

2006 Minerals Yearbook

BROMINE

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Primary uses of bromine compounds were in flame retardants (FRs), drilling fluids, brominated pesticides (mostly methyl bromide), and water-treatment chemicals. World production of bromine, in descending order and percentage of total, for 2006 was estimated to be as follows: United States, 45%; Israel, 33%; Jordan, 9%; China, 8%; and other countries, 5% (table 5). Bromine is one of two elements that are liquid at normal temperatures. Bromine is found principally in seawater, salt lakes, and underground brines associated with oil. In 2006, the quantity of bromine sold or used in the United States was 243,000 metric tons (t) valued at \$339 million (table 1). The average value of bromine sold or used was \$1.39 per kilogram (table 1).

Production

Domestic production data for bromine were developed by the U.S. Geological Survey (USGS) from a voluntary canvass of the three U.S. producers. All of the eight operations to which a canvass form was sent responded (table 2).

Bromine was recovered from brine wells in Arkansas and Michigan. In Arkansas, brine is found in the Smackover Formation at a depth of about 2,400 meters with concentrations of 4,000 to 5,000 parts per million (ppm) bromine. Brines in Michigan have an average bromine content of 2,500 ppm.

After bromine processing, the spent brine was 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).

However, The Dow Chemical Company closed its bromine recovery facility Mason County, MI, in December.

In December, TETRA Technologies, Inc., one of the leading consumers of clear brine fluids (CBRS) in the world, entered into a 23-year bromine supply agreement with Chemtura Corporation, after the closure of the Dow plant in Michigan, which had supplied TETRA recovered bromine. As part of the agreement, TETRA will invest in Chemtura's bromine operations. TETRA owns a calcium bromide plant near Magnolia, AR, that has been closed since 1988 and has about 13,400 hectares of bromine-containing brine reserves under lease near the plant. In early 2006, TETRA announced plans to reopen the Magnolia plant to recover bromine from brine reserves. However, the project was shelved after determining

that it would have taken 18 to 24 months to reconfigure the plant and the plant incurred substantial capital costs (TETRA Technologies, Inc., 2007, p. 5-6).

Recycling

Hydrogen bromide is emitted as a byproduct in many organic reactions. This byproduct waste is recycled with virgin bromine brines and is a major source of bromine production. Bromine contained in plastics, such as FRs, 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, exports, and imports, remained at an estimated 275,000 t. The United States was the world's leading market for bromine. The major consumption categories, in order of magnitude, were FRs, drilling fluids, water treatment, and pesticides. Other uses included butyl rubber, dyes, pharmaceuticals, surfactants, and photographic chemicals.

It was estimated that about 50% of the consumption of bromine was used in brominated FRs (BFR) chemicals commonly used in many domestic and industrial appliances and such equipment as computers, furniture, insulation boards, mattresses, mobile phones, televisions, textiles, and many others. About 90% of all electrical components contain BFRs.

Bromine compounds are used as a constituent of antiknock fluid in leaded fuel still used in small aircraft, farm equipment, and in third world countries.

Calcium bromide, sodium bromide, and zinc bromide, collectively referred to as clear brine fluids (CBFs), were used in the oil- and gas-well-drilling industry for high-density, solidsfree completion, packer, and workover fluids to reduce the likelihood of damage to the well bore and productive zone.

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 other produce. World trade in agriculture goods depends on the use of bromine compounds to ensure compliance with mandatory quarantine rules. Bromine compounds are also used as intermediates to make other agriculture chemicals. Methyl bromide is the leading bromine-containing pesticide in the world, but its use is 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;

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however, the United States has received annual exemptions for critical use on certain crops, such as peppers, strawberries, and tomatoes. Methyl bromide is a broad spectrum pesticide used in the control of nematodes, pathogens, pest insects, rodents, and weeds. Domestically, methyl bromide had proven to be difficult to replace because of its low cost and usefulness against a large variety of agricultural pests.

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 cylinders 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 highhumidity atmosphere, the water content of bromine can exceed 300 ppm. If the water content increases above 70 ppm, then the corrosiveness of bromine to many metals increases (Frim and Ukeles, 2007).

