

US EPA ARCHIVE DOCUMENT

BORON

A. Commodity Summary

Borates are defined by industry as any compound that contains or supplies boric oxide. A large number of materials contain boric oxide, but the three most common boron containing minerals are borax, ulexite, and colemanite.¹ Borate production in the United States is centered mainly in the Mojave Desert in southern California. Borax and kernite are mined by U.S. Borax (located in Boron, California) and borate is also recovered from brines pumped from Searles Lake.²

Borax is the most important boron mineral for the borate industry. It crushes freely, and dissolves readily in water, and its solubility and rate of solution increase with water temperature. Kernite has a higher B₂O₃ content than borax, but its excellent cleavage causes it to form fibers that mat and clog handling equipment. Being slowly soluble in water, kernite requires autoclaving or pre-refinery hydration for efficient conversion into refined products. It is currently used primarily as feed for the boric acid plant located in Boron, California.³ Colemanite is the preferred calcium-bearing borate used by the non-sodium fiberglass industry. Although it has low solubility in water, it readily dissolves in acid.⁴

The major uses of borates include: fiberglass insulation, textile or continuous-filament glass fibers, glass, detergents and bleaches, enamels and frits, fertilizers, and fire retardants.⁵ According to the U.S. Bureau of Mines, apparent domestic consumption of boric oxide in 1994 was estimated at 362 thousand metric tons.⁶

B. Generalized Process Description

1. Discussion of Typical Production Processes

There are two companies that operate borate recovery plants domestically, each using a distinctly different borate-containing source. The first plant near Searles Lake recovers borax from natural mineral-rich lake brines. The process at Searles Lake involves fractional distillation followed by evaporation. Borax is only one of the products recovered there; other products include sodium sulfate, lithium compounds, potash, and other salts. The second company, U.S. Borax, mines and processes crude and refined sodium borates, their anhydrous derivatives, and anhydrous boric acid at a plant in Kern, California.⁷

¹ Robert B. Kistler and Cahit Helvacı, "Boron and Borates," from Industrial Minerals And Rocks, 1994, p. 171.

² Ibid.

³ Ibid.

⁴ Ibid.

⁵ Ibid., p. 183.

⁶ Phyllis A. Lyday, "Boron," from Mineral Commodity Summaries, U.S. Bureau of Mines, 1995, pp. 32-33.

⁷ Phyllis A. Lyday, "Boron," from Minerals Yearbook Volume 1. Metals and Minerals, 1992, p. 249.

2. Generalized Process Flow Diagram

Exhibits 1 through 4 present the process flow diagrams for borate brine extraction and boric acid recovery. Exhibit 1 illustrates the processes used to prepare boric acid from ore in Boron, California. Exhibits 2, 3 and 4 present the methods used at two of the plants involved in the Searles Lake operations to recover borates from the brines deposits in California.

Borate Ore Processing

At the U.S. Borax facility in Boron, California, the ores are selectively mined, crushed, and stockpiled for production at two distinct facilities producing sodium borate and boric acid, respectively.

Sodium Borate Production. One facility produces sodium borate from the ore and the other produces boric acid. Since the ore used is principally tincal, which is soluble in water, after the ore is crushed, the tincal is dissolved in water. The resulting insolubles are then separated from the solution and the clarified liquor is fed to the crystallizers. Next, the crystals of sodium borate are separated from the weak solution which then can be recycled back to the dissolution step. The crystals are dried and can either be sold as borax or treated further to produce other borate materials.⁸ One of the products prepared when the crystals are cooled is sodium borate decahydrate. If sodium borate pentahydrate is the desired product, the sodium borate decahydrate can be sent to further recrystallization. Anhydrous sodium borate can be produced by thermally dehydrating either the sodium borate decahydrate or sodium borate pentahydrate.⁹ U.S. Borax also produces boric acid from ores, discussed below.

Boric Acid Production. As mentioned above, some ore from the stockpile at the U.S. Borax facility is reacted with sulfuric acid and used as feed in the production of boric acid.¹⁰ Exhibit 1 presents the process used to produce boric acid from the ore stockpile. Clays, sands and other impurities are also present in the ore. After the ore is crushed and ground, it is dissolved into an aqueous stream. Since kernite, the primary borate mineral present, is not soluble in water, sufficient sulfuric acid must be added to the dissolving unit. Next the clay and other insolubles must be removed from the aqueous stream. Rake classifiers separate out the larger material, while settling tanks and thickeners are used to remove the finer materials. The stream is then filtered further to remove any remaining insoluble materials. After filtration, the solution is pumped to crystallizers. In the crystallizers, the solution is cooled, forming a slurry containing solid boric acid crystals and a boric acid solution. Further filtration and centrifugation separate the solid boric acid, which can be dried and packaged for sale.¹¹ The remaining liquor can be further evaporated to recover a sodium sulfate co-product. If the desired product is ammonium borate, this can be prepared by reacting boric acid with ammonium hydroxide. The ratio of raw materials used determines whether the resulting product is diammonium tetraborate or ammonium pentaborate.¹²

⁸ U.S. Environmental Protection Agency, "Boron," from 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-77-2-84.

