SODA ASH

A. Commodity Summary

Six companies in Wyoming and California comprise the United States soda ash industry, which is the largest in the world. The total estimated value of domestic soda ash produced in 1994 was $650 million. According the U.S. Bureau of Mines, the six producers had a combined nameplate capacity of 11 million tons per year and operated at 83% of that capacity in 1994. Soda ash is used in many products:

- glass, 49%
- soap and detergents, 13%
- flue gas desulfurization, 3%
- chemicals, 23%
- distributors, 5%
- pulp and paper, 2%[1]

Soda ash is the common name for sodium carbonate. This alkali compound is the eleventh largest inorganic chemical, in terms of production, of all domestic inorganic and organic chemicals, excluding petrochemical feedstocks. Natural soda ash is produced from trona ore, sodium carbonate-bearing brines, or surface mineralization. All of the active facilities produce natural soda ash from sodium carbonate-rich brines or from underground mining of trona ore.[2] Synthetic soda ash can be made by one of several chemical reactions that use common raw materials for feedstocks, such as limestone, salt, and coal. Other technologies produce soda ash as a byproduct.[3] Exhibit 1 presents the names and locations of the facilities involved in the production of soda ash.

EXHIBIT 1

SUMMARY OF SODA ASH PROCESSING FACILITIES

Facility Name	Location
FMC Corporation	Green River, WY
General Chemical Partners	Green River, WY
North American Chemical Company	Argus,CA Westend, CA
Rhone-Poulenc Mine	Green River, WY
Tenneco	Green River, WY
TG Soda Ash Mine	Green River, WY

---

[1] Dennis Kostick, "Soda Ash," from Mineral Commodity Summaries, U.S. Bureau of Mines, January 1995, pp. 156-157.

[2] Dennis S. Kostick, "Soda Ash and Sodium Sulfate," from Minerals Yearbook Volume 1. Metals and Minerals, U.S. Bureau of Mines, 1992, pp. 1237-1250.

[3] Dennis Kostick, "Soda Ash," from Industrial Minerals and Rocks, 6th ed., Society for Mining, Metallurgy, and Exploration, 1994, pp. 929-955.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Soda ash from Wyoming trona is mined, crushed, dried, dissolved, filtered, recrystallized, and redried. In California, soda ash from sodium carbonate-bearing brines in solution is mined, carbonated, filtered, dried, decomposed, bleached, and recrystallized to dense soda ash. These processes are described in more detail below.

2. Generalized Process Flow Diagram

All the Wyoming trona mines use room and pillar mining with multiple entry systems. Most use a combination of one or more types of mining: conventional, continuous, longwall, shortwall, or solution.[4] The FMC Corporation is the only natural soda ash producer that uses longwall mining to augment its mining technology. Shortwall mining is used exclusively by TG Soda Ash, Inc. Since the late 1980's, most Wyoming soda ash companies have installed continuous hauling systems to replace shuttle cars. FMC Corporation has been discharging tailings and spent solutions from solution mining to its tailing ponds since about 1953. Since then, sodium carbonate decahydrate crystals have been collecting on the bottom of these ponds at a rate of 20 to 30 cm per year. In 1985, FMC began using a bucket wheel dredge to extract almost 160 kt of crystals annually from the 485 hectare pond. The crystals are slurried, dewatered, melted, and processed into soda ash in the refinery. Other producers have similar ponds where sodium carbonate decahydrate has collected since the plants were built. Because of environmental considerations and the cost of constructing and maintaining tailing ponds, all the producers now inject waste tailings underground. This will reduce the future buildup of sodium decahydrate in the tailing ponds. In addition, several of the Wyoming soda ash producers are selling their spent purge liquors that contain dissolved sodium carbonate in solution to local power utility companies for pH control of process water.[5] Trona ore must be further refined to yield a 99% pure soda ash product.

Sodium sulfate, sodium chloride, potassium chloride, and borax must be physically and chemically removed from sodium carbonate bearing brines in order to process the sodium carbonate content into refined soda ash. The Wyoming facilities use one of two processes to refine soda ash from trona ore: (1) the monohydrate process or (2) the sesquicarbonate process. The two processes are essentially the same, differing only in the sequencing of procedures. The monohydrate method is the primary process used today to make soda ash. In addition to these two processes, the North American facilities at Searles Lake produce soda ash via another operation.[6]

Monohydrate Process

In the monohydrate process, trona is crushed and calcined in rotary gas-fired calciners operating at 150-300°C. Calcining removes water and carbon dioxide from the ore, and leaves an impure product containing 85% soda ash and 15% insolubles. The thermal decomposition of trona involves the following reaction:

$$2Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O \text{ (trona)} + \text{heat} \rightarrow 3Na_2CO_3 + CO_2 + 5H_2O$$

