

BROMINE

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The quantity of bromine sold or used in the United States was 227 million kilograms (kg) valued at \$150 million. The value of bromine sold or used was 66 cents per kg. Primary uses of bromine compounds were in flame retardants (38%), drilling fluids (22%), sodium bromide solutions (10%), brominated pesticides (mostly methyl bromide) (8%), water-treatment chemicals (7%), and other including photographic chemicals and rubber additives (15%) (Chemical Marketing Reporter, 1997). International distribution of bromine production in 1996 was as follows: The United States, 50%; Israel, 30%; the United Kingdom, 6%; and other countries, 14%. The United States' portion of world production has decreased steadily since 1973, when the United States produced 71% of the world supply. The decrease in world share has been a result of environmental constraints and the emergence of Israel as the world's second largest producer. (See table 1).

Legislation and Government Programs

The Food Quality Protection Act was signed into law August 3, 1996, and became effective immediately. The law requires new standards for pesticide tolerances, expanded consumer right-to-know efforts, consideration of a pesticide's benefits, new reviews of minor-use and antimicrobial pesticides, and special consideration of infants and children. The old Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) and the Federal Food, Drug and Cosmetic Act (FFDCA) created a paradox because of the FFDCA's Delaney clause, which had prohibited any trace of a carcinogen in processed food. Pesticide residues in raw commodities, regulated under FIFRA, had no uniform standard, but residues of carcinogens in processed food, which came under FFDCA, even if they posed a negligible risk, were banned because of the Delaney clause, which was added to FFDCA in 1958. Under the new law, the Delaney clause no longer applies (Hanson, 1996).

Methyl bromide continues to be viewed as a significant ozone-depleting compound. Three potentially major anthropogenic sources of atmospheric methyl bromide have been identified (soil fumigation, biomass burning, and the exhaust of automobiles using leaded gasoline), in addition to vaporization from the ocean. Methyl bromide was listed as a Class I ozone depleting substance in the 1990 Clean Air Act, and the chemical is scheduled to be phased out in the United States by January 1, 2001. World participants, at a December 1995 Vienna meeting of the Montreal Protocol, agreed to a world phaseout of methyl bromide by 2010. The Netherlands phased out the use of methyl bromide for soil fumigation in 1992 because of concerns over ground water contamination. Denmark will ban all

agricultural uses of methyl bromide in 1998, and Sweden is expected to follow with a similar schedule. The remaining members of the European Union and Canada will cut agricultural uses by 25% in 1998. The final Montreal Protocol agreement also included a production phaseout schedule for industrial nations with a 25% reduction in 2001, a 50% reduction in 2005, and a complete phaseout in 2010. For developing nations, a freeze in 2002 on methyl bromide use will be based on average 1995-98 consumption levels. During the Vienna meeting, the treaty partners elected to defer a decision until 1997 on controlling trade in methyl bromide with countries that have not signed the protocol. This agreement will be revisited in 1997 (U.S. Environmental Protection Agency, Methyl Bromide Information, unpub. data accessed May 8, 1997, on the World Wide Web at URL <http://www.epa.gov/doc/ozone/mbr/mb4rq.html>).

Manufacturers of 15 chemicals, including one brominated compound, were asked to provide exposure information to the U.S. Environmental Protection Agency (EPA). The chemicals were selected for the project for various reasons: five were the subject of Toxic Substance Control Act (TSCA) section 8(e) significant risk notices; EPA had information suggesting that two of the substances may pose a cancer threat; and one was a high-production substance suspected of accumulating in the environment. The targeted chemicals are scheduled to be reviewed in EPA's risk management level one program (RM1), the first of two levels of decision making in the agency's program to assess the safety of existing chemicals. The data review could lead to EPA taking action under the TSCA (Chemical Marketing Reporter, 1996k).

EPA fined AmeriBrom Inc., the marketing company for Dead Sea Bromine Co. Ltd. (DSB), \$118,000 for failure to register three products. The penalty was 64% less than the fine originally proposed by the agency. The enforcement action included brominating tablets, which are used to control microorganisms in pools and spas (Chemical Marketing Reporter, 1996b).

EPA issued an advance notice of proposed rulemaking that would expand the Toxic Release Inventory (TRI) to require companies that use chemicals in industrial facilities to report information on use, also known as materials accounting. The reporting would be expanded to report on products and waste. The chemical industry objects to diverting the TRI program away from pollution prevention and risk reduction. Emissions are a better indicator of potential health threats to the community. Congress has twice considered and rejected legislation that would require materials accounting, so EPA's legal authority to collect this information is also in question

(Chemical Marketing Reporter, 1996e).

California's Department of Pesticide Regulation restricted use of methyl bromide in a bill passed in 1996 that allowed manufacturers until December 31, 1997, to complete health studies. Without the legislation, manufacturers said they would not have been able to meet the previous deadline of March 30, 1996. The bill also directed regulators to review restrictions on soil fumigant use of methyl bromide to adequately protect workers and the public from over-exposure (Chemical Marketing Reporter, 1996c).

