IODINE

A. Commodity Summary

Iodine compounds are found in seawater, seaweed, marine organisms, and brines. Iodine and its compounds are generally marketed in the form of crude iodine, resublimed iodine, calcium iodate, calcium iodide, potassium iodide, sodium iodide, and numerous organic compounds.[1] Final uses of iodine include animal feed supplements, catalysts, inks and colorants, pharmaceuticals, photographic chemicals and film, sanitary and industrial disinfectants, and stabilizers.

Japan and Chile are the largest producers of iodine in the world and account for 99% of the U.S. iodine imports. All domestic iodine production is from iodine-rich natural brines in the deep subsurface of the Anadarko basin of northwestern Oklahoma. Oklahoma production began in 1977 and at present, three companies operate a total of four facilities (three major plants and one miniplant) for the recovery of iodine. The U.S. Bureau of Mines estimates that domestic production was 2,000,000 kilograms in 1994.[2] Exhibit 1 presents the names and locations of the facilities involved in the production of iodine.

EXHIBIT 1

SUMMARY OF IODINE PROCESSING FACILITIES

Facility Name	Location
Asahi Glass Company of Japan	Woodward, OK
Iochem Corporation of Japan	Vici, OK
North American Brine Resources (miniplant)	Dover, OK
North American Brine Resources (major plant)	Woodward, OK

B. Generalized Process Description

1. Discussion of Typical Production Processes

All three facilities (Asahi Glass Company of Japan, Iochem Corporation of Japan, and North America Brine Resources) obtain iodine-rich brines from the Morrowan sandstones. Asahi Glass Company operates 22 production wells and 10 injection wells ranging in depth from 2,130 to 2,290 meters. The Iochem facility has nine production wells and four injection wells ranging in depth from 3,000 to 3,183 meters. The North American Brine Resources facility operates two production wells and three injection wells drilled to about 1,800 meters.

North American Brine Resources also operates a mini facility near Dover, OK. At the Dover facility, North American Brine Resources recovers iodine from oil-field brines collected from a number of oil and gas wells in nearby parts of northwestern Oklahoma.

Brines are separated from hydrocarbons by using the blowing-out process. Iochem Corporation and North American's Woodward facility both use this process.[3] Exhibit 2 presents a typical process flow diagram for the production of iodine from brines by the blowing-out process.

2. Generalized Process Flow Diagram

Exhibit 2 displays the blowing-out process. In the first stage of this process, hydrogen sulfide gas (contained in the brine) is removed. This gas is reacted to form sulfur compounds which are sent to a hazardous waste disposal facility. The second stage of processing is chlorine oxidation to convert iodide to iodine. The iodine is then removed from the brine by air vapor stripping (air-blowout). The waste brine is treated with lime to adjust pH and is reinjected into Class

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[1] Kenneth S. Johnson, "Iodine," from Industrial Minerals and Rocks, 6th edition, Society for Mining, Metallurgy, and Exploration, 1994, pp. 583-587.

[2] Phyllis Lyday, "Iodine," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 82-83.

[3] Phyllis A. Lyday, "Iodine," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 609-612.

IV disposal wells. The iodine vapor is absorbed by a solution of hydriodic and sulfuric acids. Sulfur dioxide is added to reduce the absorbed iodine to hydriodic acid. Most of the solution is recirculated to the absorption tower, but a bleed stream is sent to a reactor for iodine recovery. In the reactor, chlorine is added to oxidize and liberate the iodine which precipitates and settles out of solution. The settled iodine is filtered to remove waste liquor and melted under a layer of concentrated sulfuric acid. The melted iodine is then solidified either as flakes or ingots.[4]

Iodine is also recovered from oil well brines. In a settling tank, the iodine containing brine settles to the bottom and the oil rises to the top. The oil is skimmed off and processed with other oil from nearby wells. The brine is sent through a chlorinator which frees the iodine. It is then absorbed onto charcoal which is back-flushed with potassium or sodium hydroxide when full. This solution is treated with hydrochloric acid which results in a 90% crude iodine product. The spent brine is reinjected and the potassium/sodium hydroxide is recycled.[5]

3. Identification/Discussion of Novel (or otherwise distinct) Process(es)

While domestic iodine production employs the chlorine-oxidation air-blowout method for recovery of iodine, three other brine clarification processes exist. In one process, silver iodide is precipitated by the addition of a silver nitrate solution. The silver iodide is filtered and treated with scrap iron to form metallic silver and a solution of ferrous iodide. The silver is redissolved in nitric acid and recycled, and the solution is treated with chlorine to liberate the iodine. In a second process, chlorine is added after clarification to liberate the iodine as a free element in solution. Passing the solution over bales of copper wire precipitates insoluble cuprous iodides. At intervals, the bales are agitated with water to separate the adhering iodide; the bales are then recycled. The cuprous iodide suspended in the water is filtered, dried, and sold. The third process uses ion-exchange resins on brines which have been oxidized to liberate iodine. The liberated iodine, which is in the form of polyiodide, is absorbed on an anion-exchange resin. When the ion-exchange resin is saturated, it is discharged from the bottom of the column and then transferred to the elutriation column. Iodine is elutriated with a caustic solution followed by sodium chloride. The regenerated resin is returned to the absorption column. The iodine-rich elutriant is acidified and oxidized to precipitate iodine. The crude iodine is then separated in a centrifuge and
purified with hot sulfuric acid or refined by sublimation.[6]

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[4] U.S. Environmental Protection Agency, "Iodine," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-109 - 2-112.

[5] Personal Communication between ICF Incorporated and Phyllis Lyday, U.S. Bureau of Mines. October 11, 1994.

[6] "Iodine and Iodine Compounds," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., 1981, Vol. XIII, pp. 655-656.

EXHIBIT 2

THE BLOWING-OUT PROCESS

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-109 - 2-112.

The Chilean nitrate industry employs another method for iodine recovery. Iodine is extracted from caliche as sodium iodate, along with sodium nitrate. The iodate accumulates in mother liquors during crystallization of the nitrate. Part is drawn off and treated with sodium bisulfite solution. Fresh mother liquor is added to the solution to liberate the iodine. The precipitated iodine is filtered in bag filters and the iodine-free mother liquor is returned to the nitrate leaching cycle after neutralization with soda ash. The iodine cake is washed, pressed, broken up, and sublimed in retorts. The product is then crushed and packaged.[7]

4. Beneficiation/Processing Boundaries

Based on a review of the process, there are no mineral processing operations involved in the production of iodine.

C. Process Waste Streams

Existing data and engineering judgement suggest that the wastes listed below from iodine production do not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate these materials further.

1. Extraction/Beneficiation Wastes

Sulfur compounds from hydrogen sulfide removal are sent to a hazardous waste disposal facility.

Waste brine. Waste brine contains 6,800 kkg of spent brine solids per kkg of product iodine. Waste brine is processed for other solids recovery and then either used in chlor-alkali manufacture or returned to the source. Bromine, calcium chloride and magnesium hydroxide may be recovered from these spent brines.[8]

Precipitation with Chlorine

Waste bleed liquor.

Filtration

Filtrate wastes may be recycled.

Sludge.

Waste Acid.

2. Mineral Processing Wastes

None are identified.

D. Ancillary Hazardous Wastes

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents (e.g., petroleum naptha), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, waste oil (which may or may not be hazardous) and other lubricants.

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[7] Ibid.

[8] U.S. Environmental Protection Agency, Multi-Media Assessment of the Inorganic Chemicals Industry, Volume II, 1980, Chapter 9.

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