⁹ Versar, Inc., "Boron Derivatives," Multi-media Assessment of the Inorganic Chemicals Industry, Prepared for U.S. Environmental Protection Agency, August 1980, p. 2-5.

¹⁰ Ibid.

¹¹ "Comments Regarding Classification of the Boric Acid Production Line at Boron Operation of United States Borax & Chemical Corporation," Memorandum and Enclosures from W.W. Cooper, Ph.D., Senior Environmental Scientist, U.S. Borax to Mr. Lynn E. Johnson, R.E.H.S., Toxic Substances Control Program. October 3 and 11, 1991.

¹² Versar, Inc., 1980, Op. Cit., p. 2-11.

EXHIBIT 1

BORIC ACID PRODUCTION AT BORON, CALIFORNIA

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-77-2-84. (Adapted)

Brine Extraction

Operations at Searles Dry Lake in California involve the recovery of boron from brine deposits at three separate facilities: Trona, Argus, and Westend. Not all of these facilities are directly involved with the extraction of boron from brines. The Argus facility, for example, only produces soda ash, however, the carbonated liquid from this plant is used at the Westend plant. Borates can be recovered from concentrated brines prepared by either of two methods: carbonation or evaporation. Exhibit 2 presents the process flow diagrams for the method used at the Westend plant. Exhibit 3 presents the liquid-liquid extraction steps used at the Trona plant to process brine prepared by evaporation.

Westend Plant (Carbonated Liquor). Carbonation is used at the Argus facility to supersaturate the brine solution with sodium bicarbonate. As shown in Exhibit 2, the carbonated liquor from this facility is used in combination with the brine solution at the Westend facility. The Westend facility produces anhydrous sodium borate, sodium borate pentahydrate, sodium borate decahydrate, boric acid, sodium sulfate, and sodium bicarbonate. At the Westend plant, after the sodium bicarbonate has precipitated out, the brine and carbonate liquor mixture is cooled to crystallize sodium borate decahydrate. The crude sodium decahydrate is filtered out from the liquor, which can be sent for further processing to the sulfate plant. The crude sodium borate decahydrate is then heated to its melting point to remove hydrated water, thus producing anhydrous sodium borate, which can either be packaged and sold or sent to further processing. Although not shown in the Exhibit 2, the sodium borate decahydrate can be redissolved and hydrated and then cooled to form either sodium borate decahydrate or sodium borate pentahydrate. If the anhydrous sodium borate is reacted with sulfuric acid instead, the resulting product is boric acid.¹³

Trona Plant (Evaporated Brine). Evaporation processes are used in the Searles Lake operations to remove sodium chloride from the brine and to concentrate other desired constituents of the brine prior to further processing. The brine is pumped initially to solar evaporation ponds and concentrated. As the brine is evaporated, the sodium chloride concentration increases until the NaCl crystallizes out of solution. In addition, during the evaporation process, a rapid, controlled cooling selectively crystallizes various other salts including sodium bicarbonate and sodium sulfate. The concentrated brine from the evaporation ponds is then sent to the Trona plant for use as brine feedstock.¹⁴

Liquid-Liquid Extraction. The Trona facility uses a proprietary liquid-liquid extraction process to remove borate compounds from the brine. Specifically, during the process the brine is mixed with a chelating agent in a kerosene solution to remove the borates from the brine. Brine is pumped to the plant and emulsified. The emulsion is sent to a settling tank and through an API separator to break the emulsion and the extractant from the brine. The spent brine is returned to Searles Lake. The extractant is then combined with dilute sulfuric acid to convert the sodium borate to boric acid. This step produces a strip liquor containing boric acid, sodium sulfate, potassium sulfate, and sodium chloride. The strip liquor is then sent to a carbon filtration column to remove any remaining organic fractions. The filtered liquor is vacuum cooled in a boric acid crystallizer. The resulting boric acid crystals are centrifuged to separate them from the liquor, washed, dried, and packaged for sale. The resulting "mother liquor" is vacuum cooled further to crystallize the mixed sulfates, which are centrifuged to form a sulfate cake and sent to a potash production line.¹⁵

¹³ California Department of Toxic Substances Control, "Searles Lake Mining Operation," Memorandum from William Soo Hoo, Chief Counsel to Van Housman, Office of Solid Waste, U.S. Environmental Protection Agency, August 1, 1991.

¹⁴ Ibid.

¹⁵ Ibid.

