



# 2012 Minerals Yearbook

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## BROMINE

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# BROMINE

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The United States remained one of three leading bromine producers in the world along with Israel and Jordan. World production of bromine for 2012, excluding the United States, was estimated to be 505,000 metric tons (t), compared with 481,000 t in 2011 (tables 1, 6). China, Israel, Jordan, the United States, and at least six other countries produced bromine. In 2012, bromine sold or used in the United States increased compared with that of 2011, but data were withheld to avoid disclosing company proprietary data.

Bromine is one of two elements that are liquid at room temperature and is found principally as a dissolved species in seawater, evaporitic (salt) lakes, and underground brines associated with petroleum deposits. Primary uses of bromine compounds were in chemical and pharmaceutical intermediates, drilling fluids, flame retardants (FRs), pesticides, pollution control, and water treatment.

## Production

Domestic production data for bromine were developed by the U.S. Geological Survey (USGS) from a voluntary canvass of the two U.S. producers—Albemarle Corp. and Chemtura Corp., both of which responded to the survey, represented 100% of total production (table 2). Production data collected by the USGS were withheld to avoid disclosing proprietary information (table 1).

Bromine was recovered from brine wells in Arkansas, where bromine is found in the Smackover Formation at a depth of about 2,400 meters with concentrations of 5,000 to 6,000 parts per million (ppm) bromine; by comparison, seawater contains 60 to 70 ppm bromine (Hill, 2010; Albemarle Corp., 2013b, p. 8). During 2012, Albemarle was working toward expanding bromine capacity at its operations in Magnolia, AR, by drilling additional brine wells, although the company did not report the expected capacity at the completion of the project (Albemarle Corp., 2012a, p. 9, 82).

After bromine processing, the spent brine is returned underground into the production formation by class V injection wells that are regulated by the U.S. Environmental Protection Agency (EPA). The chemical composition of the spent brine is generally similar to that of the original, except that the concentration of the target elements (such as bromine and magnesium) is reduced, and the concentration of other elements (such as calcium) may have increased through substitution (U.S. Environmental Protection Agency, 1999, p. 1–2, 5).

## Recycling

Some bromide solutions were recycled to obtain elemental bromine and to prevent the solutions from being disposed of as hazardous waste. Hydrogen bromide is emitted as a byproduct

from many organic reactions. This byproduct waste is recycled with virgin bromine brines and is a major source of bromine production. Plastics containing brominated FRs (BFRs) can be incinerated as a solid organic waste, and the bromine can be recovered (Frim and Ukeles, 2007).

## Consumption

The USGS did not collect consumption data on bromine compounds. Apparent consumption of bromine in the United States, calculated by the USGS from production plus imports minus exports, increased in 2012. The major consumption categories were, in order of magnitude, FRs, pharmaceuticals and agricultural chemicals, drilling fluids, rubber, and water treatment chemicals (Albemarle Corp., 2012a, p. 52). Other uses included butyl rubber, dyes, mercury emission control, photographic chemicals, and surfactants.

Estimated bromine consumption in BFRs was slightly less than 50%; BFRs are chemicals commonly used in many domestic and industrial appliances; electronic equipment, such as computers, mobile telephones, and televisions; and other items, such as furniture, insulation boards, mattresses, and textiles. About 90% of all electrical components contain BFRs.

Calcium bromide, sodium bromide, and zinc bromide, collectively referred to as clear brine fluids, were used in the oil- and gas-well-drilling industry for high-density, solids-free completion, packer, and workover fluids to reduce the likelihood of damage to the well bore and productive zone. These high-density fluids also help to prevent migration of fluids between underground formations through the well bore. Oil and gas drilling activity in the United States, measured by the number of wells completed, was higher in 2012 than in 2011, as a result of the expanded oil drilling on private and State lands (American Petroleum Institute, 2013).

Another major use of bromine is as a water purifier and disinfectant, which is an alternative to using chlorine. Brominated compounds are used for water treatment in hot tubs and swimming pools and to control algae and bacterial growth in industrial processes.

