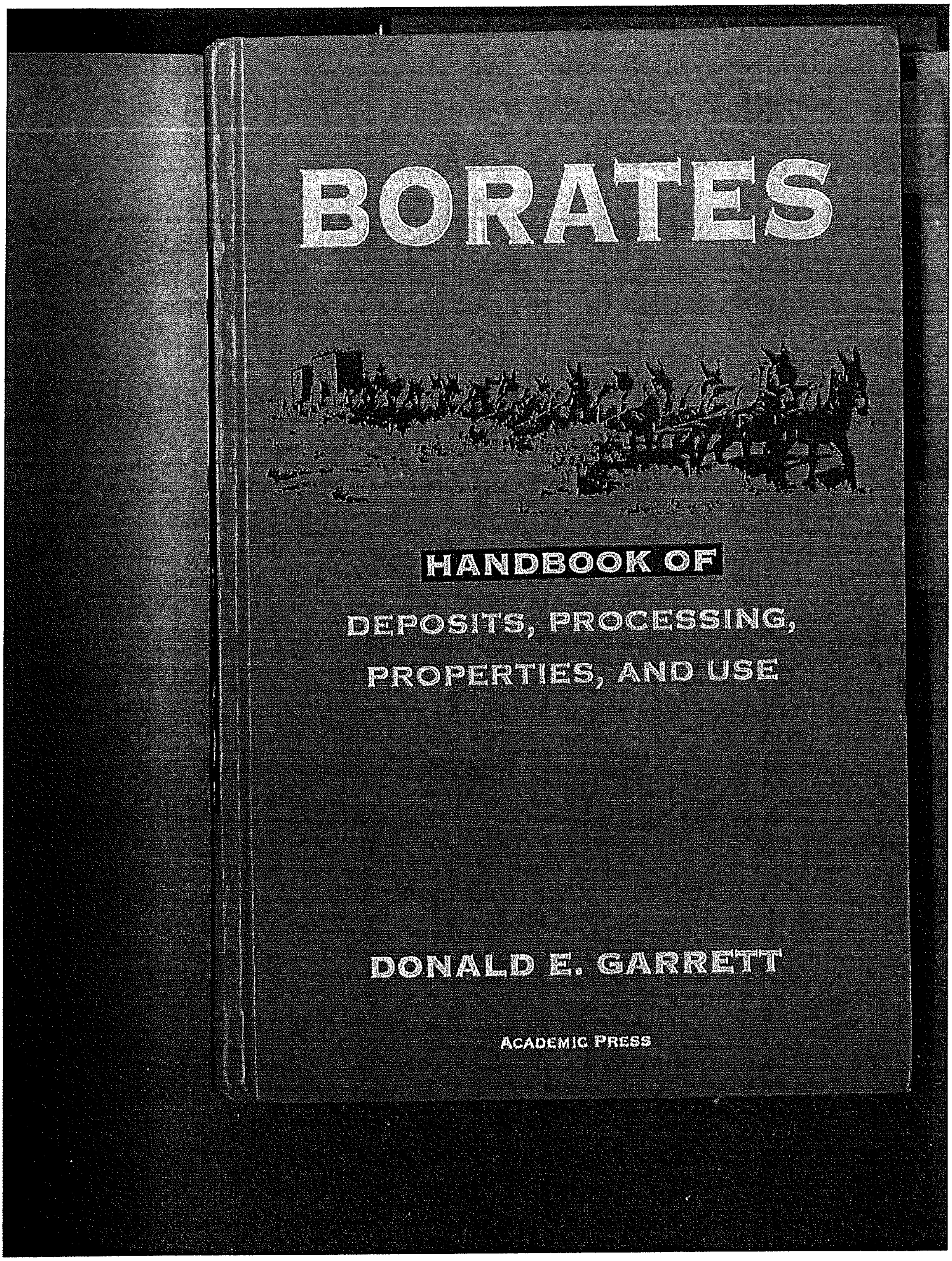

BORATES

HANDBOOK OF DEPOSITS, PROCESSING, PROPERTIES, AND USE

DONALD E. GARRETT

ACADEMIC PRESS

Borates

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Handbook of Deposits, Processing, Properties, and Use

Donald E. Garrett
SALINE PROCESSORS, INC.
OJAI, CALIFORNIA

ACADEMIC PRESS
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Front cover photograph: The 20-mule team used to haul borax from Death Valley, to Mojave, 1883–1890. (For more details, see Chapter 4, Figure 7.)

This book is printed on acid-free paper. ♾

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Contents

Chapter 1 Borate Minerals and the Origin of Borate Deposits

Chapter 2 Borax and Sassolite Deposits

Chapter 3 Calcium, Magnesium, or Silicate Buried Deposits

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Chapter 4 Calcium or Magnesium Surface (Playa or Mantle) Deposits

Chapter 5 Lake or Brine Deposits

Chapter 6 Marine Borate Occurrences: Isotropic Distribution

Chapter 7 Mining

rences: Isotropic Distribution

Chapter 8 Processing

Chapter 9 Uses of Borates

Chapter 8 Processing

The processing of each of the commercial borate minerals is a comparatively simple procedure, but the desire for good purity, low costs, high recovery and efficiency has led to many interesting and sometimes complex variations on the operations. This technology is discussed in the following section, in addition to the brief reviews given for some of the deposits in the geology chapters.

8.1 BORAX AND KERNITE

8.1.1 Argentina

8.1.1.1 Loma Blanca

S.R. Minerals (Barbados) mines borax, ulexite, and inyoite from different beds in the Loma Blanca deposit, and delivers the ore to drying pads near the mine. After drying 3–5 days, each borate is separately run through a magnetic separator to remove some of the clay, producing ores with at least 26% B_2O_3. These are then trucked 180 km southeast to a 4-hectare processing plant at Palpada (near Juju). There the ore is further crushed, kiln dried, and again sent through magnetic separators, taking the B_2O_3 content to 38%. The products can also be calcined to 54–55% B_2O_3, and sized from 2 mm to 325 mesh. Shipments are made in 45- to 50-kg sacks or 900- to 1000-kg bulk bags (Solis, 1996).

8.1.1.2 Tincalayu

The borate processing capacity of Boroquimica SAMICAF in 1990 was rated at 37,700 metric tons/year at its Campo Quijano (Quyano) plant near Salta, 227 km (250 mi) northeast of the Tincalayu mine (Norman, 1990). The 16–18% B_2O_3 ore was first given a "cold washing" treatment to remove the soluble salts and some slimes, thus raising its purity (on a dry basis) to 28% B_2O_3. Next the ore was dissolved in hot mother liquor and water, the brine settled, and the clarified hot liquor sent to tanks to cool and crystallize. When completed, the brine was decanted and the crystals removed, centrifuged, washed, and dried to produce 99.9% borax or pentahydrate. Some anhydrous product was also claimed (Dublanc, Malca, and Leale, 1993).

8.1.2 Tibet

Before the 1900s, the processing of borax from Tibet was a closely guarded secret and difficult because the sheep caravan drivers who delivered the borax "ore" coated the crystals with any available fat, oil, or grease to reduce the water-dissolving loss during transport. The Indian merchants acting as wholesalers also often adulterated the borax, making each shipment quite variable. Dissolving and recrystallization was always the first processing step, but these crystals also had to be redissolved and their brine purified. The initial solution may have required treatment by activated carbon, clay, or equivalent adsorbant to remove the organics, as well as a precipitant for some impurities, and then a bleed stream removed. For the second crystallization, perhaps only adsorbants and filtration were required. There was also a need to produce large crystals as a sign of high quality. Poor refining yielded "small crystals with a yellow color imparted by the grease with which the tincal was covered." Because of its complexity, processing became somewhat of an art, with the Dutch operation in 1773 having its "secret step," such as clarifying the initial leach solution with "the aid of the white of an egg or its equivalent slaked lime and slate." A picture of borax processing in 1556 is shown in Fig. 8.1 (Travis and Cocks, 1984).

8.1.3 Turkey

8.1.3.1 Kirka

Borax shipments from the open pit mine at Kirka began in 1972. Mined ore, −40 cm in size, was first distributed onto a 3000-metric-ton stockpile, and starting in 1974 it was was then sent to a 200-metric-ton silo to feed a 400,000-metric-ton/year washing plant (Fig. 8.2; later expanded to 600,000 metric tons/year; Anac, 1988). In it the ore was first conveyed to a series of crushers working in closed circuit with screens, where it was initially reduced to −10 cm, then to −2.5 cm with hammer mills, and finally to −6 mm with roll mills. The −2.5-cm ore had been sent to 10,000-metric-ton surge bins to be metered into the roll mills, and the mills' discharge was screened at a 1-mm (6-mesh) size. The two fractions (+6 and −6 mesh) were repulped and sent to separate scrubbers (vigorously agitated tanks). Then the 1 to 6-mm fraction was pumped to spiral classifiers (Fig. 8.3), and its coarse fraction centrifuged and sent to product bins. The original −1-mm particles were repulped in the spiral classifier's undersize slurry. Then the mixture was cycloned and the overflow sent to a hydroclassifer. Both the cyclone and hydroclassifier's underflow streams (+65 mesh) were filtered. The filter cake was added to the coarser fraction if the concentrate was to be sold directly, the mixture containing about 32% B_2O_3 and 6–8% water. It was then dried and stored in silos for shipment to the port at Bandirma. Alternately, the 6- to 65-mesh filter cake could be sent t
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Figure 8.1 Borax refining in the sixteent
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Borax Inc.)

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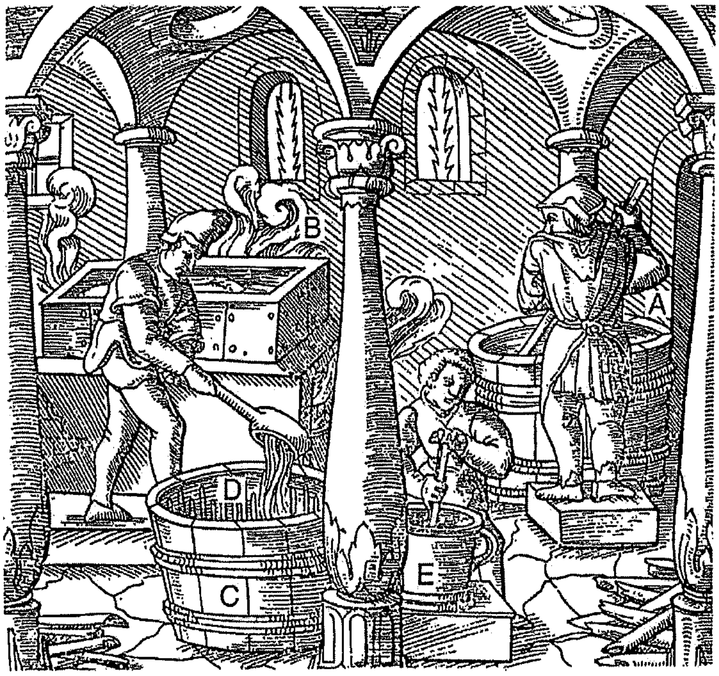

Figure 8.1 Borax refining in the sixteenth century. (A) Dissolver, (B) evaporator, (C) crystallizer, (D) copper rods, and (E) grinding. (From Travis and Cocks, 1984; picture courtesy of U.S. Borax Inc.)

65-mesh filter cake could be sent to the refinery for further processing. The overflow from the hydroclassifer was sent to a thickener, its underflow (the slimes) discarded, and the overflow brine was returned to the repulper. There was more than a 10% product loss in the washing operation (Table 8.1). In 1985 the concentrator plant operated three shifts, 7 days/week, with one of the Sunday shifts used for maintenance. There were 95 employees, and the maximum output was 2400 metric tons/day. Demircioghi (1978) reviewed the various potential borax ore beneficiation methods.

The derivatives (or purified product) plant in 1988 had a capacity of 160,000 metric tons/year of pentahydrate, 17,000 metric tons/year of borax, and 60,000 metric tons/year of anhydrous borax (Anac, 1988). The washed ore entered by conveyor belt at 50 metric tons/hr from either a stockpile or direct production. It was first dissolved in steam-heated tanks at 98°C to form a 26% $Na_2B_4O_7$ solution (saturated at 89°C). The resultant slurry was sent to countercurrent

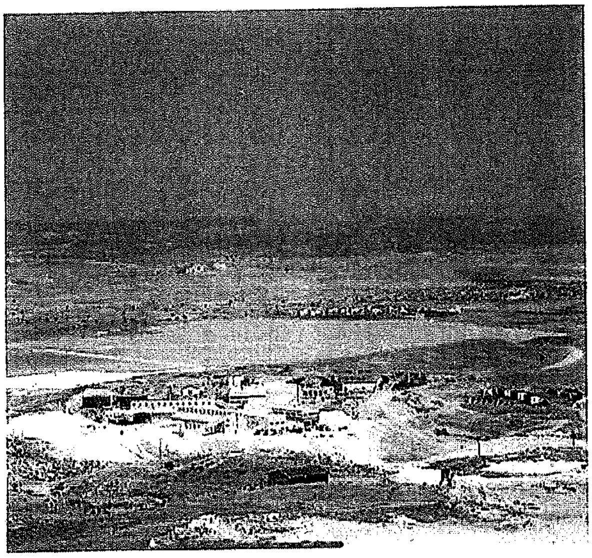

Figure 8.2 The Kirka borax processing plant. (From Etibank, 1994; pictures courtesy of Etibank.)

thickeners where the slimes were settled, washed and discarded. Gur, Turkay, and Balutcu (1994) noted that 1200 ppm (of the dry slimes present) of hydrolyzed polyacrylamide (PAM) coagulant, 10% anionic, produced a clear brine with hot, saturated high-montmorillonite slimes (with a "blue color"), but did little for high-calcite or dolomite slimes. Nonionic polyethylenoxide (PEO) gave a clear overflow with dolomite slimes at 1200 ppm, and had a slightly poorer performance at 400 ppm. Cebi, Yersel, Poslu, Behar, Nesner and Langenbrick (1994) found that 55- to 61-wt% slurries could be obtained from centrifuged (solid bowl) slimes with the aid of a coagulant, but the centrate still contained 0.4–2.6% solids.

The clear brine from the hot thickeners was next filtered in eight pressure filters and sent to a 1000-metric-ton surge tank. It then went to either of the vacuum-cooled, growth-type crystallizer circuits. In the pentahydrate unit it was cooled to 66°C at a 0.23-atm vacuum. Excess fines were removed in cyclones and redissolved to allow the production of a coarse product that could be centrifuged to a 4–5% moisture content. Borax was produced in the same manner, but the exit temperature was 46°C. The centrifuged products were dried in oil-fired rotary dryers (except one for borax, which was a steam-

Figure 8.3 Spiral classifiers at the Ki
courtesy of Etibank.)

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bagged shipment.

Part of the borax was dehydrat
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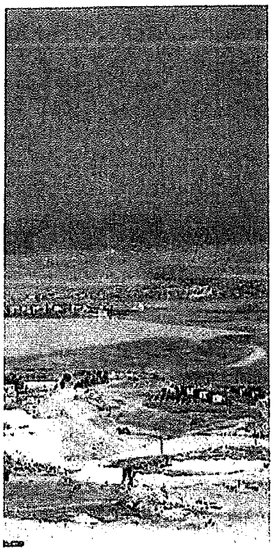

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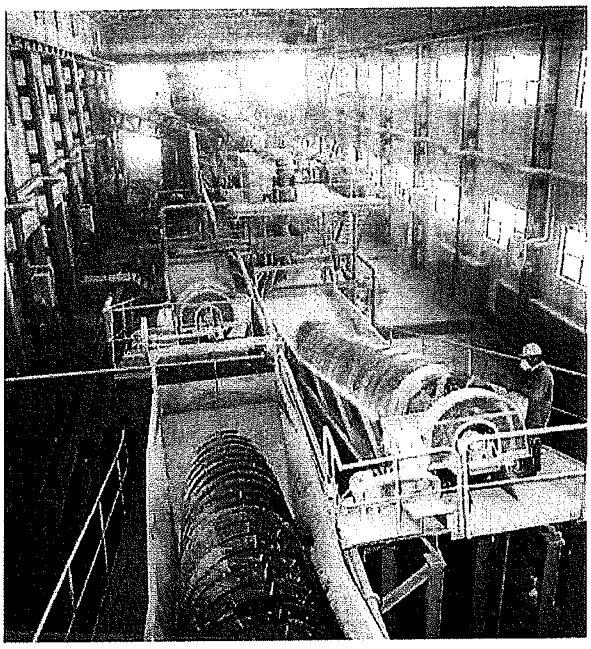

Figure 8.3 Spiral classifiers at the Kirka borax washing plant. (From Etibank, 1994; pictures courtesy of Etibank.)

Part of the borax was dehydrated in a special furnace at 1100°C to produce anhydrous borax. The resultant melt was then cooled, solidified, crushed, and screened. Oversized material was recrushed and screened, whereas the undersized material was remelted. The processing plant also had its own 3.2-megawatt power plant, both because of its remote location and to achieve better thermal efficiency with its steam-power balance. The products were trucked either to the port at Bandirma, or 18 km to a rail connection at Degirmenozu with its truck dumps into 12 small silos, and its eight 10,000-metric-ton storage buildings. Automated vibrating feeders on conveyor belts could deliver product to all of the storage buildings, and reclaim conveyors took the products to 50-ton bins over the rail lines. Three cars could be loaded simultaneously, using hopper cars for the purified products and gondolas for the concentrates. The products were weighed and analyzed before shipment, and the dust from belts and bins was returned to the plant (Dickson, 1985).

Table 8.1

Examples of the Kirka Borax Ore and Concentrator Streams[a]

A. Chemical analyses (wt%)

Elements	Ore	Concentrate	Slimes[b]
B_2O_3	26.40	34.56	15.18
MgO	7.42	2.36	13.08
CaO	5.83	1.65	11.84
SiO_2	5.60	1.54	13.58
R_2O_3	0.12	0.12	0.80
H_2O, etc.	54.63	59.77	45.52
Minerals, dry basis (wt%)			
Borax	69.11	88.43	41.44
Dolomite	13.76	4.35	23.09
Clay	11.14	2.60	27.16
Calcite	3.80	1.63	7.91
Ulexite	2.19	2.99	0.40
Total	100.00	100.00	100.00

B. Concentrate screen analyses (wt%)

Mesh size, Tyler no.	Size (mm)	Wt% on screen
+3.5	+6	3.5
5	4–6	17.5
16	1.02–4	50.5
65	0.2–1.02	28.0
−65	−0.2	0.5

[a] Albayrak and Protopapas, 1985.

[b] In some samples a high percentage of montmorillonite clay was present (Gur, Turkay, and Buluteu, 1994).

The initial plant to refine Turkish borate ore was located at the shipping port of Bandirma (Fig. 8.4), and starting in 1975 produced about 55,000 metric tons/year of borax and 35,000 metric tons/year of boric acid (made from colemanite; Anac, 1988). In 1984, 20,000 metric tons/year of sodium perborate, and in 1986 an additional 100,000 metric tons/year of boric acid capacity were added. The handling capacity of the port for refined products and concentrates was 1.5 million metric tons/year in 1995 (Norman, 1995). All of the borate operations were owned and operated by Etibank, a state-owned company.

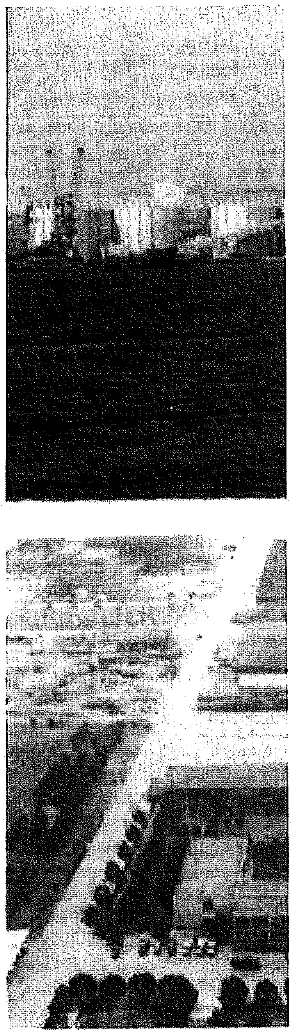

Figure 8.4 Views of the Bandirma borate
1995; pictures courtesy of Etibank.)

8.1.4 United States

8.1.4.1 Boron

A new processing plant was built in 1956 at the Kramer (boron) deposit (at the same time that it converted to open pit mining) to handle the anticipated

1
and Concentrator Streams[a]

Concentrate	Slimes[b]
34.56	15.18
2.36	13.08
1.65	11.84
1.54	13.58
0.12	0.80
59.77	45.52
88.43	41.44
4.35	23.09
2.60	27.16
1.63	7.91
2.99	0.40
100.00	100.00

б)

mm)	Wt% on screen
	3.5
6	17.5
4	50.5
1.02	28.0
	0.5

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1994).

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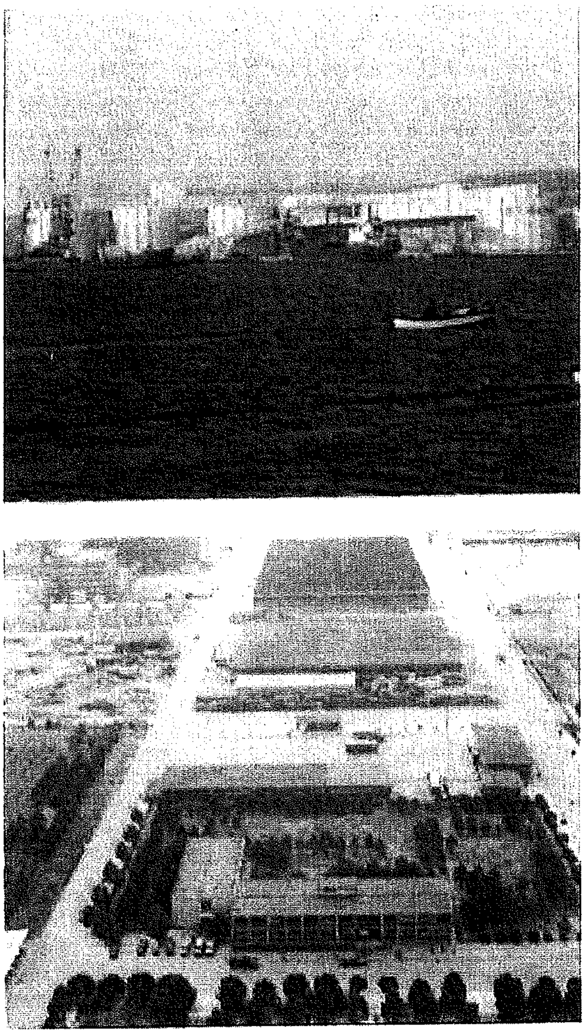
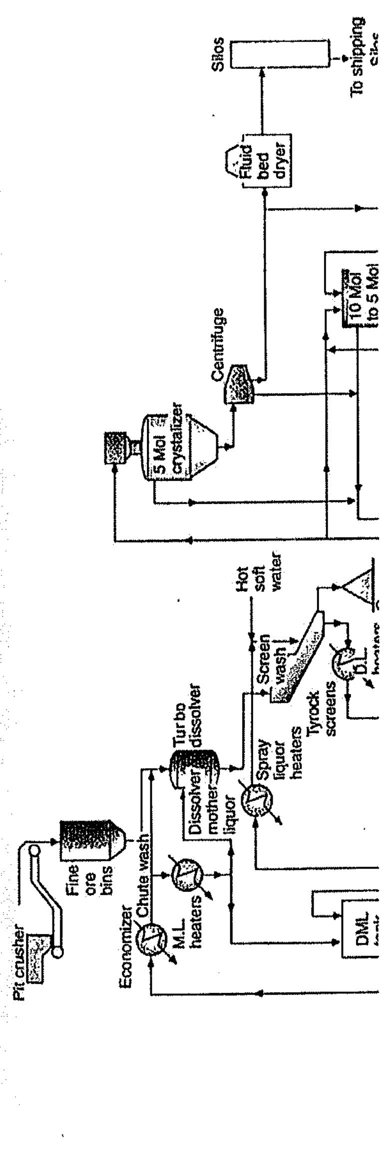


Figure 8.4 Views of the Bandirma borate processing and shipping facility. (From Etibank, 1995; pictures courtesy of Etibank.)

lower-grade ores (from 28 to 23% B_2O_3). More handling and washing capacity of insolubles was also needed, and an allowance was made for future expansion, causing the site to be enlarged to 32 hectares (0.32 km^2 or 80 acres). The high-intensity magnetic separators and some of the crude borax partial dehydration equipment (to produce pentahydrate by heating the ore to 110–121°C; Corkill, 1937) was then shut down, but the facilities to produce crude, anhydrous borax (called "Rasorite") were maintained.

In the new plant in 1958 the process started with the blending of different grades of ore, keeping the B_2O_3 content within a range of several percentage points. The −10-cm (−4-in.; also quoted as −8-in.) ore from the mine went to an automatically programmed stacker belt that discharged it in horizontal layers onto a 54,000-metric-ton, 223 × 34 × 13.7-m (730 × 112 × 45-ft) storage pile. A reclaiming tunnel 3 m (10 ft) in diameter, 244 m (800 ft) long, and 0.3 m (1 ft) deep was located under the pile, with 16 withdrawal chutes feeding a 76-cm (30-in.) conveyor belt (Dayton, 1957). However, it soon developed that outside (machine) reclaiming was necessary for all of the ore, and two overhead 1100-metric-ton/hr bucket–wheel reclaimers for each plant (borax and boric acid) were later installed (Anon., 1996b). After passing by a tramp iron magnet, the ore went to an impactor working in closed circuit with two screens to reduce its size to −1.9 cm (−3/4 in.). It was then sampled and conveyed to four 910-metric-ton (1000-ton) ore silos (Fig. 8.5). A fifth silo contained crude trona from Owens Lake to convert metaborate in the leach solution back to borax, to minimize calcite scaling, and to slightly react with the colemanite and ulexite in the ore.

The 20–25% B_2O_3 ore and a small amount of trona were removed from the silos (with some additional blending) and repulped with heated recycle brine. The slurry went in series flow through three (a fourth was maintained as a spare) 7570-liter (2000-gal) steam-jacketed, agitated dissolving tanks with internal steam coils, and having a residence time of 3–4 min. It then was passed over 1.9-cm (40-mesh; another reference said 60-mesh) Tyrock vibrating screens to remove the coarser undissolved ore, which was washed and discarded. The slurry next went to four countercurrent hot thickeners, where the slimes settled (originally aided by Separan coagulant), and were washed with the limited amount of water allowed by the plant's water balance. They were then discarded, still containing 3–4% B_2O_3. Later this mud was centrifuged (solid bowl), repulped in water (causing some difficulties because it tended to peptize to a colloidal state), combined with the screened large solids, and pumped to a tailings pond. Heat exchangers reheated the slurry as it was transferred between the 70-m- (230-ft-) diameter, covered, insulated, 2.4-m- (8-ft-) high (holding 13.2 million liters, or 3.5 million gal of slurry) thickeners. The clarified hot leach solution overflowed from the first (later also the second) of the thickeners, and was polish-filtered in six Sweetland 46.5-m^2 (500-ft^2) pressure leaf filters, except for that portion formerly made into a slightly



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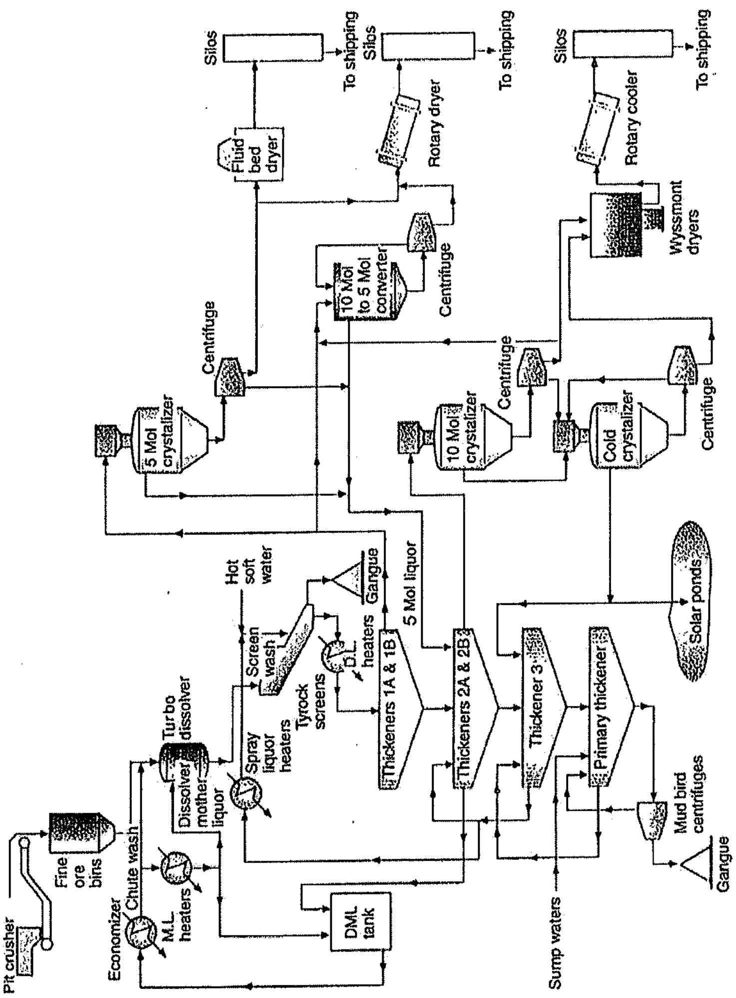

Figure 8.5 U.S. Borax's published flow sheet of its boron plant. (From Anon., 1996b; drawing courtesy of U.S. Borax Inc.)

impure product (classified as an ore, "Rasorite," to reduce European import duties).

The hot 99°C (210°F) brine next passed into one of three (a fourth was a spare) Struthers Wells, Oslo-type vacuum crystallizers, which made different products on a campaign basis. The brine was cooled to 37.8°C (100°F) when borax was being made, and 65.6°C (150°F) for pentahydrate (and formerly Rasorite). Several patents were issued (Taylor and Connell, 1953, 1956, 1957) on additives to reduce the borate supersaturation, to minimize equipment scaling, and to provide more controlled crystallization. The pentahydrate crystallizers had a 3123-l/min (825-gal/min) feed rate and 95,000-l/min (25,000-gal/min) internal circulation flow. Washouts were required on a cycle of about 4 weeks, and an organic phosphate ester defoamant was used. The product (50% +50-mesh borax; 10% +30-mesh pentahydrate) was centrifuged originally in 16 Sharples automatic basket centrifuges for the refined products, and three solid bowl centrifuges (operating at 800 rpm) for the crude pentahydrate. The later units were replaced in 1996 with vacuum belt filters, which provided much better product washing (three stages) and reduced crystal breakage and dust (from 12 to 5%). The impurities: SO_4, CO_3, Cl, and As were also reduced, as was product loading times. The moisture content did increase, however, along with caking problems, until the dryers were modified (Anon., 1996c). A dilute boric acid wash was used to reduce the product's caking tendency.

