

2007 Minerals Yearbook

ARSENIC [ADVANCE RELEASE]

ARSENIC

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In 2007, the United States produced no arsenic and relied mostly on Morocco and China, the first and second leading import sources, respectively, for arsenic trioxide (As_2O_3) and on China for arsenic metal. There has been no domestic production of arsenic trioxide or arsenic metal since 1985 following the closure of the ASARCO Incorporated copper smelter in Tacoma, WA. Arsenic trioxide was used mainly for the production of chromated copper arsenate (CCA), a pesticide-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

The U.S. Food and Drug Administration (FDA) issued a warning to consumers and recalled certain brands of mineral water that were found to contain from 454 to 674 micrograms per liter (μ g/l) arsenic; FDA's standard of quality for bottled water allows no more than 10 μ g/l (U.S. Food and Drug Administration, 2007).

Environmental Issues

Some of the noncancerous effects of arsenic exposure in humans 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, liver, lungs, and prostate (Agency for Toxic Substances and Disease Registry, 2007). Worldwide, 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 may be released by coal burning. Approximately 1 metric ton (t) of an arsenic-based compound is used annually as an additive to chicken feed. The additive converts to inorganic arsenic within the bird, and excretion of this material and its use in poultry litter introduces arsenic to agricultural fields and to runoff in parts of Delaware, Maryland, and Virginia (Hileman, 2007).

Bangladesh is one of several countries that has been severely affected by arsenic in its water supplies and researchers indicate that hundreds of thousands of people in Bangladesh are likely to die from arsenic poisoning (New York Times, The, 2007). An inexpensive (\$35 to \$40 per unit), maintenance-free, arsenic remediation system that uses easily obtained materials such as brick, charcoal, iron, and sand was developed. After laboratory and field tests, more than 30,000 units have been distributed and these will bring clean water to about 400,000 people in Bangladesh (Weiss, 2007).

Researchers estimated that 1,740 t of arsenic may be contained in the CCA-treated wood and construction debris left by Hurricane Katrina. Their findings were based on the concentration of arsenic in 53 pieces of lumber from seven sites with a mean concentration of 1.24 grams of arsenic per kilogram of wood (Cunningham, 2007).

In Hong Kong, dried squid snacks tested by the Hong Kong Consumer Council were found to contain levels of arsenic that were above the legally permitted maximum of 10 milligrams (mg). In eight of the 23 samples tested, the arsenic level was between 12.7 and 35.3 mg (German Press Agency, 2007).

Arsenic may be found in discarded electronics or "e-waste" which includes used computers, televisions, circuit boards, relays, and switches (Ohio Department of Natural Resources, 2005). Such electronics were exported from the United States and may have become part of an uncontrolled hazardous waste stream in other countries and many of the people who disassemble these electronics for recycling may be exposed to arsenic or other toxic metals (Grossman, 2005). Mobile phones and other electronic waste have been exported to Japan from southeast Asia for extraction and recycling of nonferrous metals such as arsenic, copper, gold, and lead (Metals Place, 2007).

Consumption

The major domestic consumers of arsenic, as CCA for pressure-treated wood, include Arch Wood Protection, Inc., Norwalk, CT; Osmose Wood Preserving, Inc., Buffalo, NY; and Viance, a joint venture between Rohm and Haas Company and Chemical Specialties, Inc., Charlotte, NC. However, in response to concerns about the effects of arsenic exposure on human health, domestic manufacturers of wood preservatives voluntarily reduced their use of CCA. The phaseout applied to wood used for boardwalks, decks, fencing, gazebos, picnic tables, and play structures. 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). Beginning in 2004, the global arsenic market and domestic imports of arsenic declined in response to this voluntary ban.

The United States remained the world's leading consumer of arsenic, mainly for the production of CCA. Apparent domestic consumption for arsenic was about 5,280 t in 2007, a 29% decline from about 7,450 t in 2006, and far less than the apparent consumption of 21,600 t in 2003. The estimated value of arsenic compounds and metal consumed domestically in 2007 was approximately \$5.2 million. More than 50% of the arsenic, as arsenic trioxide, was used in the wood preservative industry for nonresidential use, down from about 90% prior to 2004. 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 is also used in glassmaking as a bubble dispersant or decoloring agent. There are no data available on the percentages of arsenic used in these traditional use categories.

Since ancient times, arsenic has been used to harden copper knives and other tools. When alloyed with lead and antimony, arsenic metal is now used to harden ammunition, 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 to babbitt metals that are used for bearings. Arsenic is also used in lead shot, and minor amounts may be added to lead and antimony for use in clip-on wheel weights.