The Superfund taxes expired in December 1995 and had not been reinstated. Three Senate committees had a plan to take Superfund "offbudget" to ensure that all revenues generated by the program's special taxes on industry are used for hazardous waste site cleanups. Superfund is a trust set up from the taxes on petroleum and chemicals for cleaning up sites where no responsible party with sufficient funds can be found. Unappropriated funds can and have been redirected by lawmakers to pay for other government programs. Placed in a separate account, Superfund taxes would not be subject to the budget rules that apply to spending caps federal lawmakers have imposed on EPA and other Federal agencies. As a result, the money would be for hazardous waste cleanups and could not be used for discretionary spending. Bromine and chlorine, used to produce the bromine, are chemicals taxed to provide funds to Superfund. Since 1981 businesses in the United States have paid more than \$12 billion in taxes, including more than \$4 billion by the chemical industry. Imported bromine products do not contribute to the tax (Chemical Marketing Reporter 1996j).

The most important regulatory program established under the Clean Water Act (CWA) is the national the National Pollution Discharge Elimination System (NPDES). All point source discharges of pollutants to navigable waters must be authorized by an NPDES permit. In 1987, the CWA was amended to include specific numeric water quality standards for all toxic pollutants which could interfere with the designated uses of streams. NPDES permits issued to the oil and gas industry have become more stringent and complex. Discharge permits for Cook Inlet, AK, provide limitations for chemical additives, such as calcium bromide, sodium bromide, and zinc bromide that are used in completion and work over (upkeep) of oil and gas wells. The 1987 amendments to the CWA emphasized stricter control of toxins in waste water discharges, which State and EPA permit writers have not widely enforced. General permits proposed in 1996 for Region VI discharges into the territorial seas of Louisiana and Region X for coastal and offshore discharges in Alaska are much stricter than previous permits. Region VI and X permits now require numerical water discharge limits. For the oil and gas industry, which has large numbers of facilities in the same geographic area with similar discharges, the EPA has issued general permits. These general permits provide a set of operating and monitoring requirements. The oil and gas extraction industry is divided into five subcategories: offshore, onshore, coastal, agricultural and wildlife water use, and stripper. CWA has a goal of zero discharge of pollutants and no discharge of toxins in toxic amounts. The general permits that

have been proposed and issued in 1996 have required major changes in oil and gas industry operations. In some cases, reissued permits have required zero discharge of waste water into streams, such as, in coastal waters of Louisiana and Texas, operators have discharged water produced with oil and gas. A combination of state and EPA measures are leading toward zero discharge of produced water in coastal waters in Louisiana and Texas (Veil, 1997).

The House Ways and Means Committee ordered cancellation of the U.S. International Trade Commission's Quarterly Synthetic Organic Chemicals Report by October 1, 1996. Annual figures will not be available for 1996 and 1995 data will not appear in a finalized form. A private association was considering whether to continue gathering the information (Chemical and Engineering News, 1996).

Production

Domestic production data for bromine were developed by the U.S. Geological Survey from a voluntary survey of U.S. operations. Of the operations to which a survey request was sent, six responded representing 100% of total elemental bromine sold or used. (See table 2.)

Albemarle Corp., formerly Ethyl Corp.'s Chemical Division, and Great Lakes Chemical Corp. produced and marketed more than 60 different bromine-based chemicals from plants in Arkansas. Small amounts of unpurified bromine were produced in Michigan as a byproduct in the extraction of magnesium from brine and reprocessed in Arkansas. The Arkansas plants accounted for 96% of U.S. elemental bromine capacity at yearend 1996 and 100% of bromine sold or used. The overall result of the Albemarle expansion program was a bromine production capacity increase of 30% by 1996 (Chemical Marketing Reporter, 1995a).

Albemarle entered a request to find a customer who could use 6,000 pounds (250 gallons) of bromine in custom synthesis in California. (Paul Palmer, CBC/Chemsearch, unpub. data accessed March 27, 1996, on the World Wide Web at URL <http://www.sonic.net/chemsearch/enerchem.html>).

Great Lakes announced an expansion of a reactive flame retardant capacity for unsaturated polyester resins to be completed by the third quarter 1996 (Chemical Marketing Reporter, 1996g). On November 3, 1995, Great Lakes filed an application with the Arkansas Oil and Gas Commission to establish a third brine production unit consisting of 24,000 hectares (60,000 acres). Under Arkansas law, the company can form a unit if it owns 75% of the mining right to the brine. Murphy Oil Corp., through its subsidiary, Deltic Farm & Timber, filed for a continuance which was granted until the January 28, 1996, meeting. Deltic Farm & Timber, which owns about 4,900 hectares (12,000 acres), filed a lawsuit in U.S. District Court alleging that Great Lakes drained some brines that were owned by Deltic. The law suit also alleges that Deltic wanted to cancel leases that would restrict Great Lakes from having 75% of the leases that it needs for the brine unit. (Arkansas Democrat-Gazette, 1995).

Great Lakes earned one-half of its operating income, \$497 million in 1995, from its tetraethyl lead business (TEL) that uses bromine as a scavenger. TEL is a declining but profitable business in which Great Lakes is the only global company (Chemical Marketing Reporter, 1996h, i).