The borax was next dried in one fluid-bed, three oil-fired rotary, and seven steam-heated Wyssmont Turbo dryers. The Turbo dryers had multiple rotating trays, with rakes turning the product and advancing it from tray to tray. This provided very gentle heating to prevent dehydration of the products (except for the pentahydrate, which was purposely sold with 4.75 moles of water). Some of the borax was next partly dehydrated in four rotary kilns and then melted in four rectangular, side-fed, V-shaped-bottom, gas-fired reverbratory furnaces. The molten borax was solidified on 1.2-m- (4-ft-) diameter chilled rolls, further cooled on 0.91 × 18.3-m (3 × 60-ft) Carrier vibrating conveyors, broken with rotating-arm sheet breakers, crushed to −4 mesh in a hammer mill, and then cooled again on a 0.9 × 18-m vibrating conveyor. It was finally reduced by a hammermill to the desired particle size, and screened on Sweco screens. The fines were recycled and remelted.

The pentahydrate and anhydrous product storage was in 12 concrete silos, each 27.4 m (90 ft) tall and 10.7 m (35 ft) in diameter. Six had a combined capacity of 12,200 metric tons and were used initially for Rasorite. Three at 5300 metric tons were for the refined pentahydrate, and three at 6300 metric tons were formerly for anhydrous Rasorite. The refined borax was stored in an "angle-of-repose" warehouse because severe caking problems had been encountered when it was initially stored in the silos. When withdrawn the product was rescreened and then shipped by rail or trucks. Plant operation

was monitored from a central control
maintenance, warehouse, laboratory, b
from a fossil aquifer went to a 38-mill
and then to a 36.6-m- (120-ft-) high, 3,80
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1959). Later, boric acid fusion furnaces
drous B_2O_3 (Anon., 1965b).

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The largest was 0.49 km^2 (120 acres) a
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borate losses.) In 1985 the borax plant
the boric acid plant as needed to meet

A 46-megawatt gas turbine cogenera
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to replace five of the original six oil/gas-
a 3500-hp air blower, and evaporative a
50% excess capacity over the plant need
a 5-year pay-out period. Some plant
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automatically fill and weigh rail cars an
and shipping costs were reduced, and d
mentation and automation, as well as
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In 1985 the Rasorite line of products
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metric tons of product (Anon., 1976).
(hemispheric storage structures) were

U.S. Borax's 91,000-metric-ton/year
Los Angeles harbor (Wilmington), 240
and mud disposal costs became prohibi
ton/year, $80-million boric acid plant
at Boron. It had 12 44.5-m (146-ft; also
and featured "a continuous rotary dr

"Rasorite," to reduce European im-

sed into one of three (a fourth was a
m crystallizers, which made different
e was cooled to 37.8°C (100°F) when
0°F) for pentahydrate (and formerly
Taylor and Connell, 1953, 1956, 1957)
ersaturation, to minimize equipment
crystallization. The pentahydrate crys-
) feed rate and 95,000-l/min (25,000-
outs were required on a cycle of about
er defoamant was used. The product
pentahydrate) was centrifuged origi-
centrifuges for the refined products,
ing at 800 rpm) for the crude pentahy-
1996 with vacuum belt filters, which
g (three stages) and reduced crystal
he impurities: SO_4, CO_3, Cl, and As
ding times. The moisture content did
blems, until the dryers were modified
sh was used to reduce the product's

l-bed, three oil-fired rotary, and seven
The Turbo dryers had multiple rotating
d advancing it from tray to tray. This
t dehydration of the products (except
sely sold with 4.75 moles of water).
ydrated in four rotary kilns and then
shaped-bottom, gas-fired reverberatory
ied on 1.2-m- (4-ft-) diameter chilled
× 60-ft) Carrier vibrating conveyors,
rs, crushed to −4 mesh in a hammer
.8-m vibrating conveyor. It was finally
l particle size, and screened on Sweco
melted.
duct storage was in 12 concrete silos,
ft) in diameter. Six had a combined
used initially for Rasorite. Three at
entahydrate, and three at 6300 metric
rite. The refined borax was stored in
se severe caking problems had been
d in the silos. When withdrawn the
ed by rail or trucks. Plant operation

was monitored from a central control room, and there were administration, maintenance, warehouse, laboratory, boiler, and other buildings. Well water from a fossil aquifer went to a 38-million-liter (1-million-gal) storage tank, and then to a 36.6-m- (120-ft-) high, 3,800,000-liter (100,000-gal) pressure tank. Boiler water was treated by the lime–soda process (Anon., 1958; Garrett, 1959). Later, boric acid fusion furnaces were installed to produce some anhydrous B_2O_3 (Anon., 1965b).

Jensen and Schmitt (1985) noted that the plant had been "expanded and modified in numerous ways to increase capacity" since its original design. A new twin-boom automatic ore stacker with articulated arms (to reduce the drop height and thus dust) was installed to form separate ore stock piles for borax and kernite. Six clay-lined solar evaporation ponds were also built to recover part of the borax that was in the slimes and excess plant wash water. The largest was 0.49 km^2 (120 acres) and 12.2 m (40 ft) deep. An additional yield of 6% was claimed, bringing the stated total to 91%. (It actually may have been less than 70%, including the mine, ulexite, colemanite, and other borate losses.) In 1985 the borax plant worked 7 days/week, 3 shifts/day, and the boric acid plant as needed to meet the sales demands.

A 46-megawatt gas turbine cogeneration plant to generate 181 metric tons (400,000 lbs) of steam per hour at 173 psi and 192°C (378°F) was also built to replace five of the original six oil/gas-fired boilers. It had waste-heat boilers, a 3500-hp air blower, and evaporative air coolers to increase its efficiency. Its 50% excess capacity over the plant needs was sold to the local utility to provide a 5-year pay-out period. Some plant capacity was switched from borax to pentahydrate, and a 363-metric-tons/hr bulk-loading facility was installed to automatically fill and weigh rail cars and trucks. Automatic bagging, handling, and shipping costs were reduced, and dust control was improved. New instrumentation and automation, as well as computer assistance for plant maintenance, purchasing, and sales were also installed (Jensen and Schmitt, 1985).

In 1985 the Rasorite line of products ceased being made because the European import duties on refined products were dropped (Lyday, 1992). In 1976 twin air-supported product storage structures were erected (large plastic envelopes held to the ground by corrosion-resistant cables, with fans creating a small internal pressure). There were airlocks for the conveyor belts and personnel entry. The structures were 91 m (300 ft) long, and could store up to 91,000 metric tons of product (Anon., 1976). Later, two 18,000-metric-ton "domes" (hemispheric storage structures) were added (Anon., 1996b).

U.S. Borax's 91,000-metric-ton/year boric acid plant originally was at the Los Angeles harbor (Wilmington), 240 km (150 mi) away. However, shipping and mud disposal costs became prohibitive, so in 1980 a new 180,000-metric-ton/year, $80-million boric acid plant was built on a 0.16-km^2 (40-acre) site at Boron. It had 12 44.5-m (146-ft; also quoted at 100-ft; Anon., 1996a) silos, and featured "a continuous rotary drum reactor." It operated on kernite

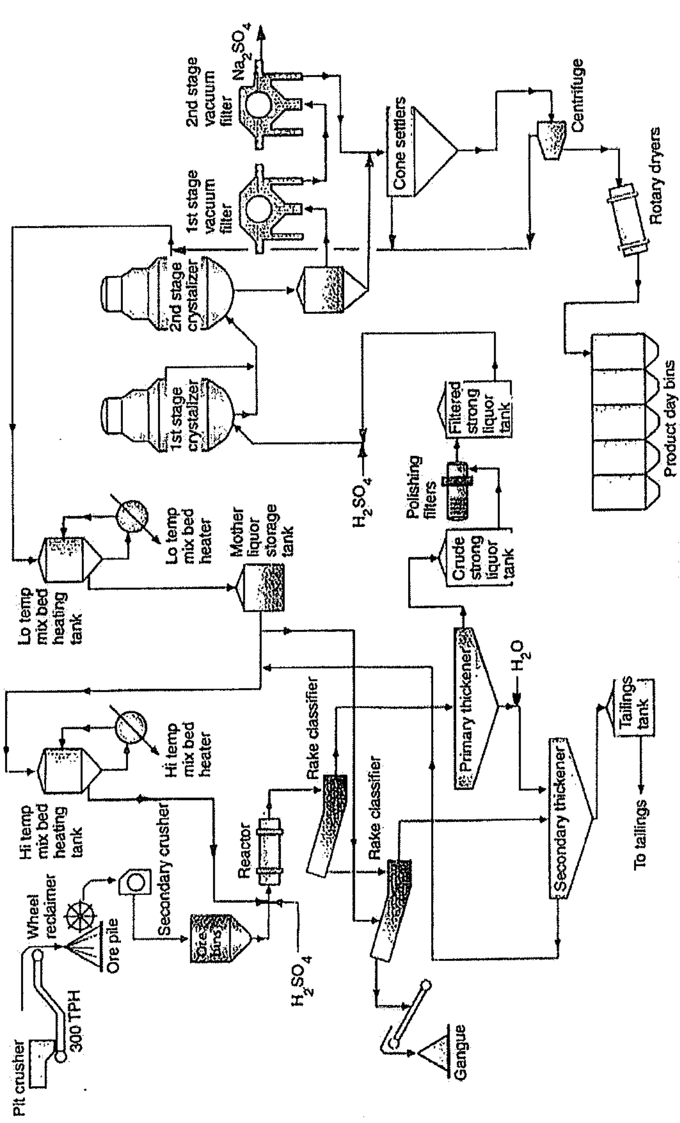


Figure 8.6 U.S. Borax's published flow sheet of its boric acid process. (Slightly modified by author, from Anon., 1996b; drawing courtesy of U.S. Borax Inc.)

ore, with its slimes and waste water be
clay-lined tailings pond. Sodium sulfate
1981).

The flow sheet for the process (Fig. 8
U.S. Borax patents that suggest reacting
that immediately precipitates by-product
cooling the solution to crystallize boric a
when used to make borax, it dissolves m
and longer leaching times, or hydration i
fine size for borax production kernite cl
mat and clog the handling equipment. T
recycle liquor in the reactor, along with p
concentration is kept just below its satura
the dissolving process, the coarse undiss
classifiers (Anon., 1996b), the slimes are
and the clarified brine is sent through po
to the final sulfuric-acid reactor, heated to
precipitated. The salt cake is thickened,
remaining brine sent to a boric acid cryst
slurry withdrawn, and the crystals thicke
After a bleed stream is removed to cont
solution is recycled to the kernite leach
introduced (i.e., 1.36 kg/5000 gal/100 p
ferrous, thus minimizing Na_2SO_4 supersa
higher-purity boric acid, the crude cake
(i.e., filtration, the precipitation of met
etc.), and the boric acid recrystallized.

On the basis of U.S. Borax's dehydr
fusion furnace such as shown in Fig. 8.7 i
drous borax or B_2O_3 (Anon., 1965b). Pa
borax) is fed into the rear of a reverb
refractory lining. As it slowly melts, it is w
on water-cooled rolls. It is next ground to
containers (U.S. Borax, 1962).

8.1.4.2 Processing

Many processing articles have been
acid production (see References), but
descriptions of the major producers' c
any, have been commercialized (which
because of space limitations so these
this chapter.

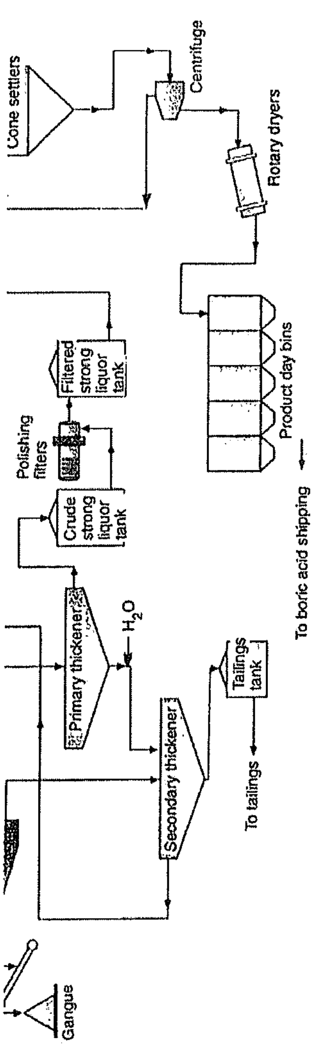


Figure 8.6 U.S. Borax's published flow sheet of its boric acid process. (Slightly modified by author; from *Anon., 1996b; drawing* courtesy of U.S. Borax Inc.)

ore, with its slimes and waste water being sent to a 0.49-km^2 (120-acre), clay-lined tailings pond. Sodium sulfate was made as a by-product (Anon., 1981).

The flow sheet for the process (Fig. 8.6) appears to follow the numerous U.S. Borax patents that suggest reacting the ore with sulfuric acid in a brine that immediately precipitates by-product sodium sulfate, removing it and then cooling the solution to crystallize boric acid. Kernite was employed because when used to make borax, it dissolves more slowly, requiring finer grinding and longer leaching times, or hydration in the mine. Also, when ground to a fine size for borax production kernite cleaves and forms fibers that tend to mat and clog the handling equipment. The kernite is added to 49°C (120°F) recycle liquor in the reactor, along with part of the sulfuric acid. The Na_2SO_4 concentration is kept just below its saturation point at that temperature. After the dissolving process, the coarse undissolved ore is then removed in rake classifiers (Anon., 1996b), the slimes are thickened, washed, and discarded, and the clarified brine is sent through polishing filters. The brine is then sent to the final sulfuric-acid reactor, heated to 99°C (210°F) and the sodium sulfate precipitated. The salt cake is thickened, filtered, washed and dried, and the remaining brine sent to a boric acid crystallizer. Here it is cooled, a boric acid slurry withdrawn, and the crystals thickened, centrifuged, washed and dried. After a bleed stream is removed to control the impurity level, the remaining solution is recycled to the kernite leach tanks. Sulfur dioxide gas could be introduced (i.e., 1.36 kg/5000 gal/100 ppmFe) to reduce the ferric iron to ferrous, thus minimizing Na_2SO_4 supersaturation and iron contamination. For higher-purity boric acid, the crude cake is redissolved, the solution purified (i.e., filtration, the precipitation of metallic impurities, carbon adsorption, etc.), and the boric acid recrystallized.

On the basis of U.S. Borax's dehydration patents (e.g. Corkill, 1937), a fusion furnace such as shown in Fig. 8.7 might be employed to produce anhydrous borax or B_2O_3 (Anon., 1965b). Partially dehydrated boric acid (as with borax) is fed into the rear of a reverbratory-type furnace to protect the refractory lining. As it slowly melts, it is withdrawn at the far end and solidified on water-cooled rolls. It is next ground to size and packaged in moisture-tight containers (U.S. Borax, 1962).

8.1.4.2 Processing

Many processing articles have been written on sodium borate or boric acid production (see References), but they do not significantly add to the descriptions of the major producers' operations given here. Also, few, if any, have been commercialized (which is the general criteria for review), because of space limitations so these articles are not further discussed in this chapter.

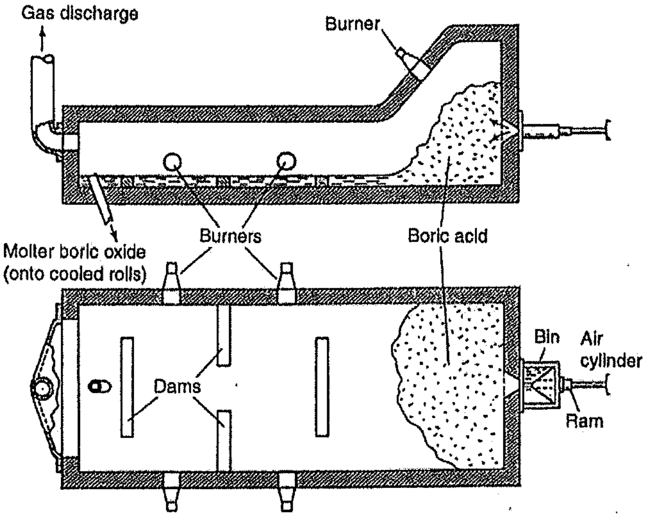


Figure 8.7 Side and top views of a borax–boric acid fusion furnace. (From U.S. Borax, 1962.)

8.1.5 Beneficiation

8.1.5.1 Magnetic Separation

Magnetic separation was used to upgrade the borax ore at the Boron plant until 1957. An early patent noted that the shale was slightly magnetic, but the borax and kernite were not. To be processed the ore was first dried and crushed to two size fractions: 1.6–3.2 mm (1/16–1/8in. or 6–10 mesh), and −1.6 mm by rolls and hammermills working in closed circuit with Tyler Hummer screens. The separation was conducted in four stages. First, tramp iron was removed. Then the ore was passed over a high-intensity induction-type Exolon magnetic roll and through a small gap between magnets. The shale was deflected slightly outward by the magnetic attraction, and a splitter blade under the falling ore divided the deflected from the free-falling portions. By repeating this separation twice, and then rerunning the product cuts, it was claimed that an 80% borax yield of a high-purity product could be obtained (Anon., 1956; Johnson, 1936). Downing (1995) claimed that borax and kernite ore were now capable of being upgraded from 60 to 90% purity by high-intensity magnetic separators, with only a 3–7% loss of their B_2O_3 content.

8.1.5.2 Borax and Boric Acid Flotation

Many articles and patents have been presented on the flotation separation of borax from other salts or gangue material. For example, Chemtob and
White (1972) and Garrett, Kallerud,
can be separated from other solubl
present) of 8–22C atom-sulfonated str
oleic acid or tall oil. Some hydrocar
also effective, as were a few seconda
15–50 g/ton. Boric acid is a naturall
selectively adhere to its surfaces, so
other substances unless a special reag
consequence, if any of the borax miner
on their surface, they could be separa
contain other articles on both borax

8.2 COLEMANITE

8.2.1 Argentina

Ulex SA's Sol de Manana mine at Sij
acite 15 km to their El Paso facility t
dried to a 42% B_2O_3, −1-mm (16-m
containers to the railroad, and from th
gasta or Tocopilla, Chile, or Buenos
salars, can also be sent to Salta to
Raymond mill to make a +45μ (325-

8.2.2 Turkey

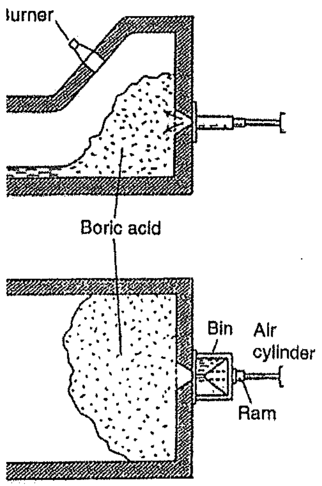
8.2.2.1 Bigadic, Emet, Espey, Kestel

In the mid-to-late 1970s large wa
facilities to produce higher-grade and
concentrates (Fig. 8.8). Products wer
purities (see Table 10.9) to meet diffe
crushed to −30 cm, and then in closed
It was next repulped to 60–75% solids,
(and the slimes removed) in a series of
discarded, and the concentrate was ce
(Albayrak and Protopapas, 1985; An

8.2.3 United States

8.2.3.1 Calico Area: Borate Mine

The borate beneficiation plant was
of Daggett, and 19.2 km (12 mi) [9.6



acid fusion furnace. (From U.S. Borax, 1962.)

rade the borax ore at the Boron plant
the shale was slightly magnetic, but
processed the ore was first dried and
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n rerunning the product cuts, it was
igh-purity product could be obtained
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led from 60 to 90% purity by high-
a 3–7% loss of their B_2O_3 content.

m

presented on the flotation separation
naterial. For example, Chemtob and

White (1972) and Garrett, Kallerud, and Chemtob (1975) noted that borax can be separated from other soluble salts by 75–500 g/ton (of the solids present) of 8–22C atom-sulfonated straight-chain fatty acids such as sulfonated oleic acid or tall oil. Some hydrocarbon sulfates such as sulfsucinates were also effective, as were a few secondary or tertiary alcohols when applied at 15–50 g/ton. Boric acid is a naturally floating material because air bubbles selectively adhere to its surfaces, something that does not happen to most other substances unless a special reagent has been added to the slurry. As a consequence, if any of the borax minerals were converted to boric acid, at least on their surface, they could be separated readily by flotation. The References contain other articles on both borax and boric acid flotation.

8.2 COLEMANITE

8.2.1 Argentina

Ulex SA's Sol de Manana mine at Sijes first hauls colemanite and hydroboracite 15 km to their El Paso facility to be hand sorted, crushed, washed, and dried to a 42% B_2O_3, −1-mm (16-mesh) product. It is shipped in bulk or containers to the railroad, and from there to customers via the ports of Antofagasta or Tocopilla, Chile, or Buenos Aires. It, along with ulexite from their salars, can also be sent to Salta to be further dried and passed through a Raymond mill to make a $+45\mu$ (325-mesh) product (Leiser, 1996).

8.2.2 Turkey

8.2.2.1 Bigadic, Emet, Espey, Kestelek

In the mid-to-late 1970s large washing plants were constructed at these facilities to produce higher-grade and more uniform colemanite and ulexite concentrates (Fig. 8.8). Products were made in different sizes, grades, and purities (see Table 10.9) to meet different market demands. The ore was first crushed to −30 cm, and then in closed-circuit stages with screens to −25 mm. It was next repulped to 60–75% solids, sent to attrition scrubbers, and classified (and the slimes removed) in a series of equipment. The −65-mesh slimes were discarded, and the concentrate was centrifuged, dried, screened, and shipped (Albayrak and Protopapas, 1985; Anac, 1988; Ozkan and Lyday, 1995).

8.2.3 United States

8.2.3.1 Calico Area: Borate Mine

The borate beneficiation plant was located at Marion, 6.4 km (4 mi) north of Daggett, and 19.2 km (12 mi) [9.6 km (6 mi); Yale, 1905] from the mine.

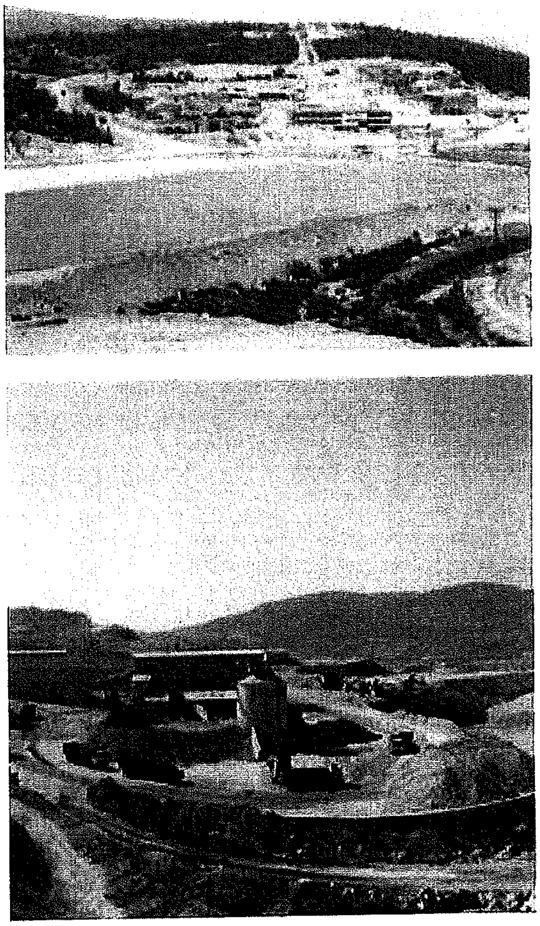
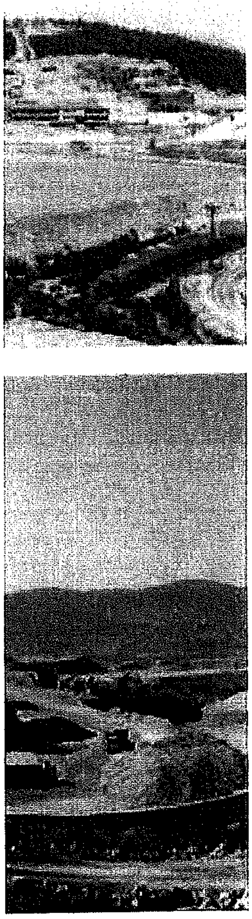


Figure 8.8 Views of the Bigadic (upper) and Emet (lower) colemanite and ulexite processing facilities. (From Etibank, 1995; pictures courtesy of Etibank.)



met (lower) colemanite and ulexite processing
f Etibank.)

The ore was first shipped by mule teams, and later by a narrow-gauge rail line with spectacular curves and a high trestle (see page 315). In 1900, after 2 years of attempted start-up, a calcining plant began processing the −35% B_2O_3 ore and fines. It used a two-hearth, 70- to 90-metric-tons/day Holthoff-Wethey reverbratory furnace fired at 500°C (932°F) by No. 6 fuel oil. The ore entered at the top, and was mixed and advanced by rabble arms (countercurrent to the flue gas) to drop holes for the lower hearth. Here the process was repeated, and the calcine left at the bottom. It was then screened, the coarse fraction rejected, and the fines shipped to refineries in Alameda, California, or Bayonne, New Jersey. The fine product averaged about 45% B_2O_3, and it took 2–4 tons of ore to produce a ton of product. Any ulexite or priceite (pandermite; called "dry bone") in the ore was lost (sometimes 50% of the ore), because it did not decrepitate, and often fused into a greenish glass.

At the Alameda (on San Francisco bay) refinery, the colemanite was ground to a fine powder by a sequence that included a Blake crusher (reducing the uncalcined ore to nut size), a coffee-type grinder (taking all of the ore to a sand size), and finally buhr mills (making it fine enough to pass through silk screens). This powder was reacted with a hot soda ash (Na_2CO_3) solution for several hours in vigorously agitated tanks. The slurry was then settled, and the mud and by-product $CaCO_3$ sent to a filter press, washed, and discarded. The clarified brine and filtrate were pumped to tanks containing many suspended wires, where the brine cooled and crystallized, producing crystals with a slightly dark color. The end liquor was then removed, and part of it returned for another leach cycle. The borax was knocked off the wires and tank walls, drained, washed, and finally redissolved and recrystallized (Bailey, 1902; Ver Planck, 1956).

At the Bayonne refinery the high-grade ore was first crushed to 1.3–3.8 cm, and then it and the calcined ore were sent to a Griffin mill, which "reduced it to the fineness of flour," so it "could pass through No. 8 silk bolting cloth." It was then sent to holding bins from which it would later be weighed and sent to a 91-metric-ton, 11,000-liter (3000-gal) tank with internal steam coils, and partly filled with recycle brine and water. Soda ash (and some bicarbonate to prevent metaborate formation) was added, and the boiling slurry agitated for a lengthy period. When complete, the slurry was pumped to steam-heated settling tanks, and 1.4–1.8 kg (3–4 lb) of glue dissolved in "3 buckets of hot water" was added as a settling agent (without it the solution was "milky-looking"). After the solids had settled a clear brine was withdrawn. The residual mud was sent to a 50-psi filter press, washed, and discarded. The brine and filtrate went to mild steel crystallizers, 2 m (6.5 ft) deep, 1.8 m (6 ft) wide, and 6.1 m (20 ft) long. Two 6.7-m (22-ft) by 5-cm (2-in.) iron pipes were laid across the tanks, with 1.5-m (5-ft) long, 6.4-mm (0.25-in.) wires on a 20-cm (8-in.) spacing extending into the tanks. After cooling 6–10 days the liquor was withdrawn and part of it returned for a new leach cycle (the bleed stream was processed separately). The borax was first knocked off the wires, since it was pure enough to be sold directly. The crystals from the sides and bottom were then removed, washed, drained, redissolved, and recrystallized. The product crystals were washed, drained, and dried in a rotary dryer by a temperature-controlled hot air stream. It was then sent to a roll crusher and screened into three product sizes: refined crystals, granulated borax, and refined screenings. A fine product was occasionally made in a cyclone pulverizer (Hanks 1883; Baily, 1902; Yale, 1905; Dupont, 1910).

8.2.3.2 Calico Area: American Borax Company

The American Borax Company treated "borate mud" at Dagget by the patented Blumenberg (1918) sulfur dioxide process. It was claimed that with it the SO_2 dissolved less silica, iron, magnesium and other impurities, and the filtration of the residue was simpler, since most of the gypsum precipitated in the ponds. The 4–20% B_2O_3 (average 7%) ore was first broken in a "rock breaker," and then crushed to −6.4 mm (−0.25 in.) in a "Chili mill." It was next conveyed to a reactor, 3 m (10 ft) in diameter and 9.1 m (30 ft) tall, filled with water. Sulfur was burned nearby at 9 psi and distributed into the base of the tower. This agitated some of the ore into a "fluidized" slurry, and was continued until much of the SO_2 began to escape from the top.

The slurry was then settled, and a dark muddy-appearing liquor was decanted and sent to a series of shallow solar evaporation ponds made of concrete and coated with an asphalt sealant, and arranged so that the liquor flowed from one pond to another. The first ponds settled much of the solids, and gypsum began to precipitate (the soluble calcium sulfite and bisulfite were oxidized by air to calcium sulfate). When this reaction was complete, the brine was pumped by a windmill to the top of a natural-draft, open cooling tower. It was distributed over the staggered baffles placed about 30 cm (1 ft) apart, and it trickled back to the solar ponds. The flow rate in the ponds was regulated so that boric acid crystallized in the last ones. When full, the ponds were drained, the residual brine recycled, the mud removed (and discarded), and boric acid shoveled onto drainage areas between the ponds. It remained there until dry, and then was shoveled into cases and shipped to refineries as about an 85% H_3BO_3 product with impurities of $CaSO_4$, $MgSO_4$, water and insolubles. The plant ran 24 hrs/day with a staff of four at night, and eight during the day. The operation was never very profitable, so it closed when the Ryan mines opened and lowered the price of borax (Yale, 1905; Keys, 1910).

