4.8 million.

In 2009, slightly more than 50% of the arsenic, as arsenic trioxide, was used in the wood preservative industry for nonresidential use. The remainder of the arsenic trioxide was used in agricultural chemicals (either directly or after conversion to arsenic acid) or in glass manufacturing applications. Arsenic acid also was used in glassmaking as a bubble dispersant or decoloring agent. No data were available on the percentages of arsenic used in these traditional use categories.

Some arsenic may be found as an impurity in copper, and alloys containing arsenic have been used to produce hardened copper tools since ancient times. Arsenic metal is used, along with antimony, to harden ammunition, in solders, and in other applications. Grids and posts in lead-acid storage batteries are strengthened by the addition of arsenic metal. Arsenic is one of several metals used as an antifriction additive in babbitt metals (alloys that are used for bearings). Minor amounts of arsenic may be added to lead for use in clip-on wheel weights. However, the EPA has encouraged the reduction of lead, a toxic metal, in wheel weights through a partnership among Federal agencies, States, automobile trade associations, environmentalists, and wheel-weight manufacturers (U.S. Environmental Protection Agency, 2009).

High-purity (99.9999%) arsenic metal is used for gallium-arsenide (GaAs), indium-arsenide (InAs), and indium-gallium-arsenide semiconductors that are widely used in computer, biomedical, communications, and electronics applications. Arsenic may be used for germanium-arsenide-selenide or GaAs specialty optical materials. Arsenic sulfide is one of several substrate materials that are used for optical thin films and interference coatings for applications in data recording media, optical communications systems, and sensors. A mobile telephone typically contains GaAs in its circuitry, of which the arsenic content is less than 1 milligram (International Precious Metals Institute, 2003). Based on reported consumption

of gallium, U.S. consumption of arsenic metal in GaAs semiconductors was approximately 20 t in 2009, which was a 50% decrease from a peak of about 40 t in 2000.

Prices

China was the world's leading producer of arsenic trioxide; however, sales were low through May 2009. In May, prices in Beijing, China, for arsenic trioxide (minimum 99%) were \$0.39 to \$0.41 per kilogram, a decrease from \$0.45 per kilogram in February. An official at a Hunan smelter indicated that no arsenic trioxide had been exported since the fourth quarter of 2008 (Metal-Pages, 2009c). In the second quarter, the 99%-pure arsenic trioxide price range in China declined to \$0.09 per kilogram, and by mid-September, the price had increased to \$0.10 per kilogram because of improved demand from customers (Metal-Pages, 2009a).

In November, prices for arsenic metal increased owing to purchases and a reduction in supplies in China. Prices for 99%-pure arsenic metal increased to \$1,247 per metric ton in November from \$1,174 per ton in October. A producer indicated that there had been some overseas purchases of arsenic metal and that consumers were expected to replenish their stocks. Prices of \$1,300 per ton were quoted; however, overseas buyers bid as low as \$1,050 to \$1,100 per ton (Metal-Pages, 2009f). By early December, there had been little change in the market, and prices were holding at \$1,248 per ton. One producer postponed restarting arsenic metal production, which had been planned for late November (Metal-Pages, 2009b). By the end of December, Chinese domestic suppliers maintained their prices of \$1,248 to \$1,292 per ton. Export prices of \$1,150 to \$1,200 per ton were reported (Metal-Pages, 2009e).

Foreign Trade

In 2009, domestic imports of arsenic compounds were 4,660 t contained arsenic, a decrease of approximately 3% compared with the 4,810 t contained arsenic in arsenic compounds imported in 2008. Arsenic trioxide contains 76% arsenic. In 2009, Morocco was the source of 74% of the arsenic trioxide imported into the United States, China was the source of 18%, and Belgium was the source of 8%. Imports of arsenic trioxide from China into the United States in 2009 decreased by 8% to 1,080 t, from 1,180 t in 2008.

In 2009, the United States imported 438 t of arsenic metal, a 16% increase compared with the 376 t of arsenic metal imported in 2008. China was the leading source of arsenic metal in 2009 and provided 370 t of arsenic metal, or 84%; however, this was an increase of 28% compared with the 288 t of arsenic metal that was imported from China in 2008. Arsenic metal was also imported from Japan (15%) and other countries.

Exports of arsenic metal from the United States in 2009 decreased to 354 t from 1,050 t in 2008. Export destinations included Honduras (64%), Colombia (21%), Guatemala (5%), and France (4%). In the Harmonized Tariff Schedule, exported materials are classified only by number and may not be inspected so as to confirm the contents of the shipping container. This may have resulted in misclassification of the exported material, and therefore, exports of material classified

as arsenic metal may vary from year to year. This classification may also include arsenic-containing “e-waste,” such as computers and other electronics destined for reclamation and recycling (Grossman, 2005; Schmit, 2008), transshipped arsenic metal used for production of small-arms ammunition (Agence France-Presse, 2005; Chicago Tribune, The, 2005), and arsenic alloyed with lead or another metal.

World Review

In 2009, commercial-grade arsenic trioxide was recovered from processing of nonferrous ores or concentrates in 13 countries. Reduction of arsenic trioxide to arsenic metal accounted for all world output of commercial-grade (99%-pure) arsenic metal.

In 2009, China produced approximately 25,000 t of arsenic trioxide and remained the world’s leading producer followed by Chile (11,000 t), Morocco (8,500 t), and Peru (4,850 t). Arsenic was also produced in China as a byproduct of gold mining from orpiment (As_2S_3) and realgar (AsS), the more common ore minerals of arsenic (Peters and others, 2002, p. 182). Arsenic trioxide was also produced in Mexico at the San Luis Potosi copper smelter.