Ambar Inc. planned to have on-stream in early 1997 a 14-millio- kilogram (30 million pound) elemental bromine facility in Manistee, MI, that will produce elemental bromine and brominated salts. Ambar would be supplied by pipeline with bromine containing brines after production of magnesium hydroxide from Martin Marietta Magnesia Specialties Inc. Ambar planned to manufacture and consume brominated well drilling fluids. Meridian Technologies Inc. was to market additional brominated salts (Chemical Marketing Reporter, 1995d). In July, Ambar was acquired by the Beacon Group Energy Investment Fund LP. Beacon entered into an agreement to purchase the 51% of Ambar currently owned by Randolph M. Moitry, the company's chairman, president and CEO and the 6% of Ambar's shares owned by Kenneth J. Boutle, an Ambar director. No change in Ambar's calcium and bromine plans will reportedly occur as a result of the acquisition (Chemical Marketing Reporter 1996a).

TETRA Technologies Inc. expanded its acreage in Magnolia, AR, from 840 hectares (2,100 acres) in 1988 to 13,355 hectares (33,000 acres) in 1996. In March, a long-term requirement contract that will supply 90% of external calcium bromide needs by the company's worldwide Oil & Gas Services operations was signed with Bromine Compounds Ltd., the largest producer of bromine and brominated compounds in the world. The company previously had held its leases in Arkansas for reserves for the Oil & Gas Service Division, but will now consider other options for the use of the bromine reserves. In 1996, TETRA acquired the clear brine fluids business of Dow Chemical Co. and entered into agreements to purchase crude bromine and build a bromine derivatives facility in Ludington, MI (TETRA Technologies Inc., 1995, 1996).

Consumption

Albemarle listed 2,700 kilograms (6,000 pounds) of bromine in bulk tank on the Chemical Recycling Wide World Web page (Paul Palmer, SBC/Chemsearch Corp., Sebastopol, CA, unpub. data accessed March 27, 1996, on the World Wide Web at URL <http://www.sonic.net/chemsearch/>). The bromine was listed as being available for custom synthesis but Special Department of Transportation permitted tanks and nickel or lead lined vessels are required to transport the bromine.

The majority of swimming pools in the United States and Canada are sanitized with chlorine, but more pools are switching to bromine compounds each year. A large number of spas already use bromine compounds. Liquid, elemental bromine forms hypobromous acid and hypobromite ions when added to water. Because of the handling problems with elemental bromine, only compounds of bromine are used for water disinfection. Bromine cannot be protected from ultra-violet light, so it is impractical to use elemental bromine for use

in outdoor pools. The tablets used in outdoor pool sanitizing contain bromine and chlorine. The chlorine is used to oxidize the bromine to produce the acid and ions. Hypobromous acid destroys bacteria, algae, or other organisms, or is decomposed by sunlight to a bromide ion, which can be reactivated by adding an oxidizer. The hypobromous acid can combine with ammonia and nitrogen compounds in the water to form bromamine that is an active sanitizer and is less odoriferous than chloramines. Therefore, in pools sanitized with bromine compounds, the chlorine odor does not exist, although it is necessary to periodically oxidize the organic waste to prevent buildup and irritation to skin and eyes (R. Chamberlin, Absolute Spa Services, Port Moody, BC, Canada, unpub. data accessed July 12, 1996, on the World Wide Web at <http://www.infomatch.com/spaguy/wtrbal.html> bromine).

Many government regulations, insurance company requirements, building codes, and voluntary industry standards define when and where flame-retardant chemicals must be used. Except where government standards exist, such as automotive and airplane components and in the State of California for mattress upholstery materials, the decision to use a flame-retardant resides with the manufacturer. Flame-retardants grew during 1995, indicating that more manufacturers are using flame-retardant additives, such as bromine. Business Communications Co. market research indicated bromine based flame-retardants had 32% of the \$718 million market in 1995 (Reisch, 1997).

Foreign Trade

The General Agreement on Tariffs and Trade (GATT) was signed into law in December 1994 and took effect January 1, 1995. GATT lowered chemical tariffs by an average of 30%. Chemicals, including bromine, are the Nation's largest export commodity, as more than 10 cents out of every export dollar is a product of the chemical industry. The agreement's intellectual property provisions include greater patent protection for products developed by American firms. GATT changes patent enforcement from 17 years from the date of issue to 20 years from the date of application. Patents issued on applications filed before June 8, 1995, will be enforceable for either 17 years from the issue date or 20 years from the filing date, whichever is longer. (See tables 3 and 4.)

World Review

France.—France's sole producer of potash at Mines de Potasse d'Alsace, S.A., part of State-owned chemicals group Entreprise Miniere et Chimique, operated two underground mines near Mulhouse in eastern France that produced byproduct bromine. Mines de Potasse d'Alsace will phase out all the French Government involvement in the operation by 2004. Marketing is through the trading subsidiary Société Commerciale de Potasse et d'Azote (Leblond, 1994). (See table 6.)

Israel.—Bromine has been produced as a byproduct from

waste bitterns associated with potash production from the Dead Sea since 1957 by Dead Sea Works (DSW). After potash is removed in solar ponds, the waste bitterns are processed with chlorine to recover bromine. The bromine-free bitterns are then processed to recover magnesium.

The Israeli Government began efforts in 1985 to sell a share of Israeli Chemical Co. Ltd. (ICL) to offset an investment program. ICL split Dead Sea Bromine Co., Ltd. (DSB) from DSW and retain an 89% share in DSB. The other 11% of DSB is owned by the public through stock on the Tel Aviv stock exchange. On October 11, 1994, the Israeli government published a tender for the sale of 25% of ICL to a single investor or group of investors. Israel Corp. (IC), Tel Aviv, bought a 24.9% share of the ICL during 1995. IC will pay \$230 million for the ICL stake. The family of Israeli business executive Shoul Eisenberg controls 50% of IC and 50% is owned by an offshore corporation Eisenberg also controls. The Government will continue to hold a 27.1% share in ICL after completion of the international offering.