Gallium arsenide (GaAs) semiconductors are used in lightemitting diodes and in semiconductors that are used in laser diodes and solar cells (Metal-Pages Ltd., 2006a). High-purity (99.9999%) arsenic metal is used for gallium-arsenide and indium-arsenide semiconductors that are used in computers and electronic devices. A mobile phone typically contains GaAs in its microelectronic circuitry, of which the arsenic content is less than 1 mg (International Precious Metals Institute, 2003). Arsenic may be used for germanium-arsenide-selenide or GaAs specialty optical materials. Indium-gallium-arsenide is used for short-wave infrared technology, and arsenic sulfide is one of several substrate materials that are used for optical thin films and interference coatings.

Based on reported consumption of gallium, U.S. consumption of arsenic metal in GaAs semiconductors was approximately 22 t in 2007, which was a decrease from a peak of about 40 t in 2000. The global GaAs industry continued to see application of its products in the automotive, defense optoelectronics, and wireless handset markets (Bosch, 2007).

Prices

In Europe, arsenic metal (minimum 99%) prices began the year at approximately \$2.26 per kilogram, were \$1.33 per kilogram in July, then rose to \$2.06 per kilogram in October, and by yearend the price was \$1.51 per kilogram (Metal-Pages Ltd., 2007f). In China, arsenic metal (minimum 99%) prices were approximately \$1.00 per kilogram at the beginning of January, then rose to \$2.33 per kg in April because of mine closures, and ended the year at \$1.88 per kilogram (Metal-Pages Ltd., 2007b, c, e).

In China, arsenic trioxide prices at the beginning of the quarter were \$450 per metric ton, then rose to \$550 per ton by March. By June, producers had focused on fulfilling their export contracts before cancellation of a 13% export tax that took place in August (Metal-Pages Ltd., 2007d). In October, one exporter reported a price of \$560 per ton, however, in general, the arsenic trioxide export market was generally sluggish, and export prices were approximately \$450 per ton by yearend (Metal-Pages Ltd., 2007a).

Foreign Trade

In 2007, domestic imports of arsenic compounds were 7,010 t contained arsenic, a decrease of approximately 26% compared with the 9,430 t (revised) contained arsenic in arsenic compounds imported in 2006. In 2007, Morocco was the source of 60% and China was the source of 35% of the arsenic imported into the United States. In 2007, the United States imported 759 t of arsenic metal, a 29% decrease compared with the 1,070 t imported in 2006. China was the leading source of arsenic metal in 2007 and provided 646 t, or 85%; however, this was a decrease of 32% compared with the 944 t that was imported from China in 2006. Arsenic metal was also imported from Japan (10%), Hong Kong (4%), and Germany (remainder).

Imports of arsenic trioxide from China into the United States decreased 60% to 3,260 t from 8,110 t in 2006. Because of the voluntary reduction in the use of CCA at yearend 2003, the total amount of arsenic trioxide imported by the United States in 2007 was 84% less than the 20,600 t of arsenic trioxide imported in 2003.

Exports of arsenic metal have increased dramatically since 2004. The export destinations for the 2,490 t of arsenic metal shipped from the United States in 2007 included the Republic of Korea (66%), Taiwan (12%), Guatemala (11%), and Japan (6%). Exported materials are classified by number in the Harmonized Tariff Schedule and this may have resulted in misclassification of exports. Exports classified as arsenic metal may include arsenic-containing "e-waste" such as computers and other electronics destined for reclamation and recycling (Grossman, 2005), transshipped arsenic metal used for production of small-arms ammunition (Agence France-Presse, 2005; Chicago Tribune, 2005), and arsenic alloyed with lead or another metal.

World Review

In 2007, 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 2007, China produced 25,000 t of arsenic trioxide and remained the world's leading producer followed by Chile (11,400 t), Morocco (8,950 t), and Peru (4,320 t). Arsenic trioxide is also produced in Mexico at the San Luis Potosi copper smelter (Southern Peru Corp., 2007). However, the overall Chinese arsenic market has weakened, and some Chinese producers have reduced or halted their production (Metal-Pages Ltd., 2007b, g). Arsenic was also produced in China as a byproduct of gold mining from orpiment and realgar, the more common ore minerals of arsenic (Peters and others, 2002, p. 182).

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 2007 and may have been stockpiled for future treatment. Production data for most countries are estimated and subject to revision.