Bromine compounds are effective pesticides, used both as soil fumigants in agriculture, particularly fruit growing, and as a fumigant to prevent pests from attacking stored grain and fresh produce. World trade in agricultural goods depends on the use of bromine compounds to ensure compliance with mandatory quarantine rules. Bromine compounds also are used as intermediates to make other agricultural chemicals. Methyl bromide is the leading bromine-containing pesticide in the world, but its use was declining owing to the ban imposed by the 1987 Montreal Protocol, which classified it as a class I ozone-depleting substance. As part of the Montreal Protocol, wealthy countries were to stop using the pesticide by 2005;

however, the United States has received annual exemptions for crops and other critical uses (for example, cucumbers, melons, orchard replants, peppers, post-harvest uses, squash, strawberries, and tomatoes). The critical use exemption is for applications where no technically or economically feasible alternatives to methyl bromide exist. In 2012, the EPA authorized use of 1,023 t or 4.0% of the historic 1991 baseline consumption of methyl bromide for approved critical uses (U.S. Environmental Protection Agency, 2012, p. 29222). Use of methyl bromide also was allowed through a quarantine and preshipment exemption for agricultural commodities and lumber. Methyl bromide is a broad spectrum pesticide used in the control of nematodes, pathogens, pest insects, rodents, and weeds. Domestically, methyl bromide has proven to be difficult to replace because of its low cost and usefulness against a large variety of agricultural pests.

The use of bromine and bromine compounds to remove mercury from flue gas emissions at coal-fired electric powerplants was an expanding use for bromine. Inorganic bromine compounds, such as calcium bromide and sodium bromide, when mixed with coal at powerplants, react with mercury in combustion zones, forming mercury compounds that are captured in scrubbers, removing 90% of mercury liberated during combustion (Chemtura Corp., 2009). Southern Research Institute (Birmingham, AL) developed a system that converts calcium bromide to elemental bromine gas, which then reacts with mercury in coal-fired powerplant flue gas to form mercuric bromide, which is captured and retained in the powerplant's wet scrubbers (Southern Research Institute, undated).

## Transportation

Bromine in bulk quantities is transported in the United States in 7,570- and 15,140-liter (L) lead-lined pressure tank railcars or 6,435- to 6,813-L nickel-clad pressure tank trailers. The trailers must be filled at least 92% full to prevent inertia effects of the heavy liquid while on the highway. International shipments by The Dead Sea Bromine Group are in 15.2- to 23.3-t lead-lined tank containers (isotanks) with a volume of 5,300 to 8,000 L. For smaller quantities, lead-lined tanks (goslars) of 3.5 t (four tanks packed on one isoframe) and drums of 400 kilograms are used. Dry nitrogen gas is recommended for use in pressure transferring bromine, although dry air may be used. The gas used must be absolutely dry or severe corrosion results. When exposed to a high-humidity atmosphere, the water content of bromine can exceed 300 ppm. If the water content exceeds 70 ppm, the corrosiveness of bromine to many metals increases (Frim and Ukeles, 2007).

## Prices

Because the bromine industry has few producers, published price lists of bromine and bromine compounds were not available. Although companies typically announce price increases by percentage increase, they normally do not publish actual price data. Price increases were announced by product categories separately, typically as elemental bromine and hydrobromic acid, BFRs, or clear brine fluids. In 2011, Albemarle announced the global minimum price for elemental

bromine, delivered, to be \$4,500 per metric ton (Albemarle Corp., 2011), but no updated information was available in 2012. Chemtura announced a price increase for methyl bromide in February (Chemtura Corp., 2012b). Albemarle announced price increases for one of the company's BFRs in April and May and increased prices on clear brine fluids in December (Albemarle Corp., 2012b, c, d). No other pricing announcements were made during 2012.

Although not exactly the same as prices, average unit values of exported and imported bromine were an indication of price trends for bromine in 2012. The average value of exported elemental bromine, including cost, insurance, and freight, was \$2,670 per metric ton, a 39% increase from \$1,920 per ton in 2011. The average values of exported ethylene dibromide and methyl bromide increased by 20% and 63%, respectively. Unit values for imported bromine compounds varied greatly, with changes ranging from a 21% decrease to a 27% increase.