ICL is a group of chemical and mineral industrial companies, with research institutes, technical facilities, and commercial and marketing services. Recovery of potash salts on a commercial scale from the Dead Sea first began in 1931. The soluble minerals exist mainly as chloride and bromine anions and magnesium, sodium, and potassium cations. Crude carnallite is harvested and the waste brines are processed for magnesium chloride and bromides. Approximately 70% of ICL's activities are devoted to the fertilizer industry, including the production of raw materials and intermediates. Current production includes potassium chloride, magnesium chloride, magnesium oxide, magnesium metal, chlorine products, bromine, caustic soda, salt, uranium, lanthanides, radium sulfate, monocalcium phosphate and/or calcium nitrate and hydrochloric acid (Lin and Schorr, 1996; Phosphorus & Potassium, 1996).

DSB production capacity for bromine, after the expansion at Sdom was 190,000 tons per year. The increase in capacity required the purchase of isotank containers. DSB has enough isotank capacity to ensure the transportation of exported bromine.

DSB has production plants at Sdom and Ramat. A 50-50 joint venture between Great Lakes and DSB came on-stream during 1996 to manufacture a flame retardant used primarily in epoxy circuit board production and other resin applications. Although demand was down when the plant came on stream, demand in the electronics industry increased at yearend. The \$22 million flame retardant plant at Ramat planned to reach capacity by 1998. Each partner of the joint venture, Tetrabrom Technologies Ltd., will market the product separately (Chemical Marketing Reporter, 1996d). Tetrabrom could eventually represent 25% of world flame retardants capacity (Chemical Marketing Reporter, 1995b).

Jordan.—Arab Potash Co. Ltd. and Albemarle were negotiating to form a joint-venture company to produce bromine from potash waste brines; ownership of the company was expected to be distributed 51% and 49%, respectively. The new company is called the Jordan Industrial Chemicals of the Dead

Sea Minerals Co. The decision to form the company follows a memorandum of understanding with Albemarle for construction of a 50,000-ton-per-year plant. The investment in the plant would be \$145 million, and the plants are to be operational by 1997 (Green Markets, 1994).

Dead Sea Bromine group and Jordan's Arab Potash Corp. Signed a memorandum of understanding to construct a \$50 million bromine plant on the Jordanian side of the Dead Sea. The 50-50 joint venture would be managed by the Jordanians and built with technical assistance by DSB. The plant was expected to be operational by 1998 (Chemical Marketing Reporter, 1995c).

Keir International, United Kingdom, has won a \$13.8 million contract to build a brine water intake system at the Dead Sea for Arab Potash Co. The project will include the construction of a 200-meter jetty supporting twin 2-meter diameter pipes for extracting brine to potash (Phosphorus & Potassium, 1995).

Turkmenistan.—A conference on the production capacities of working mines and processing enterprises of Turkmenistan listed bromine production at the Nebitdagh Iodine Factory at 3,200 tons of ferrous bromide and the Cheicken Chemical Factory at 6,400 tons of ferrous bromide (Turkmenistan Ministry of Energetics and Industry and others, 1996).

World Bank.—A world phaseout of leaded gasoline to reduce health problems in developing countries has been proposed by the World Bank. The bank believes phasing out lead could be carried out within 5 years at a cost of about 2 cents per liter. The bank is urging nations still using leaded gasoline to reduce the lead content to 0.15 grams per liter or less. All leaded gasoline contains a bromine compound that is used as a scavenger so this action would cause a decrease in the use of bromine. The bank is promoting lead phaseout schedules and financial packages through loans and guarantees to attract private investments to finance the change (Crow, 1996).

Current Research and Technology

The rate constants and equilibrium saturation capacity for the gold-bromide species are higher than those reported for the gold-cyanide system. The rate of loading increased with decreasing particle size, decreasing pH, increasing temperature, and decreasing concentration of gold in solution (Mensah-Biney, R., Reid, K.J., and Hepworth, M.T., 1996).

Stratigraphic profiles of bromine distribution from analyses of 3,045 salt samples in Colorado and Utah indicated that 29 of the salts were deposited from seawater. Averages of bromine values show variations that indicate potash and halite were concentrated in the deeper parts of the basin and other salts and carbonate rock are thicker toward the basin margins. There is a positive correlation between halite beds that have high levels of bromine and those that contain potash deposits. Bromine distribution, therefore, is a valuable tool in exploration for potash deposits in evaporites of marine origin (Raup and Hite, 1996).

The 35th Biennial Congress for the International Union for Pure and Applied Chemistry presented a program that covered

six different fields of chemistry. In the field of inorganic chemistry and solid state, there were five plenary lectures, one of which covered bromine chemistry in the atmosphere related to human activities. Recent measurements reveal that in the lower stratosphere (16-20 kilometers altitude) the effect of nitrogen oxides on ozone is outweighed by reactions of hydrogen containing radicals, such as bromine monoxide (BrO). The release of nitrogen radicals at those altitudes actually decreases the loss of ozone, because the nitrogen radicals react with the ozone destroying radicals, thereby short circuiting their destructive effect. It is estimated that nearly one-third of the photochemical loss of ozone is due to chlorine- and bromine-monoxides (Chemistry International, 1996).

