2014 Minerals Yearbook

BROMINE [ADVANCE RELEASE]

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Bromine

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The United States was one of four leading bromine producers in the world along with China, Israel, and Jordan. World production of bromine in 2014, excluding the United States, was estimated to be 441,000 metric tons (t) compared with 416,000 t in 2013 (tables 1, 6). In 2014, bromine sold or used in the United States increased compared with 2013, 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. In addition, bromine is an essential element for life and is a requirement for tissue development (McCall and others, 2014). The primary uses for bromine compounds include brominated flame retardants (BFRs), drilling fluids, and water treatment. Other applications include chemical and pharmaceutical intermediates, dyes, perfumes, pesticides, photographic chemicals, and pollution control.

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, representing 100% of total production. Production data collected by the USGS were withheld to avoid disclosing proprietary information, but capacity data for both producers were provided (table 2).

In the United States, 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., 2013, p. 8).

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).

Environment

Methyl bromide is the leading bromine-containing pesticide in the world, but its use has been 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, developed 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. For 2014, the EPA authorized use of 442 t, or 1.7% of the historic 1991 baseline consumption of methyl bromide, for approved critical uses (U.S. Environmental Protection Agency, 2014b, p. 44305). This is a decrease from the 2013 authorized use of 562 t (U.S. Environmental Protection Agency, 2013, p. 43801). 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. However, alternatives to methyl bromide do exist and vary by the benefits needed for a particular crop. The U.S. Department of Agriculture continues to research alternatives that are environmentally, technically, and economically feasible (U.S. Department of Agriculture, 2011).

In June 2014, the EPA released its final report of recommended alternatives for hexabromocyclododecane (HCBD), a BFR, following a 4-year review. HCBD is primarily used as a flame retardant in polystyrene building insulation foams. After identifying many chemicals as potential alternatives, the EPA identified three viable alternatives to HBCD, all of which were brominated. Of those, a butadiene styrene brominated copolymer was found to have the lowest hazard in terms of human health effects (U.S. Environmental Protection Agency, 2014a, p. iii, vi). The Stockholm Convention on Persistent Organic Pollutants voted in 2013 for a global ban of HBCD, which the European Union's toxics program had already classified as a "substance of very high concern" and called for its phaseout by 2015 (Stokstad, 2013).

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 BFRs can be safely incinerated as a solid organic waste, and the bromine can be recovered (Frim and Ukeles, 2007; Bromine Science and Environmental Forum, undated).

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 2014. In recent years, the leading application of bromine has been for the production of BFRs (46%), followed by clear brine fluids (16%) and water treatment (6%) (IHS Inc., 2014).

BFRs are commonly used in many household and industrial appliances; electronic equipment, such as cases for 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.

Another major use of bromine is as a water purifier and disinfectant, as an alternative to 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 also effective pesticides, used both as soil fumigants in agriculture, particularly fruit growing, and as fumigants 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. Additionally, bromine compounds are used as intermediates to make other agricultural chemicals.

Bromine and bromine compounds are also used to remove mercury from flue gas emissions at coal-fired electric powerplants (Vosteen and others, 2005). 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; Fielding, 2012). 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 is transported in bulk quantities 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 volumes 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 pressurizing bromine during transfer, 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 April 2014, Chemtura announced a price increase of up to $0.30 per kilogram for its tetrabromobisphenol A (TBBA) flame retardant for all regions and in August, as much as a 20% price increase for elemental bromine in the Asia Pacific region (Chemtura Corp., 2014b, c). In November, Israel Chemicals Ltd. (ICL) (Tel Aviv, Israel) increased its prices for elemental bromine and hydrobromic acid to their customers in the Far East by 20% (Israel Chemicals Ltd., 2014).

Notwithstanding price increases for specific products or markets, average unit values of exported and imported bromine were an indication of price trends for bromine in 2014. The average value of exported elemental bromine, including cost, insurance, and freight, was $2,599 per metric ton, a 41% increase from $1,847 per metric ton in 2013. There was no significant change in the average value of exported ethylene dibromide in 2014, and the average value of exported methyl bromide decreased by 15% (table 3). The values for imported bromine compounds varied greatly including a 66% decrease in the average value of ethylene dibromide and a 27% increase in the imported value of TBBA (table 4).