Prices

U.S. bromine prices were significantly higher in 2006 than those in 2005. The average unit value of bromine sold or used, as reported by Albemarle and Chemtura, increased to \$1.39 per kilogram in 2006 from \$0.74 per kilogram in 2005 (table 1). Both companies announced price increases for bromine and bromine compounds in the last quarter of 2006. Albemarle increased its minimum price for bulk elemental bromine to \$2,970 per metric ton delivered (Albemarle Corporation, 2006). Chemtura raised its price by 20%, but did not quote a price (Chemtura Corporation, 2006). Included in the compounds were clear brines and brine components used as oilfield completion, drill-in, and workover fluids. The price increase was the result of a rise in cost of energy, key raw materials, regulatory compliance, and transportation.

The export unit value of elemental bromine decreased by 18% in 2006. The export unit value of bromine compounds, including ethylene dibromide and methyl bromide, increased by 19% during 2006 (table 1).

The import unit value of elemental bromine increased by 98% compared with that of 2005. The import unit values of bromine compounds increased, except those for calcium bromide and potassium bromate, which decreased slightly (table 3).

World Review

Israel.—CL Industrial Products (ICL-IP) (a business unit of Israel Chemicals Ltd.), expanded its annual bromine production capacity to 250,000 metric tons per year (t/yr) from 210,000 t/yr

by removing bottlenecks in its facilities in Sdom, Israel. ICL-IP recovers bromine from Dead Sea brines (Israel Chemicals Ltd., 2006).

Outlook

Between 40% and 50% of domestic demand for bromine is for FRs. Although FR usage fluctuates along with overall cycles in the economy, assuming sustained economic growth, world consumption of FRs was expected to grow by 4% per year. 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 because they are thought to be more environmentally friendly, especially by countries concerned with recycling, such as Japan. Growth was expected to increase in BFRs overall as the Consumer Product Safety Commission approves fire safety standards for upholstered furniture in the United States and if higher flammability standards are voluntarily adopted for televisions in Europe.

Overall global consumption for bromine was expected to grow at an average annual rate of 1.6% through 2010 (Frim and Ukeles, 2007). The Fredonia Group forecast FR value to grow in the United States by 6.5% per year through 2008 with volumes rising by 3.2% per year to more than 453,600 t.

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, digital technology will likely replace film in these applications during the next decade.

Bromine use in CFBs is highly dependent on fluctuations in the oil and gas drilling industry. This use was expected to grow at 3% to 4% per year through 2010 based on projections of increased oil and gas exploration (Frim and Ukeles, 2007).

Bromine water treatment chemical use was expected to show modest growth during the next several years. Bromine was used in both residential and commercial swimming pools, hot tubs, and whirlpools. In addition, bromine was used to treat industrial cooling water. 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.

References Cited

Albemarle Corporation, 2006, Albemarle to raise prices of elemental bromine: Albemarle Corporation press release, October 10, 1 p.

Chemtura Corporation, 2006, Chemtura to raise elemental bromine pricing: Chemtura Corporation press release, December 8, 1 p.

Frim, R., and Ukeles, S.D., 2007, Bromine: Mining Journal, v. 59, no. 6, June,

Israel Chemicals Ltd., 2006, ICL Industrial Products announces significant addition to its bromine production capacity: Israel Chemicals Ltd. press release, April 11, 1 p.

TETRA Technologies, Inc., 2007, Form 10K—2006: Securities and Exchange Commission, 114 p.

U.S. Environmental Protection Agency, 1999, The class V underground injection control study—Spent brine flow wells: U.S. Environmental Protection Agency EPA/816-R-99-014i, 27 p.

Other

U.S. Geological Survey Publications

Bromine. Ch. in Mineral Commodity Summaries, annual. Evaporites and Brines. Ch. in United States Mineral Resources, Professional Paper 820, 1973.

Bromine. Ch. in Mineral Facts and Problems, U.S. Bureau of Mines Bulletin 675, 1985.

Bromine Science and Education Forum.