## Foreign Trade

Bromine exports were about 9% lower than those in 2011 (tables 1, 3). The value of exported elemental bromine and bromine compounds increased by 35% compared with that of 2011 because of price increases for bromine compounds imposed in 2011. Elemental bromine imports were about 58% higher than those of 2011, but total imports of bromine and bromine compounds were 12% higher. Overall, the import value for elemental bromine and bromine compounds increased by 12% in 2012.

## World Review

The U.S. share of world bromine production has decreased as other countries have strengthened their positions as world producers of elemental bromine. Israel, the United States, Jordan, China, Japan, and Turkmenistan, in descending order, had the leading bromine production capabilities in 2012, although none of these countries operated at capacity (tables 2, 5). Actual production did not necessarily reflect capacity.

**China.**—In China, bromine operations are in Shandong Province. In the past, many unlicensed bromine facilities operated in the area, but since 2006, the Shandong Provincial government and the Government of China had closed down unlicensed operations. Only six companies were thought to be licensed to produce bromine.

Bromine production capacity was available for only one company in China. For that reason, China's estimated bromine production is substantially higher than the capacity listed in table 5. Although specific information, by operation, was not available, the bromine operating capacity in China likely was about 150,000 metric tons per year (t/yr).

Gulf Resources, Inc., one of the leading bromine producers in China, announced the discovery of an underground brine deposit in Sichuan Province with six to seven times the bromine content of the deposits at which the company operates in Shandong Province. Further exploration was planned to delineate the size of the deposit and estimate the quantity of bromine contained in it (Gulf Resources, Inc., 2012).

**India.**—Chemtura announced an agreement to acquire the bromine assets of Solaris ChemTech Industries Ltd., the leading bromine producer in India. The purchase included two elemental bromine production operations, a facility that produces multiple bromine compounds, and a research and development center. Headquarters for the new unit were expected to be in New Delhi. Chemtura intended to expand the bromine units and implement proprietary technology to improve productivity and efficiency at the operations. In addition, the acquisition will expand Chemtura's presence in the region (Chemtura Corp., 2012a; Syrett, 2012).

**Israel.**—ICL Industrial Products (Tel Aviv) was one of the world's leading producers of elemental bromine, with approximately 40% of global capacity. In 2012, ICL produced 174,000 t of elemental bromine. ICL processes brines from the Dead Sea, which contain more than 10,000 ppm of bromine, a much higher concentration than the next richest source found in U.S. brine wells, which contain 5,000 to 6,000 ppm (Albemarle Corp., 2013b, p. 8).

**Jordan.**—Jordan Bromine Co. (a joint venture between Albemarle and Arab Potash Co.) on the Dead Sea continued its project to double elemental bromine capacity to 100,000 t/yr bromine. Although the first phase of the project was scheduled for completion in late 2012, the commissioning was delayed until early 2013. Completion of phase two to double bromine derivative capacity was expected by mid-2013 (Albemarle Corp., 2013a).

The Natural Resources Authority (NRA) of Jordan reported bromine production in 2011 to be 148,000 t (Natural Resources Authority, 2012, p. 29). Even when fully operational, the expansion project at Jordan Bromine was not expected to reach that level of elemental bromine production. No reports indicated that more than one bromine producer operated in Jordan, although the Government data indicated that Jordan may have become the world's leading bromine producer. Discrepancies between reported capacity and production estimates made by the NRA in 2008–11 and estimated production for 2012 possibly could be the result of double counting of bromine production and derivative compounds.

## Outlook

Between 40% and 50% of domestic consumption of bromine is for FRs. In 2012, demand for FRs, particularly in the construction and electronics industries, increased as the economy recovered. Although FR usage fluctuates along with overall cycles in the economy, world consumption of FRs is expected to increase, assuming sustained economic growth. Recycling efforts in Europe for BFR plastics in electrical usage, which are easier to recycle than some other FR compounds, may increase the demand for BFR products. Use of BFRs, however, will likely increase at a slower pace than FRs in general because of legislative mandates and customer demand for more environmentally friendly materials.