Changes in the average imported and exported values of particular bromine compounds corresponded with their applications. For example, the decrease in the average price of imported ethylene dibromide mirrors the continuing decrease in its uses. Ethylene dibromide is highly toxic to humans and had been primarily used as an antiknock additive in leaded gasoline and as a fumigant. Following the ban of ethylene dibromide as a soil and grain fumigant in 1984 and the complete ban of leaded gas by 1996, it was approved for only limited uses including the treatment of felled logs for bark beetles and termites or as an intermediate for dyes, resins, waxes, and gums (Agency for Toxic Substances and Disease Registry, 1992, p. 1, 84; U.S. Environmental Protection Agency, 1996, p. 28763). Additionally, the increase in the average value of imported TBBA, one of the most widely used BFRs, reflected the steady demand for BFRs in the manufacture of electronics.

Foreign Trade

In terms of bromine content, total bromine exports in 2014 were about 6% lower than those in 2013; however, the value of exported elemental bromine and bromine compounds increased by 19% compared with that of 2013 (tables 1, 3). Total imports

of bromine and bromine compounds increased by 63% during the same period, with a 38% increase in value from that of 2013 (tables 1, 4). In particular, imports of calcium bromide were six times greater than those of 2013, and sodium bromide and potassium bromide imports were more than double. These compounds, which also increased their share of total imported bromine materials to 20% compared to 13% in 2013, are commonly used as dense, clear brine drilling fluids and for mercury flue gas removal. Ammonium bromide, commonly used as a BFR, remained the dominant imported bromine product, in terms of quantity, accounting for approximately 71% of imported materials in 2014.

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. In 2014, China, Israel, Jordan, and the United States led in bromine production capacity (tables 2, 5). Actual production did not necessarily reflect capacity (tables 5, 6).

China.—In China, bromine operations were in Shandong Province. In the past, many unlicensed bromine facilities operated in the area, but the Shandong Provincial government and the Government of China have closed down many small, unlicensed operations (Gulf Resources, Inc., 2010).

Because bromine production capacity was available for only one company in China, estimated production listed in table 6 is substantially higher than the capacity listed in table 5. Gulf Resources, Inc., the leading bromine producer in China, produced approximately 20% of all bromine consumed in China (Gulf Resources, Inc., 2014b). The company operated more than 4,000 brine wells, with combined production capacity of 46,300 metric tons per year, on leased land with 50-year mineral rights (Gulf Resources, Inc., 2014a). For its 2014 fiscal year, Gulf Resources announced a 4% decrease in bromine revenue compared with that of 2013, which was attributed to lower prices (Gulf Resources, Inc., 2015).

Israel.—ICL Industrial Products (Tel Aviv) processed brines from the Dead Sea and was a world leader in the production of elemental bromine with an estimated production of 190,000 t in 2014 (table 6). In August, Albemarle Corp. and ICL entered into a joint venture for manufacturing ICL's FR–122P polymeric flame retardant and Albemarle's GreenCrest™ polymeric flame retardant, which were designed to replace HBCD. The partners will own and operate a 2,400-metric-ton-per-year (t/yr) plant in the Netherlands, which ICL was currently operating, and a 10,000-t/yr plant in Israel, which opened in late 2014 (Albemarle Corp., 2014; Bloomberg Business, 2014). In October, Israel's Committee for the Review of Policy with Respect to Royalties on Natural Resources, commonly referred to as the Sheshinski II Committee, recommended a progressive tax on profits from the development of the country's natural resources. The goal of the surtax (a tax on excess profits) was to share a portion of the proceeds from natural resources with the people of Israel (Udasin, 2014). The Committee's final report recommended a surtax of 25% after a company reached an annual profit of 14% and a surtax of 42% when the annual return was greater than 20%. Following the final recommendations from the Sheshinski II Committee, ICL responded by freezing a $1 billion investment program, warned that the new policy might result in a reduced workforce, and claimed the surtax would limit its ability to invest in the Negev region, thereby greatly affecting the local economy (Globes, 2014; Udasin, 2014). In late November, however, ICL postponed the layoff of 144 employees and began negotiations with workers for a streamlining plan at the company (Azulai, 2014).

Jordan.—Jordan produced an estimated 100,000 t of bromine in 2014 (table 6). Jordan Bromine Co. (JBC), a joint venture between Albemarle and Arab Potash Co., processed 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., 2013, p. 8).

Outlook

Worldwide, BFRs account for the largest consumption of bromine with domestic and international fire safety standards regulating the flammability of construction, home furnishing, and electronic products. However, environmental and toxicological questions regarding particular BFR products continued to be assessed in 2014. Additionally, fire safety standards were amended in the State of California in January. In response to the new standards, Chemtura filed a lawsuit in the Superior Court of California claiming that the "smolder-only" test for upholstered furniture in California weakened fire safety standards (Chemtura Corp., 2014a; State of California, Department of Consumer Affairs, 2013). Questions of fire safety as well as environmental and human health concerns in relation to BFRs likely will continue to be tested in coming years.

