

# 2007 Minerals Yearbook

**BROMINE [ADVANCE RELEASE]** 

# **Bromine**

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Domestic survey data and tables were prepared by Michelle B. Blackwell, statistical assistant, and the world production table was prepared by Linder Roberts, international data coordinator.

Primary uses of bromine compounds were in flame retardants (FRs), drilling fluids, water treatment, and brominated pesticides (mostly methyl bromide). World production of bromine, for 2007 was estimated to be 387,000 metric tons (t), excluding the United States, compared with 400,000 t in 2006 (table 5). The world producers of bromide include China, Israel, Jordan, and the United States, and seven other countries (table 5). The United States has been the world's leading producer of bromine; however, the U.S. portion of world production has decreased steadily since 1973 when the United States produced 71% of the world supply. Bromine is one of two elements that are liquid at normal temperatures. It is found principally in seawater, salt lakes, and underground brines associated with oil. In 2007, the quantity and value of bromine sold or used in the United States decreased from the amount of 243,000 t valued at \$339 million that was produced in 2006 (table 1).

#### **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. The two U.S. bromine producers, Albemarle Corp. and Chemtura Corp., responded to the survey, representing 100% of total production (tables 1, 2). In December 2006, the Dow Chemical Company closed its bromine recovery facility in Mason County, MI; therefore, production and stock data were withheld from publication to avoid disclosing company proprietary data.

Bromine was recovered from brine wells in Arkansas, where 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; by comparison, seawater contains 65 ppm bromine.

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

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. Plastics containing bromine 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, decreased from 2006. 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.

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

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.

Another major use of bromine is as a water purifier/disinfectant, which is an alternative to using chlorine. Brominated compounds are used for water treatment in swimming pools and hot tubs and are also used 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 other 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 is declining owing to the ban imposed by the 1987 Montreal Protocol, which classified it as a class I ozonedepleting 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 critical use on certain crops, such as peppers, strawberries, and tomatoes. In 2007, EPA authorized 6,230 t or 24.4% of the historic 1991 baseline consumption of methyl bromide for approved critical uses (U.S. Environmental Protection Agency, 2006, p. 12). 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 high-humidity 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 higher in 2007 than in 2006. Albemarle announced price increases for bromine and bromine compounds in the last quarter of 2007. Albemarle increased the global price of its bulk elemental by 7% delivered, which would be a minimum value of \$3,178 per metric ton delivered (Albemarle Corp., 2006, 2007). Chemtura raised its price by 20% in December 2006, but did not quote a price (Chemtura Corp., 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 the cost of energy, key raw materials, regulatory compliance, and transportation.

The export unit value of elemental bromine decreased by 10% in 2007. The export unit value of bromine compounds, including ethylene dibromide and methyl bromide, was estimated to have increased by 16% during 2007 (table 1).

The import unit value of elemental bromine decreased by 9% compared with that of 2006. The import unit values of bromine compounds increased, except for the other bromine compounds, which showed a decrease even though there was a lack of trade data for some of these compounds (tables 1, 3).

#### **World Review**

The United States part in the world's bromine production has decreased as other countries have strengthened their positions as world producers of elemental bromine. China, Israel, Japan, and Jordan have the largest bromine production capabilities (table 4).

*China.*—Gulf Resources, Inc. became China's leading bromine producer, with a market share of 20%. Gulf Resources has doubled its annual bromine production to approximately

26,700 t with 1.9 million t of proven and probable reserves (Gulf Resources, Inc., 2008).

Israel.—ICL Industrial Products (ICL-IP) (a business unit of Israel Chemicals Ltd.) increased its price of bromine by approximately 15%. The reason for the increase was that bromine production and marketing required significant investments in infrastructure of logistics and feed stock supply (Israel Chemicals Ltd., 2007). Currently, the company is upgrading its fleet of bromine isotanks. ICL-IP is continually investing funds to sustain improvements in their bromine infrastructure.

#### 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 increase by 4% per year through 2010 (Frim and Ukeles, 2007). 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 when the Consumer Product Safety Commission approves fire safety standards for upholstered furniture in the United States and if more stringent flammability standards are voluntarily adopted for televisions in Europe.

The Fredonia Group forecast FR global bromine consumption to rise 4.7% annually through 2011 (Fredonia Group Inc., 2007). The increase will be driven by the use of FRs in developing countries as they begin to develop more stringent flammability standards and begin to use more plastic materials. The Asian/Pacific region is the leading consumer of FRs, with consumption rising 7% per year. More moderate growth in FR use is expected for markets in North America and Western Europe; however, gains are expected to outpace those that took place from 2001 to 2006. Above-average gains in the demand for FRs will take place in Latin America, Eastern Europe, and the Africa/Mideast region.