Between 6.8 to 9 million kilograms (15 to 20 million pounds) of methyl bromide are used each year in California, primarily for preplant soil fumigation. Although methyl bromide is important to agriculture its absence would have a small effect on most of California's agriculture. The United Nations Methyl Bromide Technical Options Committee concluded that alternatives exist or are at an advanced stage of development for more than 90% of methyl bromide use (James Liebman, Pesticide Action Network North American Regional Center, San Francisco, CA, unpub. data accessed on May 8, 1997, on the World Wide Web at URL <http://www.cdpr.ca.gov/doc/dprdocs/methbrom/mb4chg.html>).

Researchers at the University of California, Riverside, proposed methyl iodide as a replacement for methyl bromide in soil fumigation (S. R. Yates, U. S. Salinity Laboratories, Riverside, CA, unpub. data accessed May 8, 1997, on the World Wide Web at URL <http://www.ars.usda.gov/is/mba/april96/yatest.html>). However, there is little information regarding methyl iodide's behavior in agricultural soils. It is important that any decision to use alternative fumigants should balance environmental consequences and economic implications. Because methyl iodide has a longer half-life, this may cause delays in planting. If the soil needs venting to reduce photo-toxicity, an increase in total emissions into the atmosphere related to methyl bromide may result.

Dr. Vincent Patrick in consultation with the Australian Minerals Industry Research Association developed a low-toxicity heavy liquid called LST that can replace bromoform and tetrabromoethane chemicals traditionally used to separate minerals from gangue. The low-viscosity aqueous solution is made of tungsten polyanions and uses acetone and alcohol. LST should prove attractive to companies producing diamonds, mineral sands, industrial ores, and heavy metals like tantalum and tin (Australian Science & Technology Newsletter, 1996).

Molybdenum trioxide studies with bromine polymers produce more char than chlorine type polymers in the solid phase of the fire. Char has been found to restrict the spread of fire by removing the fuel source. Few aromatic products were formed (Musselman, 1996).

Outlook

Petroleum.—Demand for bromine as a gasoline additive has

declined each year since the EPA issued regulations in the 1970's to reduce the lead in gasoline. In the United States bromine, in the form of ethylene dibromide or EDB, is used as a "scavenger" for the lead to keep the lead from depositing in the engine. In 1979, the amount of bromine sold reached a peak of 225 million kilograms. The rapid decline to 141 million kilograms in 1986 was a direct result of the limits on lead in leaded gasoline. The European Community continued discussions to reduce lead levels in gasoline. Bromine in petroleum additives is expected to continue to decline over the long-term. Federal laws enacted to encourage alternative forms of power in automotive engines are likely to have a depressive effect on bromine demand. The Clean Air Act Amendments of 1990 have an amendment that will require mobile sources, such as cars and trucks, to use the most effective technology possible to control emission. Electric cars that do not require bromine gasoline additives are already on the market in California.

Sanitary Preparations.—Bromine has found usage in indoor swimming pools, hot tubs, and whirlpools. The sanitary preparation field is an area where bromine has been found to be safer than its substitutes because bromine has a higher biocidal activity level for the same amount of product. Applications in the pulp and paper industry, in cooling towers, and Government-regulated food-washing applications are growth areas. The use of bromine will continue to grow in sanitary preparation, closely following the gross national product in real growth.

Fire Retardants.—A study by Business Communications Co. (BCC) expected the domestic flame-retardant industry to reach sales of \$924 million by the year 2000. Bromine-based flame-retardant chemicals are expected to grow at a 6.4% annual average growth rate. BCC states flame retardancy represents bromine's largest domestic use (Chemical Marketing Reporter, 1996f).

Other Uses.—Usage of calcium, sodium, and zinc bromides in well-drilling fluids decreased during the 1980's as the domestic petroleum industry suffered a severe recession. Oil field chemicals used in drilling, completion and work over, and production operations have remained significantly more profitable internationally than in the United States. The competition market included corrosion inhibitors, bactericides, viscosities and defoamers, as well as commodities such as calcium chloride and calcium bromide brines used to maintain well productivity. Because of the significant benefits of bromine compounds in the well-drilling fluids area, usage is expected to grow at the rate of 2% per year.

References Cited

- Arkansas Democrat-Gazette [Little Rock], 1995, Fight over rights to pump out brine depends on value: November 28, p. 1D.
- Australian Science & Technology Newsletter, 1996, Heavy liquid lowers toxic waste: Department of Foreign Affairs and Trade, June, p. 4.
- Chemical & Engineering News, 1996, Association may collect organic chemical data: Chemical & Engineering News, v. 74, no. 39, p. 18.
- Chemical Marketing Reporter, 1995a, Albemarle project on target: Chemical Marketing Reporter, v. 248, no. 6, p. 4.
- 1995b, Financial newsfront—Kemper analyst sees Great Lakes as long-term buy: Chemical Marketing Reporter, v. 248, no. 2, p. 26.