The calcinate is dissolved with hot water and sent to evaporative, multiple-effect crystallizers or mechanical vapor recompression crystallizers where sodium carbonate monohydrate crystals precipitate at 40-100°C. This is below the transition temperature of monohydrate to anhydrous soda ash. The insoluble portion of the ore containing shale and shortite are collected by clarifiers, filtered, and washed to recover any additional alkali before they are piped as a slurry to tailing ponds or injected underground. Some companies pass the liquor through activated carbon beds prior to crystallization to remove trace organics solubilized from the oil shale so that the organics do no interfere with crystal growth rate. The crystals are sent from the crystallizers to hydroclones and dewatered in centrifuges. The centrifuge cake is conveyed to steam tube dryers where the crystals are dehydrated into anhydrous soda ash at 150°C, screened, and sent to storage or shipment. The final product made by the monohydrate process is dense soda ash.[7] Exhibit 2 presents a process flow diagram for the monohydrate process.

Sesquicarbonate Process

---

[4] Ibid.

[5] Ibid.

[6] Ibid.

[7] Ibid.

The sesquicarbonate process, the second process used to process Wyoming trona, produces light to intermediate grades of soda ash crystals. The trona is crushed, dissolved in hot mother liquor, clarified, filtered, and passed to cooling crystallizers where crystals of sodium sesquicarbonate precipitate. Activated carbon is added to filters to control the organics that interfere with crystal growth. The sodium sesquicarbonate is hydrocloned, centrifuged, and calcined using gas or indirect steam heat. Dense soda ash can be made by calcining the sodium sesquicarbonate at 350°C.[8] Exhibit 3 presents a process flow diagram of the sesquicarbonate process.

Searles Lake Process

At the North American Chemical Company facility at Searles Lake, complex brines are first treated with carbon dioxide gas in carbonation towers to convert the sodium carbonate in solution to sodium bicarbonate, which will precipitate under these conditions. The sodium bicarbonate is separated from the remainder of the brine by settling and filtration and is then calcined to convert the product back to soda ash. The decarbonated brine is cooled to recover borax and Glauber's salt. A second dissolving, precipitating with carbon dioxide, filtering, and calcining the light soda ash to dense soda ash, results in a refined product of better than 99% sodium carbonate.[9] Exhibit 4 presents the Searles Lake process.

Sodium Bicarbonate

Sodium bicarbonate, baking soda, is manufactured by percolating carbon dioxide gas through a carbonation tower containing a saturated soda ash solution. The sodium bicarbonate precipitate is collected, filtered, centrifuged, dried, screened, and packaged. Three of the five sodium bicarbonate producers are also soda ash producers.[10]

Sodium Hydroxide

Sodium hydroxide, or chemical caustic soda, is made from lime and soda ash by the following reaction:

$$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCo_3 + 2NaOH$$

---

[8] Ibid.

[9] U.S. Bureau of Mines, 1992, Op. Cit., pp. 1237-1250.

[10] Dennis Kostick, 1994, Op. Cit., pp. 929-955.

EXHIBIT 2

THE MONOHYDRATE PROCESS

Graphic Not Available.

Source: "Soda Ash: Mineral Processing Waste Generation Profile"

EXHIBIT 3 Graphic Not Available.

THE SESQUICARBONATE PROCESS

Source: "Soda Ash: Mineral Processing Waste Generation Profile"

EXHIBIT 4

THE SEARLES LAKE PROCESS

Graphic Not Available.

Source: 1988 Final Draft Summary Report of Mineral Industry Processing Wastes, 1988, pp. 2-43 - 2-46.

The lime is slaked and added to dissolved soda ash to produce chemical caustic soda. Calcium carbonate is precipitated from the reaction, calcined back to lime, and recycled. FMC uses about half of its caustic soda to produce captive sodium cyanide for precious metal recovery at its gold operation. [11]

Sodium Sesquicarbonate

Sodium sesquicarbonate is a hydrated compound containing soda ash and sodium bicarbonate. Trona ore is first crushed and dissolved to separate the insoluble impurities. The sodium compounds in solution are then clarified, filtered, crystallized, centrifuged, calcined, and recovered as long needle-shaped monoclinic crystals of sodium sesquicarbonate. FMC has a 50 ktpy sodium sesquicarbonate facility that sells mainly to the detergent industry. [12]

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

None identified.