8.2.3.3 Calico Area: Palm Borate, Western Mineral Companies

These companies also leached borate mud: Palm with sulfur dioxide, and Western with sulfuric acid. Sulfur was burned at Palm under pressure and distributed into the bottom of a 76,000-liter (20,000-gal) agitated (by a slowly revolving rake) redwood tank. When excessive SO_2 came off the top the burner was shut off and the tank allo
to solar ponds, and the mud filtered.
over a natural-draft cooling tower (Y
the four Calico companies processing
ore with sulfuric acid in agitated tanks
ing the heavy muds to recover more of
produced a very weak brine, which was
brine could reach temperatures up to
piles of brush to increase the evaporati
last ponds at a rate of 27 metric tons/

8.2.3.4 Coastal Mountain Area: Lan

Four oil-burning colemanite calcine
furnaces (each producing 36 metric
producing 54 metric tons/day). Fine-ca
calciners and recovered in cyclone du
by rail to the Lang siding on the Sou
to several eastern refineries (Gay and

8.2.3.5 Death Valley Region: Borax

Tenneco's Boraxo mine in Death
1970s by trucks 50 km (31 mi) to a
Nevada (13 km north of Death Valle
a 30-cm (12-in.) grizzly, the oversize m
by belts to a hammermill that reduce
repulped to a 55% slurry at a rate of
(40 × 40-in.) attrition scrubbers. The
ore) were removed in a 1.2 × 7.2-m
sprays on the coarse solids to reduce fi
slurry (the fines) was sent to a 25-cm (
were returned to the classifier. The
solids sent to a tailings pond (from w
and the thickener overflow returned to
solids (containing only about 3% −1
went to a stockpile where further d
increased 3–5% in the washing step a
ulexite was present the loss increase
rated capacity was 45 metric tons/hr, b
72 metric tons/hr, and with wet or hig
The plant had its own water wells.

A front-end loader took the washec
apron feeder (also stated to be two sli
delivered it to a 2.1 × 12.8-m (7 ×

rax was first knocked off the wires,
tly. The crystals from the sides and
ned, redissolved, and recrystallized.
ed, and dried in a rotary dryer by a
It was then sent to a roll crusher
fined crystals, granulated borax, and
casionally made in a cyclone pulver-
; Dupont, 1910).

ompany

ed "borate mud" at Dagget by the
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of $CaSO_4$, $MgSO_4$, water and insolu-
taff of four at night, and eight during
profitable, so it closed when the Ryan
 borax (Yale, 1905; Keys, 1910).

estern Mineral Companies

e mud: Palm with sulfur dioxide, and
burned at Palm under pressure and
-liter (20,000-gal) agitated (by a slowly
excessive SO_2 came off the top the

burner was shut off and the tank allowed to settle. Clarified brine was sent to solar ponds, and the mud filtered. Second-stage pond brine was pumped over a natural-draft cooling tower (Yale, 1905). Western was the largest of the four Calico companies processing "mud," but the company leached the ore with sulfuric acid in agitated tanks operating near the boiling point. Washing the heavy muds to recover more of the boric acid after the first decantation produced a very weak brine, which was concentrated in solar ponds. The pond brine could reach temperatures up to 60°C (140°F), and it was pumped over piles of brush to increase the evaporation. Crude boric acid crystallized in the last ponds at a rate of 27 metric tons/day (Bailey, 1902).

8.2.3.4 Coastal Mountain Area: Lang

Four oil-burning colemanite calciners were employed at Lang: two wedge furnaces (each producing 36 metric tons/day), and two rotary kilns (each producing 54 metric tons/day). Fine-calcined colemanite was blown from the calciners and recovered in cyclone dust collectors. The product was shipped by rail to the Lang siding on the Southern Pacific Railroad, and from there to several eastern refineries (Gay and Hoffman, 1954).

8.2.3.5 Death Valley Region: Boraxo

Tenneco's Boraxo mine in Death Valley shipped its 18–20% ore in the 1970s by trucks 50 km (31 mi) to a processing plant near Lathrop Wells, Nevada (13 km north of Death Valley Junction). The ore was dumped onto a 30-cm (12-in.) grizzly, the oversize manually reduced, and the undersize fed by belts to a hammermill that reduced it to −6.4 mm (−¼ in.). It was then repulped to a 55% slurry at a rate of 45 metric tons/hr and sent to 1 × 1-m (40 × 40-in.) attrition scrubbers. The −65-mesh particles (about 33% of the ore) were removed in a 1.2 × 7.2-m (48-in. × 23.5-ft) spiral classifier, with sprays on the coarse solids to reduce fines carry-over. The classifier underflow slurry (the fines) was sent to a 25-cm (10-in.) cyclone, and its underflow solids were returned to the classifier. The cyclone's overflow was thickened, the solids sent to a tailings pond (from which 75% of the water was recycled), and the thickener overflow returned to the ore repulper. The coarse classifier solids (containing only about 3% −150-mesh particles and 15–18% water) went to a stockpile where further draining occurred. Their B_2O_3 content increased 3–5% in the washing step and there was a 15% colemanite loss. If ulexite was present the loss increased because of its friability. The plant's rated capacity was 45 metric tons/hr, but with dry ore it could be as much as 72 metric tons/hr, and with wet or high clay ore as low as 27 metric tons/hr. The plant had its own water wells.

A front-end loader took the washed ore to a hopper with a variable-speed apron feeder (also stated to be two slide-plates and a belt feeder). Belts then delivered it to a 2.1 × 12.8-m (7 × 42-ft) 10.9 metric tons/hr (12 tons/hr) rotary dryer, heated in counterflow by gas from the calciner, which entered at 343°C and left at 93°C. The coarser entrained solids from this flue gas were cycloned and added to the dryer discharge. The gas then went to a wet scrubber. The ore to the dryer averaged 9% moisture, 22% B_2O_3, and left at 177°C. It then entered (for about a 30-min residence time) the 2.4 × 12.8-m (8 × 42-ft) countercurrent-flow, direct contact stainless steel rotary calciner with lifters only at its front end. The flow rate of the gas in the dryer was 2.8- to 3.1-m/sec (9.2- to 10-ft/sec), and it left at 427°C. This entrained the decrepitated colemanite, which was recovered by six cyclones operating in parallel. The product was split into two size fractions (+ and −40 mesh), and cooled in air classifiers before being sent to silos. Part of the air from these coolers was used for combustion in the No. 2 fuel oil burners. Typical calciner recoveries were 70% (giving a 60% overall recovery), or a yield of 1 part product per 2.7 parts of ore. The plant operated with 37 people 24 hrs/day, 7 days/week, and shipped 47–49% B_2O_3 colemanite. The product specifications were >47.5% B_2O_3, <0.3% Fe_2O_3 and <0.9% SO_3, and since low-grade ore could not meet them, ore blending was practiced.

Later, equipment was added to crush the calciner tailings and screen them at 35 mesh. The undersize contained about 50% of the tailings B_2O_3 at a 30% B_2O_3 grade. A 10 to 35 mesh fraction was then processed on (air) density-classification tables, with a B_2O_3 yield of 70%, and 30% B_2O_3 product. The −35 mesh and this fraction combined with the calcine gave an overall yield of 71%.

The +40 mesh product was trucked to rail loading facilities in North Las Vegas, whereas the undersize was sent in 22.7 metric-ton (25-ton) pneumatic trucks to a modern, converted talc-grinding plant at Dunn Siding, 48 km (30 mi) west of Baker, California. It was unloaded into 109-metric-ton (120-ton) storage or blending silos, and then sent to a Raymond mill (with its built-in air classifier) to produce −70-mesh particles. From there it went to five 109-metric-ton product silos, and then was shipped in 75-metric-ton (85-ton) hopper cars. The plant had nine bag filters for dust control, and employed 25 people (Walters, 1975; Evans, Taylor and Rapp, 1976; Smith and Walters, 1980).

8.2.3.6. Death Valley Region: Billie

After the Boraxo mine had closed, ore from the Billie mine was also sent to the Lathrop Wells processing plant (Fig. 8.9). It was crushed and ball-milled to −32.5 mesh, and deslimed (at 70 mesh) to reach 37% B_2O_3. The 32.5–70 mesh fraction was then floated to produce a 42–45% B_2O_3 product (Lyday, 1996; Norman and Johnson, 1980).

8.2.3.7 Death Valley Region: Lila C, Ryan

From 1907 to 1916 the Lila C mine processed its lower-grade ore in a mill on the site. The ore was first reduced in size to −2.5 cm (−1 in.) by a roll

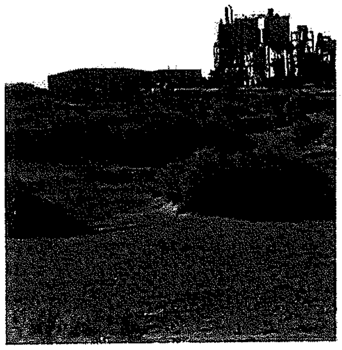

Figure 8.9 The Lathrop Wells (or

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Death Valley Junction. Ore from the
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fired at 704°C (1300°F) by crude oil.
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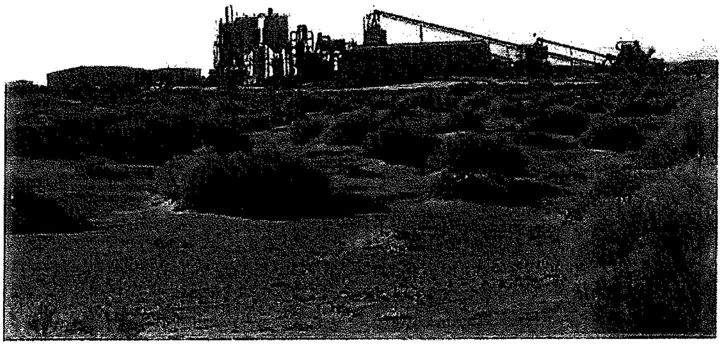


Figure 8.9 The Lathrop Wells (or Amargosa Valley) borate processing plant.

crusher, and sent through an indirectly heated, oil-fired rotary kiln with a flame temperature of 650°C (1200°F). The calcined ore was then screened, and the fine fraction shipped to the Bayonne refinery. The coarse material went to a tailings pile (Gale, 1912).

During 1916–1928 the dominant colemanite mines in Death Valley were at Ryan. Their "first-grade" ore went directly to refineries at Bayonne or Alameda, but the fines and lower-grade ore was sent to a calcining plant at Death Valley Junction. Ore from the Upper Biddy (Biddy McCarthy or Ryan), Lower Biddy, Grand View, Lizzie V Oakley, Played Out and Widow mines was first reduced to −5 cm (−2 in.) in a gyratory crusher, and then to −2.2 cm (−⅞ in.) in 61-cm (24-in.) roll crushers. Conveyor belts took the ore to two 73-metric-ton (80-ton) storage bins, which in turn fed six 1.8 × 15.2-m (6 × 50-ft) dual-tube, indirectly heated rotary calciners (Fig. 8.10). They were fired at 704°C (1300°F) by crude oil. The calcined ore was screened in double-deck units to +6.4-mm (¼-in), 6.4-mm to 24-mesh, and −24 mesh fractions. The −24-mesh material was immediately sent to the product silos, whereas the other fractions (56% of the ore with a 4% B_2O_3 content) went to silos for further processing. Both oversize fractions of calcine were reground in roll crushers and rescreened at 24 mesh. Each fraction was repulped, and the +24 mesh calcine was sent to Hartz jigs, while the undersize went to Wilfrey tables (density separators). The light colemanite fractions were thickened in drag

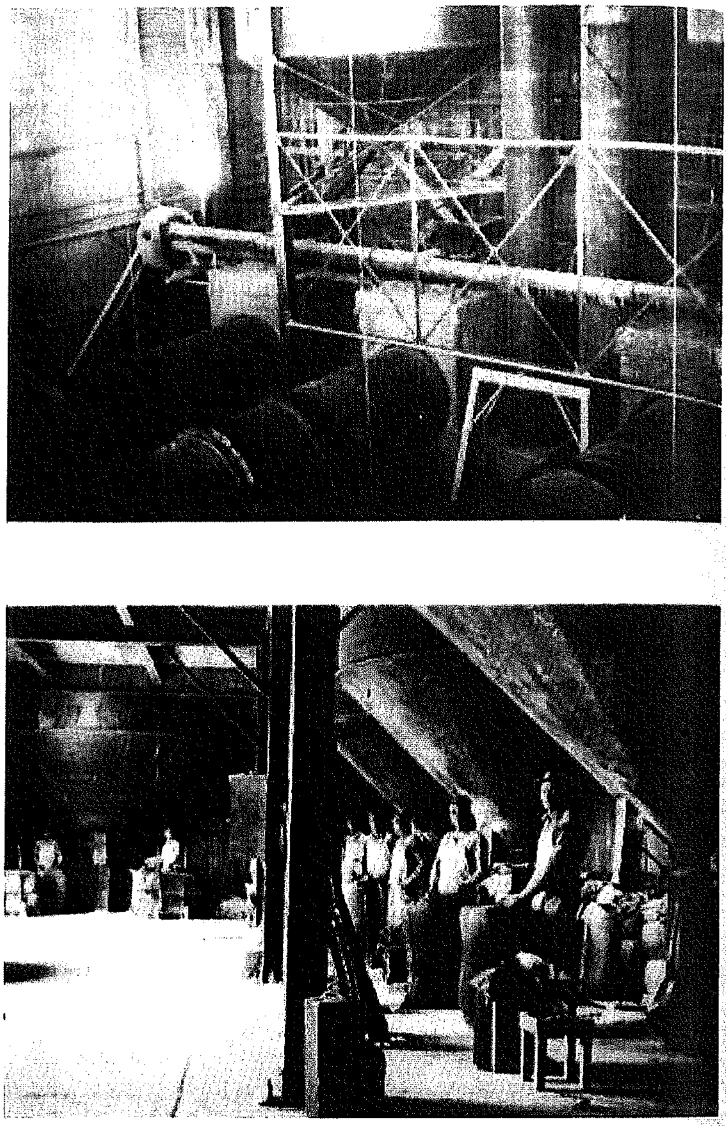
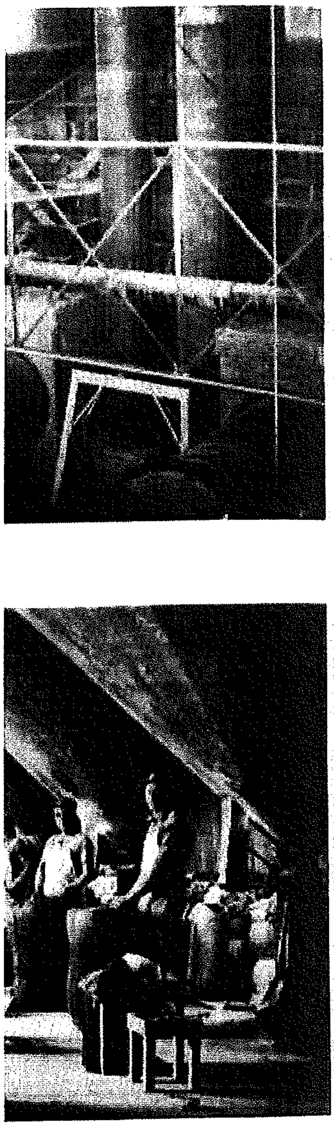


Figure 8.10 Roasting colemanite and bagging the concentrates at Death Valley Junction. (From Ver Planck, 1956; used with permission of the California Department of Conservation, Division of Mines and Geology.)



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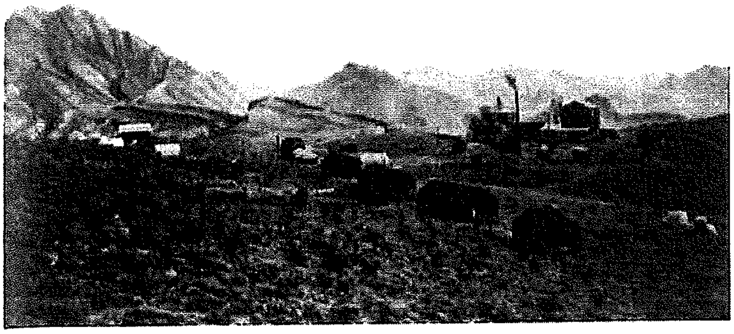

Figure 8.11 West End Chemical Company camp and mill at the Anniversary mine. Buildings from lower right to center: Club house, bunk house, boaring house, office; Upper right: processing plant. (From Castor, 1993; reprinted courtesy of the Nevada Bureau of Mines and Geology.)

(ladder) classifiers, filtered, and dried in table dryers. The combined calcine and low density streams were bagged for shipment, and contained 42–45% B_2O_3, with an overall B_2O_3 recovery of 85%. The plant capacity was 272 metric tons/day of ore; 85 men were employed; and power was supplied by a 500-hp diesel engine (Hamilton, 1921).

8.2.3.8 Muddy Range, Nevada: Callville Wash

The processing plant (Fig. 8.11) of the Anniversary Mine also employed the calcining process. An aerial tramway from the mine dumped ore into a bin at the plant, and from there it was withdrawn and crushed to −2.5 cm (1 in.). It was next fed into a 1.5 × 18.3-m (5 × 60-ft) indirectly heated, oil-fired rotary kiln (two kilns; Papke, 1976) whose flame temperature was kept at a minimum to avoid fusing the ore. The discharged calcine was screened, and the fine product hauled 43 km to the railway. The newly developed 4.6-metric-ton (5-ton) tractors or truck and trailers were used, and supplies brought back on the return trip. The production was 68 metric tons/day in 1923, and 50 people were employed in the mine, mill, and trucking operations. Electric power was provided by oil- (27 gravity-) fired engine–generator sets, and plant water from shallow 12.2-m (40-ft) wells at the site. Drinking water was hauled from the railroad (Young, 1924).

8.2.4 Processing

There have been many other processes developed to recover the boron values from colemanite, as indicated in the References and the following examples.

The chlorine, or Moore, process was used during the 1800s in England, with chlorine introduced into an agitated slurry of powdered colemanite at 70°C. When the chlorine began to escape the slurry was allowed to settle. The clear liquid was next decanted and sent to crystallizers to cool, and when withdrawn, was recycled until its calcium chloride and other salt content began to interfere with the borax crystallization.

In a similar process colemanite was treated with hydrochloric acid in an agitated, boiling slurry. When the reaction was completed the slurry was settled and the clear liquor sent to crystallizers for the fractional crystallization of $CaCl_2$ and H_3BO_3. In the Bigot process, 100 parts of fine colemanite were heated with 150 parts of ammonium sulfate in a closed vessel. After the reaction was complete further heating drove off the ammonia, and it was reacted with sulfuric acid to form ammonium sulfate to be recycled. The solids were then leached with water, and boric acid crystallized from the solution (Bailey, 1902). Winkler (1907) reported on a German process in which flue gas (CO_2) under pressure was forced into an agitated pressure vessel containing a colemanite–water slurry until the solution was saturated with $Ca(HCO_3)_2$. The pressure was then released, precipitating $CaCO_3$, and the cycle repeated until the colemanite was dissolved. The remaining slurry was settled, the liquor drained off, and boric acid crystallized. The process was stated to be less expensive, and the boric acid contained fewer impurities than with acid leaching.

8.2.5 Beneficiation

8.2.5.1 Calcining, Gravity Separation

When colemanite is to be *calcined,* the ore is usually crushed to −1.9 or −2.5 cm (¾ or 1 in.; smaller if it is to be deslimed) and heated in a calciner to about 450–500°C (850–930°F; well below the normal mixed borate ore fusion point of 485–550°C). In the residence time of most calciners, 85–90% of the colemanite decrepitates to a predominantly −28 to −35 mesh size. If the flue gas velocity is greater than 2–5 m/sec (4–15 ft/sec), most of the colemanite is entrained and carried out to be recovered in dust collectors. If the kiln is indirectly fired, or if it has a low flue-gas velocity, the colemanite can be separated by vibrating screens. The hot flue gas from the dust collector or indirect fired kiln is often sent through a colemanite ore rotary dryer to remove its free moisture content (sometimes up to 16%), carry out some clay, and preheat the ore. In the dryer the flue gas often leaves at 90–120°C (194–265°F), and the ore is heated to >149°C (300°F). Both the calciner and dryer are operated in a counterflow manner to increase the ore's exit temperature, and to effect better efficiency (Miles, 1973; there are many articles on calcining in the References).

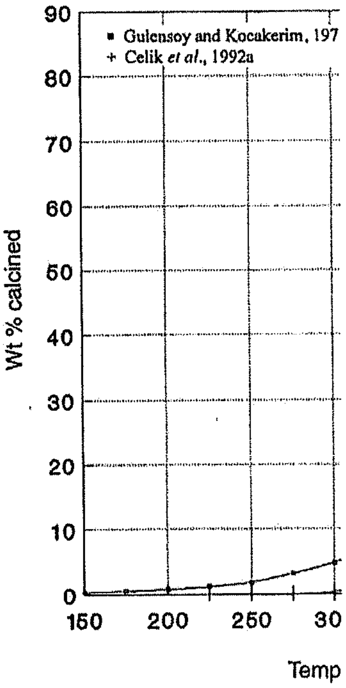

Figure 8.12 Col

Small-scale laboratory calcining te
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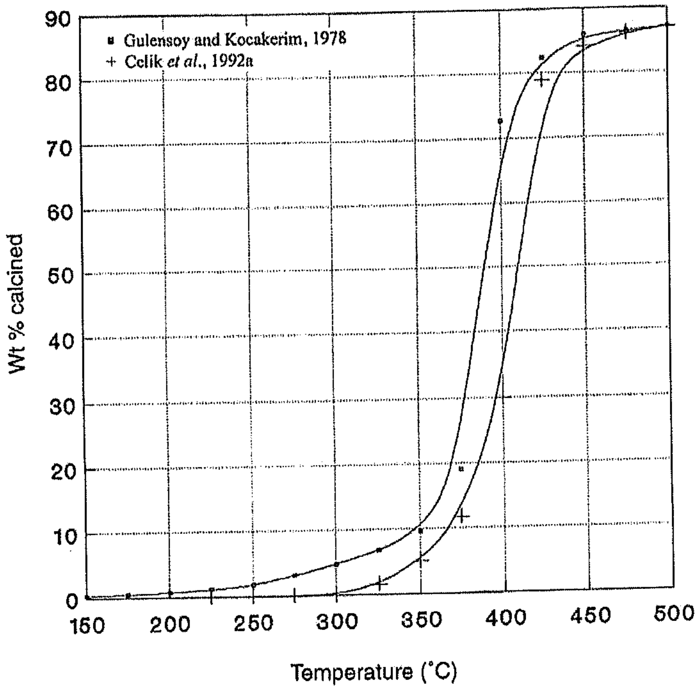

Figure 8.12 Colemanite calcination.

Small-scale laboratory calcining tests with about 15 min of heating have been made on hand-picked, high-purity Turkish (Bigadic) colemanite (Fig. 8.12). Regardless of the ore size (19–0.6 mm; 0.74 in.–10 mesh) or time (15 min–5 hr), at 500°C, 87–89% of the colemanite decrepitated to a −0.2-mm (65-mesh) size. With 10- to 16-mesh ore, the same results were obtained in 10 min. Ulexite did not decrepitate, but as much as 20% of the 10- to 16-mesh ulexite could pass through a −65-mesh screen merely because of its friability and ease of grinding (Atman and Baysal, 1973; Celik, Uzunoglu, and Arslan, 1992a).

Many studies have also been made on the *gravity separation* of the coarse residue from colemanite calcining (see References), such as that by Emrullahoglu, Kara, Tolun, and Celik (1993). They employed the rejects (43% of the total, 19.5% of the B_2O_3) from a pilot plant test calcining 0.2- to 25-mm (1-in. to 65-mesh), 30% B_2O_3 Turkish (Bigadic) colemanite ore. On screening, the +1-mm (+16-mesh) fraction contained 11.6% B_2O_3, and was 60% of the sample's weight. It was ground to −16 mesh and screened to two fractions: 1–0.5 mm (16–32 mesh) and −0.5 mm. They were then separately repulped and run over a laboratory diagonal concentrating table. The (light) concentrate plus middling analyses for the 1- to 0.5-mm and −0.5-mm fractions were 45.5wt%, 51.9% B_2O_3 and 42.2wt%, 51.0% B_2O_3, respectively. Microscopic studies indicated a 1-mm liberation size, and the densities were: calcined colemanite 1.85, and the gangue 2.72 g/cc.

Heavy media separation has also been attempted on both calcined and uncalcined ore. Pure colemanite's density is 2.42–2.43 g/ml, whereas calcite's is 2.71 g/ml, indicating that a gravity separation might be possible. However, in both laboratory and plant tests with 3- to 25-mm Turkish colemanite ore, the separation was poor. With +50-mm ore, a 15% recovery of 43% B_2O_3 was obtained. The liberation size was a problem, but because some calcite cocrystallized with colemanite, and the gangue was a clay–calcite mixture, the density difference was blurred (Ozkan and Lyday, 1995).

8.2.5.2 Flotation, Desliming

The flotation separation of colemanite from lower-grade and fine ores appears to be the most economical processing method. It can give reasonably high yields and selectivity, and its processing equipment and costs are much less than those for calcining. Sodium oleate ($C_{17}H_{33}COONa$) can be a good collector, but it is not selective in the presence of calcite. Sodium dodecyl benzene sulfonate [$CH_3(CH_2)_{11}C_6H_4SO_3Na$] is not quite as good a collector, but is reasonably selective when calcite is present. Floating a 48- to 200-mesh 50% mixture of calcite and colemanite with 10^{-4} mole/l of sulfonate gave a 90% colemanite product, but only a 40% yield. At 8×10^{-4} to 10^{-3}mole/l, the recovery was nearly complete, but there was no separation. Yarar (1985) and Yarar and Mager (1979a and b) reported concentrates of 41% B_2O_3 or higher with this reagent on Turkish colemanite ore. The flotation solutions had a pH of 9 ± 0.4, and contained 42.3 ppmB.

Barwise (1992), and Simon and Barwise (1993) suggested using ~1.5kg/ton of Na or NH_4 dialkyl (i.e., dinonyl, dilauryl or di-isodicyl) sulfosuccinate as the collector for both colemanite and ulexite Turkish ores. The branched chain nonyl salts were preferred. Mixing 50–80% of the collector with 2–30% water, 10–40% of a dihydric or >15C monohydric alcohol, and grinding to −60 mesh (desliming at −400 mesh) was recommended. Realgar and stibnite have been partially removed from −150-mesh ore by flotation with potassium amyl xanthate, mercaptobenzothiazole, or butyl xanthogen ethyl formate. In one test with 38% B_2O_3 Turkish ore, the As was reduced to 270 ppm, with an 82% B_2O_3 recovery by a sequential As–colemanite flotation. Sawyer and ed 11.6% B_2O_3, and was 60% of the nesh and screened to two fractions: They were then separately repulped trating table. The (light) concentrate 5-mm and −0.5-mm fractions were)% B_2O_3, respectively. Microscopic e, and the densities were: calcined c.

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Wilson (1973) found that above 75°C 80–98% of the arsenic could be floated with only a 2–8% borate loss. The arsenic either self-floated or could be assisted by C_2–C_5 xanthates or mineral oils. Other flotation articles are given in the References.

The *desliming* step on colemanite or ulexite ore usually results in a relatively high B_2O_3 loss. For instance, a 24.5% B_2O_3 Turkish colemanite ore had a 20% loss (and 35% B_2O_3) after one attrition stage when deslimed at −53μ (270 mesh). With higher-grade ore (28.4% B_2O_3), after four desliming stages at 270 mesh the grade was 40.5% B_2O_3, and the recovery 78.6% (Ozkan and Lyday, 1995). At Death Valley the loss is 15–25% at −65 mesh.

8.2.5.3 Magnetic, Electrostatic, Optical

Tests on the magnetic separation of dry Sijes (Argentina) colemanite ore indicated the presence of some magnetite, but most of the magnetic material (iron) was in the adhering clay and tuff. When 30- to 80-mesh colemanite was slowly passed under a strong electromagnet positioned above a right angle belt (with a 3-mm gap between the ore and the belt) the B_2O_3 yield was 92%, and the Fe_2O_3 content was reduced from 0.47 to 0.28%. The ore's B_2O_3 increased by 0.7–1.5% (Flores and Villagran, 1992).

In a series of laboratory and pilot plant tests the colemanite–ulexite slimes (10.7% B_2O_3) from leaching borax at U.S. Borax were air-dried and then crushed into three fractions: 4–10 mesh, 10–70 mesh, and −70 mesh. The first two were separately processed in three-stage magnetic separators with an average B_2O_3 recovery of 52%, and a 26% B_2O_3 product. The slimes' montmorillonite clay contained a small amount of pyrrhotite (FeS). In 1995, 14 million tons of slimes were in U.S. Borax's five solar ponds, and it was projected that a magnetic separation process could equal the mining cost (on a B_2O_3 basis) of borax. A 77 tons/hr plant was being considered (Downing, 1995).

Kaytaz, Onal, and Guney (1986) studied the *electrostatic* separation of Turkish colemanite, and felt that it could be moderately successful. Celik and Yasar (1995), and Yasar, Hancer, Kaytaz, and Celik (1994) achieved good electrostatic recoveries of 9- to 20-mesh pure-white colemanite in the laboratory at room temperature, and with beige colemanite at 50°C. With black colemanite the recovery at 80°C was only 60%. They noted that the conductivity of colemanite, borax, and ulexite largely depends on their impurities, particularly strontium and lithium, and that colemanite behaved as an insulator with both static and beam-type electrodes. *Optical sorting* tests on colemanite from Emet gave poor results, except for the removal of realgar (it is bright red). The minerals all looked the same to the machine because of the trapped (or surface-adhering) clay or tuff. Wetting the ore assisted in the color distinction, but greatly hindered its rejection (Ozkan and Lyday, 1995).