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 increase by 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.

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#### GENERAL SOURCES OF INFORMATION

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#### Other

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

Bromine Science and Education Forum.

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

(Metric tons and thousand dollars)

	HTS <sup>2</sup> number	2003	2004	2005	2006	2007
United States:	TITS Humber					
Bromine sold or used: <sup>3</sup>						
Quantity	<del></del>	216,000	222,000	226,000	243,000	W $^4$
Value		155,000	191,000	168,000	339,000	W 4
Apparent consumption		256,000	274,000	277,000	275,000	W 4
Exports: <sup>5</sup>		·	·	·	·	
Elemental bromine: <sup>6</sup>	2801.30.2000					
Quantity		2,280	2,700 <sup>r</sup>	2,910 <sup>r</sup>	4,470 <sup>r</sup>	5,660
Value		3,090	3,250 <sup>r</sup>	3,990	5,370 <sup>r</sup>	6,090
Bromine compounds: <sup>7</sup>		,	,		,	
Gross weight		7,160 <sup>6</sup>	7,850 <sup>6</sup>	8,130 6	9,430 6	6,260 8
Contained bromine		6,040	6,600	6,830	7,920	5,280
Value		11,800	13,800	12,800	17,600	13,600 e
Imports: <sup>6, 9</sup>		,	,	,	,	
Elemental bromine:	2801.30.2000					
Quantity		1,920	2,650	2,740	807	2,270
Value		1,450	2,000	2,300	1,340	3,440
Bromine compounds:		· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·	,	
Ammonium bromide:	2827.59.2500					
Gross weight		46,600	59,700	58,200	37,200	21,700
Contained bromine		38,000	48,700	47,500	30,300	17,700
Value		21,100	27,400	30,400	43,600	38,800
Calcium bromide:	2827.59.2500	,	.,		- ,	/
Gross weight		9		922 8	4,350 8	1,820 8
Contained bromine		7		727	3,500 <sup>r</sup>	1,460
Value		4 e		645 <sup>e</sup>	3,000 e	1,440 e
Potassium bromate:	2829.90.0500				,	
Gross weight		36	54	122	103	55
Contained bromine		17 <sup>r</sup>	26	58	50	26
Value		111	163	394	328	236
Potassium bromide: <sup>10</sup>	2827.51.0000					
Gross weight		497	598	434 8	159 8	187 8
Contained bromine		334	401	291	107	126
Value <sup>e</sup>		1,210	1,800	1,310	500	646 e
Sodium bromate:	2829.90.2500	,	,			
Gross weight		967	992	950	852	467
Contained bromine		512	525	503	451	247
Value		2,010	1,930	1,800 e	1,850	1,060
Sodium bromide:10	2827.51.0000	,	· · · · · · · · · · · · · · · · · · ·		,	
Gross weight <sup>8</sup>		3,670	4,610	4,530	4,750	6,330
Contained bromine		2,850 <sup>r</sup>	3,580	3,520	3,690	4,920
Value <sup>e</sup>		5,660	5,300	5,400	7,100	11,300 e
Other compounds:		- 7	- /	-,	.,	,
Gross weight <sup>11</sup>		4,530 <sup>r</sup>	7,140	6,090	6,800	5,460
Contained bromine		2,820 <sup>r</sup>	4,800 <sup>r</sup>	3,830 <sup>r</sup>	4,120 <sup>r</sup>	3,420
Value 11		8,892 <sup>r</sup>	13,500	13,500	20,370 <sup>r</sup>	16,200
World, production <sup>e</sup>		494,000 <sup>r</sup>	565,000 <sup>r</sup>	631,000 <sup>r</sup>	643,000 <sup>r</sup>	387,000
See footnotes at end of table.		,000	,	,	,000	227,000

See footnotes at end of table.

# TABLE 1—Continued SALIENT BROMINE AND BROMINE COMPOUNDS STATISTICS<sup>1</sup>

United States closing at the end of 2006.

TABLE 2 ELEMENTAL-BROMINE-PRODUCING PLANTS IN THE UNITED STATES IN 2007

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 2
Chemtura Corp.	do.	El Dorado Central	do.	NA
Do.	do.	El Dorado South	do.	NA
Total				71 3
Do.	do.	Marysville West	do.	36
Do.	do.	Newell	do.	23
Total	·			59
Grand Total				278

Do., do. Ditto. NA Not available.