Increased demand for FRs would be driven by the use of FRs in developing countries as they begin to adopt more stringent flammability standards and begin to use more plastics. Countries in Asia and the Pacific region likely would be the leading consumers of FRs. Above-average gains in the demand for FRs

were expected to take place in Africa, Eastern Europe, the Middle East, and Latin America. More moderate growth in FR use was expected for markets in North America and Western Europe.

Bromine use in clear brine fluids is highly dependent on fluctuations in the oil and natural gas drilling industry. Consumption of clear brine fluids in crude oil and natural gas drilling was expected to increase as demand for these commodities increases. Expectations for drilling increasingly deep and high-pressure oil and gas formations, especially using deep water hydraulic fracturing techniques, increase the likelihood of greater demand for clear brine fluids (Albemarle, 2012a, p. 53).

Bromine water treatment chemical use was expected to show modest growth during the next several years. Bromine has been found to be safer than its substitutes in sanitary preparations because bromine has a higher biocidal activity level for the same volume of product. The use of bromine compounds was expected to continue increasing in the hot tub, spa, and swimming pool sector as a gentler disinfectant than chlorine. Global demand for water treatment products was projected to increase in developing markets, such as China and India, as a result of continued industrial expansion and increased efforts to expand access to safe water supplies.

Bromine use in photography is declining as digital imaging replaces film in consumer and professional photography. Most feature films for movie theater presentation are shot using printed film; however, the use of digital technology was expected to increase and overtake film in these applications during the next decade.

The market potential for bromide-based technologies to remove mercury emissions at coal-fired powerplants is an area of potential growth for the industry. Using bromide compounds for abatement of mercury emissions appears to be more cost effective compared with other materials, such as chlorine-, fluorine-, or iodine-base compounds. The EPA issued regulations for reducing mercury emissions at powerplants by an estimated 91% within 4 years of 2011, when the rule took effect, were likely to increase demand for bromine and bromine compounds for that application (U.S. Environmental Protection Agency, 2011).

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### Other

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TABLE 1  
SALIENT BROMINE STATISTICS<sup>1</sup>

(Metric tons and thousand dollars)

	2008	2009	2010	2011	2012
United States:					
Bromine sold or used: <sup>2</sup>					
Quantity	W	W	W	W	W
Value	W	W	W	W	W
Exports: <sup>3</sup>					
Quantity (Br equivalent)	9,640	6,130	8,150	7,150	6,430
Value	16,200	12,500	22,300	18,400	24,900
Imports for consumption: <sup>4,5</sup>					
Quantity (Br equivalent)	41,200	36,000	45,400	47,300 <sup>r</sup>	53,100
Value	97,300	81,000	88,900	104,000 <sup>r</sup>	116,000
Apparent consumption	W	W	W	W	W
World, production <sup>6</sup>	415,000	320,000 <sup>r</sup>	644,000 <sup>r</sup>	481,000 <sup>r</sup>	505,000

<sup>r</sup>Estimated. <sup>r</sup>Revised. W Withheld to avoid disclosing company proprietary data.

<sup>1</sup>Data are rounded to no more than three significant digits.

<sup>2</sup>Elemental bromine sold as such to nonproducers, including exports, or used by primary U.S. producers in preparing bromine compounds.

<sup>3</sup>Export values are free alongside ship.

<sup>4</sup>Source: U.S. Census Bureau or PIERS (see table 4).

<sup>5</sup>Import values are cost, insurance, and freight.

<sup>6</sup>Excludes U.S. production.

TABLE 2  
ELEMENTAL-BROMINE-PRODUCING PLANTS IN THE UNITED STATES IN 2012

State and company	County	Plant	Production source	Capacity <sup>1</sup> (thousand metric tons)
Arkansas:				
Albemarle Corp.	Columbia	Magnolia South	Well brines	NA
Do.	do.	Magnolia West	do.	NA
Do.	Union	Satellite plants	do.	NA
Total				148 <sup>2</sup>
Chemtura Corp.	do.	El Dorado Central and El Dorado South	do.	71 <sup>3</sup>
Do.	do.	Marysville West	do.	36
Do.	do.	Newell	do.	23
Total				59
Grand total				278

Do., do. Ditto. NA Not available.