- 1995c, Israel and Jordan plan bromine plant: *Chemical Marketing Reporter*, v. 248, no. 16, p. 5.
- 1995d, U.S. bromine market poised for Ambar's entry in 1996: *Chemical Marketing Reporter*, v. 248, no. 1, 1995, p. 5, 19.
- 1996a, Ambar is selling to beacon group: *Chemical Marketing Reporter*, v. 250, no. 3, p. 15.
- 1996b, AmeriBrom pays fine for violating EPA pesticide rule: *Chemical Marketing Reporter*, v. 249, no. 26, p. 34.
- 1996c, California restricts methyl bromide: *Chemical Marketing Reporter*, v. 250, no. 23, p. 26.
- 1996d, Closing market developments—Great Lakes starts up joint venture tbba unit: *Chemical Marketing Reporter*, v. 249, no. 16, p. 4.
- 1996e, EPA advances plan for chemical use reporting: *Chemical Marketing Reporter*, v. 250, no. 24, p. 3, 36.
- 1996f, Flame retardants market set to reach \$924: *Chemical Marketing Reporter*, v. 249, no. 22, p. 20.
- 1996g, Great Lakes expands in flame retardants: *Chemical Marketing Reporter*, v. 249, no. 1, p. 4.
- 1996h, Great Lakes eyes Ciba stabilizers: *Chemical Marketing Reporter*, v. 249, no. 14, p. 7.
- 1996i, Great Lakes share price moves south: *Chemical Marketing Reporter*, v. 250, no. 24, p. 3.
- 1996j, Superfund may go "off Budget": *Chemical Marketing Reporter*, v. 249, no. 8, p. 7.
- 1996k, 15 Chemicals targeted for EPA study: *Chemical Marketing Reporter*, v. 249, no. 23, p. 8.
- 1997, Chemical Profile: *Chemical Marketing Reporter*, v. 251, no. 13, p. 37.
- Chemistry International, 1996, Istanbul 1995: *Chemistry International*, v. 18, no. 1, p. 1-5.
- Crow, Patrick, 1996, World Bank urges lead phaseout: *Oil & Gas Journal*, v. 94, no. 24, p. 36.
- Green Markets, 1994, Jordan forms large holding company: *Green Markets*, v. 18, no. 8, p. 8.
- Hanson, David, 1996, Regulation after Delaney: *Chemical & Engineering News*, v. 74, no. 39, p. 38-39.
- Leblond, D. 1994, EMC looks to trade after MDPA closure: *European Chemical News*, v. 61, p. 23.
- Lin, I.J., and Schorr, M., 1996, Exploitation of Israel's P and K resources: *Phosphorus & Potassium*, no. 206, p. 25-30.
- Mensah-Biney, R., Reid, K.J., and Hepworth, M.T., 1996, Kinetics of gold-bromide loading onto activated carbon: *American Institute of Mining, Metallurgical, and Petroleum Engineers, Society for Mining, Metallurgy, and Exploration Inc.*, Preprint 96-73, 9 p.
- Musselman, Larry, 1996, Update and new developments in endothermic flame retardants: *Industrial Minerals 96*, Toronto, October 22-23.
- Phosphorus & Potassium, 1995, Jordan-Keir wins APC's brine water intake contract: *Phosphorus & Potassium*, no. 201, p. 13.
- 1996, Exploiting Dead Sea potash: *Phosphorus & Potassium*, no. 202, p. 26-33.
- Turkmenistan Ministry of Energetics and Industry, Turkmenistan Ministry of Construction Material, and "Turkmengeology" Industrial Association on Geological Prospect Works, 1996, The solid raw mineral resources of Turkmenistan: Ashgabat, Turkmenistan, Turukmenistan Ministry of Energetics and Industry, Turkmenistan Ministry of Construction Material, and "Turkmengeology" Industrial Association on Geological Prospect Works, p. 3.
- Raup, O.B., and Hite, R.J., 1996, Bromine geochemistry of chloride rocks of the middle Pennsylvanian Paradox Formation of the Hermosa Group, Paradox Basin, Utah and Colorado: *U.S. Geological Survey Bulletin 2000-M*, 117 p.
- Reisch, M.S., 1997, Flame retardants sales heat up: *Chemical & Engineering News*, v. 75, no. 8, p. 19.
- TETRA Technologies, Inc., 1995, TETRA Technologies, Inc., 1995 annual report: The Woodlands, TX, 57 p.
- 1996, TETRA Technologies, Inc., 1996 annual report: The Woodlands, TX, p 11.
- Veil, J.A., 1997, NPDES permits have increased emphasis on control of toxic pollutants: *Oil & Gas Journal*, v. 94, no. 1, p. 46-52.

SOURCES OF INFORMATION

U.S. Geological Survey Publications

Bromine. Ch. in *Minerals Yearbook*, annual.¹

Bromine. Ch. in *Mineral Commodity Summaries*, annual.¹

Smith, O.I., Jones, C.L., Culbertson, W.C., Ericksen, G.E., and Dyni, J.R., 1973 *Evaporites and brines*, in Brobst, D.A., and Pratt, W.P., eds., *United States mineral resources*: U.S. Geological Survey Professional Paper 820, p. 197-216.

Other

Bromine. Ch. in *Mineral Facts and Problems*, 1985.