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

		2006		2007		
	$HTS^3$	Gross weight	Value <sup>4</sup>	Gross weight	Value <sup>4</sup>	
Compound	number	(metric tons)	(thousands)	(metric tons)	(thousands)	Principal sources, 2007
Hydrobromic acid	2811.19.3000	240	\$347	669	\$662	Israel, 99%; other, 1%.
Ethylene dibromide	2903.30.0500	103	764			
Methyl bromide	2903.30.1520	235	1,140			
Dibromoneopentyl glycol	2905.50.3000			915	NA NA	Israel, 99%; other, 1%.
Tetrabromobisphenol A	2908.10.2500	930	3,780	1,380	NA NA	Israel, 97%; China, 3%.
Decabromodiphenyl oxide and						
octabromodiphenyl oxide	2909.30.0700	5,290	14,300 <sup>r</sup>	4,790	15,500	Israel, 93%; China 6%; other, 1%.
Total		6,800	20,400 r	7,750	16,100	

Revised. NA Not available. -- Zero.

Source: U.S. Census Bureau.

<sup>&</sup>lt;sup>e</sup>Estimated. <sup>r</sup>Revised. W Withheld to avoid disclosing company proprietary data. -- Zero.

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

<sup>&</sup>lt;sup>2</sup>Harmonized Tariff Schedule of the United States.

<sup>&</sup>lt;sup>3</sup>Elemental bromine sold as such to nonproducers, including exports, or used by primary U.S. producers in preparing bromine compounds.

<sup>&</sup>lt;sup>4</sup>U.S. production data are withheld because of proprietary data requirements that resulted from a bromine recovery facility in the

<sup>&</sup>lt;sup>5</sup>Export values are free alongside ship.

<sup>&</sup>lt;sup>6</sup>Source: U.S. Census Bureau.

<sup>&</sup>lt;sup>7</sup>Includes methyl bromide and ethylene dibromide.

<sup>&</sup>lt;sup>8</sup>Source: The Journal of Commerce Port Import/Export Reporting Service.

<sup>&</sup>lt;sup>9</sup>Import values are cost, insurance, and freight.

<sup>&</sup>lt;sup>10</sup>"Potassium bromide" and "Sodium bromide" import data are reported by a mutual HTS number, 2827.51.0000.

<sup>&</sup>lt;sup>11</sup>Data for these compounds are detailed in table 3.

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

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

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

<sup>&</sup>lt;sup>1</sup>These data detail the information included in table 1 under "Imports, bromine compounds, other compounds."

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

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

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

<sup>&</sup>lt;sup>5</sup>Source: The Journal of Commerce Port Import/Export Reporting Service.

TABLE 4 WORLD BROMINE ANNUAL PLANT CAPACITIES AND SOURCES AS OF DECEMBER 31,  $2007^1$ 

		Capacity (metric	
Country and company or plant	Location	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.

Do. Ditto. NA Not available.

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

#### (Metric tons)

Country <sup>3</sup>	2003	2004	2005	2006	2007
Azerbaijan	2,000	2,000	2,000	2,000	2,000
China	75,000 <sup>r</sup>	80,000 <sup>r</sup>	105,000 <sup>r</sup>	124,000 <sup>r</sup>	130,000
France	100 <sup>r</sup>	r	r	r	
Germany <sup>4</sup>	388 5	248 5	274 5	431 5	1,612 5
India	1,500	1,500	1,500	1,500	1,500
Israel	176,000 5	202,000 5	207,048 5	179,000 5	159,400 5
Italy	r	r	r	r	
Japan	20,000	20,000	20,000	20,000	20,000
Jordan	<sup>5</sup>	34,000 <sup>r</sup>	66,000 <sup>r</sup>	69,000 <sup>r</sup>	69,000
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	r	r			
United States <sup>6</sup>	216,000 5	222,000 5	226,000 5	243,000 5	W
Total	494,000 r	565,000 r	631,000 r	643,000 r	387,000 7

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

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

<sup>&</sup>lt;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>&</sup>lt;sup>2</sup>Table includes data available through May 15, 2008.

<sup>&</sup>lt;sup>3</sup>In 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.

<sup>&</sup>lt;sup>4</sup>Includes bromides and oxides.

<sup>&</sup>lt;sup>5</sup>Reported figure.

<sup>&</sup>lt;sup>6</sup>Sold or used by producers.

<sup>&</sup>lt;sup>7</sup>U.S. production data are withheld because of proprietary data requirements that resulted from a bromine recovery facility in the United States closing at the end of 2006.