Using advanced metallurgical techniques, 17 different metals, including arsenic, copper, gold, and silver were recycled from

connectors, circuit boards, and other metal scrap by Dowa Eco-System Co., Ltd., Japan, for reuse in electric substrates, films, and other electronics applications (Dowa-Eco-System Co., Ltd., 2007). Furakawa Denshi Co., Ltd., a Japanese company, developed technology to recover arsenic and gallium from used semiconductors and the company planned to recycle the arsenic to meet Japanese requirements for environmental protection (Metal-Pages Ltd., 2006b).

Outlook

The voluntary decision by the wood preservative industry to eliminate CCA as a wood preservative for certain wood products at yearend 2003 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 for automotive uses, military and space applications, solar cells, and telecommunications equipment. World sources of arsenic, as arsenic trioxide and arsenic metal become available from nonferrous metal processing, are expected to be sufficient to meet projected needs.

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TABLE 1 ARSENIC SUPPLY-DEMAND RELATIONS¹

(Metric tons of arsenic content)

	2003	2004	2005	2006	2007
U.S. supply:					
Imports:					
Metal	990	872	812	1,070	759
Compounds	20,800	6,150	8,330	9,430 ^r	7,010
Total	21,700	7,020	9,150	10,500 ^r	7,770
Distribution of U.S. supply:					
Exports ²	173	220	3,270	3,060	2,490
Apparent demand	21,600	6,800	5,870 ^r	7,450 ^r	5,280
Estimated U.S. use:					
Agricultural chemicals	860	850	NA	NA	NA
Glass	660	650	NA	NA	NA
Wood preservatives	19,200	4,450	NA	NA	NA
Nonferrous alloys and electronics	660	650	NA	NA	NA
Other	200	200	NA	NA	NA
Total	21,600	6,800	5,870 ^r	7,450 ^r	5,280

^rRevised. NA Not available.

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

	20	06	2007		
	Quantity	Value	Quantity	Value	
Class and country	(metric tons)	(thousands)	(metric tons)	(thousands)	
Arsenic trioxide:					
Belgium	369	\$268	267	\$178	
Bolivia	90	45	120	60	
Chile	110	40			
China	8,110	3,830	3,260	1,680	
Germany	64	241			
Hong Kong	329	178			
Morocco	3,320	1,370	5,580	2,220	
Spain	r	^r			
United Kingdom	. 14	53	(2)	4	
Total	12,400	6,020	9,220	4,140	
Arsenic acid:					
China	16	16			
France	6	33			
Germany			5	14	
Mexico	2	3			
Taiwan			7	14	
Total	24	52	12	28	
Arsenic sulfide, China	75	179	103	241	
Arsenic metal:					
China	944	1,290	646	1,750	
Germany	6	846	4	689	
Hong Kong	16	12	32	42	
Japan	84	1,470	77	927	
Thailand	. 19	15			
United Kingdom	4	11			
Total	1,070	3,640	759	3,410	

^rRevised. -- Zero.

 $^1\text{Data}$ are rounded to no more than three significant digits; may not add to totals shown. $^2\text{Less}$ than 1/2 unit.

Source: U.S. Census Bureau.

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

(Metric tons)

Country ⁴	2003	2004	2005	2006	2007
Belgium	1,000	1,000	1,000	1,000	1,000
Bolivia	276 5	168 5	120 5	240 ^r	200
Canada	250	250	250	250	250
Chile	11,600	11,500	11,700	11,700 ^r	11,400
China	40,000	30,000	30,000	30,000	25,000
France	r	^r	^r	^r	
Iran	275 5	89 ⁵	100	100	100
Japan	- 40	40	40	40	40
Kazakhstan	1,500	1,500	1,500	1,500	1,500
Mexico	1,729 5	1,829 5	1,664 5	1,595 ^{r, 5}	1,600
Morocco	- 6,872 ⁵	6,866 ⁵	8,939 ⁵	8,900 ⁵	8,950 ⁵
Peru ⁶	4,640 ^{r, 5}	3,037 ^{r, 5}	3,150 ^{r, 5}	4,399 ^{r, 5}	4,321 5
Portugal	25 ^r	15 ^r	15 ^r	15 ^r	15
Russia	- 1,500	1,500	1,500	1,500	1,500
Total	69,700 ^r	57,800 ^r	60,000 ^r	61,200 ^r	55,900

^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 April 1, 2008.

⁴Austria, Hungary, the Republic of Korea, Serbia and Montenegro, South Africa, Spain, 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.

⁶Output of Empresa Minera del Centro del Perú (Centromín Perú) as reported by the Ministerio de Energía y Minas.