<sup>1</sup>Actual production capacity is limited by brine availability.

<sup>2</sup>Cumulative capacity of Magnolia South, Magnolia West, and Satellite plants.

<sup>3</sup>Cumulative capacity of El Dorado Central and El Dorado South plants.

TABLE 3  
U.S. EXPORTS OF BROMINE AND BROMINE COMPOUNDS<sup>1,2</sup>

Compound	HTS <sup>3</sup> number	2011			2012		
		Gross weight (metric tons)	Br equivalent (metric tons)	Value <sup>4</sup> (thousands)	Gross weight (metric tons)	Br equivalent (metric tons)	Value <sup>4</sup> (thousands)
Elemental bromine	2801.30.2000	4,580	4,580	\$8,790	3,730	3,730	\$9,960
Other compounds:							
Ethylene dibromide	2903.31.0000	1,490	1,260	4,940	854	726	3,420
Methyl bromide	2903.39.1520	1,540	1,300	4,670	2,340	1,970	11,500
Grand total		7,610	7,150	18,400	6,930	6,430	24,900

<sup>1</sup>These data detail the information included in table 1 under "Exports."

<sup>2</sup>Data are rounded to no more than three significant digits; may not add to totals shown.

<sup>3</sup>Harmonized Tariff Schedule of the United States.

<sup>4</sup>Declared cost, insurance, and freight valuation.

Source: U.S. Census Bureau.

TABLE 4  
U.S. IMPORTS OF BROMINE AND BROMINE COMPOUNDS<sup>1,2</sup>

Compound	HTS <sup>3</sup> number	2011			2012			Principal sources in 2012
		Gross weight (metric tons)	Br equivalent (metric tons)	Value <sup>4</sup> (thousands)	Gross weight (metric tons)	Br equivalent (metric tons)	Value <sup>4</sup> (thousands)	
Elemental bromine	2801.30.2000	997	997	\$2,200	1,580	1,580	\$3,910	Israel, 54%; Jordan, 42%.
Inorganic bromine compounds:								
Ammonium bromide	2827.59.2500	37,200	30,300	49,600	48,700	39,700	67,800	Israel, 93%.
Calcium bromide <sup>5</sup>	2827.59.2500	3,350 <sup>r</sup>	2,680 <sup>r</sup>	7,170 <sup>r, e</sup>	327	261	551 <sup>e</sup>	Israel, 62%; China, 38%.
Potassium bromate	2829.90.0500	71	34	447	36	17	224	China, 100%.
Potassium bromide <sup>5,6</sup>	2827.51.0000	968	650	1,910 <sup>e</sup>	1,210	814	2,320 <sup>e</sup>	China, 86%.
Sodium bromate	2829.90.2500	746	395	3,110	1,080	571	4,370	China, 100%.
Sodium bromide <sup>5,6</sup>	2827.51.0000	7,530	5,850	11,100 <sup>e</sup>	7,420	5,760	11,800 <sup>e</sup>	Israel, 76%; China, 24%.
Organic bromine compounds:								
Decabromodiphenyl oxide and octabromodiphenyl oxide	2909.30.0700	3,690	2,950	15,500	2,600	2,080	13,900	Israel, 90%; China, 10%.
Dibromoneopentyl glycol <sup>5</sup>	2905.59.3000	--	--	--	19	11	75 <sup>e</sup>	Israel, 100%.
Ethylene dibromide	2903.31.0000	23	20	113	8	7	211	China, 95%.
Hydrobromic acid	2811.19.3000	2,110	2,080	3,600	1,250	1,240	2,550	Israel, 65%; France, 18%.
Methyl bromide	2903.39.1520	373	314	2,720	302	254	2,330	Israel, 73%; China, 20%.
Tetrabromobisphenol A	2908.19.2500	1,750	1,030	6,320	1,370	806	5,950	Israel, 93%.
Grand total		58,800 <sup>r</sup>	47,300 <sup>r</sup>	104,000 <sup>r</sup>	65,900	53,100	116,000	

<sup>e</sup>Estimated. <sup>r</sup>Revised. -- Zero.