8.3 ULEXITE, PROBERTITE, AND OTHER BORATES

8.3.1 Argentina

The flow sheet of a typical boric acid plant processing ulexite in the Lerma Valley near Salta is shown in Fig. 8.13 (Pocovi, Latre, and Skaf, 1994). The ulexite is in the form of air-dried, hand-sorted nodules or slabs containing 22–25% B_2O_3, 4–15% Cl, 1–6% SO_4 and 9–34% acid insolubles. It is first

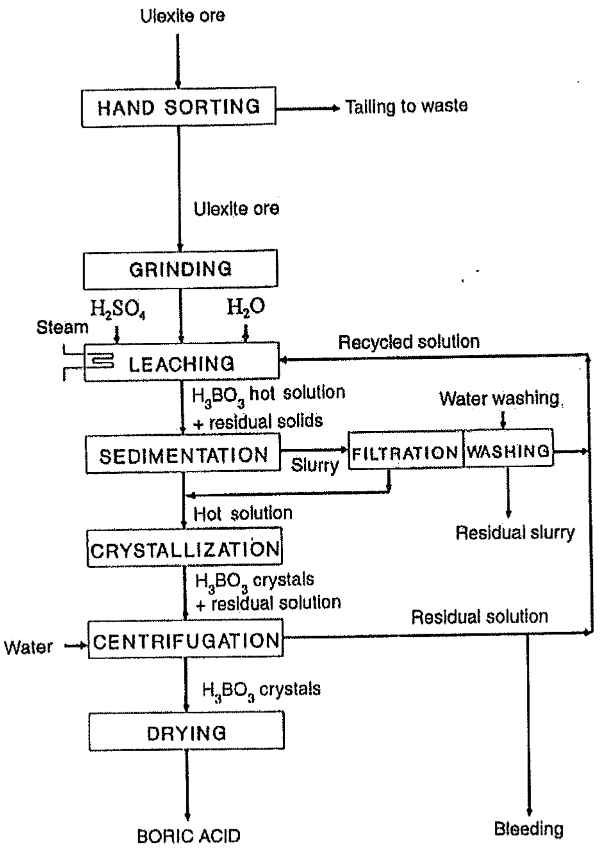

Figure 8.13 Flow sheet of a typical boric acid plant near Salta, Argentina in 1994. (From Pocovi, Latre, and Skaf, 1994; reprinted by permission of Chapman Hall.)

ground, and then batch leached wit
agitated tanks with steam coils. Wh
(with a coagulant) to a steam-heated
liquor is withdrawn. The insolubles
pulped and sent to a tailings pond.
filtrate are pumped to agitated batch
lates through internal cooling coils. W
and partially recycled to the leach
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the Na_2SO_4 formed during leaching,
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These authors suggested that the
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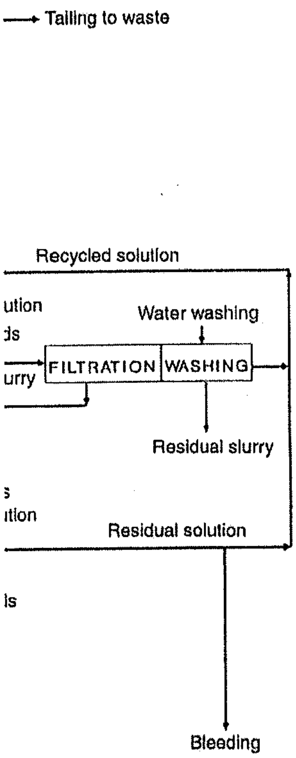
containing 36–40% B_2O_3, 0.2–0.9% C
bles, with a 78–87% B_2O_3 recovery. T
be returned to the salar. As a second
the Salta plants to crystallize salt cak
disposing of it (Pocovi *et al.*, 1994).

Among the individual operators, I
was 25 km from Buenos Aires, with
plans for an increase to 300 metric to
34% B_2O_3, 5–7% Cl, 3–4% SO_4, 15–
Maggie mine was sent (1500 metric t
500 metric tons/month of boric acid. I
acid solution from a local sugar mill

8.3.2 Bolivia

In 1995 Corban S.A.'s Oruro plant
B_2O_3 ulexite from the Salar de Uyuni
to 37–40% B_2O_3, and then ground to
with crude trona mined from the n
the reaction was complete the solut
crystallized. The borax was removed,
fired dryer, producing 90–100 tons/mo
was 200 tons/month of borax and 100
tons/month of 37% B_2O_3, and 200 to
shipped by trucks to the railhead at S
Brazil or Iquique, Chile for distribut

lant processing ulexite in the Lerma
(Pocovi, Latre, and Skaf, 1994). The
d-sorted nodules or slabs containing
nd 9–34% acid insolubles. It is first



id plant near Salta, Argentina in 1994. (From
ission of Chapman Hall.)

ground, and then batch leached with sulfuric acid at 60–80°C in baffled, agitated tanks with steam coils. When dissolved the residual slurry is sent (with a coagulant) to a steam-heated settler, and after it has settled the clear liquor is withdrawn. The insolubles are also removed, filtered, washed, repulped and sent to a tailings pond. The solution from the settler and the filtrate are pumped to agitated batch crystallizers where cooling water circulates through internal cooling coils. When cool, the residual brine is removed and partially recycled to the leach tank. The boric acid crystals are then repulped, pumped from the tank, centrifuged, washed, and dried in a parallel-flow hot-air rotary dryer. The product is kept below 95°C to prevent its dehydration to metaboric acid. The bleed steam from the end liquor removes the Na_2SO_4 formed during leaching, along with the NaCl and Na_2SO_4 that were in the ore. The disposal of this brine and the mud into tailings ponds has resulted in a serious pollution problem, and represents a major recovery loss.

These authors suggested that the operators crush, grind, and wash the ulexite at the salars before shipping it to Salta. Even with ulexite's low density of 1.7 g/cc, a hydrocyclone separation of a crushed ore slurry gave concentrates containing 36–40% B_2O_3, 0.2–0.9% Cl, 0.4–0.7% SO_4 and 4–16% acid insolubles, with a 78–87% B_2O_3 recovery. The slimes and water-soluble salts would be returned to the salar. As a second step, evaporators should be installed in the Salta plants to crystallize salt cake (Na_2SO_4) as a by-product rather than disposing of it (Pocovi *et al.*, 1994).

Among the individual operators, BoroSur S.A.'s boric acid plant in 1990 was 25 km from Buenos Aires, with a capacity of 550 metric tons/year, and plans for an increase to 300 metric tons/month (Norman, 1990). Ulexite (20–34% B_2O_3, 5–7% Cl, 3–4% SO_4, 15–20% insolubles, 5–10% water) from the Maggie mine was sent (1500 metric ton/month) to Salta in 1992 to produce 500 metric tons/month of boric acid. It was leached by a residual hydrochloric acid solution from a local sugar mill (Battaglia and Alonso, 1992).

8.3.2 Bolivia

In 1995 Corban S.A.'s Oruro plant received up to 5000 tons/month of 20% B_2O_3 ulexite from the Salar de Uyuni's Rio Grande area. It was first air-dried to 37–40% B_2O_3, and then ground to a fine size and reacted in a boiling slurry with crude trona mined from the nearby Salar de Collpa Laguna. When the reaction was complete the solution was settled, decanted, cooled, and crystallized. The borax was removed, centrifuged, washed, and sent to a gas-fired dryer, producing 90–100 tons/month of borax in 1995. The plant capacity was 200 tons/month of borax and 100 tons/month of pentahydrate. About 300 tons/month of 37% B_2O_3, and 200 tons/month of 40% B_2O_3 ulexite were also shipped by trucks to the railhead at Santa Cruz, and from there to Corumba, Brazil or Iquique, Chile for distribution (Lyday, 1995). The plant and mine employed 40 full-time, and 200 part-time workers. A second company, Minera Tierra, employed 120 people, and in 1993 operated a 10,000-tons/year boric acid plant. Some of their ulexite was washed and roasted to a 42% B_2O_3 content (Lyday, 1994).

8.3.3 Chile

In the late 1800s all of the borax manufactured in Germany was from ulexite mined in Chile's Salars Ascotan, Maricunga and Pedernal, or Argentina's Rosario. Ascotan's ulexite was generally superior, with much less gypsum, and a B_2O_3 content of 34% compared to the 12–24% of the others. The ulexite nodules were first ground to a smaller size, and then to very fine particles in a "disintegrator." Next, 1.25 metric tons of the fine ore were placed in a vigorously agitated, boiling (by live steam injection) tank with 5–6.25 metric tons of water and a slight excess of soda ash. Trona or sodium bicarbonate could also be used, and were slightly favored, since if added in accidental great excess, metaborate would not be formed. A small excess of soda ash, however, did aid in speeding the borax crystallization. The leaching reaction tended to cause foaming, which was controlled by turning off the steam and spraying cold water on the boiling surface.

When the ore was dissolved, the steam and agitation were stopped and the mixture settled. The clear liquor at 30–35°Be (1.26–1.32 g/ml) was then pumped into 1000- to 1500-liter rectangular steel tanks and cooled for 3–4 days. (The density variability depended on the amount of sodium sulfate and other salts from the impurities and gypsum.) After crystallization was complete the brine was removed and recycled, except for a bleed stream, which was cooled in the winter to crystallize glauber salt ($Na_2SO_4 \cdot 10H_2O$), and then this end liquor, or all of the brine in the summer, evaporated to crystallize the non–borax salts. The residual liquor from the evaporators was sent back to the borax crystallizers. The mud from the leaching step was filtered, washed (with hot water), repulped, and again filtered. The wash water went to the leach tank, and the filtrate to the crystallizer.

The crude borax from this operation usually contained 40–50% borax, 40% sodium sulfate, and 10% salt. It was dissolved in boiling water to obtain a 30°Be (1.26 g/ml) solution, and the iron and organics oxidized and precipitated by sodium hypochlorite, and then settled. The clear liquor was decanted and sent to insulated 8- to 10-m^3 rectangular insulated steel vessels with wooden lids. This allowed very slow cooling to grow large, hard, colorless, and clear borax crystals. After 10–14 days the temperature was 33°C, and the residual brine was drained off. By this temperature control the other salts did not crystallize, and fairly pure borax was obtained. The residual liquor was either used for leaching or boiled to crystallize Na_2SO_4, and then cooled to recover borax. The 20-cm thick layer of borax was removed from the crystallizer walls,

drained, washed, and then dried f
small crystals were screened an
"packed into 300- to 400-kilo bar
purity) for shipment (Witting, 18
In more recent times, Quibora
Arica, for processing. The plant
capacity, and two 6000 kg/hr boile
ated freshwater from the plant's 1
1200–1500 ppmNaCl). The plant's
and dry the ore to make a 36.5%
Some ore was also ground, screen
boric acid in one of two agitated, s
solution was settled, sent to 250-p
stainless steel, water-cooled tanks
ened, centrifuged, washed, and d
dryers. A production capacity of
boric acid was claimed. The pro
Antafagasta (Leiser, 1996; Lyday
boric acid as a by-product from t
plant was announced for 1998.
process on the solar-evaporated p

8.3.4 China

The Chinese borate skarn depo
metric tons/year of szaiblyite in 1
capacity was 77,000–110,000 tons
of boric acid in 1994 (Lyday, 199
metric tons/year of boron–iron o
the basis of their "recent success
Su and Yu (1980) reported that
being done by an alkaline digestio
of magnesia and other insolubles.
on the processing of this type of

8.3.5 Peru

The Inka Bor group at the La
at the salar, and then crushed, sc
was next cooled and passed throu
of the iron and clay. This was fo
year of a +10-mesh agricultural
calcined ulexite could be shipped

workers. A second company, Minera
93 operated a 10,000-tons/year boric
washed and roasted to a 42% B_2O_3

ctured in Germany was from ulexite
cunga and Pedernal, or Argentina's
ly superior, with much less gypsum,
the 12–24% of the others. The ulexite
ize, and then to very fine particles in
ns of the fine ore were placed in a
m injection) tank with 5–6.25 metric
la ash. Trona or sodium bicarbonate
avored, since if added in accidental
formed. A small excess of soda ash,
crystallization. The leaching reaction
trolled by turning off the steam and
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n and agitation were stopped and the
0–35°Be (1.26–1.32 g/ml) was then
ular steel tanks and cooled for 3–4
on the amount of sodium sulfate and
m.) After crystallization was complete
xcept for a bleed stream, which was
r salt ($Na_2SO_4 \cdot 10H_2O$), and then this
mmer, evaporated to crystallize the
m the evaporators was sent back to
he leaching step was filtered, washed
iltered. The wash water went to the
llizer.
sually contained 40–50% borax, 40%
ssolved in boiling water to obtain a
nd organics oxidized and precipitated
d. The clear liquor was decanted and
r insulated steel vessels with wooden
row large, hard, colorless, and clear
perature was 33°C, and the residual
ture control the other salts did not
ained. The residual liquor was either
Na_2SO_4, and then cooled to recover
s removed from the crystallizer walls,

drained, washed, and then dried for 24 hr in a "drying chamber" at 30°C. The small crystals were screened and reprocessed, and the larger ones were "packed into 300- to 400-kilo barrels lined with blue paper" (to signify high purity) for shipment (Witting, 1888).

In more recent times, Quiborax trucks their ulexite to El Aquila, north of Arica, for processing. The plant had six diesel generators with a 2375-kWhr capacity, and two 6000 kg/hr boilers. A 200-m^3/day reverse osmosis unit generated freshwater from the plant's 1500-m^3/day brackish water wells (containing 1200–1500 ppmNaCl). The plant's capacity to wash, deslime in cyclones, filter, and dry the ore to make a 36.5% B_2O_3 product in 1995 was 30,000 tons/year. Some ore was also ground, screened, and reacted with sulfuric acid to produce boric acid in one of two agitated, steam-heated reaction vessels. The hot leach solution was settled, sent to 250-psi filter presses, and then cooled in agitated stainless steel, water-cooled tanks to crystallize boric acid. It was next thickened, centrifuged, washed, and dried in one of two inverted U-shaped flash dryers. A production capacity of 24,000–30,000 tons/year of 99–99.9% pure boric acid was claimed. The product was exported from Arica, Iquiqui or Antafagasta (Leiser, 1996; Lyday, 1995). Production of 18,000 tons/year of boric acid as a by-product from the large Salar de Atacama's Minsal potash plant was announced for 1998. It will probably be made by a salting-out process on the solar-evaporated potash end liquor as described on page 384.

8.3.4 China

The Chinese borate skarn deposits had the capacity for processing 120,000 metric tons/year of szaiblyite in 1995 (Norman, 1996), and the country's total capacity was 77,000–110,000 tons/year of borax and 10,000–18,000 tons/year of boric acid in 1994 (Lyday, 1994). A new plant with a capacity of 110,000 metric tons/year of boron–iron ore in Liaoning was announced in 1995, on the basis of their "recent success in separating boron from this type of ore." Su and Yu (1980) reported that in 1980 all the borate ore processing was being done by an alkaline digestion. This left a large residue ("muddy waste") of magnesia and other insolubles. There are many articles in the References on the processing of this type of ore.

8.3.5 Peru

The Inka Bor group at the Laguna Salinas in 1995 air-dried their ulexite at the salar, and then crushed, screened, and sent it to a rotary calciner. It was next cooled and passed through a strong magnetic field to remove some of the iron and clay. This was followed by screening, and about 5000 tons/year of a +10-mesh agricultural grade, and 15,000 tons/year of −10-mesh calcined ulexite could be shipped to customers directly from the salar. The company built medical facilities and housing for its workers at the Salar, equipped with television, communication, electricity, heating, and cooling. Some of the ulexite was shipped directly to a 12,000-tons/year boric acid plant in Lima where it was reacted with sulfuric acid in steam-heated, agitated reaction vessels. The hot slurry was next sent to a drum filter, and the filtrate polished in a filter press. The clear liquor was then cooled to crystallize boric acid, which was centrifuged, washed, dried, and packaged. Most of the products were shipped from the ports of Callao and Matarani (Leiser, 1996).

8.3.6 Russia

In 1939 three plants (Slavyansk, Buiskii, and Leningrad) produced borax and boric acid from Inder borate ore (Moshkareva *et al.*, 1971). The Slavyansk plant used a soda ash leach, whereas at Buiskii borax was produced by acid leaching and then reacting the boric acid with soda ash. The combined capacity of the three plants was about 25,000–30,000 metric tons/year of boron compounds (Gale, 1964). Some ascharite and hydroboracite ores were beneficiated from 15–25% B_2O_3 to 44% B_2O_3 by crushing, washing, desliming, and a short-contact leach to remove the NaCl. Lower-grade ores were upgraded to 18–20% B_2O_3 (occasionally 34% B_2O_3) by a density separation process.

Datolite ores from the skarn deposits with 3–15% B_2O_3 have been upgraded to >16% B_2O_3 by density separation or flotation. Ludwigite-type ores with 4% B_2O_3 have been upgraded to 10% B_2O_3 by a magnetic removal of the accompanying magnetite. The ore was then sintered with calcite, and the residue acid leached to produce 64,000 metric tons/year of B_2O_3 products in 1964, and 68,000 metric tons of B_2O_3 in 1968. An anhydrous borax plant was established in 1972 (Matterson, 1980). Kistler and Helvaci (1994) reported that low-grade borosilicates from the Bor deposit were first crushed and then processed in a complex plant employing magnetic separators, heavy media, and flotation. The concentrate was dried, acidified, and calcined before being converted to boric acid or borax.

8.3.7. United States

8.3.7.1 Death Valley Region: Boraxo, Billie

The ulexite–probertite ore from Tenneco's Boraxo mine averaged 28% B_2O_3 (70% equivalent ulexite), and was shipped directly by 22.7-metric-ton (25-ton) end-dump trucks the 61 km to their Dunn Siding, California plant. The ore size was −15 cm (6 in.), and it was first fed to a double rotor impactor in closed circuit with 2.5-cm (1-in.) screens. It was then conveyed to a Raymond mill to make either −70- or −200-mesh products, which were pneumatically conveyed to a 544-metric-ton (600-ton) or two 204 metric-ton (225-ton) silos. The impactor discharge could also be sent to a 10-mesh-screen and hammermill circuit. Each product analyzed 25–30%
pneumatically, and the −10-mesh produc
metric-ton (90-ton) rail cars (Evans *et al.*,
tion of ore from the Billie mine was alsc
(Norman and Johnson, 1980).

8.3.8 Processing

Many leaching processes have also b
borate ores, as indicated in the References
and Gulensoy's (1977) study of the alka
to reduce metaborate formation) leaching
some forms of ulexite (i.e., "camel tooth,"
harder to dissolve than others (i.e., "com
mesh a preliminary roast at 390°C was re
of the ores with a 1-hour, 85–88°C leach.
yields of either ulexite could be obtained,
reduced the yields to 91–96%. The initial
that cut as well as ground because of ulexi
might require 100 parts of 33% B_2O_3 fir
and 10 of $NaHCO_3$ to produce 117 parts

When *priceite* was processed in the 1
soda ash (some boric acid or bicarbonate
at 60 psi pressure overnight. The leached
filtered, washed, and discarded. The cla
56°C to crystallize pentahydrate, or to a lo
1910). The acid or alkaline leaching of u
in the literature, as have magnesium borat
as indicated in the References.

8.3.9 Beneficiation

8.3.9.1 Flotation

Studies on the flotation separation of
made by Celik and Bulut (1996). They fo
10^{-5}M sodium dodecylsulfate (SDS)] eas
pH of 9.3, but did not float ulexite. Cationi
hydrochloride (DAH)] floated both mine
the presence of negatively charged clay pa
of both ores were ground to 65–100 mesh,
cite was floated with isopropyl naphthale
starch. The ore was first deslimed with th
and then conditioned with 100 g/ton of

ousing for its workers at the Salar,
on, electricity, heating, and cooling,
to a 12,000-tons/year boric acid plant
lfuric acid in steam-heated, agitated
t sent to a drum filter, and the filtrate
r was then cooled to crystallize boric
d, and packaged. Most of the products
and Matarani (Leiser, 1996).

skii, and Leningrad) produced borax
oshkareva *et al.*, 1971). The Slavyansk
Buiskii borax was produced by acid
with soda ash. The combined capacity
),000 metric tons/year of boron com-
hydroboracite ores were beneficiated
hing, washing, desliming, and a short-
-grade ores were upgraded to 18–20%
sity separation process.
with 3–15% B_2O_3 have been upgraded
r flotation. Ludwigite-type ores with
B_2O_3 by a magnetic removal of the
then sintered with calcite, and the
metric tons/year of B_2O_3 products in
1968. An anhydrous borax plant was
Kistler and Helvaci (1994) reported
r deposit were first crushed and then
g magnetic separators, heavy media,
l, acidified, and calcined before being

Billie

nneco's Boraxo mine averaged 28%
s shipped directly by 22.7-metric-ton
their Dunn Siding, California plant.
as first fed to a double rotor impactor
s. It was then conveyed to a Raymond
products, which were pneumatically
or two 204 metric-ton (225-ton) silos.
t to a 10-mesh-screen and hammermill

circuit. Each product analyzed 25–30% B_2O_3, with the finer ones loaded pneumatically, and the −10-mesh product by belt. They were shipped in 82-metric-ton (90-ton) rail cars (Evans *et al.*, 1976). The ulexite–probertite fraction of ore from the Billie mine was also shipped to the Dunn Siding plant (Norman and Johnson, 1980).

8.3.8 Processing

Many leaching processes have also been suggested for ulexite or other borate ores, as indicated in the References. An example of these is Demircioglu and Gulensoy's (1977) study of the alkaline (Na_2CO_3, with some $NaHCO_3$ to reduce metaborate formation) leaching of Turkish ulexite. They found that some forms of ulexite (i.e., "camel tooth," large masses of crystals) were much harder to dissolve than others (i.e., "compact" ore). When ground only to 20 mesh a preliminary roast at 390°C was required to obtain >90% yields for all of the ores with a 1-hour, 85–88°C leach. However, with fine grinding 98–99% yields of either ulexite could be obtained, but losses in the muds after filtration reduced the yields to 91–96%. The initial grinding step was best done in mills that cut as well as ground because of ulexite's fibrous nature. A typical process might require 100 parts of 33% B_2O_3 finely ground ulexite, 12 of Na_2CO_3, and 10 of $NaHCO_3$ to produce 117 parts of borax (Dupont, 1910).

When *priceite* was processed in the 1800s in France it was leached with soda ash (some boric acid or bicarbonate was also added) in heated autoclaves at 60 psi pressure overnight. The leached slurry was then settled and the mud filtered, washed, and discarded. The clarified leach solution was cooled to 56°C to crystallize pentahydrate, or to a lower temperature for borax (Dupont, 1910). The acid or alkaline leaching of ulexite has been extensively covered in the literature, as have magnesium borates and borosilicates (as from skarns), as indicated in the References.

8.3.9 Beneficiation

8.3.9.1 Flotation

Studies on the flotation separation of ulexite from colemanite have been made by Celik and Bulut (1996). They found that anionic surfactants [i.e., 6.7 10^{-5}M sodium dodecylsulfate (SDS)] easily floated colemanite at its natural pH of 9.3, but did not float ulexite. Cationic reagents [i.e., 10^{-4}M dodecylamine hydrochloride (DAH)] floated both minerals, but were adversely affected by the presence of negatively charged clay particles. In these tests perfect crystals of both ores were ground to 65–100 mesh, and conditioned 10 min. Hydroboracite was floated with isopropyl naphthalene sulfate, turpentine, kerosene, and starch. The ore was first deslimed with the aid of 500 g/ton of sodium silicate, and then conditioned with 100 g/ton of oleic acid, 400 g/ton of kerosene, 50 g/ton of pine oil, and the naphthalene sulfate. Yields of 81–92% were reported, of a 18–34% B_2O_3 product (Ozkan and Lyday, 1995). There have also been rather intensive studies on the flotation of borosilicate ores from the large skarn deposits (see the References).

8.3.9.2 Electrostatic, Magnetic, Others

Experimental tests by Fraas and Ralston (1942) have been made on the electrostatic separation of ulexite from synthetic bentonite mixtures. The "ore" was coated with benzoic acid at 150°C, and then passed through a cupric sulfide plate electrostatic separator. With 1.7% of 20- to 32-mesh ulexite, 61% was recovered in the first pass with a 95.5% purity; an additional 13.8% was recovered on the second pass with a 65.6% purity; and 4.9% more at an 18.8% purity on the third pass. Similar studies were made by Yasar *et al.* (1994). At Loma Blanca magnetic separation was used on ulexite, inyoite, and borax ores, first at the mine where the ore was dried, ground, and fed to magnetic separators to produce >26% B_2O_3 ore. Then it was trucked to Palpala (near Jujuy) where additional magnetic separation produced a >38% B_2O_3 product (Solis, 1996). At the Laguna Salinas, Peru, magnetic separation also removed some clay from 20,000t/yr of air-dried ulexite ore (Lyday, 1995).

Many studies (including pilot plant tests) on beneficiation procedures have been made for borosilicate and borosilicate–magnetite ores, including ascharite, danburite, datolite, garnierite, and ludwigite. The methods included density separators, heavy media, flotation, laser and x-ray luminescence, neutron absorption, and roasting. Rapid boron analytical procedures were also examined. Each of these subjects is considered in the References.

8.4 BRINE

8.4.1 Searles Lake

8.4.1.1 Evaporation (Main Plant Cycle)

In 1916 a plant was built at Searles Lake to process brine by plant evaporation, and large scale borax production was initiated in 1919. The lake's brine, a complex mixture containing about 35% dissolved solids (Table 8.2), is saturated with all of the solid phases present in each zone. Since the crystal and brine compositions vary somewhat, the wells have been drilled in the most favorable locations. Casings are cemented in the holes to within a short distance of the bottom, and pumps with 4.3-m (14-ft) suction capability are mounted in them to bring brine to the plants.

The plant evaporation process of the former American Potash & Chemical Corporation treated about 3 million gallons of upper structure brine per day in a continuous, cyclic process. Brine was first mixed with recycle liquor and

Tat

Typical Brine Analyses for the Se

	Lake brine, 19
Constituent	Upper
KCl	4.90
Na_2CO_3	4.75
$NaHCO_3$	0.15
$Na_2B_4O_7$	1.58
$Na_2B_2O_4$	—
Na_2SO_4	6.75
Na_2S	0.12
Na_3AsO_4	0.05
Na_3PO_4	0.14
NaCl	16.10
H_2O	65.46
WO_3	0.008
Br	0.085
Li_2O	0.018
I	0.003
F	0.002

[a] Bixler and Sawyer, 1957; Garrett, 1960.

evaporated to the potash saturation p
chloride, licons ($NaLi_2PO_4$), and bu
were removed and hydraulically clas
and Na_2SO_4 products to be obtain
next cooled to 38°C (100°F) in gentle,
resulting potash removed. Since the l
cooling step, it was only its high sup
lution.

The "mother liquor" (called ML-
where it contacted a thick seed bed
(see Figs. 8.14 and 8.15). The crystalli
and a large conical section on the top.
or the top of the lower cylindrical, hi
Pentahydrate crystals were removed
relatively clear overflow brine came
section). This provided considerable
the liquor and the solids. The overflo

ene sulfate. Yields of 81–92% were
)zkan and Lyday, 1995). There have
ie flotation of borosilicate ores from
ences).

lston (1942) have been made on the
n synthetic bentonite mixtures. The
0°C, and then passed through a cupric
h 1.7% of 20- to 32-mesh ulexite, 61%
5.5% purity; an additional 13.8% was
5% purity; and 4.9% more at an 18.8%
were made by Yasar *et al.* (1994). At
used on ulexite, inyoite, and borax
ıs dried, ground, and fed to magnetic
Then it was trucked to Palpala (near
ation produced a >38% B_2O_3 product
ru, magnetic separation also removed
ılexite ore (Lyday, 1995).
sts) on beneficiation procedures have
ate–magnetite ores, including aschar-
dwigite. The methods included density
and x-ray luminescence, neutron ab-
ytical procedures were also examined.
the References.

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ıke to process brine by plant evapora-
vas initiated in 1919. The lake's brine,
% dissolved solids (Table 8.2), is satu-
nt in each zone. Since the crystal and
wells have been drilled in the most
ted in the holes to within a short dis-
4.3-m (14-ft) suction capability are
plants.
former American Potash & Chemical
llons of upper structure brine per day
as first mixed with recycle liquor and

Table 8.2

Typical Brine Analyses for the Searles Lake Main Plaint Cycle (wt%)[a]

Constituent	Lake brine, 1960 Upper	Lake brine, 1960 Lower	Plant brine ML-1	Plant brine ML-2
KCl	4.90	3.50	11.67	11.82
Na_2CO_3	4.75	6.50	6.77	7.55
$NaHCO_3$	0.15	—	—	—
$Na_2B_4O_7$	1.58	1.55	9.77	7.16
$Na_2B_2O_4$	—	0.75	—	—
Na_2SO_4	6.75	6.00	1.93	1.99
Na_2S	0.12	0.30	1.00	1.01
Na_3AsO_4	0.05	0.05	—	—
Na_3PO_4	0.14	0.10	0.20	0.21
NaCl	16.10	15.50	6.77	7.38
H_2O	65.46	65.72	61.09	61.51
WO_3	0.008	0.005	—	—
Br	0.085	0.071	0.64	0.66
Li_2O	0.018	0.009	—	—
I	0.003	0.002	0.07	0.71
F	0.002	0.001	—	—

[a] Bixler and Sawyer, 1957; Garrett, 1960.

evaporated to the potash saturation point, and in so doing, crystallizing sodium chloride, licons ($NaLi_2PO_4$), and burkeite ($2Na_2CO_3 \cdot Na_2SO_4$). These salts were removed and hydraulically classified, allowing pure Li_2CO_3, Na_2CO_3, and Na_2SO_4 products to be obtained. The clear, concentrated liquor was next cooled to 38°C (100°F) in gentle, growth-controlled crystallizers, and the resulting potash removed. Since the borax also became saturated during this cooling step, it was only its high supersaturation tendency that kept it in solution.

The "mother liquor" (called ML-1) was then sent to special crystallizers where it contacted a thick seed bed to crystallize crude borax pentahydrate (see Figs. 8.14 and 8.15). The crystallizers had closed impellers at the bottom, and a large conical section on the top. The ML-1 was introduced in the middle, or the top of the lower cylindrical, high-circulation, high-seed-density section. Pentahydrate crystals were removed from the bottom as a 36% slurry, and a relatively clear overflow brine came off the top of the upper conical (settling section). This provided considerable residence time (about 40 min) for both the liquor and the solids. The overflow liquor went to a thickener to remove

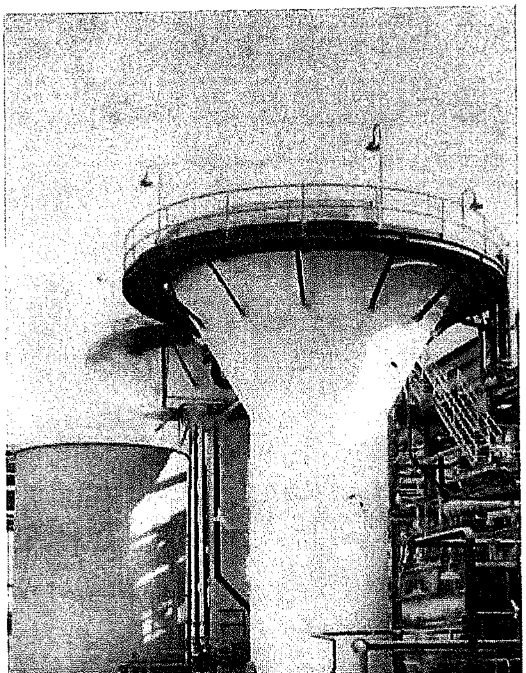


Figure 8.14 Searles Lake crude borax pentahydrate feed tank (left), crystallizer (center) and thickenter (bottom). (From Bixler and Sawyer, 1957; reprinted with permission from the American Chemical Society; copyright 1957.)