Wildhelm, M.J., and Williams, K.C., 1994, Bromine resources, *in* Carr, D.D., ed., *Industrial rocks and minerals*: Society of Mining, Metallurgy, and Exploration, Inc., p. 187-189.

¹Prior to January 1996, published by the U.S. Bureau of Mines.

TABLE 1
SALIENT BROMINE AND BROMINE COMPOUNDS STATISTICS 1/

(Thousand kilograms and thousand dollars)

	H.T.S.U.S. 2/ Number	1992	1993	1994	1995	1996
United States:						
Bromine sold or used: 3/	--					
Quantity		171,000	177,000	195,000	218,000	227,000
Value		\$125,000	\$123,000	\$155,000	\$186,000	\$150,000
Exports: 4/ 5/						
Elemental bromine:	2801.30.2000					
Quantity		5,320	6,010	6,470	3,220	2,920
Value		\$5,540	\$7,440	\$7,270	\$3,790	\$3,970
Bromine compounds: 6/	(7/)					
Gross weight		20,000	15,800	13,700	13,300	13,100
Contained bromine		16,900	13,400	11,500	11,200	1,110
Value		\$26,400	\$21,800	\$21,100	\$19,900	\$22,100
Imports: 4/ 8/						
Elemental bromine:	2801.30.2000					
Quantity		851	850	319	2,220	415
Value		\$522	\$513	\$194	\$1,460	\$305
Bromine compounds:						
Ammonium bromide:	2827.59.2500					
Gross weight		1,790	1,240	1,120	288 9/	11,700 10/
Contained bromine		1,460	1,010	917	235 9/	9,370 10/
Value		\$2,870	\$2,020	\$1,850	\$832 e/ 9/	\$9,580 10/
Calcium bromide:	2827.59.2500					
Gross weight		5,370	9,650	14,700	730 9/	--
Contained bromine		4,290	7,720	11,700	584 9/	--
Value		\$3,210	\$3,740	\$5,380	\$262 e/ 9/	--
Potassium bromate:	2829.90.0500					
Gross weight		407	280	166	275	462
Contained bromine		195	134	79	132	221
Value		\$1,250	\$892	\$538	\$933	\$1,750
Potassium bromide:	2827.51.0000 11/					
Gross weight		883	1,180	1,280	171 9/	NA
Contained bromine		592	790	858	115 9/	NA
Value		\$1,660	\$2,170	\$2,270	\$420 e/ 9/	NA
Sodium bromate:	2829.90.2500					
Gross weight		176	290	276	944	1,200
Contained bromine		93	153	146	500 r/	634
Value		\$469	\$725	\$714	\$2,360	\$3,030
Sodium bromide:	2827.51.0000 11/					
Gross weight		1,100	1,270	1,400	1,400 r/ 9/	NA
Contained bromine		852	983	1,090	1,070 9/	NA
Value		\$1,620	\$1,730	\$1,770	\$2,550 r/ e/ 9/	NA
Other compounds:	2903.30.1550					
Gross weight		11,700	12,500	14,300	5,850 r/ 12/	6,520
Contained bromine		7,160	7,600	8,680	4,880 r/ 12/	5,090
Value		\$21,500	\$36,500	\$42,600	NA	\$14,900
World: Production: e/		397,000	396,000	412,000	432,000	452,000

e/ Estimated. r/ Revised. NA Not available.

1/ Data are rounded to three significant digits.

2/ "Harmonized Tariff Schedule of the United States".

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

4/ Bureau of the Census.

5/ Export values are "Free-alongside-ship" (f.a.s.).

6/ Bureau of the Census. Includes methyl bromine and ethylene dibromide.

7/ Data for these compounds are derived from HTSUS numbers 2903.30.0500 and 2903.30.1500 information.

8/ Import values are "Cost, insurance, and freight" (c.i.f.).

9/ The Journal of Commerce Port Import/Export Reporting Service.

10/ The respective data for "Bromides/Bromines and Oxides" of Ammonium, Calcium and Zinc are combined and reported here.

11/ "Bromides of sodium" or "potassium" import data are usually reported by a mutual HTSUS number, 2827.51.0000.

12/ Certain compounds reported for 1995 are not included in the total.

TABLE 2
ELEMENTAL BROMINE-PRODUCING PLANTS IN THE UNITED STATES, 1996

State and company	County	Plant	Production source	Capacity 1/ (million kilograms)
Arkansas:				
Albemarle Corp.	Columbia	Magnolia	Well brines	120
Arkansas Chemicals, Inc.	Union	El Dorado	do.	25
Great Lakes Chemical Corp.	do.	do.	do.	70
Do.	do.	Marysville	do.	60
Michigan:				
The Dow Chemical Co.	Mason	Ludington 2/	do.	15
Total 3/			(Plants) 5	290

1/ Actual production capacity is limited by brine availability.

2/ Bromine produced at this plant is reprocessed in Arkansas.

3/ Chemical Marketing Reporter, Vol. 251, No. 13, p. 37.