4. Beneficiation/Processing Boundaries

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

C. Process Waste Streams

1. Extraction/Beneficiation Wastes

Extraction and beneficiation wastes include **overburden**, **tailings**, and **spent dissolution wastes**. The trona ore dissolution wastes are sent to tailings ponds. Waste tailings are injected underground.

Monohydrate Process Waste Streams

Ore insolubles. About 110 to 150 kg per kkg of ore insolubles are generated. These insolubles are transported to evaporation ponds for disposal.[13]

Filter aid and **carbon absorbent.** The waste generation for these wastes ranges from about 0.5 to 2 kg per kkg of product. Spent carbon absorbent and spent filter aids are sent to on-site evaporation ponds for disposal.[14]

Scrubber water. Scrubber liquor is recycled to the process for recovery of additional product.[15]

Particulates from crushing and calcination are generated. The calciner offgases contain carbon dioxide. Airborne particulate emissions from crushing are about 1.5 kg per kkg of product. From calcination, emissions are about 95 kg per kkg or product. The particulates from crushing and conveying are collected in bags and recycled to the ore bin which feeds the calciners. Residual emissions from the bag collectors are 0.015 kg per kkg of product. Particulates from the calciner consist of raw sodium carbonate dust. These particulates are passed through dry cyclones and electrostatic precipitators in series. The overall removal efficiency is 99.5%, resulting in residual particulates of 0.28 kg per kkg of product. Collected particulate is periodically recycled to the calciner.[16]

At the Tenneco Corporation facility in Green River, WY, tailings generated from the calcining process are discharged to the tailings tank. The tailings tank also receives fly ash and bottom ash generated from using coal to fire the calcining kiln and the steam boiler. This waste is treated in a thickening tank by adding anionic and cationic flocculants to the tailings to increase the solids content from approximately 10 to 50% solids. The waste is then disposed

---

[11] Ibid.

[12] Ibid.

[13] Ibid.

[14] Ibid.

[15] Ibid.

[16] Ibid.

of in one of two waste management units, (1) the tailings pond, or (2) the mine void. The mine void is located in an old mine shaft approximately 800 feet below ground. Tailings which will be disposed of in the mine void are first accumulated in a holding tank adjacent to the mine shaft. The tailings are gravity fed into the mine when the holding tank fills. Tailing supernatant that accumulates in the mine is collected in a sump and periodically pumped and disposed of in the tailings pond. Eighty percent of the time thickened tailings are disposed of in the mine void and the remainder of the time thickened tailings are disposed of directly in the tailings pond.[17]

Airborne emissions from product drying, cooling, and packaging are generated from the monohydrate process. These wastes are controlled by the use of baghouses and wet scrubbers, with the recovered materials being recycled to the process. Emissions from the sodium carbonate drier are generated at about 2 kg per kkg of product. After wet scrubbing, residual emission is 0.02 kg per kkg of product. Product cooling generates about 0.7 kg of emissions per kkg of product. After bag dust collection, the residual emission is 0.005 kg per kkg of product. Product screening, storing, and packaging generates 1.4 kg of emissions per kkg of product. After bag dust collection, residual emission is 0.005 kg per kkg of product.[18]

Purge liquor. Purge liquor from calcining is often sold as a sulfur neutralizer or dust suppressant. At the California facility, purge liquor is produced in the brine operation and is sent back into the lake.

Mother liquor is a possible waste stream from centrifugation. This waste stream is recycled.

Trona ore processing waste is generated from the purification of calcined material.

At the Stauffer Chemical Company facility in Green River, WY, trona ore processing waste is generated at each of five calcining rakes after dissolution and purification. Waste from trona ore processing is pumped to a tank and combined with sluice water from a tailings pond so the waste can be pumped to one of the three on-site surface impoundments designated to receive the waste. The waste sent to the three impoundments contains approximately 10% sodium carbonate. As water evaporates the sodium carbonate dries forming sodium decahydrate.[19]

At General Chemical in Green River, WY, 1,451,488 metric tons of this waste was generated in 1988. This waste was characterized by a pH of 11.5. The waste is either sold or sent to an unlined surface impoundment.[20]

At the Tg Soda Ash facility in Green River, WY, 580 million gallons of this waste were reported in 1988. This waste reportedly had a pH of 11.5. The waste was sent to a surface impoundment lined with in-situ clay for solids precipitation and dewatering.[21]

Sesquicarbonate Process Waste Streams

Trona ore particulates are generated from crushing, drying, and calcination. About 1.5 kg per kkg of trona ore particulates are generated from crushing. About 2 kg per kkg of particulates are generated by drying operations. Approximately 95 kg per kkg of particulates are produced by calcination. Particulate emissions from drying and packaging are controlled by wet scrubbers and dry bag collectors, respectively. Emissions after control average 0.02 kg per kkg from the driers and 0.02 kg per kkg from the product packaging operations. Solids recovered from the dry bag collectors are recycled to product storage. Emissions from ore calcination are also collected and recycled.[22]

---

[17] U.S. Environmental Protection Agency, Mineral Processing Waste Sampling Survey Trip Reports, Tenneco Corporation, Green River, WY, August 1989.