EXHIBIT 2

**BORATE BRINE PROCESSING AT SEARLES LAKE, CALIFORNIA
Westend Plant (Carbonated Liquor Feedstock)**

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-77-2-84. (Adapted)

EXHIBIT 3

**BORATE BRINE PROCESSING AT SEARLES LAKE, CALIFORNIA
Trona Plant (Liquid-Liquid Extraction)**

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-77-2-84. (Adapted)

Potash/Borax Line. The potash/borax line is part of the Trona plant that produces pentahydrate borax, anhydrous borax, potassium chloride (potash), and potassium sulfates. As shown in Exhibit 4, brine is pumped to the plant from the evaporation ponds and sent to further evaporation. Following the evaporation, some of the concentrated brine is fed to tanks and vacuum cooled. Following this, the resultant halite is slurried, filtered, washed, and sent back to Searles Lake with the spent liquor. After the drying step, the solution is cooled and the potassium chloride that precipitates out can be sold as a product. The remaining brine is mixed with the sulfate cake from the liquid-liquid extraction process and potassium sulfate is precipitated. Following the precipitation of potassium chloride, the residual solution can be cooled to allow sodium borate pentahydrate to precipitate out from the remaining solution. This is then redissolved, hydrated, and filtered, producing dehydrated borax products (i.e., sodium borate decahydrate or sodium borate pentahydrate). The decahydrate borax can be further processed by heating to remove hydrated water, thus producing anhydrous sodium borate.¹⁶ At Searles Lake the same processes are also used to produce chemicals including sodium chloride, soda ash, and potassium chloride. These solids are precipitated from the brine solution as the solution evaporates.¹⁷

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

None Identified.

4. Beneficiation/Extraction Boundary

EPA established the criteria for determining which wastes arising from the various mineral production sectors come from mineral processing operations and which are from beneficiation activities in the September 1989 final rule (see 54 Fed. Reg. 36592, 36616 codified at 261.4(b)(7)). In essence, beneficiation operations typically serve to separate and concentrate the mineral values from waste material, remove impurities, or prepare the ore for further refinement. Beneficiation activities generally do not change the mineral values themselves other than by reducing (e.g., crushing or grinding), or enlarging (e.g., pelletizing or briquetting) particle size to facilitate processing. A chemical change in the mineral value does not typically occur in beneficiation.

Mineral processing operations, in contrast, generally follow beneficiation and serve to change the concentrated mineral value into a more useful chemical form. This is often done by using heat (e.g., smelting) or chemical reactions (e.g., acid digestion, chlorination) to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical and chemical structure of the incoming ore or mineral feedstock such that the materials leaving the operation do not closely resemble those that entered the operation. Typically, beneficiation wastes are earthen in character, whereas mineral processing wastes are derived from melting or chemical changes.

EPA approached the problem of determining which operations are beneficiation and which (if any) are processing in a step-wise fashion, beginning with relatively straightforward questions and proceeding into more detailed examination of unit operations, as necessary. To locate the beneficiation/processing "line" at a given facility within this mineral commodity sector, EPA reviewed the detailed process flow diagram(s), as well as information on ore type(s), the functional importance of each step in the production sequence, and waste generation points and quantities presented above in this section.

EPA determined that for the boric acid production process within this specific mineral commodity sector, the beneficiation/processing line occurs between preparation and acidification of ore. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where a significant chemical change to the ore occurs (sodium borate (ore) reacts with sulfuric acid to produce boric acid and sodium sulfate). EPA also determined that the sodium borate and the brine extraction production processes do not generate any mineral processing wastes. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents the mineral processing waste streams generated after the beneficiation/processing line in section C.2, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

¹⁶ Ibid.

¹⁷ Versar Inc., 1980, Op. Cit., p. 2-7.

Borate Ore Processing

Gangue. Gangue solids are generated from the initial dissolution step during the production of sodium borate decahydrate. In 1980, these waste were reported as generally inert insolubles, although they contained 0.08 percent natural arsenic mineral realgar. The solid wastes from ore residues and evaporation wastes were sent to on-site lined evaporation ponds.¹⁸

Wastewater. Process wastewater from washing contains dissolved borax and other salts may be sent to lined evaporation ponds.¹⁹

From Brines

Spent Solvents, Crud, and Waste Brine. The brine extraction process generates waste brine and spent solvents. The plant extract or crud generated during the recovery of boron from brines at the Trona plant contains arsenic and halogens and is ignitable.²⁰

Particulate Emissions. Particulates generated from drying operations are collected in dry bags and recycled. In 1980, the wastes were generated at approximately 14 kg per kkg of product.²¹

¹⁸ Ibid.

¹⁹ Versar, Inc., 1980, Op. Cit., p. 2-7.

²⁰ California Department of Toxic Substances Control, Memorandum from William Soo Hoo, Director, to Sylvia K. Lowrance, Office of Solid Waste, U.S. Environmental Protection Agency, May 8, 1992.

²¹ Versar, Inc., 1980, p. 2-5.

EXHIBIT 4

**BORIC ACID PRODUCTION AT SEARLES LAKE, CALIFORNIA
Trona Plant (Potash/Borax Production)**

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-77-2-84. (Adapted)

2. Mineral Processing Wastes

Boric Acid Production

Spent Sodium Sulfate. Crystallization produces sodium sulfate. Existing data and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Waste Liquor. Some of the liquor remaining after the boric acid is filtered off contains arsenic. In 1980, one site reported that the arsenic was present as a natural impurity in the ore used to make the sodium pentahydrate. Another site reported returning the arsenic-containing wastes to the original subterranean brine source. Low, medium, and high annual waste generation rates were estimated as 300 metric tons/yr, 150,000 metric tons/yr, and 300,000 metric tons/yr, respectively. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity for arsenic. This waste is recycled and is classified as a spent material.

Underflow Mud. Existing data and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

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 naphtha), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors.

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