${\it TABLE~1}$ SALIENT BROMINE AND BROMINE COMPOUNDS STATISTICS 1

(Metric tons and thousand dollars)

	HTS ² number	2002	2003	2004	2005	2006
United States:						
Bromine sold or used: ³						
Quantity		222,000	216,000	222,000	226,000	243,000
Value		166,000	155,000	191,000	168,000	339,000
Apparent consumption		232,000	256,000	274,000	277,000	275,000
Exports: ^{4, 5}						
Elemental bromine:	2801.30.2000					
Quantity		6,070	2,280	2,840	2,710	4,320
Value		4,680	3,090	2,070	3,990	5,180
Bromine compounds: ^{4, 6}		,	,	,	*	
Gross weight		8,000	7,160	7,850	8,130	9,430
Contained bromine		6,750	6,040	6,600	6,830	7,920
Value		13,600	11,800	13,800	12,800 ^r	17,600
		13,000	11,000	13,600	12,000	17,000
Imports: ^{4,7}	2001 20 2000					
Elemental bromine:	2801.30.2000	2.020	4.020	2.650	2.740	207
Quantity		2,020	1,920	2,650	2,740	807
Value		1,530	1,450	2,000	2,300	1,340
Bromine compounds:	2027 50 2500					
Ammonium bromide:	2827.59.2500					
Gross weight		17,800 ^r	46,600	59,700 ^r	58,200	37,200
Contained bromine		14,500 ^r	38,000 ^r	48,700 ^r	47,500 ^r	30,300
Value		9,050 ^r	21,100	27,400 ^r	30,400	43,600
Calcium bromide:	2827.59.2500					
Gross weight		164	9		922 8	4,350 8
Contained bromine		131	7		727 ^r	3,500
Value		100 e	4 e		645 r, c	3,000
Potassium bromate:	2829.90.0500					
Gross weight		76 ^{r, 8}	36 ^r	54	122	103
Contained bromine		40 ^r	19 ^r	26	58	50
Value		248 ^r	111 ^r	163	394	328
Potassium bromide:9	2827.51.0000					
Gross weight		171 8	497	598	434 8	159 8
Contained bromine		115	334	401	291	107
Value ^e		417	1,210	1,800	1,310	500
Sodium bromate:	2829.90.2500					
Gross weight		1,020	967	992	950	852
Contained bromine		539	512	525	503	451
Value		2,020	2,010	1,930	1,800 r, e	1,850
Sodium bromide:9	2827.51.0000					
Gross weight ⁸		2,980	3,670	4,610	4,530 ^r	4,750
Contained bromine		2,320	2,940	3,580	3,520 ^r	3,690
Value ^e		4,600	5,660	5,300	5,400 ^r	7,100
Other compounds:						
Gross weight ¹⁰		4,920	5,460 ^r	7,140 ^r	6,090 ^r	6,800
		3,620 ^r	4,140 ^r	5,780 ^r	4,870 °	5,300
Contained bromine		3,020	4,140	5,700	T,070	
		10,800 ^r	12,600 ^r	13,500 ^r	13,500 ^r	23,400

See footnotes at end of table.

TABLE 1—Continued SALIENT BROMINE AND BROMINE COMPOUNDS STATISTICS¹

 ${\it TABLE~2}$ ELEMENTAL-BROMINE-PRODUCING PLANTS IN THE UNITED STATES IN 2006

State and company Arkansas:	County	Plant	Production source	Capacity ¹ (thousand metric tons)
Albemarle Corporation	Columbia	Magnolia South	Well brines	(2)
Do.	do.	Magnolia West	do.	(2)
Do.	Union	Satellite plant	do.	148 ²
Chemtura Corporation	do.	El Dorado Central	do.	(3)
Do.	do.	El Dorado South	do.	71 3
Do.	do.	Marysville West	do.	36
Do.	do.	Newell	do.	23
Michigan, The Dow Chemical Company	Mason	Ludington ⁴	do.	9
Total				287

¹Actual production capacity is limited by brine availability.

^eEstimated. ^rRevised. -- Zero.

¹Data are rounded to no more than three significant digits.