Arsenic-containing residues and smelter dusts recovered from nonferrous metals plants in several countries may not have been processed to recover commercial-grade arsenic trioxide in 2009 and may have been stockpiled for future treatment. Production data for most countries were estimated and subject to revision.

Outlook

At yearend 2003, the voluntary decision by the wood preservative industry to eliminate CCA as a wood preservative for certain wood products has led to a decline in U.S. consumption and a decline in arsenic trioxide production in China. The use of alternative wood preservatives and wood alternatives, such as concrete, plastic, or wood composites, will continue to substitute for CCA wood preservatives. Borate-treated wood is resistant to insects and fungal decay, but its use is recommended only for interior or weather-shielded applications. Specific industrial applications, such as marine timber, plywood roofing, and utility poles, are expected to continue to use CCA-treated wood. High-purity arsenic is expected to continue to be used by the electronics industry for GaAs semiconductors. Effects of the global economic decline slowed GaAs industry growth; however, GaAs was expected to continue to represent the principal semiconductor technology, mainly for defense applications, through 2013. Overall, the GaAs market was expected to increase to \$4.5 billion by 2013 (Anwar, 2010). World sources of arsenic, as arsenic trioxide and arsenic metal from nonferrous metal processing, are expected to be sufficient to meet projected needs.

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TABLE 1
ARSENIC SUPPLY-DEMAND RELATIONSHIPS¹

(Metric tons of arsenic content)

	2005	2006	2007	2008	2009
U.S. supply, imports:					
Metal	812	1,070	759	376	438
Compounds	8,330	9,430	7,010	4,810	4,660
Total	9,150	10,500	7,770	5,180	5,100
Distribution of U.S. supply:					
Exports ²	3,270	3,060	2,490	1,050	354
Apparent demand	5,870	7,450	5,280	4,130	4,740

¹Data are rounded to no more than three significant digits; may not add to totals shown.

²Metal only.

TABLE 2
U.S. IMPORTS FOR CONSUMPTION OF ARSENIC PRODUCTS¹

Class and country	2008		2009	
	Quantity (metric tons)	Value (thousands)	Quantity (metric tons)	Value (thousands)
Arsenic trioxide:				
Belgium	654	\$413	514	\$297
Bolivia	30	15	--	--
China	1,180	599	1,080	440
Germany	5	17	--	--
Morocco	4,460	1,860	4,530	1,970
Spain	(2)	16	10	36
Total	6,320	2,920	6,130	2,740
Arsenic acid:				
France	89	639	--	--
Germany	(2)	2	--	--
Indonesia	19	22	--	--
Japan	4	11	3	11
Taiwan	3	7	--	--
Total	115	682	3	11
Arsenic sulfide:				
China	-- ²	-- ²	--	--
France	(2)	5 ²	--	--
Italy	(2)	6	77	334
Total	(2)	11	77	334
Arsenic metal:				
China	288	792	370	993
Germany	5	761	1	276
Japan	84	1,050	67	613
United Kingdom	--	--	(2)	5
Total	376	2,610	438	1,890

¹Revised. -- Zero.

¹Data are rounded to no more than three significant digits; may not add to totals shown.

²Less than ½ unit.

Source: U.S. Census Bureau.

TABLE 3
ARSENIC TRIOXIDE: ESTIMATED WORLD SMELTER PRODUCTION, BY COUNTRY^{1,2,3}

(Metric tons)

Country ⁴	2005	2006	2007	2008	2009
Belgium	1,000	1,000	1,000	1,000	1,000
Bolivia	120 ⁵	90 ⁵	--	74 ^{r,6}	100
Canada	250	250	250	250	250
Chile	11,700	11,700	11,400	10,000	11,000
China	30,000	30,000	25,000	25,000	25,000
Iran	100	100	100	100	100
Japan	40	40	40	40	40
Kazakhstan	1,500	1,500	1,500	1,500	1,500
Mexico	1,664 ⁵	1,595 ⁵	1,600	513	500
Morocco	8,939 ⁵	8,900 ⁵	8,950 ⁵	8,800	8,500
Peru ⁷	3,150 ⁵	4,399 ⁵	4,321 ^{r,5}	4,822 ^{r,5}	4,850 ^p
Portugal	15	15	15	15	15
Russia	1,500	1,500	1,500	1,500	1,500
Total	60,000	61,100	55,700	53,600 ^r	54,400

^pPreliminary. ^rRevised. -- Zero.

¹Including calculated arsenic trioxide equivalent of output of elemental arsenic compounds other than arsenic trioxide where inclusion of such materials would not duplicate reported arsenic trioxide production.

²World totals and estimated data have been rounded to no more than three significant digits; may not add to totals shown.

³Table includes data available through March 24, 2010.

⁴Austria, Hungary, the Republic of Korea, Serbia and Montenegro (listed as an individual entity but dissolved their union in June 2006), South Africa, Ukraine, the United Kingdom, and Zimbabwe have produced arsenic and (or) arsenic compounds in previous years, but information is inadequate to make estimates of output levels, if any.

⁵Reported figure.

⁶Estimated exports of arsenic trioxide reported by Bolivia's Ministry of Mines and Metallurgy (2009).

⁷Output of Empresa Minera del Centro del Perú (Centromin Perú) as reported by the Ministerio de Energía y Minas.