[18] Ibid.

[19] Ibid.

[20] RTI survey for General Chemical Partners, Green River, WY, 1988, ID# 100388.

[21] RTI Survey for Tg Soda Ash, Green River, WY, 1988, ID# 100206.

[22] U.S. Environmental Protection Agency, Multi-Media Assessment of the Inorganic Chemicals Industry, Volume III, August 1980, Chapter 13.

Scrubber water is generated from air pollution control devices. This is recycled to recover additional product.[23]

Ore residues. About 110 to 150 kg per kkg or ore residues, chiefly shale, are generated in the initial steps.[24]

Spent carbon and filter wastes from carbon absorption and filtration range from 0.5 to 2.0 kg per kkg per product. Waste filter aids and carbon absorbents are washed to the evaporation ponds for final disposal. Solid wastes from initial ore leaching are slurried to tailings ponds to settle out suspended materials and then to the final disposal ponds which serve as evaporation ponds from which there is no discharge.[25]

Suspended particulate matter is generated by the use of wet scrubbers for air pollution control, resulting in wastewater containing 2 kg per kkg of suspended particulates.[26]

Purge liquor from calcining. This waste is often sold as a sulfur neutralizer or dust suppressant.

Mother liquor from centrifugation. This waste stream is often recycled.

Searles Lake Process Waste Streams

Calciner offgases. About 170 kg of water vapor and 415 kg of carbon dioxide per kkg of soda ash are generated by calcination of the sodium bicarbonate intermediate. These offgases are cooled to recover water for other on-site uses and for use in product purification. After water removal, the carbon dioxide in recycled to the initial process calcination step.[27]

Particulate emissions from driers. These emissions are controlled by dry collectors, and the recovered solids are recycled to the process. Residual airborne particulate emissions are less than 1 kg per kkg of product.[28]

Spent brine. Spent brine from the initial carbonation and filtration steps contains about 16,000 kg per kkg of product of unrecovered sodium carbonate and other raw brine constituents. The spent brine contains about 65% water, 16% sodium chloride, and 19% of other constituents including sodium sulfate, borax, and potassium chloride. This waste stream is combined with other waterborne waste streams and returned to the brine source.[29]

Waste mother liquor. This waste stream is generated from product recrystallization and contains principally unrecovered sodium carbonates, along with smaller amounts of other raw brine constituents such as sodium sulfate, borax, and potassium chloride. This waste stream is combined with other waterborne waste streams and returned to the brine source.[30]

2. Mineral Processing Wastes

None identified.

D. Ancillary Hazardous Wastes

---

[23] Ibid.

[24] Ibid.

[25] Ibid.

[26] Ibid.

[27] Ibid.

[28] Ibid.

[29] Ibid.

[30] Ibid.

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.

BIBLIOGRAPHY

"Alkali and Chlorine Products." Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed. 1992. Vol. I. pp. 876.

Kostick, Dennis S. "Soda Ash." From Industrial Minerals and Rocks. 6th ed. Society for Mining, Metallurgy, and Exploration. 1994. pp. 929-955.

Kostick, Dennis. "Soda Ash." From Mineral Commodity Summaries. U.S. Bureau of Mines. January 1995. pp. 156-157.

Kostick, Dennis. "Soda Ash and Sodium Sulfate." From Minerals Yearbook Volume 1. Metals and Minerals. U.S. Bureau of Mines. 1992. pp. 1237-1250.

Kostick, Dennis. "Soda Ash." From Mineral Facts and Problems. U.S. Bureau of Mines. 1985. pp. 741-755.

RTI survey for General Chemical Partners, Green River WY. 1988. ID# 100388.

RTI Survey for Tg Soda Ash, Green River, WY. 1988. ID# 100206.

U.S. Environmental Protection Agency. Mineral Processing Waste Sampling Survey Trip Reports. Tenneco Corporation, Green River, WY. August 1989.

U.S Environmental Protection Agency. "Soda Ash." From 1988 Final Draft Summary Report of Mineral Industry Processing Wastes. 1988. pp. 2-43--46.

U.S. Environmental Protection Agency. Multi-Media Assessment of the Inorganic Chemicals Industry. Vol. III. August 1980. Chapter 13.