Bromine use in clear brine drilling fluids is highly dependent on fluctuations in the natural-gas- and oil-drilling industry. As such, demand for clear brine fluids for oil and gas drilling was strong in 2014 owing to worldwide increases in the number active drilling rigs (Baker Hughes Inc., 2015; U.S. Energy Information Administration, 2014). However, a future decrease in crude oil prices and the number of active drilling rigs would likely lessen demand for clear brine drilling fluids.

Use of bromine in chemical water treatment is expected to show modest growth during the next several years. Bromine has been found to be safer than its substitutes in sanitary preparations and has a higher biocidal activity level for the same volume of product. The use of bromine compounds is expected to continue to increase in the hot tub, spa, and swimming pool sector as a gentler disinfectant than chlorine. Global demand for water treatment products is 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.

The market 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.

These regulations are likely to increase demand for bromine and bromine compounds for that application (U.S. Environmental Protection Agency, 2011).

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

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TABLE 1
SALIENT BROMINE STATISTICS[1]

(Metric tons and thousand dollars)

	2010	2011	2012	2013	2014
United States:					
Bromine sold or used:[2]					
Quantity	W	W	W	W	W
Value	W	W	W	W	W
Exports:[3]					
Quantity (Br equivalent)	7,950 r	6,800 r	6,400 r	7,860 r	7,400
Value	21,400 r	18,100 r	24,700 r	23,200 r	27,600
Imports for consumption:[4, 5]					
Quantity (Br equivalent)	45,400	47,500 r	53,600	36,700 r	59,800
Value	91,900 r	107,000 r	121,000	88,800 r	123,000
Apparent consumption	W	W	W	W	W
World, production[e, 6]	371,000	389,000	370,000	416,000 r	441,000

[e]Estimated. [r]Revised. W Withheld to avoid disclosing company proprietary data.
[1]Data are rounded to no more than three significant digits.
[2]Elemental bromine sold as such to nonproducers, including exports, or used by primary U.S. producers in preparing bromine compounds.
[3]Export values are free alongside ship.
[4]Source: U.S. Census Bureau and PIERS.
[5]Import values are cost, insurance, and freight.
[6]Does not include U.S. production.

TABLE 2
ELEMENTAL-BROMINE-PRODUCING PLANTS IN THE UNITED STATES IN 2014

State and company	County	Plant	Production source	Capacity[1] (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 [2]
Chemtura Corp.	do.	El Dorado Central and El Dorado South	do.	71 [3]
Do.	do.	Marysville West	do.	59
Grand total				278

Do., do. Ditto. NA Not available.
[1]Actual production capacity is limited by brine availability.
[2]Total capacity of Magnolia South, Magnolia West, and Satellite plants.
[3]Total capacity of El Dorado Central and El Dorado South plants.

TABLE 3
U.S. EXPORTS OF BROMINE AND BROMINE COMPOUNDS[1]

Compound	HTS[2] number	2013 Gross weight (metric tons)	2013 Br equivalent (metric tons)	2013 Value[3] (thousands)	2014 Gross weight (metric tons)	2014 Br equivalent (metric tons)	2014 Value[3] (thousands)
Elemental bromine	2801.30.2000	5,420 r	5,420 r	$10,000 r	3,420	3,420	$8,890
Other compounds:							
Ethylene dibromide	2903.31.0000	532	453	2,080	135	115	526
Methyl bromide	2903.39.1520	2,360	1,990	11,100	4,590	3,860	18,200
Grand total		8,310 r	7,860 r	23,200 r	8,150	7,400	27,600

[r]Revised.
[1]Data are rounded to no more than three significant digits; may not add to totals shown.
[2]Harmonized Tariff Schedule of the United States.
[3]Declared cost, insurance, and freight valuation exports are free alongside ship.

Source: U.S. Census Bureau.