²Harmonized Tariff Schedule of the United States.

³Elemental bromine sold as such to nonproducers, including exports, or used by primary U.S. producers in preparing bromine compounds.

⁴Source: U.S. Census Bureau.

⁵Export values are free alongside ship.

⁶Includes methyl bromine and ethylene dibromide.

⁷Import values are cost, insurance, and freight.

⁸Source: The Journal of Commerce Port Import/Export Reporting Service.

 $^{^9}$ "Potassium bromide" and "Sodium bromide" import data are reported by a mutual HTS number, 2827.51.0000.

 $^{^{10}}$ Data for these compounds are detailed in table 3.

²Cumulative capacity of Magnolia South, Magnolia West, and satellite plants.

³Cumulative capacity of El Dorado Central and El Dorado South plants.

⁴Bromine produced at this plant was reprocessed in Arkansas. Plant was closed on December 31, 2006.

 $\label{eq:table 3} \text{U.S. IMPORTS OF OTHER BROMINE COMPOUNDS}^{1,\,2}$

		2005		2006		
	HTS ³	Gross weight	Value ⁴	Gross weight	Value ⁴	
Compound	number	(metric tons)	(thousands)	(metric tons)	(thousands)	Principal sources, 2006
Hydrobromic acid	2811.19.3000	222	\$286	240	\$347	Israel, 96%; other, 4%.
Ethylene dibromide	2903.30.0500	499	337	103	764	Israel, 100%.
Methyl bromide	2903.30.1520	327	1,620	235	1,140	Israel, 100%.
Dibromoneopentyl glycol	2905.50.3000	r	r			Israel, 99%.
Tetrabromobisphenol A	2908.10.2500	414	1,480	930	3,780	Israel, 96%; India, 2%; Japan, 2%.
Decabromodiphenyl oxide and						
octabromodiphenyl oxide	2909.30.0700	4,630	9,790	5,290	17,300	Israel, 99%; other, 1%.
Total		6,090 ^r	13,500 ^r	6,800	23,400	_

^rRevised. --Zero.

Source: U.S. Census Bureau.

 ${\it TABLE~4}$ WORLD BROMINE ANNUAL PLANT CAPACITIES AND SOURCES AS OF DECEMBER 31, 2006^1

		Capacity	
Country and company or plant	Location	(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	Sdom	250,000	Bitterns of potash production from surface brines
Italy, Societa Azionaria Industrial Bromo Italiana	Margherita di Savoia	900	Seawater bitterns from salt production.
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.

NA Not available.

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¹These data detail the information included in table 1 under "Imports, bromine compounds, other compounds."

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

³Harmonized Tariff Schedule of the United States.

⁴Declared cost, insurance, and freight valuation.

¹Excludes U.S. production capacity, which is detailed in table 2.

 ${\it TABLE~5}$ BROMINE: ESTIMATED WORLD REFINERY PRODUCTION, BY COUNTRY $^{1,\,2}$

(Metric tons)

Country ³	2002	2003	2004	2005	2006
Azerbaijan	2,000	2,000	2,000	2,000	2,000
China	42,000	42,000	43,000	43,000	43,000
France	2,000	2,000	2,000	2,000	2,000
Germany ^{4, 5}	413 ^r	388 ^r	248 ^r	274 ^r	431
India	1,500	1,500	1,500	1,500	1,500
Israel ⁵	185,000	176,000	202,000	207,048 ^r	179,000
Italy	300	300	300	300	300
Japan	20,000	20,000	20,000	20,000	20,000
Jordan	5	5	46,000 5	50,000 ^r	50,000
Spain	100	100	100	100	100
Turkmenistan	150	150	150	150	150
Ukraine	3,000	3,000	3,000	3,000	3,000
United Kingdom	24,500	25,000	1,000		
United States ^{5, 6}	222,000	216,000	222,000	226,000	243,000
Total	503,000	488,000	543,000 ^r	556,000 ^r	545,000

^rRevised. -- Zero.

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

²Table includes data available through May 15, 2007.

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

⁴Includes bromides and oxides.

⁵Reported figure.

⁶Sold or used by producers.