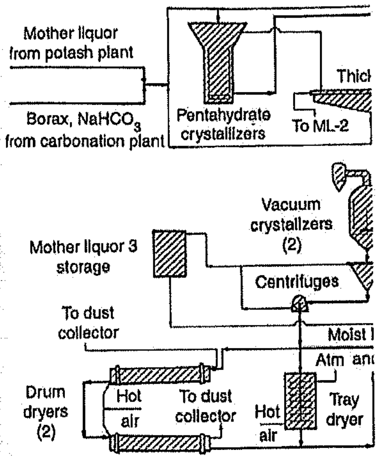


Figure 8.15 Flowsheet for production c (From Garrett, 1960; reproduced by permissio tion, Inc.)

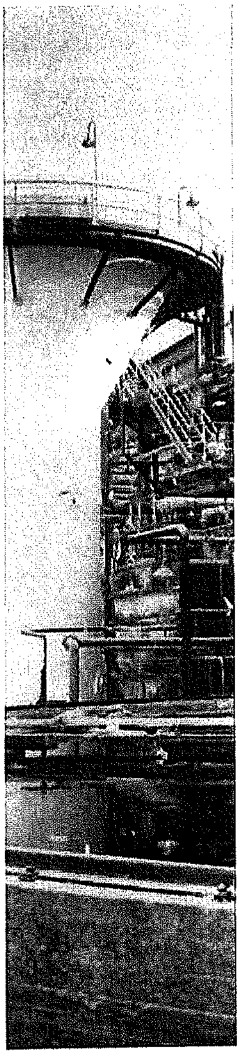
the last of its solids (occasionally 6– with fresh lake brine and returned to carbonation plant (accompanied by s borate to tetraborate) joined the pe brine contains some metaborate, and of the evaporators:

$$Na_2B_4O_7 + Na_2CC$$

To increase the borax yield per reaction is reversed by bicarbonate:

$$2NaHCO_3 + 2Na_2B$$

Foaming in the crystallizers or th fine crystals out the top, but it was m feed tank, level control to keep the occasional use of a defoamant. The was further thickened in a liquid c thickener underflow to two 4-m (13- remaining portion of the thickener u



lrate feed tank (left), crystallizer (center) and
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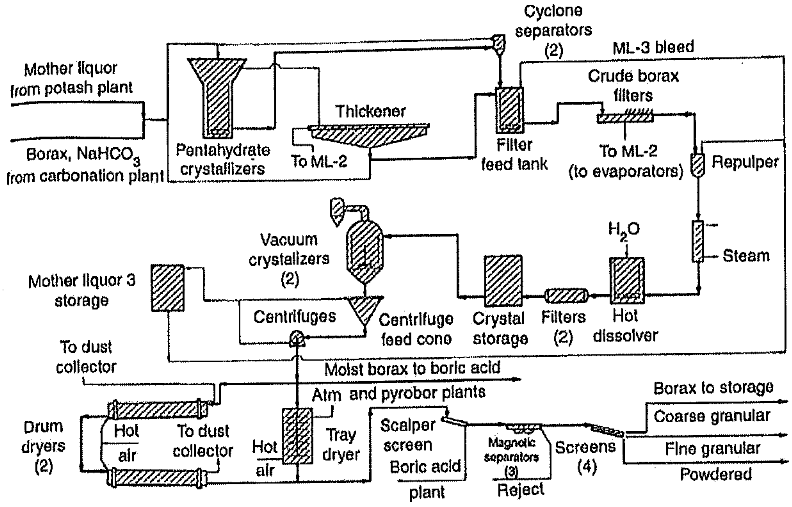


Figure 8.15 Flowsheet for production of borax from Searles Lake; evaporation process. (From Garrett, 1960; reproduced by permission of the Society for Mining, Metallurgy and Exploration, Inc.)

the last of its solids (occasionally 6–8%), and then (as ML-2) it was blended with fresh lake brine and returned to the evaporators. Borax from the separate carbonation plant (accompanied by some sodium bicarbonate to convert metaborate to tetraborate) joined the pentahydrate in the crystallizers. The lake brine contains some metaborate, and more was formed at the high temperature of the evaporators:

$$Na_2B_4O_7 + Na_2CO_3 \rightarrow 2Na_2B_2O_4 + CO_2 \qquad (1)$$

To increase the borax yield per cycle (metaborate is very soluble), this reaction is reversed by bicarbonate:

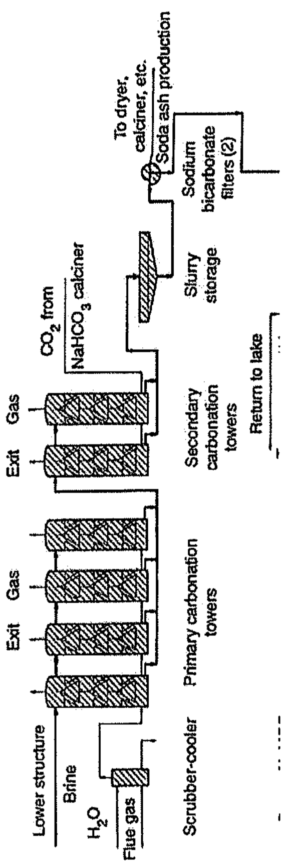
$$2NaHCO_3 + 2Na_2B_2O_4 \rightarrow 2Na_2B_4O_7 + CO_2 \qquad (2)$$

Foaming in the crystallizers or thickeners could be a problem in floating fine crystals out the top, but it was minimized by deaeration in the crystallizer feed tank, level control to keep the pumps under positive pressure, and the occasional use of a defoamant. The underflow stream from the crystallizers was further thickened in a liquid cyclone, and then sent with part of the thickener underflow to two 4-m (13-ft) flat bed, scroll-discharged filters. The remaining portion of the thickener underflow was returned to the crude pentahydrate crystallizer feed tank as seed crystals. The pentahydrate was washed on the filters with borax refinery end liquor (called ML-3) before it was discharged, and the filtrate returned to the thickeners. Analytical samples were taken on a 2- to 4-hr schedule to ensure the proper control of the process. Typical liquor concentrations are given in Table 8.2.

The crude pentahydrate was next repulped and redissolved in 88°C (190°F) refinery end liquor (ML-3), and further heated with steam sparging to 93°C (200°F) in the dissolver tanks. This brine was sent through polishing filters, and then to vacuum crystallizers where either high-purity borax [cooled to 49°C (120°F)] or pentahydrate [cooled to 60°C (140°F)] could be produced with heavy seed beds of either crystal. Caustic soda was added to increase the pH from 9.2–9.4 to 9.6–9.8 to form larger, chunkier crystals, and oleic acid to prevent crystal twinning and agglomeration. The product was originally dewatered in five continuous, automatic Sharples centrifuges to a moisture content of 3.5–6%, but later was separated in a screen bowl centrifuge. The crystals not going to the boric acid or anhydrous borax plants were dried in hot air [43–52°C (110–125°F)] rotary or Wyssmont shelf dryers, and then screened for shipment (Garrett, 1960).

8.4.1.2 Carbonation

The second process for recovering borax from Searles Lake brines was by carbonation, starting in 1926 at West End, 1946 at Trona, and 1976 at Argus. The three operations were slightly different, but they can still be described together. Primarily lower-structure brine, with its richer borax and sodium carbonate content, was introduced into the top of large carbonating towers. There it was contacted by compressed makeup CO_2 in flue gas, lime kiln gas, or CO_2 from an MEA unit, distributed into the base of the towers. One plant produced fine bubbles with agitators, and another used sieve plates to reduce the bubble size and provide a more even gas distribution. The absorbed CO_2 converts the Na_2CO_3 in the brine to $NaHCO_3$, which being only slightly soluble in the NaCl-saturated brine, crystallizes. The slurry from the primary towers is then sent to secondary towers where it absorbs CO_2 returned from the bicarbonate calciner, and the carbonation is complete (see Fig 8.16). The bicarbonate crystallized in the towers is centrifuged (or was filtered), and sent through equipment to convert it to high-purity dense soda ash. The remaining brine and centrate are blended with fresh lower-structure brine (with its metaborate content) to convert the pentaborate ($Na_2B_{10}O_{16}$) formed during carbonation back to tetraborate. The mixed brine is then sent to vacuum crystallizers where it is cooled in the presence of a heavy seed bed, and borax is crystallized. Slurry is withdrawn from the crystallizers, thickened, and centrifuged (or was filtered). The overflow is further cooled and sent to glauber salt crystallizers, which also produces a little more borax. In each plant the final brine is routed through heat exchangers to provide some cooling, and



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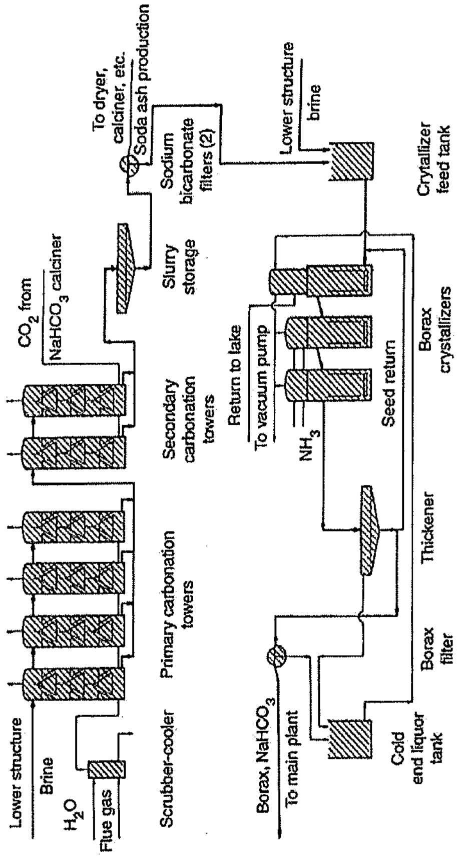

Figure 8.16 Flowsheet for production of borax from Searles Lake; carbonation process, old plant. (From Garrett, 1960; reproduced by permission of the Society for Mining, Metallurgy and Exploration, Inc.)

then returned to the lake. The crude borax is next redissolved to form pure products (Garrett, 1960, 1992). Lowry (1926) obtained one of the early patents on the process, and Helmers (1929) received a patent on the blending-of-brines concept.

8.4.1.3 Other Products

A full range of borate products had been made at Searles Lake, including borax, pentahydrate, anhydrous borax, boric acid, and B_2O_3. The boric acid process started with refined borax centrifuge cake and hot water being sent to a dissolving tank, along with heated recycle end liquor and part of the sulfuric acid. A pentaborate solution was formed, which was polish-filtered and further heated to 99°C (210°F). The remaining sulfuric acid was then added, converting the pentaborate to boric acid. This solution was sent to a vacuum crystallizer cooled to 30°C (86°F) by a barometric condenser operating with cooling-tower water. Boric acid was crystallized, and then withdrawn, centrifuged, and dried in a steam-tube dryer. Most of the process equipment was made of a special stainless steel to minimize corrosion. A USP grade of boric acid was also produced by dissolving technical boric acid, filtering the solution, and recrystallizing the product. A small excess of sulfuric acid was added to the refined product leach liquor in order to improve the crystal size and color.

The boric acid end liquor was sent through heat exchanger-condensers in the crystallizer's vapor head, and returned to the main plant cycle. There the by-product sodium sulfate was concentrated and recovered more economically than by installing a separate evaporator. (Its boric acid content also helped reduce metaborate in the ML-2.) The design of this single-pass system took advantage of two unique solubility features. First, for solutions saturated with both boric acid and sodium sulfate, there is maximum Na_2SO_4 solubility at 30°C (86°F; see Fig. 11.6). Therefore, a reaction solution cooled to this temperature has a maximum single-pass boric acid yield of 88%. Sodium sulfate saturation was maintained by recycling some of the end liquor. Secondly, the feed borax's solubility was greatly enhanced by adding only about 40% of the total sulfuric acid to form the very soluble sodium pentaborate ($Na_2B_{10}O_{16}$). If boric acid or sodium sulfate were allowed to crystallize immediately, it would be very hard to control their crystal size and purity. Consequently, enough end liquor was recycled to hold all of the boric acid in solution at 82°C (180°F) until the final sulfuric acid was added (Garrett, 1960; Garrett and Rosenbaum, 1958a, 1958b).

8.4.1.4 Dehydration

To save on shipping costs, and for some special purposes, considerable borax, and some boric acid is sold in the anhydrous form. They are produced

by partially dehydrating borax or bc
melting it in fusion furnaces. At the
Company's plant, to make $Na_2B_4O_7$ th
about 70% of the hydrate water froı
granular borax. If borax fines or pent
to the extent that some blew out of
dense enough to make an adequate
first passed over a weigh-feeder and w
bins. From there a variable-speed cha
the rotary calciners' feed screw. The
diameter and 21.3 m (70 ft) long, an
countercurrent by the 704–816°C (130
ciner dust was recovered first by dry a
was sent to the borax/pentahydrate r
nearly saturated with water and at abo
efficiency. The hot, partially dehydrat
to feed storage bins for the three fusio
with a small amount of sodium nitrat
the lake brine and oil burners), to tl
furnace. The hoppers distributed calci
between the furnace walls, allowing it
and cutters then forced the calcined b

Inside the furnaces a direct, oil-fire
down the furnace walls, and the hot flı
on its way to the calciners. The borax
melting and flowing to the seal lip at
had the melt flow into chain conveyc
min) for the length of the building. (
in the melt to promote crystallization b
As the molds traveled they slowly co
then dumped, and the crystals ground
anhydrous borax still converted to the
when poured into the molds). The m
and solidified on a chilled roll, produci
or glass form that was difficult to grin

The furnace walls were lined with
and water jacketed to further protec
borax attacks all commercial refracto
required between the wall and the
1200–1430°C (2200–2600°F) at the fir
zone [borax melts at 743°C (1370°F)]
the molds onto a toothed roll that re
which were sent to storage bins. The

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arrett, 1960; Garrett and Rosenbaum,

some special purposes, considerable
anhydrous form. They are produced

by partially dehydrating borax or boric acid in rotary calciners, and then melting it in fusion furnaces. At the former American Potash & Chemical Company's plant, to make $Na_2B_4O_7$ three rotary-drum calciners first removed about 70% of the hydrate water from either wet centrifuge cake or dried granular borax. If borax fines or pentahydrate were used, the crystals puffed to the extent that some blew out of the calciners, and the calcine was not dense enough to make an adequate seal in the fusion furnaces. The borax first passed over a weigh-feeder and went to any of the three calciner storage bins. From there a variable-speed chain feeder withdrew and delivered it to the rotary calciners' feed screw. The three calciners were 2.4 m (8 ft) in diameter and 21.3 m (70 ft) long, and two were heated cocurrent, and one countercurrent by the 704–816°C (1300–1500°F) fusion furnace flue gas. Calciner dust was recovered first by dry and then by wet scrubbers, and the dust was sent to the borax/pentahydrate refinery. The flue gas left the calciners nearly saturated with water and at about 52°C (125°F), providing good thermal efficiency. The hot, partially dehydrated borax from the calciners then went to feed storage bins for the three fusion furnaces. It was next conveyed, along with a small amount of sodium nitrate (a bleaching agent for organics from the lake brine and oil burners), to the feed hoppers rotating around each furnace. The hoppers distributed calcined borax through a 20-cm (8-in.) gap between the furnace walls, allowing it to pile up and seal this opening. Plows and cutters then forced the calcined borax into the furnace.

Inside the furnaces a direct, oil-fired flame impinged on the borax sliding down the furnace walls, and the hot flue gas passed out the bottom (Fig. 8.17) on its way to the calciners. The borax almost completely dehydrated before melting and flowing to the seal lip at the base of the furnaces. Two furnaces had the melt flow into chain conveyor molds traveling at 6.7 m/min (22 ft/min) for the length of the building. (A very small amount of water was left in the melt to promote crystallization by minimizing its tendency to supercool). As the molds traveled they slowly cooled and crystallized. The molds were then dumped, and the crystals ground and sized quite easily (about 5% of the anhydrous borax still converted to the amorphous phase as it quickly cooled when poured into the molds). The melt from the third furnace was cooled and solidified on a chilled roll, producing the much more abrasive amorphous or glass form that was difficult to grind.

The furnace walls were lined with either cast or brick refractory material, and water jacketed to further protect the steel structure. However, molten borax attacks all commercial refractories, so a constant layer of calcine was required between the wall and the melt. The furnace temperatures were 1200–1430°C (2200–2600°F) at the fire box, and 980°C (1800°F) in the fusion zone [borax melts at 743°C (1370°F)]. Anhydrous borax was emptied from the molds onto a toothed roll that reduced it to −3.8-cm (1.5-in.) particles, which were sent to storage bins. The final grinding and screening was done

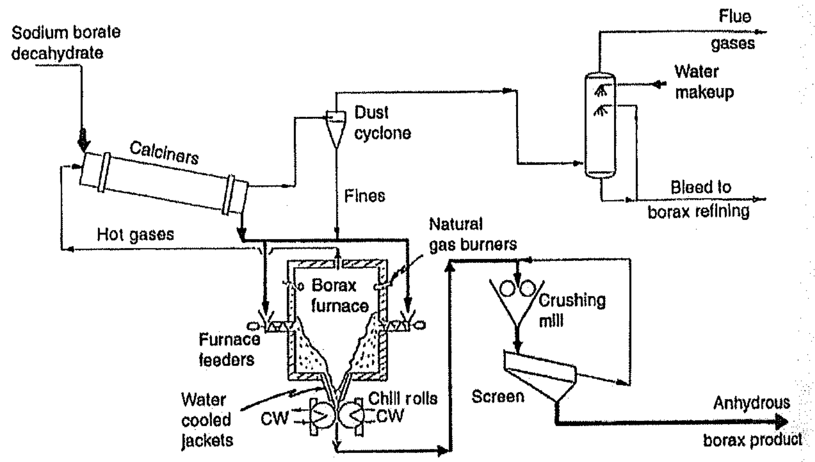

Figure 8.17 Searles Lake anhydrous borax plant flowsheet. (From Garrett, 1960; reproduced by permission of the Society for Mining, Metallurgy and Exploration, Inc.)

in a dry rod mill working with screens to produce three product sizes: +7, 7–16, and −16 mesh. Dust smaller than 80 mesh was recycled and remelted. The 1.6-mm- (1/16-in.-) thick sheet of anhydrous borax from the chilled roll was similarly crushed, screened, and stored (Bixler and Sawyer, 1957; Garrett, 1960). Anhydrous boric acid, or B_2O_3, could also be produced, but it was dehydrated and fused in a special calciner. The energy requirements to dehydrate boric acid to B_2O_3 have been estimated by Finlay (1952).

8.4.1.5 Late 1990s Operation

On April 1, 1996, the operator at that time, the North American Chemical Company, shut down the main plant cycle and produced boron products only from carbonation plant brine and solvent extraction. To partly make up for the lost borax capacity two changes were made: The brine flow rate was increased, and waste heat from a power plant's flue gas was used to preheat the "solution mining" injection brine. At the West End plant the 4000 gal/min carbonation/borax/glauber-salt plant's end liquor was heated to about 37°C (98°F), and the 3000 gal/min for the carbonation plant (it formerly was 2000 gal/min) and the 1000 gal/min (it was 667 gal/min) blending brine for the borax/glauber-salt plants at West End was withdrawn at about 27°C (80°F). This was a 6.7°C (12°F) increase, and raised the brine's $Na_2B_4O_7$ content from ~1.2% to 1.6–1.8%.

Brine from the carbonation plant
to West End, and blended with lake
was first cooled with cooling-tower
at 16.4–16.7°C (61.5–62°F), and finall
to crystallize borax. The crystallizers
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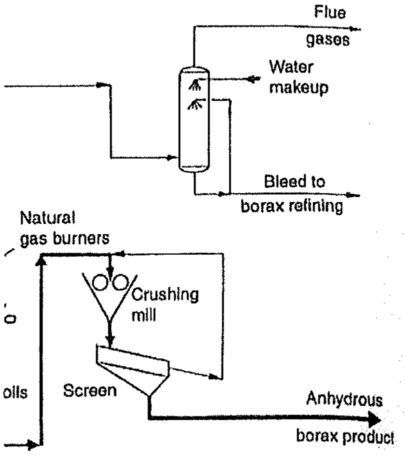
crystallized in the first effects, 10 or
The final slurry was sent to three w
solids advanced to the centrifuges,
crystallizers to increase the slurry d
The underflow solids were then redis
The borax product was centrifuged
pusher-type centrifuges. The clarifie
the glauber-salt crystallizers for furth
compressors were used for the com

Part of the crude borax cake from
hrs during the evening on a private r
trucks to the Trona plant for conv
borax. At West End the borax was
the cake at 85–88°C (185–190°F) to
then polish-filtered and recrystallize
crystallizers at 60°C (140°F), with coo
barometric condensers. The pentahy
and washed in two-stage pusher cen
sent to storage, and loaded for ship
water to freshwater by reverse osm
with a waste-heat boiler (and the inj
units, and Evapco cooling towers co
ing coils.

At the Trona plant, borax cake fr
borax end liquor (ML3), and sent t
spare) polishing filters (using a cellulo
next sent to vacuum crystallizers wi
Disodium hydrogen phosphate was
the chunkiness of the crystals; a sligh
caustic soda; and 30–50 ppm of a
crystallizers were cooled as far as pos
ter condensers, which in the summer
A slurry was withdrawn from the cr
four-stage pusher centrifuge. The ca
wash water containing a small amo
reduce the Na_2SO_4 to less than 10 pp
rotary dryer with steam-heated hot



lant flowsheet. (From Garrett, 1960; reproduced
urgy and Exploration, Inc.)

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Brine from the carbonation plant was sent from Trona (the Argus plant) to West End, and blended with lake brine to a pH of 8.3–8.5. This mixture was first cooled with cooling-tower water, then with glauber salt end liquor at 16.4–16.7°C (61.5–62°F), and finally with ammonia coolers to 18.3°C (65°F) to crystallize borax. The crystallizers were arranged in two parallel lines, one with three units in series, and the other with two. About 85% of the borax crystallized in the first effects, 10 or 15% in the second, and 5% in the third. The final slurry was sent to three wet vibrating screens, with the oversized solids advanced to the centrifuges, the mid-sized fraction returned to the crystallizers to increase the slurry density, and the fines sent to a thickener. The underflow solids were then redissolved in the feed solution and recycled. The borax product was centrifuged and washed in three two-stage, 700-mm pusher-type centrifuges. The clarified brine from the thickener was sent to the glauber-salt crystallizers for further cooling. Six 1000- to 1500-ton ammonia compressors were used for the combined cooling load.

Part of the crude borax cake from the West End plant was transported 12 hrs during the evening on a private road in 41-metric-ton (45-ton) off-highway trucks to the Trona plant for conversion to purified borax and anhydrous borax. At West End the borax was converted to pentahydrate by dissolving the cake at 85–88°C (185–190°F) to form a 23–24% borax solution. It was then polish-filtered and recrystallized in bottom-agitated, draft-tube baffled crystallizers at 60°C (140°F), with cooling supplied by glauber-salt end liquor in barometric condensers. The pentahydrate crystals were withdrawn, dewatered, and washed in two-stage pusher centrifuges, dried in gas-fired rotary dryers, sent to storage, and loaded for shipment. The plant also converted brackish water to freshwater by reverse osmosis, and had a 19-megawatt gas turbine with a waste-heat boiler (and the injection brine heaters), large refrigeration units, and Evapco cooling towers containing 1.2-m (4-ft) ammonia condensing coils.

At the Trona plant, borax cake from West End was dissolved in water and borax end liquor (ML3), and sent through two (another was available as a spare) polishing filters (using a cellulosic-type filter aid). The clarified brine was next sent to vacuum crystallizers with 45-rpm internal "pachuca" impellers. Disodium hydrogen phosphate was added (instead of oleic acid) to increase the chunkiness of the crystals; a slight "excess alkalinity" was maintained with caustic soda; and 30–50 ppm of an antifoamant was often required. The crystallizers were cooled as far as possible with cooling-tower water in barometer condensers, which in the summer were occasionally 40–43°C (104–109°F). A slurry was withdrawn from the crystallizers, thickened, and then sent to a four-stage pusher centrifuge. The cake was washed with about 5 gal/min of wash water containing a small amount of boric acid to prevent caking and reduce the Na_2SO_4 to less than 10 ppm. The product was dried in a counterflow rotary dryer with steam-heated hot air and some direct gas firing, with the flue gas leaving at 43–49°C (110–120°F). The product was screened at +30 mesh, −30 mesh (98% +40 mesh), and −40 mesh. Cold end liquor from the crystallizer was used in the first effect's barometer condenser, and recycled.

In the anhydrous borax plant, only one of the three melting furnaces was usually operated, at a capacity of about 140 tons/day, and with the burner design changed to improve its fuel efficiency. Water jacketing of the furnace shell was also eliminated except at the lip where melted borax flowed onto a chilled roll. There was a 2–4 tons/day pilot plant to produce >99% B_2O_3, and a plant to make 1–1.5 tons/hr of a noncaking, very finely divided (20 lb/ft^3) boric acid powder for anticeptical use (De Nuz, 1996).

8.4.2 Owens Lake

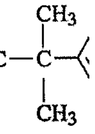
During the early 1900s several companies operated small soda ash plants on Owens Lake, and a few such as the Pacific Alkali Company also recovered borax. They operated from 1926 to 1967 at Bartlett, California, employing the Kuhnert process. Brine from the lake was pumped 4 km (2.5 mi) to solar ponds where the borax content rose from about 2.6 to 4%. The brine was next carbonated with 14–15% CO_2 flue gas (for the makeup CO_2) in 16 carbonation towers, 24 m (80 ft) tall and 1.5 m (5 ft) in diameter. Sodium sesquicarbonate was formed; and after it was removed from the carbonated brine the end liquor was blended with solar pond brine, and cooled to obtain 1800 metric tons/year of borax. Columbia Southern (Pittsburgh Plate Glass) purchased the plant in 1944, expanded it 300% in 1958, and closed it in 1967 (Garrett, 1992).

8.4.3 Miscellaneous Processes

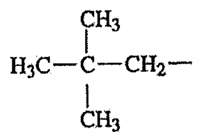
8.4.3.1 Solvent Extraction

Boron has a strong tendency to form ring structures with oxygen atoms, as indicated by the many borate compounds in nature. Similary, boron—oxygen—carbon bonding can be very strong, such as a hydrogen ion being liberated from an OH group (used for boron analyses) in mannitol in order to form B—O—C rings. This property also allows the selective extraction of boron from brines, or the removal of a boron contaminant. The first patent on this concept was by Garrett (1961), then Garrett, Weck, Marsh, and Foster (1963), and later many others (e.g., Weck, 1969). It was noted that some alcohols, polyols, acids, and ketones have borax extraction coefficients of up to 10 (at equilibrium the boron concentration in the solvent is 10 times that in the extracted brine). Specific organic polyols were then synthesized to achieve maximum boron extraction from basic solutions (it is much easier to extract from acidic solutions). They had high distribution coefficients (10–150), low solubility in water, good stability, high selectivity, and were easy to regenerate, stable, safe and inexpensive. The
boric acid recovery plant was built in
end liquors or lake brines.

The specific solvent used in the p
saligenins were very effective, such a
(with a coefficient of 122):



The 1963 patent claimed to have favore
6-methylol-phenol (with a coefficient



As an example of the effectiveness of s
ture, 800 ml/min of solvent–carrier (on
contacted 500 ml/min of a 1.05% Na_2B
loaded solvent was then stripped in f
min of 1N sulfuric acid. The extract
5.2% K_2SO_4, and no CO_3, Cl, or S
90–95°C to crystallize the potassium–
to crystallize boric acid. About 27 ppm
brine, and 44 ppm in the stripping s
storage life in the boron complex fo
capacity in 1 week at 60°C (below 25°

A general description of the proces
given by Havighorst (1963) and An
(3000–4000 gal/min) of end liquor was
solvent in a single extraction stage,
returned to the lake. The loaded solve
rent stripping with dilute sulfuric acid.
to the brine extraction stage. The b
through a semicontinuous carbon-ad
amount of solvent and organics in th

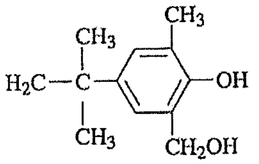
. The product was screened at +30
-40 mesh. Cold end liquor from the
arometer condenser, and recycled.
e of the three melting furnaces was
140 tons/day, and with the burner
ncy. Water jacketing of the furnace
where melted borax flowed onto a
t plant to produce >99% B_2O_3, and
aking, very finely divided (20 lb/ft^3)
e Nuz, 1996).

nies operated small soda ash plants
cific Alkali Company also recovered
7 at Bartlett, California, employing
was pumped 4 km (2.5 mi) to solar
m about 2.6 to 4%. The brine was
gas (for the makeup CO_2) in 16
d 1.5 m (5 ft) in diameter. Sodium
was removed from the carbonated
lar pond brine, and cooled to obtain
a Southern (Pittsburgh Plate Glass)
300% in 1958, and closed it in 1967

ring structures with oxygen atoms,
ds in nature. Similary, boron—oxy-
, such as a hydrogen ion being liber-
n analyses) in mannitol in order to
o allows the selective extraction of
oron contaminant. The first patent
n Garrett, Weck, Marsh, and Foster
ck, 1969). It was noted that some
borax extraction coefficients of up
ation in the solvent is 10 times that
polyols were then synthesized to
basic solutions (it is much easier to
gh distribution coefficients (10–150),
selectivity, and were easy to regen-

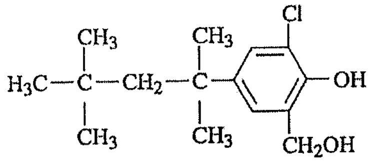
erate, stable, safe and inexpensive. The results were so successful that a large boric acid recovery plant was built in 1963 at Searles Lake to process plant end liquors or lake brines.

The specific solvent used in the plant has not been disclosed, but the saligenins were very effective, such as 4-tertiary butyl-6-methylol saligenin (with a coefficient of 122):



(1)

The 1963 patent claimed to have favored 2-chloro-4 (1,1,3,3)tetramethylbutyl-6-methylol-phenol (with a coefficient of 100):



(2)

As an example of the effectiveness of solvent (2), in one test at room temperature, 800 ml/min of solvent–carrier (one part solvent and three parts kerosene) contacted 500 ml/min of a 1.05% $Na_2B_4O_7$, pH 10 brine in a single stage. The loaded solvent was then stripped in four countercurrent stages with 800 ml/min of 1N sulfuric acid. The extract contained 6.1% H_3BO_3, 2.8% Na_2SO_4, 5.2% K_2SO_4, and no CO_3, Cl, or $S^=$. The extract was first evaporated at 90–95°C to crystallize the potassium–sodium salts, and then cooled to 35°C to crystallize boric acid. About 27 ppm of the organics remained in the stripped brine, and 44 ppm in the stripping solution. The (2) solvent had a better storage life in the boron complex form, loosing only 2% of its extraction capacity in 1 week at 60°C (below 25°C was recommended).