TABLE 3
YEAREND 1996 PRICES 1/ FOR ELEMENTAL BROMINE AND SELECTED COMPOUNDS

Product	Value (Cents)	
	Per pound	Per kilogram
Ammonium bromide, National Formulary (N.F.), granular, drums, carlots, truckloads, f.o.b. works	110 - 131	242 - 289
Bromine:		
Drums, truckloads, works 2/	123	271
Bulk, tank cars, works 2/	56 - 68	123 - 150
Bromochloromethane, drums, bulk, f.o.b. Magnolia, AR	127	280
Ethyl bromide, technical, 98%, drums, truckloads	127	280
Ethylene dibromide, drums, carloads	57	126
Hydrobromic acid, 48%, drums, carloads, truckloads, f.o.b.	42	93
Hydrogen bromide, anhydrous, cylinders, 2,500 pounds, truckloads	475	1,047
Methyl bromide, tank cars	77	170
Potassium bromate, granular, powdered, 200-pound drums, carloads, f.o.b. works	179	395
Potassium bromide, N.F., granular, drums, carloads, f.o.b. works	110 - 112	242 - 247
Sodium bromide, technical, truckloads	70	154

1/ Source: Chemical Marketing Reporter. Current Prices of Chemicals and Related Materials. Vol. 250, No. 27, Dec. 30, 1996, pp. 20-27.

2/ Delivered prices for drums and bulk shipped west of the Rocky Mountains, 1 cent per pound higher. Bulk truck prices 1 to 2 cents higher per pound for 30,000-pound minimum.

TABLE 4
U.S. IMPORTS OF OTHER BROMINE COMPOUNDS 1/ 2/

Compounds	H.T.S.U.S. 3/ Number	1995		1996		Principal sources, 1996
		Gross weight (kilograms)	Value 4/ (thousands)	Gross weight (kilograms)	Value 4/ (thousands)	
Hydrobromic acid	2811.19.3000	125	\$143	179	\$215	Israel 78%; Netherlands 22%.
Ethylene dibromide	2903.30.0500	836	599	3	43	United Kingdom 100%.
Methyl bromide	2903.30.1520	3,540	4,470	3,530	6,230	Israel 100%.
Dibromoneopentyl glycol	2905.50.3000	--	--	1,000	3,480	Do.
Tetrabromobisphenol A	2908.10.2500	8	NA	349	699	Israel 95%; Netherlands 5%.
Decabromodiphenyl oxide and octabromodiphenyl oxide	2909.30.0700	1,340	3,050	1,460	4,190	Israel 100%.
Total		5,850 r/ 5/	NA	6,520	14,900	

r/ Revised. NA Not available.

1/ These data detail the information included in table 1, imports of "Other Bromine Compounds".

2/ Data are rounded to three significant digits.

3/ Harmonized Tariff Schedule of the United States.

4/ Declared c.i.f. valuation.

5/ Certain compounds reported in 1995 are not included in that year's total.

Source: Bureau of the Census.

TABLE 5
WORLD BROMINE ANNUAL PLANT CAPACITIES 1/ AND SOURCES, DECEMBER 31, 1996

Country and company	Location	Capacity (thousand kilograms)	Source
Azerbaijan:			
Neftechala Bromine Plant	Baku	5,000	Underground brines.
China:			
Laizhou Bromine Works	Shandong	30,000	Do.
France:			
Atochem	Port-de-Bouc	13,600	Seawater.
Mines de Potasse d'Alsace S.A.	Mulhouse	2,300	Bitterns of mined potash.
India:			
Hindustan Salts Ltd.	Jaipur		Seawater bitterns from salt production.
Mettur Chemicals	Mettur Dam	1,500	
Tata Chemicals	Mithapur		
Israel:			
Dead Sea Bromine Co. Ltd.	Sdom	190,000	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.
Spain:			
Derivados del Etilo S.A.	Villaricos	900	Do.
Turkmenistan			
Nebitag Iodine Plant	Vyshka	3,200	Underground mines.
Cheicken Chemical Plant	Balkan	6,400	Do.
Ukraine			
Perekopskry Bromine Plant	Krasnoperckopsk	3,000	Do.
United Kingdom:			
Associated Octel Co. Ltd.	Amlwch	30,000	Seawater.

1/Excludes U.S. production capacity. See table 2.

TABLE 6
BROMINE: ESTIMATED WORLD REFINERY PRODUCTION, BY COUNTRY 1/ 2/

(Thousand kilograms)

Country 3/	1992	1993	1994	1995	1996
Azerbaijan	5,000	4,000	3,000	2,000	2,000
China	16,650	24,600 r/	31,400 r/	30,000 r/	30,000
France	3,200 4/	2,290	2,190 r/	2,260 r/	2,200
Germany	-- r/	-- r/	-- r/	-- r/	--
India	1,300	1,400	1,400	1,500	1,500
Israel	135,000	135,000	135,000	135,000	135,000
Italy	300	300	300	300	300
Japan	15,000	15,000	15,000	15,000	15,000
Spain	250	200	200	200	200
Turkmenistan	12,000	10,000	8,000	7,000	7,000
Ukraine	7,000	5,000	4,000	3,500	3,000
United Kingdom	29,903 4/	27,423 4/	33,800 r/	26,200 r/	28,000
United States 5/	171,000 4/	177,000 4/	195,000 4/	218,000 4/	227,000 4/
Total	397,000	402,000 r/	429,000 r/	441,000 r/	451,000

r/ Revised.

1/ World totals, U.S. data, and estimated data are rounded to three significant digits; may not add to totals shown.

2/ Table includes data available through Apr. 24, 1997.

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

4/ Reported figure.

5/ Sold or used by producers.