TABLE 4

U.S. IMPORTS OF BROMINE AND BROMINE COMPOUNDS[1]

Compound	HTS[2] number	2013 Gross weight (metric tons)	2013 Br equivalent (metric tons)	2013 Value[3] (thousands)	2014 Gross weight (metric tons)	2014 Br equivalent (metric tons)	2014 Value[3] (thousands)	Principal sources in 2014
Elemental bromine	2801.30.2000	2,600	2,600	$7,850	2,050	2,050	$6,160	Israel, 99%.
Inorganic bromine compounds:								
Ammonium bromide	2827.59.2500	31,500	25,700	47,900	52,300	42,700	69,500	Israel, 96%.
Calcium bromide[4]	2827.59.2500	418 r	334 r	788 r	2,720	2,170	5,120	Brazil, 47%; Israel, 53%.
Potassium bromate	2829.90.0500	53	25	330	34	16	213	China, 100%.
Potassium bromide[4, 5]	2827.51.0000	644	432	1,330	1,380	926	2,380	China, 99%.
Sodium bromate	2829.90.2500	895	474	3,350	1,140	601	4,540	China, 99%.
Sodium bromide[4, 5]	2827.51.0000	4,960	3,850	7,860	11,200	8,690	19,300	Israel, 78%; China, 17%.
Organic bromine compounds:								
Decabromodiphenyl oxide and octabromodiphenyl oxide	2909.30.0700	662	546	2,930 r	506	417	2,260	China, 92%.
Dibromoneopentyl glycol	2905.59.3000	942	557	5,340 r	935	553	4,950	Israel, 79%; China, 21%.
Ethylene dibromide	2903.31.0000	7	6	145	36	31	255	China, 94%.
Hydrobromic acid	2811.19.3000	986	974	2,740	1,050	1,040	2,810	Israel, 90%.
Methyl bromide	2903.39.1520	394	332	2,240	172	145	859	Israel, 100%.
Tetrabromobisphenol A	2908.19.2500	1,490	873	5,950	889	523	4,540	Israel, 84%; China, 16%.
Grand total		45,500 r	36,700 r	88,800 r	74,400	59,800	123,000	

[r]Revised.

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

[2]Harmonized Tariff Schedule of the United States.

[3]Declared cost, insurance, and freight valuation.

[4]Source: PIERS.

[5]Potassium bromide and sodium bromide import data are reported under a common HTS number.

Source: U.S. Census Bureau.

TABLE 5

SELECTED WORLD BROMINE ANNUAL PLANT CAPACITIES AND SOURCES AS OF DECEMBER 31, 2014[1]

Country and company or plant	Location	Capacity (metric tons)	Source
China, Gulf Resources, Inc.	Shandong	46,300	Underground brines.
India:			
Hindustan Salts Ltd.	Kharaghoda	1,350	Seawater bitterns from salt production.
Solaris ChemTech Industries, Ltd.	Khavda	NA	Do.
Tata Chemicals Ltd.	Mithapur	150	Do.
Total		NA	
Israel, ICL Industrial Products	Sodom	280,000	Bitterns of potash production from surface brines.
Japan, Tosoh Corp.	Tokuyama	24,000	Seawater.
Jordan, Jordan Bromine Co. Ltd.	Safi	100,000	Bitterns of potash production from surface brines.
Turkmenistan:			
Cheleken Chemical Plant	Cheleken Region	NA	Seawater.
Nebitdag Iodine Plant	Vyshka	NA	Underground brines.
Ukraine, Perekop Bromine Plant	Krasnoperekopsk	NA	Do.

Do. ditto. NA Not available.

[1]Does not include U.S. production capacity.

TABLE 6

BROMINE: ESTIMATED WORLD PRODUCTION, BY COUNTRY[1, 2]

(Metric tons)

Country[3]	2010	2011	2012	2013	2014
Azerbaijan	3,500	3,500	3,500	3,500	3,500
China	100,000	100,000	105,000	110,000	110,000
Germany[4]	1,500 [5]	1,600	1,600	1,500	1,500
India	1,600	1,600	1,700	1,700	2,100
Israel	184,696 [5]	202,313 [5]	173,940 [5]	184,943 [r, 5]	190,000
Japan	25,000	25,000	30,000	30,000	30,000
Jordan	50,000	50,000	50,000	80,000	100,000
Turkmenistan	445	460	480	500	500
Ukraine	4,100	4,100	4,100	4,100	3,500
United States	W	W	W	W	W
Total[6]	371,000	389,000	370,000	416,000 [r]	441,000

W Withheld to avoid disclosing company proprietary data; not included in total.

[1]World totals and estimated data are rounded to no more than three significant digits; may not add to totals shown.

[2]Includes data available through June 1, 2015.

[3]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.

[4]Includes bromides and oxides.

[5]Reported figure.

[6]Does not include U.S. production.