A general description of the process as it was first operated (Fig. 8.18) was given by Havighorst (1963) and Anon. (1963). About 11,000–15,000 l/min (3000–4000 gal/min) of end liquor was first contacted with the polyol–kerosene solvent in a single extraction stage, and the stripped brine (raffinate) was returned to the lake. The loaded solvent was sent to four stages of countercurrent stripping with dilute sulfuric acid, and the stripped solvent was returned to the brine extraction stage. The boric acid strip liquor was next passed through a semicontinuous carbon-adsorption column to remove the small amount of solvent and organics in the brine. The brine was then sent to a

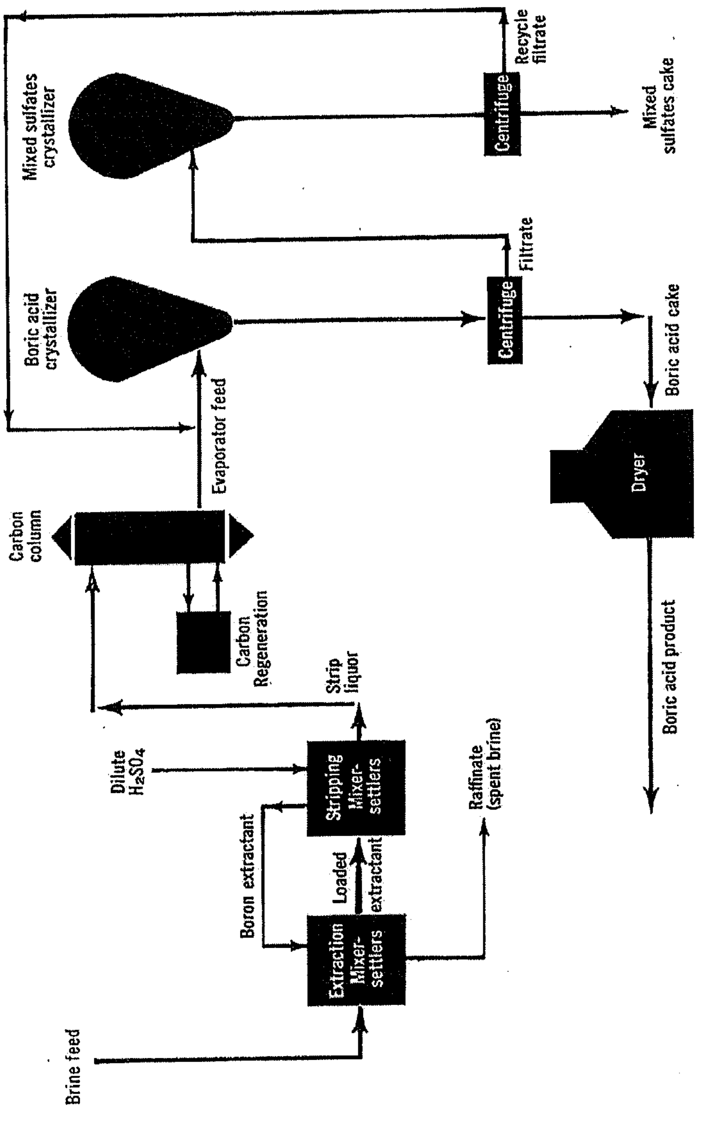


Figure 8.18 The Searles Lake borax solvent extraction process. (From Anon, 1963; reprinted with permission of the American Chemical Society, copyright 1963.)

Figure 8.19 Evaporator–crystallizers fc

65°C growth-type glaserite–salt cake ev
it was joined by boric acid crystallizer o
was maintained just below boric acid's
withdrawn. The salts were centrifugec
glaserite reactor to form potassium sul

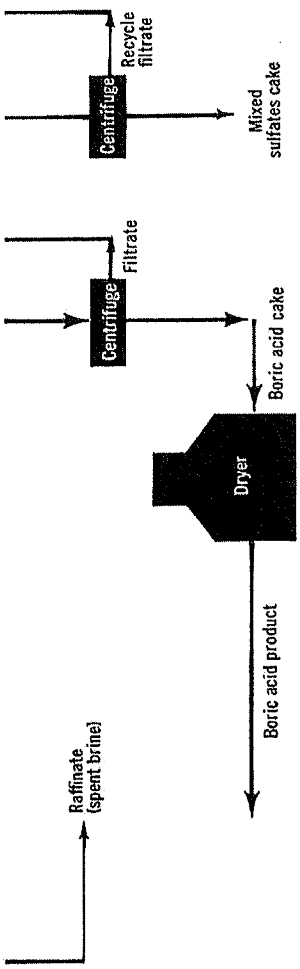


Figure 8.18 The Searles Lake borax solvent extraction process. (From Anon., 1963; reprinted with permission of the American Chemical Society; copyright 1963.)

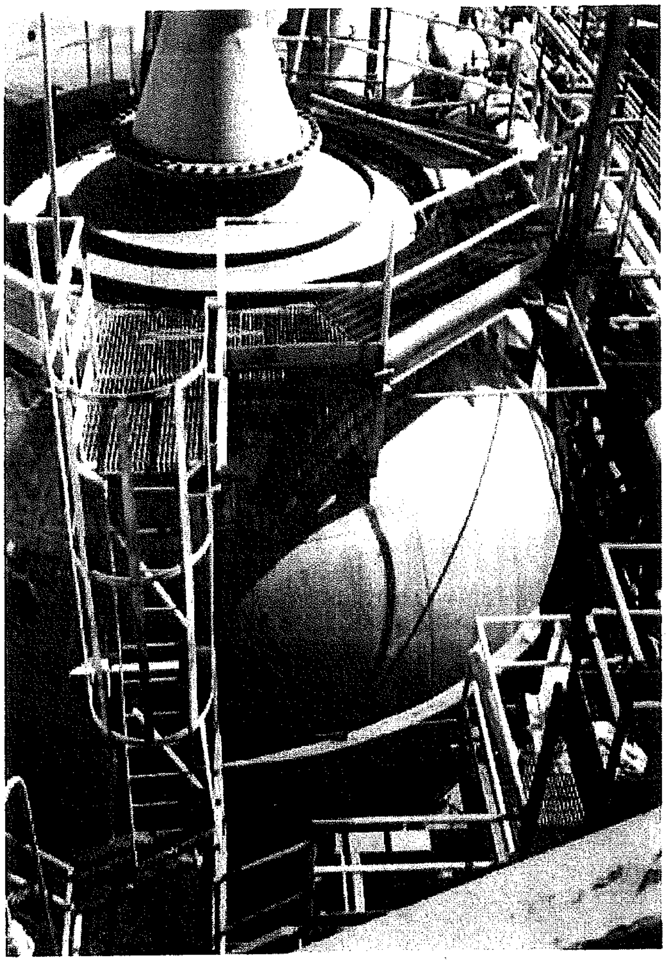


Figure 8.19 Evaporator–crystallizers for the boric acid solvent extraction plant.

65°C growth-type glaserite–salt cake evaporator–crystallizer (Fig. 8.19), where it was joined by boric acid crystallizer overflow and centrate. The concentration was maintained just below boric acid's solubility, and a slurry was constantly withdrawn. The salts were centrifuged, washed, and sent to the main plant's glaserite reactor to form potassium sulfate, a valuable by-product. The mixed

salt crystallizer's overflow brine and centrate was then sent to the boric acid crystallizer.

This unit was operated at the lowest temperature obtainable from cooling-tower water in a barometric condenser, nominally 35°C, and its brine was maintained at a concentration just below that at which the other salts would crystallize. A slurry of boric acid was constantly withdrawn, thickened, centrifuged, and washed. The product was then sent to a multiple hearth-type dryer for gentle drying (to prevent metaboric acid formation). A +99.9% product was obtained with only 0.05% SO_3 and 0.029% Na. The boric acid crystallizer's overflow stream and centrate were returned to the mixed sulfate evaporator to repeat the cycle. A bleed stream was occasionally sent to the extraction plant's acid stripper to control any H_2SO_4 buildup. The operator's skill, computer programs, and extensive instrumentation allowed the plant to have a rapid startup and essentially trouble-free operation. It very likely produces the most inexpensive boric acid in the world.

The solvent extraction plant by 1996 had changed slightly, and was operating well over its design capacity at 150 metric tons/day of H_3BO_3. The solvent loading was still done as a single stage, but originally the solvent–brine mixing was accomplished in four agitated tanks in series. It was found that the fourth vessel was unnecessary, and the third added very little borax and began to form an emulsion. Consequently, only two were used. The flow rates in the plant were about 1800–1950 gal/min of fresh brine at 34°C (94°F), and 3200 gal/min of a solvent–kerosine mixture. The brine from the loading tanks (at a pH of 8.9) was sent to three lines of settlers where the two phases were separated, and finally to an API settler. The stripped brine contained up to 100 ppm of organics, and the government had set limits of 17 ppm for it to be returned to the lake. Consequently, it was sent to three parallel lines (650 gal/min each) of Wemco Depurators (flotation-like cells) where the organics were removed as a froth or vapor. The former was collected and reused, whereas the vapor and fumes from every part of the plant were sent to the power plant's burners. The organics in the brine were reduced to less than 10 ppm.

The loaded solvent was next given five (the last one was a water wash) countercurrent mixing and settling stages (Fig. 8.20) at 38°C (100°F) with dilute sulfuric acid. The mixer–settler tanks were made of concrete with a fiberglass lining, and each of the other tanks were lined with fiberglass. Some emulsion constantly formed (partly from the solvent's degradation), so it was separated, treated to break the emulsion, and returned to the system. Since the solvent was acidic by nature, and always contained some entrained acid, it tended to precipitate a small amount of sodium bicarbonate from the brine. To minimize this, a few percent of water was added, but some still formed, along with the emulsion, so the plant had to be cleaned about once per year. This was difficult because of the tank covers, vents, and emergency quench system.

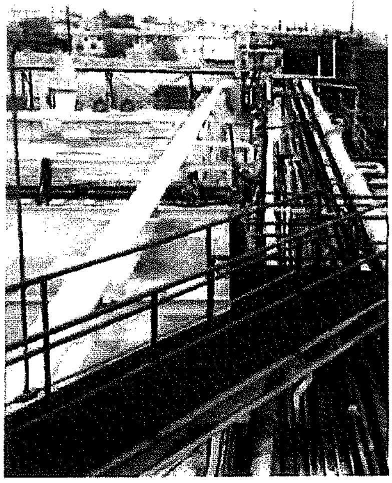


Figure 8.20 Solvent–acid mixers (to the righ
of the Searles Lake boric acid solvent extraction

The organic solvent was always main
the brine as droplets within it. If the p
be disrupted, and there could be a ma
plant consumed about 20,000 gal/24 hr of
makeup solvent once per week. This r
and 6000 gal of kerosene. The solvent
extraction plant (Fig. 8.21) with nonyl
reactants. The nonyl phenol provided g
viously used P10 octyl phenol. The extr
and partially computer controlled, req
handled the sulfuric acid receiving and
responsible for the P20 synthesis and its

The processing facilities for the boric
the Trona plant, far from the brine extra
containing 10–15 ppm of organics, so i
7.6-m (25-ft) adsorption column, 1.6 m (
to 16-mesh activated carbon. Every few
out through six withdrawal pipes at the
hot water (second effect condensate), a
next sent to a 1.2-m- (49-in.-) diameter,

centrate was then sent to the boric

temperature obtainable from cooling-
r, nominally 35°C, and its brine was
w that at which the other salts would
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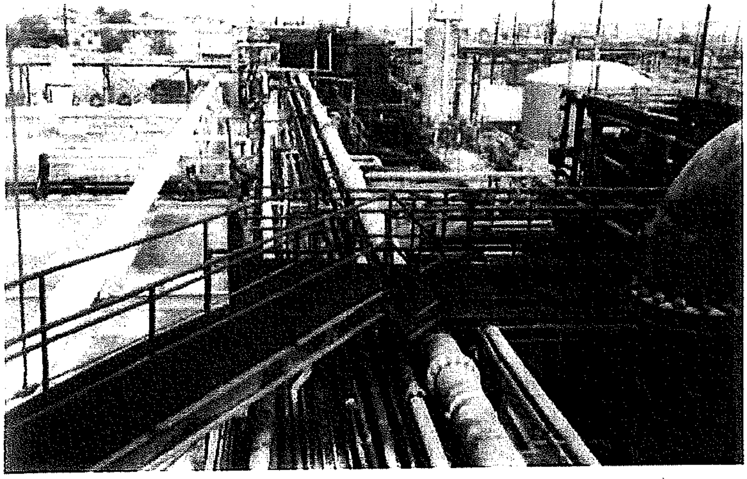


Figure 8.20 Solvent–acid mixers (to the right) and the totally covered settlers (to the left) of the Searles Lake boric acid solvent extraction plant.

The organic solvent was always maintained as the continuous phase, with the brine as droplets within it. If the phases were reversed, the flow would be disrupted, and there could be a major foam or emulsion problem. The plant consumed about 20,000 gal/24 hr of concentrated sulfuric acid, and added makeup solvent once per week. This required 4000 gal of the P_2O solvent and 6000 gal of kerosene. The solvent was manufactured adjacent to the extraction plant (Fig. 8.21) with nonyl phenol and chlorine as two of the reactants. The nonyl phenol provided greater solvent stability than the previously used P10 octyl phenol. The extraction plant was highly instrumented and partially computer controlled, requiring only one operator, who also handled the sulfuric acid receiving and unloading. A second operator was responsible for the P20 synthesis and its raw material handling (Mata, 1996).

The processing facilities for the boric acid strip solution are located across the Trona plant, far from the brine extraction unit. The brine enters the plant containing 10–15 ppm of organics, so it is first sent (downflow) through a 7.6-m (25-ft) adsorption column, 1.6 m (62 in.) in diameter, filled with 3-mm to 16-mesh activated carbon. Every few days a portion of the bed is flushed-out through six withdrawal pipes at the column's base, drained, washed with hot water (second effect condensate), and blown partially dry with air. It is next sent to a 1.2-m- (49-in.-) diameter, six-tray Hershoff furnace where the

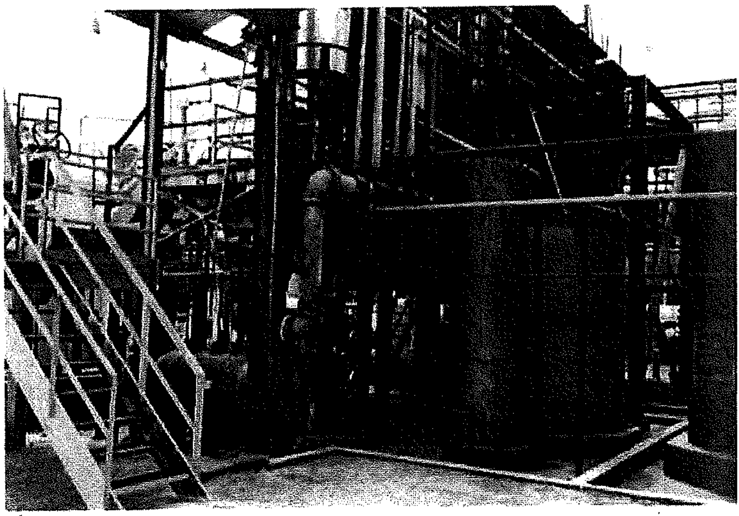


Figure 8.21 The solvent manufacturing facilities for the Searles Lake boric acid solvent extraction plant.

organics are burned at 650–760°C (1200–1400°F). This regenerates the carbon, and it, along with 180 kg (400 lb) of makeup carbon, is sent to a holding tank to be slurried back into the column.

The brine is next sent to two hemispherically-domed evaporator–crystallizers (see Fig. 8.19) where it is joined by recycle liquor and circulated through titanium heat-exchanger tubes at 19,000 gal/min. Water is evaporated, and salt cake and glaserite are crystallized, which are removed, settled, and dewatered in a 1 × 1.5-m- (40 × 60-in.-) solid bowl centrifuge. In 1996 this cake was being repulped and returned to the lake. The overflow brine and centrate are then cooled in the second stage growth-type crystallizer circulating at 22,000 gal/min. Boric acid is crystallized and a slurry withdrawn, settled, and dewatered in a 900-mm, four-stage pusher centrifuge (Fig. 8.22). The product is washed in two of the stages, and the centrate and overflow brine are returned to the circuit. The cake is dried in a gas-fired rotary dryer and pneumatically transported to a storage silo. Caking is prevented by removing the transport air at the top and blowing cold air into the silo at its base. Normally, the product is 88% +60 mesh, but upsets can occur, perhaps caused by changes in the stripping sulfuric acid (i.e., the acid's copper content can randomly change from 30–400 ppm). The evaporator–crystallizer are made of 316 extra-low carbon (elc) stainless steel, and rubber-lined and acid-brick-lined for the entire first stage, and f
stage. Without the acid brick there
organics in the brine. Process lines
must be replaced periodically (De-N

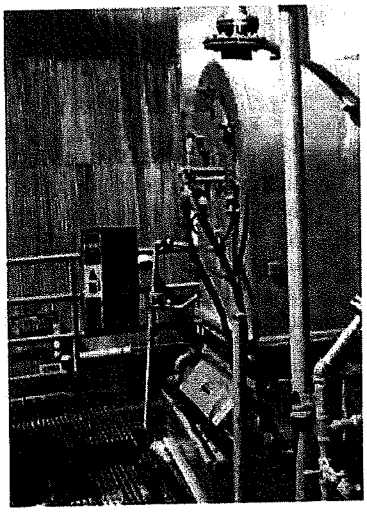
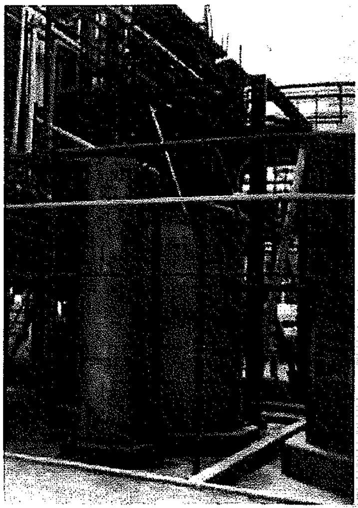


Figure 8.22 Boric acid centrifu

Several other commercial boron li
but they are for removing small amo
of magnesium chloride solutions (No
or high-purity magnesium oxide. A si
of lithium chloride solutions for high
both cases boron can cause serious p
is important. Off-the-shelf diols or al
cients, are employed because of the ac
demands. Usually, the boron is mere

8.4.3.2 *Ion Exchange*

The unique chemical properties th
by solvent extraction also apply to io
literature on this subject (see the R
of boron-specific resins have been av
XE-243R (Anon., 1965a; Kunin and
which contains pentahydroxyhexyl a



ities for the Searles Lake boric acid solvent

-1400°F). This regenerates the carbon,
eup carbon, is sent to a holding tank

emispherically-domed evaporator–
ined by recycle liquor and circulated
t 19,000 gal/min. Water is evaporated,
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-) solid bowl centrifuge. In 1996 this
to the lake. The overflow brine and
ge growth-type crystallizer circulating
zed and a slurry withdrawn, settled,
e pusher centrifuge (Fig. 8.22). The
and the centrate and overflow brine
dried in a gas-fired rotary dryer and
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but upsets can occur, perhaps caused
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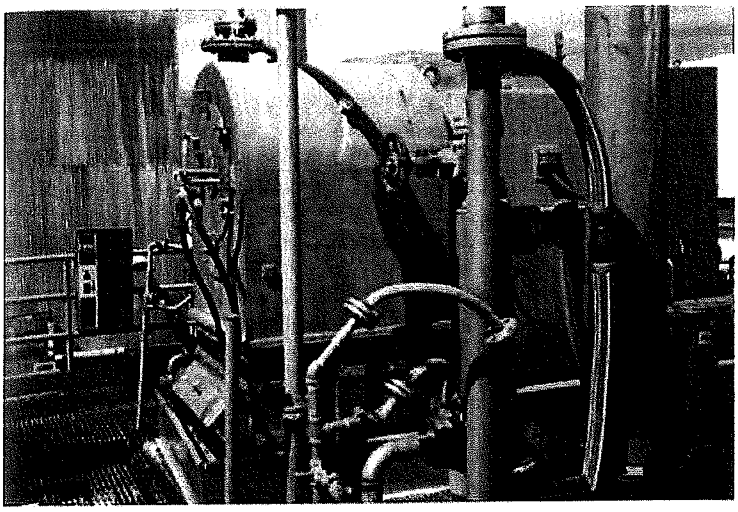

Figure 8.22 Boric acid centrifuge for the solvent extraction plant.

lined for the entire first stage, and for the lower 3 m (10 ft) of the second stage. Without the acid brick there was gradual rubber damage from the organics in the brine. Process lines are made of 316 elc stainless steel and must be replaced periodically (De-Nuz, 1996).

Several other commercial boron liquid extraction systems have been built, but they are for removing small amounts of impurities, as in the purification of magnesium chloride solutions (Norsk Hydro, 1974) for magnesium metal, or high-purity magnesium oxide. A similar process is used for the purification of lithium chloride solutions for high-purity lithium compounds or metal. In both cases boron can cause serious problems, so its nearly complete removal is important. Off-the-shelf diols or alcohols, with their 2–5 distribution coefficients, are employed because of the acidic solutions and much simpler removal demands. Usually, the boron is merely precipitated from the extractant.

8.4.3.2 Ion Exchange

The unique chemical properties that allow boron to be selectively removed by solvent extraction also apply to ion exchange resins. There is considerable literature on this subject (see the References), and experimental quantities of boron-specific resins have been available. The first of these was Amberlite XE-243R (Anon., 1965a; Kunin and Preuss, 1964; Lyman and Preuss, 1957), which contains pentahydroxyhexyl and tetrahydroxy pentyls, including sorbityl and mannityl (the preferred polyol was hydrogenated glucose in the presence of methylamine, or N-methyl–glucamine). The polyol was attached to a monovinyl resin base containing 0.5–50% $CH_2{=}C{=}$ groups. The resin weighed 40–45 lb/ft^3; had an exchange capacity of 2.4–2.5 meq/ml, 5.7 mg B/ml, or 0.36 lbB/ft^3 of resin; and contained 56–60% water. The capacity was flow-rate dependent, and the resin had to be regenerated with 10% H_2SO_4 (3 lb H_2SO_4/ft^3 of resin), followed by removal of the sulfate with 4% NaOH or NH_4OH (4 lb NaOH or 3 lb NH_4OH/ft^3). Suggested uses were removing boron from irrigation water or magnesium chloride brine. However, with most solutions there was no period of complete boron removal, the breakthrough curve was gradual, and the capacity dropped with each cycle. The elute concentration averaged about 0.2% H_3BO_3 in a large excess of H_2SO_4 (Chemtob, 1971). Very much improved boron-specific resins have been prepared by Garrett and Weck (1958). In one test on a Searles Lake end liquor (0.5% $Na_2B_4O_7$), the borax was completely removed, the resin capacity was 8 mgB/ml, and elution with pH 3 acid gave a 6% H_3BO_3 solution and completely regenerated the resin.

8.4.3.3. Salting Out

With a number of the boron-containing lakes (i.e., many of the playas in South America and China), a salting-out process for recovering boric acid would appear to be practical, especially if it were a by-product. Such a process has been developed by Garrett and Laborde (1983), starting with a solar-evaporated brine that had already produced the maximum K_2SO_4 KCl and/or lithium as the primary products of the operation. When sufficiently concentrated, boric acid can be crystallized (it is quite insolulble in a saturated NaCl brine) by adding sulfuric acid, either in a cyclic in-plant procedure, or by harvesting a boric acid mixture from solar ponds and separating the mixture by flotation.

Salting-out has been the method of boric acid production from the Chilean nitrate plants, and is usually combined with iodine recovery, where pH adjustment is also required. This production has been practiced only periodically and in rather small amounts. However, the large potash plant now operating on the Salar de Atacama has announced the production of 18,000 metric tons/year of boric acid beginning in 1998. In their pilot plant tests (Pavlovic, Parada, and Vergara, 1983), boric acid could be precipitated when its concentration was greater than 21 g/liter H_3BO_3. The optimum pH after acid addition was 2.0 for 25–50 g/liter of H_3BO_3 brine, requiring about 0.21 g of H_2SO_4/g H_3BO_3. A brief water wash gave high-purity boric acid. An identical process has been proposed by Gao, Yang, and Huang (1993) for a Chinese playa (Lake Da Chaidan). They suggested adding the acid to the brine when the MgB_3O_7 content was above 35 g/liter (48 g/liter of H_3BO_3). The acid requirement was 0.30 g/g H_3BO_3, and the optimum terminal pH was 3.0.

8.5 HEALTH AND SAFETY

8.5.1 Worker Studies: Toxicology

A number of reports have described
of borate processing plant and mine w
separate U.S. OSHA and U.S. Bora
employees who were exposed to bo
slightly healthier lung functions than t
there were no adverse lung or respirat
to borax, kernite, boric acid, or their
also found no adverse health effec
workers, as was the case with the
(Kasparov and Yakubovskii, 1970).
exposure variability of dust contact by
by Woskie, Shen, Eisen, Finkel, Smi

More specific toxicologic informati
who noted that borax and boric acid
(Table 8.3), with the official LD_{50} (the
die), as g/kg of body weight, being
Chronic toxicity studies over a two-y
g/kg LD_{50}, respectively, values only
kg). Substances with LD_{50}s greater t
The minimum lethal dose of borate
but an intake of 4 g/day was reporte
of 20 g of boric acid for neutron cap
Fish have survived 30 min in a satura
longer in strong borax solutions.

Levinskas (1964) presented some
a study in which 144 humans ingest
acid, with a 50% mortality rate. How
of boric acid were ingested by hum
effects, indicating that toxicity varies
symptoms for adults can be nausea, m
weakness, and excitement or depressi
tion, convulsions, coma, and deliriu
(like "boiled lobster skin") may cove
membranes, for a day or two.

Skin irritation with borate dusts
with the borate cleaners and ointme
Occasionally, there is a mild allergi
plants or mines its alkalinity at hig
respiratory tract. In a study of 629 w

as hydrogenated glucose in the pres-
mine). The polyol was attached to a
50% $CH_2=C=$ groups. The resin
capacity of 2.4–2.5 meq/ml, 5.7 mg
tained 56–60% water. The capacity
d to be regenerated with 10% H_2SO_4
moval of the sulfate with 4% NaOH
/ft^3). Suggested uses were removing
n chloride brine. However, with most
te boron removal, the breakthrough
ed with each cycle. The elute concen-
a large excess of H_2SO_4 (Chemtob,
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n a Searles Lake end liquor (0.5%
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6% H_3BO_3 solution and completely

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it were a by-product. Such a process
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operation. When sufficiently concen-
quite insolulble in a saturated NaCl
a cyclic in-plant procedure, or by
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as been practiced only periodically
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the production of 18,000 metric tons/
eir pilot plant tests (Pavlovic, Parada,
precipitated when its concentration
optimum pH after acid addition was
ring about 0.21 g of H_2SO_4/g H_3BO_3.
acid. An identical process has been
993) for a Chinese playa (Lake Da
cid to the brine when the MgB_3O_7
H_3BO_3). The acid requirement was
nal pH was 3.0.

8.5 HEALTH AND SAFETY

8.5.1 Worker Studies: Toxicology

A number of reports have described the effects of borate dust on the health of borate processing plant and mine workers. Kistler and Helvaci (1994) noted separate U.S. OSHA and U.S. Borax studies at the Boron deposit on 800 employees who were exposed to borate dust. It was found that they had slightly healthier lung functions than the U.S. national average, indicating that there were no adverse lung or respiratory effects even from long-term exposure to borax, kernite, boric acid, or their dehydrated products. Kasparov (1971) also found no adverse health effects from boric acid dust on production workers, as was the case with the fibrogenic activity of borosilicate dusts (Kasparov and Yakubovskii, 1970). Studies on the sampling methods and exposure variability of dust contact by sodium borate workers have been made by Woskie, Shen, Eisen, Finkel, Smith, Smith, and Wegman.

More specific toxicologic information has been provided by Sprague (1972), who noted that borax and boric acid have a relatively low toxicity for animals (Table 8.3), with the official LD_{50} (the dosage at which half of the test animals die), as g/kg of body weight, being 6.05 for borax and 5.14 for boric acid. Chronic toxicity studies over a two-year period gave values of 5.00 and 3.00 g/kg LD_{50}, respectively, values only 2–3 times that of aspirin (salt is 3.75 g/kg). Substances with LD_{50}s greater than 2.0 are not classified as dangerous. The minimum lethal dose of borates for humans has not been established, but an intake of 4 g/day was reported without incident, and medical dosages of 20 g of boric acid for neutron capture therapy have caused no problems. Fish have survived 30 min in a saturated boric acid solution, and can survive longer in strong borax solutions.

Levinskas (1964) presented some slightly less optimistic LD_{50} data, noting a study in which 144 humans ingested 15–30 g of borax, or 2–5 g of boric acid, with a 50% mortality rate. However, in another study 15- to 30-g doses of boric acid were ingested by hundreds of patients with no serious toxic effects, indicating that toxicity varies with age and the individual. Ingestion symptoms for adults can be nausea, mild shock, vomiting, diarrhea, headaches, weakness, and excitement or depression. Children may have meningeal irritation, convulsions, coma, and delirium. An intense scarlatina form of rash (like "boiled lobster skin") may cover the entire body, including the mucous membranes, for a day or two.