<sup>1</sup>These data detail the information included in table 1 under "Imports for consumption."

<sup>2</sup>Data are rounded to no more than three significant digits; may not add to totals shown.

<sup>3</sup>Harmonized Tariff Schedule of the United States.

<sup>4</sup>Declared cost, insurance, and freight valuation.

<sup>5</sup>Source: PIERS.

<sup>6</sup>Potassium bromide and sodium bromide import data are reported under a common HTS number, 2827.51.0000.

Source: U.S. Census Bureau.

TABLE 5  
SELECTED WORLD BROMINE ANNUAL PLANT CAPACITIES AND SOURCES AS OF DECEMBER 31, 2012<sup>1</sup>

Country and company or plant	Location	Capacity (metric tons)	Source
Azerbaijan, Neftechala Bromine Plant	Baku	4,000	Underground brines.
China, Laizhou Bromine Works	Shandong	43,000	Do.
India:			
Hindustan Salts Ltd.	Jaipur	NA	Seawater bitterns from salt production.
Mettur Chemicals Ltd.	Mettur Dam	NA	Do.
Tata Chemicals Ltd.	Mithapur	NA	Do.
Total		1,500	
Israel, ICL Industrial Products	Sodom	280,000	Bitterns of potash production from surface brines.
Japan, Toyo Soda Manufacturing Co. Ltd.	Tokuyama	20,000	Seawater.
Jordan, Jordan Bromine Co. Ltd.	Safi	50,000	Bitterns of potash production from surface brines.
Spain, Derivados del Etilo S.A.	Villaricos	900	Seawater.
Turkmenistan:			
Cheleken Chemical Plant	Cheleken Region	4,740	Do.
Nebitdag Iodine Plant	Vyshka	2,370	Underground brines.
Ukraine, Perekop Bromine Plant	Krasnoperekopsk	3,000	Do.

Do. ditto. NA Not available.

<sup>1</sup>Excludes U.S. production capacity, which is detailed in table 2.

TABLE 6  
BROMINE: ESTIMATED WORLD PRODUCTION, BY COUNTRY<sup>1,2</sup>

(Metric tons)

Country <sup>3</sup>	2008	2009	2010	2011	2012
Azerbaijan	3,500	3,500	3,500	3,500	3,500
China	135,000	93,000 <sup>r</sup>	100,000 <sup>r</sup>	100,000 <sup>r</sup>	100,000
Germany <sup>4</sup>	1,680 <sup>5</sup>	985 <sup>5</sup>	1,500 <sup>5</sup>	1,900 <sup>r,5</sup>	1,500
India	1,500	1,500	1,500	1,500	1,500
Israel <sup>5</sup>	164,042	127,689	184,696	202,313 <sup>r</sup>	174,000
Japan	20,000	20,000	20,000	20,000	20,000
Jordan	85,000 <sup>5</sup>	69,000 <sup>5</sup>	329,000 <sup>5</sup>	147,988 <sup>r,5</sup>	200,000
Spain	-- <sup>r</sup>	-- <sup>r</sup>	-- <sup>r</sup>	-- <sup>r</sup>	--
Turkmenistan	150	150	150	150	150
Ukraine	4,416 <sup>5</sup>	4,121 <sup>5</sup>	4,100	4,100	4,100
United States <sup>6</sup>	W	W	W	W	W
Total	415,000	320,000 <sup>r</sup>	644,000 <sup>r</sup>	481,000 <sup>r</sup>	505,000

<sup>r</sup>Revised. W Withheld to avoid disclosing company proprietary data; not included in total. -- Zero.

<sup>1</sup>World totals, U.S. data, and estimated data are rounded to no more than three significant digits; may not add to totals shown.

<sup>2</sup>Table includes data available through September 27, 2013.

<sup>3</sup>In addition to the countries listed, several other nations, including Iran, were thought to produce bromine, but output data were not reported; available general information is inadequate to formulate reliable estimates of output levels.

<sup>4</sup>Includes bromides and oxides.

<sup>5</sup>Reported figure.

<sup>6</sup>Sold or used by producers.