Skin irritation with borate dusts or solutions is usually not a problem, with the borate cleaners and ointments being less irritating than pure soap. Occasionally, there is a mild allergic response, and with workers in borate plants or mines its alkalinity at high dust levels can cause irritation of the respiratory tract. In a study of 629 workers at a borax plant and mine, com-

Table 8.3

Toxicity of Borax, Boric Acid and Other Borates[a]

A. LD_{50} of borax and boric acids in animals, oral

	Borax			Boric acid		
Sex & strain	LD_{50} (g/kg)	Equiv. boron (gB/kg)	Experimental limits (g/kg)	LD_{50} (g/kg)	Equiv. boron (gB/kg)	Experimental limits (g/kg)
Long Evans male rats	6.1	0.69	3.5–10.4	3.2	0.55	—
Sprague Dawley female rats	5.0	0.57	4.3–5.8	4.1	0.71	3.6–4.6
Sprague Dawley male rats	4.5	0.51	4.1–5.0	3.5	0.60	3.0–4.0
Mice, guinea pigs[b]	>3.92 ± 1.42[c]	—	—	>3.27 ± 2.07[c,d]	—	—
B. As A, intravenous						
Mice[b]	1.32	—	—	—	—	—
Mice, rat, rabbit, dog[b]	—	—	—	1.6 ± 0.79	—	—
Rabbit, cat[b]	0.41 ± 0.34 (sodium perborate monohydrate)					
Rabbit[b]	>0.3[c] (sodium metaborate)					
C. As A, subcutaneous						
Mice, rat, dog, guinea pigs[b]	—	—	—	1.48 ± 0.53	—	—
D. As A, intraperitoneal						
Mice, rats[b]	—	—	—	>0.8[c]	—	—

E. Minimum lethal dose of borates for minnows

	LD_{50}, (mg/l or 1000 ppm)	
Substance	Distilled water	Hard water
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	19,000–19,500	19,000–19,500
Anhydrous borax ($Na_2B_4O_7$)	3,000–3,300	7,000–7,500
Boric acid (H_3BO_3)	1,600–1,750	3,700–4,000
Sodium chloride	10,000	11,500–12,000

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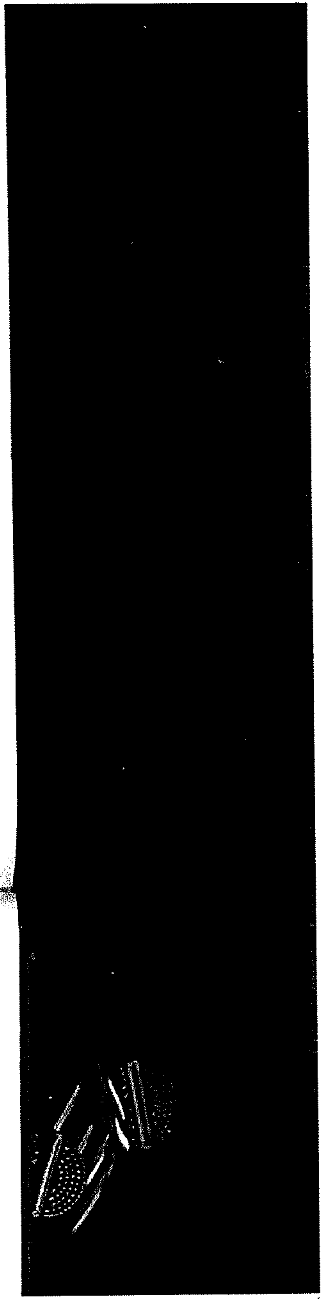
[a] Sprague, 1972.

[b] Levinskas, 1964.



A. LD_{50} of borax and boric acids in animals, oral

Sex & strain	Borax LD_{50} (g/kg)	Borax Equiv. boron (gB/kg)	Borax Experimental limits (g/kg)	Boric acid LD_{50} (g/kg)	Boric acid Equiv. boron (gB/kg)	Boric acid Experimental limits (g/kg)
Long Evans male rats	6.1	0.69	3.5–10.4	3.2	0.55	—
Sprague Dawley female rats	5.0	0.57	4.3–5.8	4.1	0.71	3.6–4.6
Sprague Dawley male rats	4.5	0.51	4.1–5.0	3.5	0.60	3.0–4.0
Mice, guinea pigs[b]	>3.92 ± 1.42[c]	—	—	>3.27 ± 2.07[c,d]	—	—
B. As A, intravenous						
Mice[b]	1.32	—	—	—	—	—
Mice, rat, rabbit, dog[b]	—	—	—	1.6 ± 0.79	—	—
Rabbit, cat[b]	0.41 ± 0.34 (sodium perborate monohydrate)					
Rabbit[b]	>0.3[c] (sodium metaborate)					
C. As A, subcutaneous						
Mice, rat, dog, guinea pigs[b]	—	—	—	1.48 ± 0.53	—	—
D. As A, intraperitoneal						
Mice, rats[b]	—	—	—	>0.8[c]	—	—

E. Minimum lethal dose of borates for minnows

Substance	LD_{50}, (mg/l or 1000 ppm) Distilled water	LD_{50}, (mg/l or 1000 ppm) Hard water
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	19,000–19,500	19,000–19,500
Anhydrous borax ($Na_2B_4O_7$)	3,000–3,300	7,000–7,500
Boric acid (H_3BO_3)	1,600–1,750	3,700–4,000
Sodium chloride	10,000	11,500–12,000

[a] Sprague, 1972.
[b] Levinskas, 1964.
[c] No toxic effect noted at this dosage.
[d] Not guinea pig, but including rat, rabbit, and dog.

plaints of symptoms of mouth, nose or throat dryness, dry cough, nose bleeds, sore throat, productive cough, shortness of breath, and chest tightness were common for workers with daily average exposures of 4.0 mg/m^3 of borate dust, and infrequent at exposures of 1.1 mg/m^3 (5.7 and 2.2, respectively, Woskie *et al.*, 1994). No damage was done, however, even with prolonged and/or high levels of exposure, except perhaps for some FEV$_1$ decline for cumulative high-level dust ($\geq$80 mg/m^3 years) exposure of smokers (Garabrant, Bernstein, Peters, Smith and Wright, 1985). The American Conference of Governmental Industrial Hygienists in 1980 recommended dust exposure limits of 1.0 mg/m^3 for anhydrous borax and pentahydrate, 5.0 mg/m^3 for borax, 2 mg/m^3 for boric acid, and 15 mg/m^3 for boric oxide.

There is little information on the mechanism of borate toxicity, other than a decreased oxygen uptake by brain tissue contacted by borates, but the effect is largely overcome by the addition of glucose or pyruvate. Borates may possibly interfere with protein formation and glutamine synthesis in brain tissue. In acute poisoning studies with animals, gross pathologic changes were minimal, but microscopic studies showed renal glomerular and tubular damage. There is no proven therapy for boric acid ingestion, but with laboratory animals large doses of Ringer's solution and plasma given intravenously have been very helpful, as has D-glucose. With infants, exchange transfusions and intravenous infusion of multiple electrolyte have been successfully used (Levinskas, 1964).

Normal boron blood levels in humans are on the order of 0.1–10 ppm, but 74.8 ppm was observed in an infant who drank a boric acid solution (with no visible sign of toxicity). Boron is rapidly excreted in unchanged form by the kidneys, and in one human test 500 mg of boric acid was injected intravenously. It was excreted rapidly in the urine, demonstrating a half-life of 21 hours and complete elimination in 96 hours. In chronic exposure tests, doses of 2500 and 5000 ppm of boric acid in the diet of mice over a 2-year period showed no evidence of carcinogenicity. Boron in the diet is normal at an ingestion rate of 10–20 mg/day, with foods varying from 0.002 mg (milk) to 0.279 mg (apple sauce) per helping. The boron is rapidly and completely absorbed, but there is no accumulation in the body (Raymond and Butterwick, 1992). When tested on a cellular level, borax and its ores were toxic only to mammalian cells (cytotoxicity; 50% plating efficiency). At a high concentration (800–3200 mg/liter of cells), they appeared to have no mutagenic effect, and were not significantly tumor forming (oncogenic; Landolph, 1985).

Borates, however, do have some toxicity to insects. High concentrations can control fly larvae in manure piles, dog runs, and the like, and powdered boric acid is effective in controlling cockroaches. Borates have been used as mild antiseptics in pharmaceutical applications for literally centuries, but are not strong enough for most modern uses. Sudden large amounts of borates can reduce the efficiency of sewage treatment organisms, but these organisms

can adapt to more continuous high le
of 430 ppm can protect wood against
protects against termites. Where th
however, is in plants, since a very narr
an essential fertilizer and their being

8.5.2 Environment

There have been a large number o
environment, such as summarized by
fish, the "lowest observable effect con
with the early life stages of rainbow tr
However, in natural waters no effect
rainbow trout have been found in C
fish species have shown a similar or hig
trations have been found beneficial
raising carp production by 7.6%, an
The range of several LD$_{50}$ tests was
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Grazing animals have not been stu
were found in heifers exposed to 120
ppm was not acutely toxic. The safe to
ppmB in water. However, it was fou
grazing on soils with 30–300 ppmB, d
40 ppmB feed. In an extensive inves
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can adapt to more continuous high levels of borates. Boric acid impregnation of 430 ppm can protect wood against the house borer, and 1% impregnation protects against termites. Where the borate concentration is most critical, however, is in plants, since a very narrow margin exists between borates being an essential fertilizer and their being toxic (see Table 9.2; Sprague, 1972).

8.5.2 Environment

There have been a large number of studies on the effect of boron in the environment, such as summarized by Raymond and Butterwick (1992). With fish, the "lowest observable effect concentration (LOEC)" of boron was found with the early life stages of rainbow trout at 0.1 ppmB in reconstituted waters. However, in natural waters no effect was noted even at 17 ppm, and healthy rainbow trout have been found in California streams with 13 ppmB. Other fish species have shown a similar or higher boron tolerance. Low boron concentrations have been found beneficial for some fish growth, such as 0.4 ppmB raising carp production by 7.6%, and rohu benefiting from 1 mgB/fish/day. The range of several LD_{50} tests was 5–3000 ppmB for freshwater fish and 12–90 ppm for seawater fish. Amphibians have been found to respond to boron in a similar manner. A concentration of 30 ppmB was found to reduce the photosynthesis of half the phytoplankton tested, and 50 ppm decreased the growth rate of 5 of 19 species. In sewage tests 20 ppmB had no effect on activated sewage treatment, and 200 ppmB produced no inhibition of anaerobic sludge digestion.

Grazing animals have not been studied extensively, but no signs of toxicosis were found in heifers exposed to 120 ppmB in their drinking water, and 300 ppm was not acutely toxic. The safe tolerance level was estimated to be 40–150 ppmB in water. However, it was found that sheep developed enteritis when grazing on soils with 30–300 ppmB, drinking water with 1–20 ppmB, or eating 40 ppmB feed. In an extensive investigation of boron's effect on rivers and water courses in England, Waggot (1969) came to the conclusion that there was no toxicity problem, and that both natural boron removal (i.e., adsorption on clays, etc.) and sewage treatment appeared to be capable of maintaining a low boron concentration in the country's rivers and water courses (Raymond and Butterwick, 1992).

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Chapter 9 | Uses of Bora

9.1 GLASS

Borates and their derivatives find an unus
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The production of borosilicate glass, how
amounting to about 55% of the total U.S.
into glass production of fiberglass for in
and also as specialty glass products for
resistance and many other uses. Boron's e
in the late 1800s, and by the late 1930s
well recognized. By the 1940s fiberglass, hi
and specialty glasses were being made in
of various glass compositions using bora

In general, boron considerably reduc
provides good resistance to vibration, hi
and improves its toughness, strength, c
also greatly reduces the viscosity of the
features, and others, allow it to form su
specialty applications. E-glass was the ini
positions such as C- and D-glass were
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glasses greatly improved the fiberglass fo
fiberglass is both very strong and resista
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Molten glass is sufficiently viscous fo
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Chapter 9 | Uses of Borates

9.1 GLASS

Borates and their derivatives find an unusually large range of uses, as indicated in Tables 9.6, 10.7 and Fig. 10.3, and briefly discussed in the following section. The production of borosilicate glass, however, is by far the largest single use, amounting to about 55% of the total U.S. consumption in 1990. Borates enter into glass production of fiberglass for insulation, fabrics and reinforcement, and also as specialty glass products for household, laboratory, optical, heat resistance and many other uses. Boron's effect on glass was initially established in the late 1800s, and by the late 1930s its usefulness in fiberglass was also well recognized. By the 1940s fiberglass, high-durability and performance glass, and specialty glasses were being made in large continuous furnaces. Examples of various glass compositions using borates are given in Table 9.1.

In general, boron considerably reduces the thermal expansion of glass, provides good resistance to vibration, high temperatures and thermal shock, and improves its toughness, strength, chemical resistance and durability. It also greatly reduces the viscosity of the glass melt as it is being made. These features, and others, allow it to form superior glass for many industrial and specialty applications. E-glass was the initial textile fiberglass, and other compositions such as C- and D-glass were later used. Iron, arsenic, and sulfate are usually undesirable constituents in the boron source. The high-boron glasses greatly improved the fiberglass for both fabrics and insulation. Modern fiberglass is both very strong and resistant to destructive conditions such as elevated temperatures, burning, chemicals other than alkalies, bacterial and fungal attack, and high-energy radiation. However, it will not elongate under stress, and is comparatively brittle. Much of it is employed in batting form as nonflammable thermal insulation, and it is the load-bearing fiber imbedded in heat and/or catalyst-curable resin for many structural and other applications. It is woven into fabrics for higher-temperature industrial uses, or for decorative purposes when nonflammability and resistance to sunlight are important, such as with draperies and curtains.

Molten glass is sufficiently viscous for it to be drawn into uniform fibers, which are then cooled and solidified (Figs. 9.1 and 9.2). To reduce brittleness, the filaments are made smaller (filament fineness is known as *denier*) than organic fiber, and special protective coatings are added so they will not cut and abrade each other when woven into fabrics. The extremely high surface-

Table 9.1
Typical Glass Compositions Containing Boron (wt%)[a]

	D-Glass[b]	[c]	[d]	Pyrex[b]	[e]	[f]	[g]	[h]	E-Glass[b]		[i]	C-Glass[b]
B_2O_3	<23	22.5	15.0	13.5	13.0	12.0	11.5	9.6	7.0	6–8	7.0	5
SiO_2	72–75	65.0	74.0	80	81.0	3.0	69.5	74.7	55.0	53–55	61.0	60–65
CaO	—	—	—	—	—	—	—	0.9	21.8	17–22	9.0	14
Al_2O_3	—	5.2	1.0	2	2.0	11.0	—	5.6	15.0	14–15	4.0	3.5–6
MgO	<3	—	—	—	—	—	—	—	0.5	1.0	3.5	3
Na_2O	—	7.2	4.0	4.5	4.0	—	9.0	—	0.5	0.8	14.5	10
Fe_2O_3	—	—	—	—	—	—	—	—	—	0.3	—	0.5
TiO_2	—	—	—	—	—	—	—	—	—	0.5	—	—
PbO	—	—	6.0	—	—	74.0	—	—	—	—	—	—
BaO	—	—	—	—	—	—	3.0	2.2	—	—	—	—
K_2O	—	—	—	—	—	—	7.0	0.5	—	—	1.0	—

[a] Gagin, 1985.
[b] Russell, 1991.
[c,d] Electronic glass.
[e] Corning 7740 heat and chemical-resistant glass.
[f] Solder glass for sealing electrical components.
[g] Optical lenses.
[h] Older chemical-resistant glass.
[i] Soft glass for making insulation by rotary fiberization; C-, D-, and E-Glass are for fiberglass.

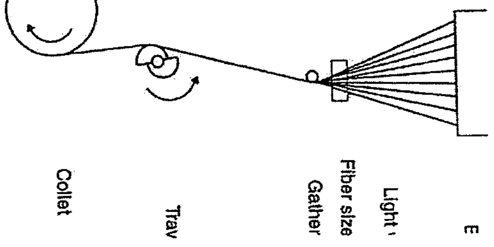

Figure 9.1 Extruding molten borate glass fib
Russell, 1991; reprinted by permission of Industr

to-volume ratio that results from use of
that the surfaces be protected against
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E-glass is an alkali-free calcium–ma
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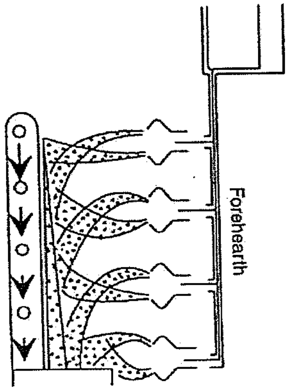

Figure 9.2 Glass-melting furnace, fiber-extr
fiberglass insulation mats. (From Russell, 1991; r

PbO	—	—	6.0	—	—	74.0	—	—	—	—	—	—
BaO	—	—	—	—	—	—	3.0	2.2	—	—	—	—
K_2O	—	—	—	—	—	—	7.0	0.5	—	—	1.0	—

[a] Gagin, 1985.
[b] Russell, 1991.
[c,d] Electronic glass.
[e] Corning 7740 heat and chemical-resistant glass.
[f] Solder glass for sealing electrical components.
[g] Optical lenses.
[h] Older chemical-resistant glass.
[i] Soft glass for making insulation by rotary fiberization; C-, D-, and E-Glass are for fiberglass.

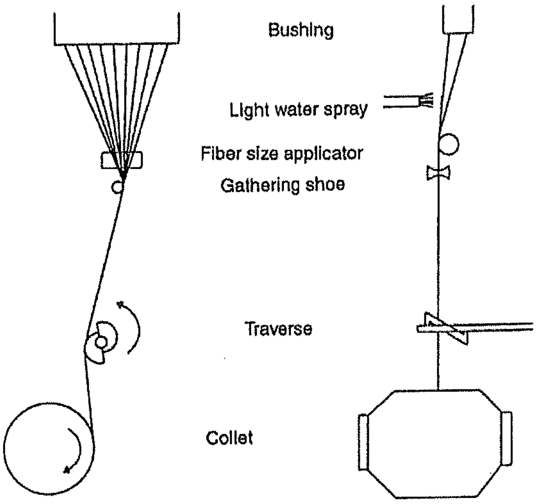

Figure 9.1 Extruding molten borate glass fibers from nozzles fed by a glass furnace. (From Russell, 1991; reprinted by permission of Industrial Minerals.)

to-volume ratio that results from use of such small filament sizes also requires that the surfaces be protected against the action of alkalies, even those as mild as soaps and detergents (Mark and Atlas, 1966).

E-glass is an alkali-free calcium–magnesium borosilicate, and when used for textile fiber glass its raw material requirements are more demanding than in the production of insulation. The silica is first ground to a very fine powder

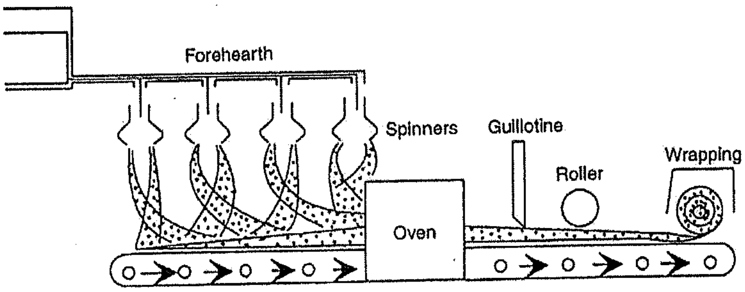

Figure 9.2 Glass-melting furnace, fiber-extruding nozzles, and finishing equipment to form fiberglass insulation mats. (From Russell, 1991; reprinted by permission of Industrial Minerals.)

to speed its melting, while the limestone, fluorspar, colemanite, and boric acid can be used with larger particle sizes. The raw materials are first weighed and blended before being fed into the furnace. The temperature in the upper portion of the furnace is about 1600°C, and the glass is withdrawn from its base at about 1300°C (the furnace is nominally at a temperature of 1400–1450°C). Because boric acid has significant volatility, the dust from the flue gas, which can contain up to 30% B_2O_3 and 20% Na_2O, is collected and recycled.

When melted to a uniform viscosity (partly controlled by the amount of boron), the glass flows through a submerged throat into a canal and a forehearth that feeds the various production lines. The melt is then forced through as many as 200 electrically heated platinum alloy bushings (nozzles) per furnace. There are usually 500 or more individual filaments drawn from tiny orifices in each nozzle, usually 6–9 μ in size, although they can be as small as 1.5 μ. The filaments are then rapidly cooled and coated with a binder or sizing compound from sprays, or by being rolled over a sizing applicator. The filaments are next combined on a high-speed winder to form a single strand as a textile yarn, which can be formed into mats, chopped strands, or other products (Russell, 1991; Roskill, 1993).

In another process the glass from the furnace flows into a rapidly rotating dish (spinner) with several thousand small holes in its perimeter. As it rotates the molten glass is forced through the holes and formed into filaments ("fiberized"). The fibers are cooled and sprayed with a resinous binder to make a "wool," which is collected on a conveyor. The speed of the spinner determines the product's grammage (weight per unit area). The wool is next sent through an oven at 280°C for curing, and then trimmed, chopped, and either stacked or rolled before final packing. If the wool is for pipe insulation, the uncured glass is separated into pelts on the forming conveyor and converted into pipe sections by a winding machine, which wraps the pelt around a heated mandrel with the wall thickness of the pipe determined by a set of counter-rollers. The formed sections are then passed through a curing oven and split; faced with cloth, paper or aluminum foil, and packaged (Russell, 1991).

The two basic boron products used in the 1940s for glass were boric acid and borax, but as the demand increased, an effort was made to reduce the delivered costs of the borates. Anhydrous borax became widely used, but by the 1970s the standard purified product for E-glass in textiles became five-mole borax (the pentahydrate) because it is much easier and cheaper to produce. For insulation fiberglass, colemanite and ulexite began to be used, usually containing 34–48% B_2O_3. Colemanite melted better in existing furnaces, so the processing and blending problems to produce a uniform, adequately pure product were then given more attention. Washing the ore for partial clay removal (and/or flotation) helped to remove impurities, increase the B_2O_3 content and improve the ore's consistency.

The choice of boron raw materials was also influenced by the size and type of glass-melting facilities. E-glass is prodı
as 68 metric tons/day) with heat exchan
air. Using colemanite in place of limes
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All commercial fiberglass has some vı
destroy the bond with the organic binder.
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reinforces and protects the fibers from bri
of applications to such things as sporting
tanks, reinforcing mats, electric applianc
aircraft, and many other products. They
tensile strength, high modulus of elasticit
glass (Gagin, 1985).

As the boron content increases in man
tion occurs during heating, which is the ba
After phase separation, regular melting a
later heat treatment forms a highly dissen
that can be leached with hot acids. The pc
899°C (1650°F) to a solid, transparent 96
to acids and thermal shock. The presint
as a desiccant or as a catalyst support.

In another application, sodium borates
glass for improved acid-resistance by re
glass, such as Nos. e and h in Table 9.1
good for most chemical uses. The bora
shape and forms a network structure witl
expansion of vitreous silica more than
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in many products.

There are a large number of comn
containing glasses. For instance, the boro
piping, reaction columns and gauge gla
shock and retain its dimensional stability
assembled with flanged fittings, and is av
very chemical resistant and has smooth

fluorspar, colemanite, and boric acid
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consistency.
also influenced by the size and type

of glass-melting facilities. E-glass is produced in large gas-fired furnaces (such as 68 metric tons/day) with heat exchangers for preheating the combustion air. Using colemanite in place of limestone and boric acid allowed faster batch melting, sometimes increased furnace output, and yielded better fuel efficiency. Ulexite is usually a replacement for borax, but its effect on batch melting was not as pronounced as that of colemanite in the production of E-glass, since it replaces some of the soda ash, a very active flux. When purity or color are critical, the refined boric acid or sodium borates are used because both colemanite and ulexite usually contain much more iron, arsenic, sulfate or other harmful impurities.

All commercial fiberglass has some vulnerability to water, which tends to destroy the bond with the organic binder. Partly for this reason, and for added strength and ease of use, textile fiberglass is often mixed with plastics. This reinforces and protects the fibers from brittle failure, and allows a wide variety of applications to such things as sporting equipment, roofing, shingles, storage tanks, reinforcing mats, electric appliances, components of automobiles and aircraft, and many other products. They benefit from the light weight, high tensile strength, high modulus of elasticity and chemical stability of the fiberglass (Gagin, 1985).

As the boron content increases in many glass compositions a phase separation occurs during heating, which is the basis for the high-silica Vycor products. After phase separation, regular melting and forming techniques are used, but later heat treatment forms a highly disseminated, interconnected borate phase that can be leached with hot acids. The porous structure is then sintered above 899°C (1650°F) to a solid, transparent 96% silica glass with a good resistance to acids and thermal shock. The presintered porous glass may also be used as a desiccant or as a catalyst support.

In another application, sodium borates can be used in producing high-silica glass for improved acid-resistance by replacing some of the soda ash. This glass, such as Nos. e and h in Table 9.1 has a lower alkali content, which is good for most chemical uses. The borax in glass retains a trigonal planar shape and forms a network structure with the silica. This reduces the thermal expansion of vitreous silica more than network-modifying ions, making it more resistant to thermal shock. Borates also reduce the surface leaching of water or alkalies by inhibiting the removal of alkali ions, which can destroy the silica network. This causes frosting of the glass surface, which is detrimental in many products.

There are a large number of commercial applications for the borate-containing glasses. For instance, the borosilicate glass used for industrial glass piping, reaction columns and gauge glass is designed to withstand thermal shock and retain its dimensional stability to 400°C (750°F). The piping is easily assembled with flanged fittings, and is available in a wide range of sizes. It is very chemical resistant and has smooth, pore-free surfaces, which improve the fluid flow and resists scaling (Shelley, 1994). Other specialty glasses have been developed with a wide range of B_2O_3 contents. Sodium vapor lamps may contain up to 36% B_2O_3, and low x-ray absorption glass up to 83% B_2O_3. Most, however, are in the 1–34% B_2O_3 range, and include glass for electron tubes, optical fibers and filters, pharmaceutical applications, laboratory and kitchen ware (such as Pyrex), vacuum flasks, sealed-beam headlights, high-performance lights, electrical equipment with seals to metals, high-voltage insulators, and many others. Borax also enhances the quality of art and optical glasses (Anon., 1995b).

9.2 ABRASIVES AND REFRACTORIES

The boride compounds are very hard (about 9 on Mohs' scale; diamonds are 10), and are used as abrasives and refractories. They have a basic chemical formula with a limited range of compositions, and a high thermal and electrical conductivity. These compounds can be produced by reacting mixtures of powdered metal with boron at 1800–2000°C, and then compressing and sintering the residue into the desired shapes. Very pure borides may be prepared by sintering in a vacuum or an inert atmosphere near the melting point. They also may be produced by reducing B_2O_3 or KBF_4 with aluminum, magnesium or potassium, but the borides are impure, and further purification is difficult. High-purity borides also may be deposited on a filament in an atmosphere of boron tribromide, hydrogen and methane. Boride coatings are prepared with arc plasma or high-powered carbon dioxide lasers. Technical-grade borides with 67–76.5% boron are produced by reacting B_2O_3, finely divided coke, and the desired metal in an electric furnace.

Boron carbide (pure B_4C contains 78.3% boron) may be produced in the same manner at 1400–2300°C, but without the metal, or at lower temperatures (1400–1800°C) with Mg in a H_2 atmosphere, and then leached with HCl and boiling HF. The latter product is very hard and has good electrical conductivity as well as a high compressive strength and melting point (2450°C). It is chemically inert, but remains stable in an oxidizing environment only to about 800–1000°C. It is used as a polishing agent, for sandblast nozzles and in nuclear shielding. A composite of boron carbide and fiberglass has been developed that can stop a 30-caliber bullet at point-blank range, and was used for seats in the AH-10 Cobra attack helicopter. A silicoboron carbonitride ($Si_3BC_{4.3}N_2$) has extraordinarily high thermal stability (i.e., up to 2000°C; Anon., 1996d).

Boron nitride (BN; "white graphite") is produced by the thermal decomposition of boron–nitrogen compounds, such as $B(NH_3)_3$ and $BF_3{\cdot}NH_3$, has a hexagonal graphite-like platelet structure, and sublimes above 2980°C. It is similar to graphite in directional properties, has good machinability, high thermal conductivity, excellent resistance to thermal shock, a low density, and

is an electrical insulator. It resists air oxi
by many molten metals, slags, or glasse
as a solid, powder, or aerosol, and its
nozzles and lubricants (Luehrsen and O
zon, is produced by applying high temp
(1 million psi) to the hexagonal BN. It
and polishing ferrous metals and supera
continuous heavy-duty ability than tun
coolants.

Borides of chromium, hafnium, titani
are high-melting-point materials with ve
tance, electrical conductivity, and resi
boride (TiB_2) has been used as anvils, b
crucibles. Aluminum boride (AlB_{12}) is a
and polishing, while zirconium diborid
metal atomization (Lyday, 1985; Roskil

9.3 AGRICULTURE

9.3.1 Function of Boron in Plants

Boron is essential to plant growth, bein
However, high concentrations of boron
narrow range of concentration betwee
The exact function of boron in plants i
to several processes, such as the transl
of various organic compounds within th
ability of boron with poloyls facilitates
cant increase in the oxygen uptake b
addition of 5 ppmB to a sucrose foliar sp
tion of sucrose in the plant when a 10 pp
of bean and tomato plants. Boron is kr
on the hormone action in plants, the a
absorption of CO_2 from the air, and th

Another important function of boro
deficiency alters the cell walls, making
phloem parenchyma and ground pare
thicker. This appears to result from
carbohydrates into wall material. A bo
sulted in less lignification and a reductio
and nucleic acid syntheses. Without ad
of cell walls also may be altered. With b

ley, 1994). Other specialty glasses have
f B_2O_3 contents. Sodium vapor lamps
x-ray absorption glass up to 83% B_2O_3.
)$_3$ range, and include glass for electron
ıaceutical applications, laboratory and
n flasks, sealed-beam headlights, high-
.ent with seals to metals, high-voltage
ɔ enhances the quality of art and optical

ORIES

(about 9 on Mohs' scale; diamonds are
fractories. They have a basic chemical
ıitions, and a high thermal and electrical
. produced by reacting mixtures of pow-
'C, and then compressing and sintering
/ery pure borides may be prepared by
ıosphere near the melting point. They
)$_3$ or KBF_4 with aluminum, magnesium
ure, and further purification is difficult.
sited on a filament in an atmosphere of
ane. Boride coatings are prepared with
lioxide lasers. Technical-grade borides
reacting B_2O_3, finely divided coke, and
ɔe.
78.3% boron) may be produced in the
ıout the metal, or at lower temperatures
ıphere, and then leached with HCl and
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and melting point (2450°C). It is chemi-
oxidizing environment only to about
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ide and fiberglass has been developed
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A silicoboron carbonitride ($Si_3BC_{4.3}N_2$)
lity (i.e., up to 2000°C; Anon., 1996d).
') is produced by the thermal decompo-
such as $B(NH_3)_3$ and $BF_3{\cdot}NH_3$, has a
ture, and sublimes above 2980°C. It is
ɔperties, has good machinability, high
ıce to thermal shock, a low density, and

is an electrical insulator. It resists air oxidation up to 1400°C and is not wetted by many molten metals, slags, or glasses, but it can hydrolyze. It is available as a solid, powder, or aerosol, and its uses include crucibles, molten metal nozzles and lubricants (Luehrsen and Ott, 1990). A cubic boron nitride, Borazon, is produced by applying high temperatures (1400–1700°C) and pressure (1 million psi) to the hexagonal BN. It is used for cutting, honing, lapping, and polishing ferrous metals and superalloys. It has a higher cutting rate and continuous heavy-duty ability than tungsten carbide, and does not require coolants.

Borides of chromium, hafnium, titanium, zirconium, and many other metals are high-melting-point materials with very good strength, hardness, wear resistance, electrical conductivity, and resistance to chemical attack. Titanium boride (TiB_2) has been used as anvils, bearings, bearing liners, jet nozzles and crucibles. Aluminum boride (AlB_{12}) is a substitute for diamond dust in grinding and polishing, while zirconium diboride (ZrB_2) is used in spray nozzles for metal atomization (Lyday, 1985; Roskill, 1993).

9.3 AGRICULTURE

9.3.1 Function of Boron in Plants

Boron is essential to plant growth, being one of the 16 basic plant nutrients. However, high concentrations of boron are also toxic, resulting in a relatively narrow range of concentration between too much and too little (Table 9.2). The exact function of boron in plants is still unclear, but it has been related to several processes, such as the translocation, or the control of the amount of various organic compounds within the plant. It appears that the complexing ability of boron with poloyls facilitates the movement of sugars, and a significant increase in the oxygen uptake by root tissue was observed with the addition of 5 ppmB to a sucrose foliar spray. Also, there was a greater distribution of sucrose in the plant when a 10 ppmB solution was applied to the leaves of bean and tomato plants. Boron is known to enhance the effects of sugars on the hormone action in plants, the amount of photosynthesis, the rate of absorption of CO_2 from the air, and the growth of plant roots.

Another important function of boron is with cell growth and structure. A deficiency alters the cell walls, making most of them thinner, except for the phloem parenchyma and ground parenchyma cell walls, which are made thicker. This appears to result from an alteration in the condensation of carbohydrates into wall material. A boron deficiency in sunflower tissue resulted in less lignification and a reduction in RNA, causing changes in protein and nucleic acid syntheses. Without adequate supplies of boron the growth of cell walls also may be altered. With bean plants a boron deficiency reduced

Table 9.2

Boron in the Soil Solution and Tissue Analysis for Best Plant Growth[a]

	Boron concentration in soil solution for best growth (ppm)	Lowest soil solution concentration for injury (ppmB)	Best tissue analyses (ppmB)	Typical application rates[b] (lbsB/acre)
A. Sensitive Plants				
Bermuda grass	—	—	7–20[b]	1–2[b]
Blackberry (*Rubus* sp.), Raspberry	Trace, <0.5[c]	1, 0.3–0.5[d]	30–60[b]	—
Cherry (*Prunus arium L.*)	1, 0.5–0.75[c]	5, 0.3–0.5[d]	25–60,[b] 30[c]	1–2[b]
Citrus, Lemon (*Citrus limonia osbeck*)	Trace, <0.5[c] 0.5–0.75[b]	1, 0.3–0.5[d]	30–100[b]	1–2[b]
Cowpea (*Vigna sinensis, Torner, Savl.*)	Trace, 0.5–0.75[c]	5, 0.3–0.8[d]	—	—
Elm (*Cimusamericana L.*)	1, <0.5[c]	1	—	—
Fig (*Ficus carica L.*)	1, 0.5–0.75[c]	5, 0.5–0.8[d]	—	—
Grape (*Vitisrinifera L.*)	1, 0.5–0.75[c]	5, 0.5–0.8[d]	40–60,[b] 50[c]	1.5–3[b]
Jerusalem artichoke (*Helianthus tuberosus L.*)	1, 0.75–1.0[c]	1	—	—
Kidney bean (*Phaseolus vulgaris L.*)	1, 0.75–1.0[c]	1, 0.8–1.0[d]	—	—
Larkspur (*Delphinium* sp.)	1, 0.5–1.0[c]	5	—	—
Lupine (*Lupinus hurtwegi Lindl.*)	1, 0.75–1.0[c]	5	—	—
Pansy (*Viola tricolor L.*)	Trace, 0.5–1.0[c]	5	—	—
Peach (*Prunus persica L. Batsch*)	1, 0.5–0.75[c]	5, 0.3–0.5[d]	—	—
Pears	0.75[b]	—	30–60,[b] 50[c]	1–2[b]
Persimmon (*Diospyros kaki L.f.*)	1, 0.5–0.75[c]	1, 0.5–0.8[d]	—	—
Plum	0.75[b]	0.3–0.5[d]	30–60[b]	2–4[b]
Strawberry (*Fragaria* sp.)	1, 0.75–1.0[c]	5, 0.8–1.0[d]	25–50[b]	1–2[b]
Violet (*Viola odorata L.*)	Trace, 0.5–1.0[c]	5	—	—
Walnuts	1[b]	0.5–0.8[d]	40–100,[b] 400[c]	2–4[b]
Zinnia (*Zinnia elegans Jacq.*)	Trace, 0.5–1.0[c]	1	—	—
Bean, mung; cucumber; garlic; peanut; sesame; sugar cane; sunflower; wheat	0.75–1.0[c]	0.5–0.8[d]	6–20,[b] 5,[c] 8–20[g]	0.5–1[b]
Almonds; apricot; avocado; figs, Kadota; pecan	0.5–0.75[c]	0.3–0.8[d]	20–45,[b] 20–70[g]	—
B. Semi-tolerant plants				
Alfalfa (*Medicago sativa L.*)	10,	15,	30–70,[b]	1–4[b]

Cowpea (*Vigna sinensis, Torner, Savl.*)	Trace, 0.5–0.75[c]	5, 0.3–0.8[d]	—	—
Elm (*Cimusamericana L.*)	1, <0.5[c]	1	—	—
Fig (*Ficus carica L.*)	1, 0.5–0.75[c]	5, 0.5–0.8[d]	—	—
Grape (*Vitisrinifera L.*)	1, 0.5–0.75[c]	5, 0.5–0.8[d]	40–60,[b] 50[e]	1.5–3[b]
Jerusalem artichoke (*Helianthus tuberosus L.*)	1, 0.75–1.0[c]	1	—	—
Kidney bean (*Phaseolus vulgaris L.*)	1, 0.75–1.0[c]	1, 0.8–1.0[d]	—	—
Larkspur (*Delphinium* sp.)	1, 0.5–1.0[c]	5	—	—
Lupine (*Lupinus hurtwegi Lindl.*)	1, 0.75–1.0[c]	5	—	—
Pansy (*Viola tricolor L.*)	Trace, 0.5–1.0[c]	5	—	—
Peach (*Prunus persica L. Batsch*)	1, 0.5–0.75[c]	5, 0.3–0.5[d]	—	—
Pears	0.75[b]	—	30–60,[b] 50[e]	1–2[b]

Persimmon (*Diospyros kaki L.f.*)	1, 0.5–0.75[c]	1, 0.5–0.8[d]	—	—
Plum	0.75[b]	0.3–0.5[d]	30–60[b]	2–4[b]
Strawberry (*Fragaria* sp.)	1, 0.75–1.0[c]	5, 0.8–1.0[d]	25–50[b]	1–2[b]
Violet (*Viola odorata L.*)	Trace, 0.5–1.0[c]	5	—	—
Walnuts	1[b]	0.5–0.8[d]	40–100,[b] 400[e]	2–4[b]
Zinnia (*Zinnia elegans Jacq.*)	Trace, 0.5–1.0[c]	1	—	—
Bean, mung; cucumber; garlic; peanut; sesame; sugar cane; sunflower; wheat	0.75–1.0[c]	0.5–0.8[d]	6–20,[b] 5,[e] 8–20[g]	0.5–1[b]
Almonds; apricot; avocado; figs, Kadota; pecan	0.5–0.75[c]	0.3–0.8[d]	20–45,[b] 20–70[g]	—
B. Semi-tolerant plants				
Alfalfa (*Medicago sativa L.*)	10, 4–6[c]	15, 4–6[d]	30–70,[b] 80[e]	1–4[b]
Apples	1[b]	—	30–50,[b] 25[e]	1–3[b]
Barley (*Hordeum vulgare L.*)	Trace, 2–4[c]	5, 1–2[d]	6–20[b]	—
Broccoli; brussel sprouts; cucumber	1–2[c]	—	25–50,[b] 30–60[e]	1–3,[b] 3–4,[f] 2–5[e]
Cabbage (*Brassica oleracea var. capitata L.*)	1, 2–4[c]	10, 1–2[d]	25–50,[b] 40[e]	1–3,[f] 2–3,[b] 3–4[f]
Calendula (*Calendula officinalis L.*)	Trace	5	—	—
California Poppy (*Eschscholtzia californica Cham.*)	5, 2–4[c]	5	—	—
Carrot (*Daucus carota L.*)	Trace, 1–2[c]	10, 1–2[d]	25–70,[b] 30–200[e]	1–2,[b] 2–3[f]

continues

Table 9.2 (*continued*)

	Boron concentration in soil solution for best growth (ppm)	Lowest soil solution concentration for injury (ppmB)	Best tissue analyses (ppmB)	Typical application rates^b (lbsB/acre)
Cauliflower	2–4^c	—	30–60,^{b} 25–50^c	2–3,^{b} 2–5,^{c} 3–4^c
Celery (*Apium graveolens L.*)	15, 2–4^c	15, 1–2^d	25–50^b	2–3,^{b} 1–3,^{c} 2–3^f
Collards	—	—	30–60^b	1–3^b
Corn (*Zea mays L.*)	1, 2–4^c	5, 2–4^d	10–20,^{b} 25^e	1–2,^{b} 0.5–1^f
Eggplant	—	—	40–50^b	1–2^b
Kentucky bluegrass (*Poa pratensis L.*)	5, 2–4^c	1	—	—
Lettuce (*Lactucca sativa L.*)	5, 2–4^c	1, 1–2^d	25–50,^{b} 27–43^e	1–2^{b,f}
Lima bean (*Phaseolus tunatus L.*)	Trace, 0.75–1.0^c	1, 0.8–1.0^d	30–40^b	1–2^b
Milo (*Sorghum vulgare Pers.*)	Trace	5	—	—
Mustard (*Brassica sp.*)	1, 2–4^c	10	—	—
Oats (*Avena sativa L.*)	5, 2–4^c	5, 4–6^d	8–20^g	—
Onion (*Allium cepa L.*)	Trace, 0.5–0.75^c	1, 0.5–0.8^d	25–50^b	1–2,^{b} 0.5–1^f
Parsley (*Petroselinum crispum, Mill., Nym.*)	5, 4–6^c	15, 4–6^d	—	—
Pea (*Pisum sativum L.*)	1, 1–2^c	5, 0.8–1^d	25–50^b	1^b
Peanut	0.75^b	—	25–50^b	0.5–1,^{b} 0.5–0.75^g
Potato (*Solanum tuberosum L.*), pumpkin	1, 1–2^c	1, 1–2^d	20–40^b	1–2,^{b} 0.5–1^f
Radish (*Raphanus sativus L.*)	1, 1–2^c	10, 1–2^d	20–50,^{b} 45^e	1–2^{b,f}
Red pepper (*Capsicum frutescens L.*)	Trace, 1–2^c	5, 0.8–1	40–100^b	1^b
Rhubarb, spinach	—	—	40–60^b	1–2^{b,f}
Rutabaga	—	—	25–60^b	1–2^b
Soybean	0.5^b	—	20–60^b	0.5–1^{b,g}
Squash	—	2–4^d	30–40^b	1–2,^{b} 0.5–1^f
Sweet potato (*Ipomoca batatas, L., Lam.*)	Trace, 0.75–1.0^c	5, 0.5–0.8^d	20–40,^{b}	1^b 0.5–1^f
Tobacco (*Nicotiana tomentosa Ruiz and Pav.*)	15, 2–4^c	10, 2–4^d	20–50,^{b} 100^e	0.5–1^{b,g}
Tomato (*Lycopersicon esculentium Mill.*)	10, 4–6^c	5, 4–6^d	30–80,^{b} 100^e	1–2^{b,f}
Vetch (*Vicia atropurpurea Desf.*)	5, 4–6^f	5	—	1^b
Watermelon	—	—	—	1–2^b

		1–2^{a}	27–43^{c}	
Lima bean (*Phaseolus tunatus L.*)	Trace, 0.75–1.0^{c}	1, 0.8–1.0^{d}	30–40^{b}	1–2^{b}
Milo (*Sorghum vulgare Pers.*)	Trace	5	—	—
Mustard (*Brassica sp.*)	1, 2–4^{c}	10	—	—
Oats (*Avena sativa L.*)	5, 2–4^{c}	5, 4–6^{d}	8–20^{g}	—
Onion (*Allium cepa L.*)	Trace, 0.5–0.75^{c}	1, 0.5–0.8^{d}	25–50^{b}	1–2,^{b} 0.5–1^{f}
Parsley (*Petroselinum crispum, Mill., Nym.*)	5, 4–6^{c}	15, 4–6^{d}	—	—
Pea (*Pisum sativum L.*)	1, 1–2^{c}	5, 0.8–1^{d}	25–50^{b}	1^{b}
Peanut	0.75^{b}	—	25–50^{b}	0.5–1,^{b} 0.5–0.75^{g}
Potato (*Solanum tuberosum L.*), pumpkin	1, 1–2^{c}	1, 1–2^{d}	20–40^{b}	1–2,^{b} 0.5–1^{f}

Radish (*Raphanus sativus L.*)	1, 1–2^{c}	10, 1–2^{d}	20–50,^{b} 45^{c}	1–2^{b,f}
Red pepper (*Capsicum frutescens L.*)	Trace, 1–2^{c}	5, 0.8–1	40–100^{b}	1^{b}
Rhubarb, spinach	—	—	40–60^{b}	1–2^{b,f}
Rutabaga	—	—	25–60^{b}	1–2^{b}
Soybean	0.5^{b}	—	20–60^{b}	0.5–1^{b,g}
Squash	—	2–4^{d}	30–40^{b}	1–2,^{b} 0.5–1^{f}
Sweet potato (*Ipomoca batatas, L., Lam.*)	Trace, 0.75–1.0^{c}	5, 0.5–0.8^{d}	20–40,^{b}	1^{b} 0.5–1^{f}
Tobacco (*Nicotiana tomentosa Ruiz and Pav.*)	15, 2–4^{c}	10, 2–4^{d}	20–50,^{b} 100^{c}	0.5–1^{b,g}
Tomato (*Lycopersicon esculentium Mill.*)	10, 4–6^{c}	5, 4–6^{d}	30–80,^{b} 100^{c}	1–2^{b,f}
Vetch (*Vicia atropurpurea Desf.*)	5, 4–6^{f}	5	—	1^{b}
Watermelon	—	—	—	1–2,^{b} 0.5–1^{f}
C. Tolerant plants				
Artichoke (*Cynara scolymus L.*)	5, 2–4^{c}	5, 2–4^{7}	—	—
Asparagus (*Asparagus officinalis L.*)	5, 10–15^{c}	25, 10–15^{d}	40–65^{b}	1–2^{f}
Common beet (*Beta vulgaris L.*)	5, 4–6^{c}	15	30–70,^{b} 80^{c}	1–2,^{b} 3–4^{f}
Cotton (*Gossypium hirsutum L.*)	10, 6–10^{c}	10, 6–10^{d}	30–50,^{b} 30–80^{c}	0.5–2,^{b} 1–2^{c}
Leaf beet (*Beta vulgaris var. cicla L.*)	5	25	—	—
Muskmelon (*Cucumis melo L.*)	5	15	25–50^{b}	1–2^{b}
Oxalis (*Oxalis bowiei Herb.*)	10	—	—	—
Parsnips	—	—	25–70^{b}	1–2,^{b} 2–3^{f}

continues

Table 9.2 (*continued*)

	Boron concentration in soil solution for best growth (ppm)	Lowest soil solution concentration for injury (ppmB)	Best tissue analyses (ppmB)	Typical application rates[b] (lbsB/acre)
Sorghum	6–10[c]	4–6[d]	1–2[b]	8–20[b]
Sugar beet (*Beta vulgaris var. crassa Alef.*)	5, 4–6[c]	15, 4–6[d]	30–70,[b] 50[c]	1–3[b]
Sunflower	—	—	1–2[b]	40–60[b]
Sweet clover (*Melilotus indica L., All.*)	5, 2–4[c]	10, 4–6[d]	20[h], 25–50[b] 45[c]	0.5–2,[b] 1–2[h]
Sweet pea (*Lathyrus odoratus L.*)	10, 2–4[c]	15	—	—
Turnip (*Brassica rapa L.*)	5, 2–4[f]	25, 1–2[d]	25–60,[b] 50[c]	1–3,[b] 2–4,[c] 3–4[f]

[a] Sprague, 1972.
[b] Segars, 1987.
[c] Maas, 1986.
[d] Raymond and Butterwick, 1992 (quoting 1929 and 1944 references).
[e] Anon., 1994.
[f] Mack, 1986.
[g] Garratte, 1983.
[h] Flannery, 1985.

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the cell division and decreased the mov
root sections. There was an increased mo
possibility that boron is involved in cell
of cell elongation.

Finally, boron is involved in enzymati
glucose-1-phosphate into starch by starc
effect on the synthesis of plant hormo
appears to be less nucleic acid in boron-d
by adding nucleic acid to the plants' so
in peanut plants, the total nitrogen and
normal, but the protein and DNA were

9.3.2 Boron's Quantitative Effects on

Table 9.2 contains guidelines on the toler
boron concentration in the soil solution
the lowest concentration for injury. It is
widely different boron requirements and
local conditions and the availability of
increase in potassium induced a boron
quired if phosphorus was low or the nit
calcium also can induce a boron deficienc
on cotton can sometimes be ineffective
of boron in the soil solution on the gro
Fig. 9.3. In general, soil solution and
(Fig. 9.4).

The concentration of boron in plant l
and mild leaf injury may occur at or below
in the greatest growth. Boron may acc
yellowing or burning, even though the bor
matic tissues is insufficient for their most
less than 15 or 20 ppmB are associated
of 200 ppm are required for symptoms

It appears necessary to move the bo
liquid flow to the root area, rather than
other nutrients). Once boron reaches the
cytoplasmic membranes into the root
concentration in the soil solution is gen
tissue. The rate of uptake for boron is
nutrients, possibly because of the need
be adsorbed by it, and then to be desorbe
be transported to utilization and immobi
plant. The uptake of boron can be reduc

Sweet pea (*Lathyrus odoratus L.*)	10, 2–4[c]	15	—	—
Turnip (*Brassica rapa L.*)	5, 2–4[f]	25, 1–2[d]	25–60,[b] 50[e]	1–3,[b] 2–4,[e] 3–4[f]

[a] Sprague, 1972.
[b] Segars, 1987.
[c] Maas, 1986.
[d] Raymond and Butterwick, 1992 (quoting 1929 and 1944 references).
[e] Anon., 1994.
[f] Mack, 1986.
[g] Garratte, 1983.
[h] Flannery, 1985.

the cell division and decreased the movement of glucose into pectin in the root sections. There was an increased movement into cellulose, indicating the possibility that boron is involved in cell wall bonding, or the stretching phase of cell elongation.

Finally, boron is involved in enzymatic reactions such as the conversion of glucose-1-phosphate into starch by starch phosphorylase. It may also have an effect on the synthesis of plant hormones regulating plant growth. There appears to be less nucleic acid in boron-deficient tissue, and it can be increased by adding nucleic acid to the plants' soil solution. Without adequate boron in peanut plants, the total nitrogen and certain amino acids were higher than normal, but the protein and DNA were reduced.

9.3.2 Boron's Quantitative Effects on Growth

Table 9.2 contains guidelines on the tolerance of plants to boron, the optimum boron concentration in the soil solution and plant tissue for best growth, and the lowest concentration for injury. It is evident that different experts suggest widely different boron requirements and tolerances, probably on the basis of local conditions and the availability of other nutrients. With soybeans, an increase in potassium induced a boron deficiency, and more boron was required if phosphorus was low or the nitrate was high. The presence of high calcium also can induce a boron deficiency, and increased nitrogen application on cotton can sometimes be ineffective without increased boron. The effect of boron in the soil solution on the growth of a few plants is illustrated in Fig. 9.3. In general, soil solution and plant tissue analyses correlate well (Fig. 9.4).

The concentration of boron in plant leaves may vary from 2 to 3875 ppm, and mild leaf injury may occur at or below the boron concentration that results in the greatest growth. Boron may accumulate in the older leaves, causing yellowing or burning, even though the boron supply to actively enlarge meristematic tissues is insufficient for their most rapid growth. In general, tissue levels less than 15 or 20 ppmB are associated with deficiency, while levels in excess of 200 ppm are required for symptoms of boron excess.

It appears necessary to move the boron in the soil solution primarily by liquid flow to the root area, rather than by diffusion (the mechanism of most other nutrients). Once boron reaches the plant root, transport across selective cytoplasmic membranes into the root cells occurs, even though the boron concentration in the soil solution is generally much lower than in the root tissue. The rate of uptake for boron is also much slower than that of other nutrients, possibly because of the need for boron to react with the root, or be adsorbed by it, and then to be desorbed into the plant's fluids. It then must be transported to utilization and immobilization sites in other portions of the plant. The uptake of boron can be reduced by a factor of 4 as the soil solution

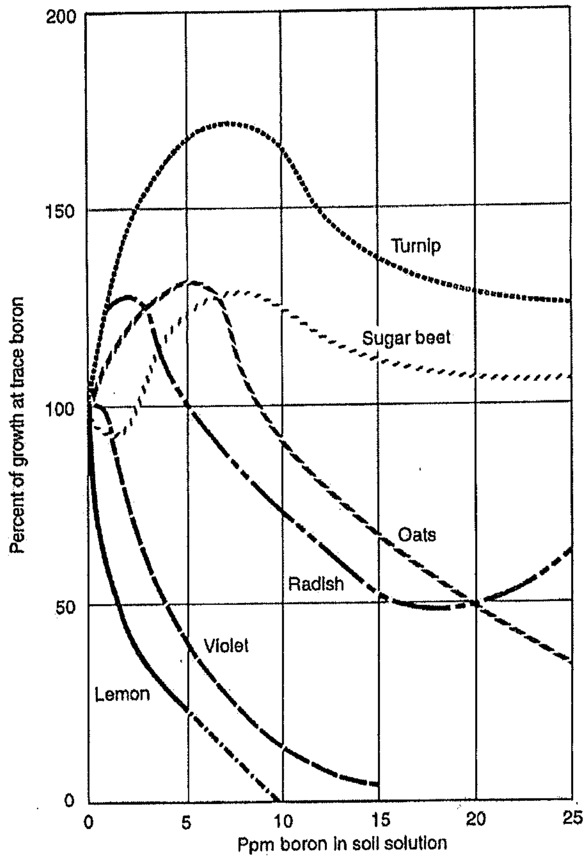


Figure 9.3 Effect of boron concentration in the soil solution on plant growth. (From Sprague, 1972; drawing courtesy of U.S. Borax Inc.)

changes from pH 4 to pH 8, and increases over the range of 10–30°C (followed by a sharp reduction above 35°C). Increase in light intensity also increases the rate of boron uptake.

Irrigation water with 5 ppmB in California has damaged walnut and citrus orchards, resulting in rules or regulations for the water's boron concentration. No more than 0.3 to 1 ppmB is suggested for water used on sensitive plants, and less than 1–2 ppmB is recommended for semitolerant plants. These recommendations do not allow for difference
other growth factors, and thus are usu
conditions (Sprague, 1972).

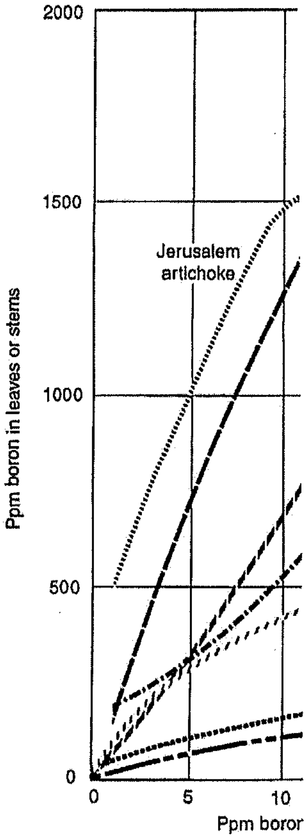
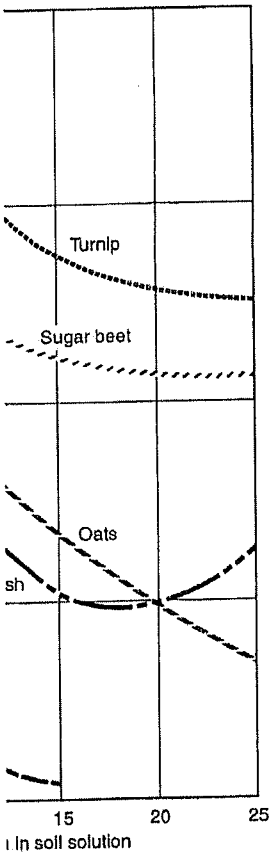


Figure 9.4 Boron concentration in plant tiss
(From Sprague, 1972; drawing courtesy of U.S. B

9.3.3 Boron Deficiency Symptoms and

9.3.3.1 Natural Boron in Soils

Some of the common symptoms of b
9.3. The average boron content in all pla



soil solution on plant growth. (From Sprague,

over the range of 10–30°C (followed
ase in light intensity also increases

rnia has damaged walnut and citrus for the water's boron concentration. for water used on sensitive plants, or semitolerant plants. These recommendations do not allow for differences in soils, climate, use conditions, or other growth factors, and thus are usually the limits for the most adverse conditions (Sprague, 1972).

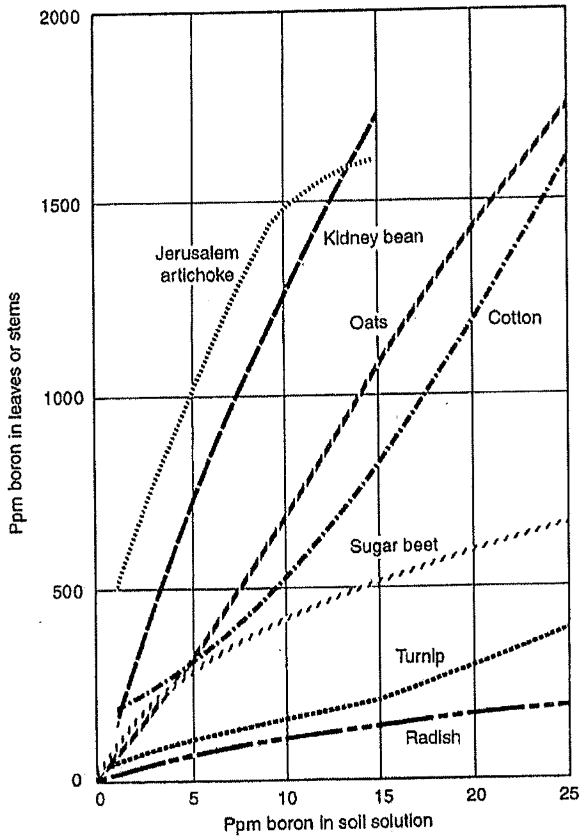


Figure 9.4 Boron concentration in plant tissue related to the content in the soil solution. (From Sprague, 1972; drawing courtesy of U.S. Borax Inc.)

9.3.3 Boron Deficiency Symptoms and Fertilization Rates

9.3.3.1 Natural Boron in Soils

Some of the common symptoms of boron deficiencies are listed in Table 9.3. The average boron content in all plants, on a dry matter basis, is 20 ppmB

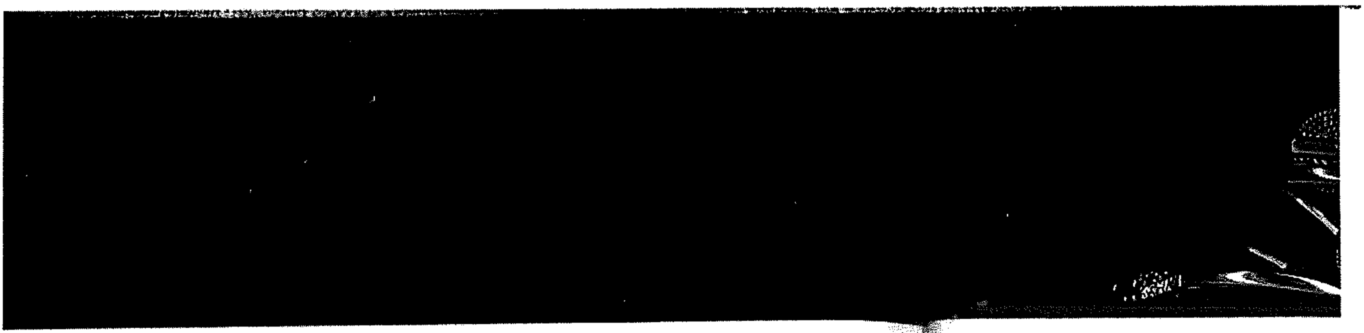


Table 9.3
Boron Deficiency Symptoms[a]

	Visible symptoms
Field crops	
Alfalfa	Death of terminal bud, rosetting, yellow top, little flowering, poor pod set and yellowing with short internodes in new growth.
Clover	Poor stands, growth and color. Reduced flowering and seed set.
Corn	Short, bent cobs, barren ears, bland stalks and poor kernel development.
Cotton	Shedding of squares and young bolls, ringed or banded leaf petioles with dieback of terminal buds, ruptures at base of squares, dark fluid exuding from ruptures, internal discoloration at base of boll, small half-opened bolls and green leaves until frost. Hard to defoliate.
Peanut	Dark hallow area in center of the nut called "hollow heart."
Soybean	Yellow leaves, chlorotic between veins, downward curling of leaf tips, crinkling of leaves, dieback of tips, no flowering and roots stunted.
Sugar beet	Yellowing or drying of leaves, cracking of the leaf midrib, brown discoloration of internal tissue ("black heart" or "hart rot"), and rotting of the crown.
Sweet corn	Elongated, watery or transparent stripes later becoming white on newly formed leaves, and dead growing points.
Tobacco	Leaf puckering and deformed buds.
Fruit crops	
Apple	Pitting, skin discolored, cracking and corking core.
Apricot	Twigs die back and fruit fails to set.
Citrus	Thickened rind, gum pockets near axis, discolored patches, die back and rosetting.
Grape	"Hen and chick" symptom, and dead main shoots.
Pear	Blossom blast, pitting, internal corking and bark cankers.
Strawberry	Pale chlorotic skin of fruit, cracking and die back.
Walnut	Die back from shoot tips, and leaf fall.
Vegetable crops	
Beet (red)	External spotting, cracking and canker.
Broccoli	Hollow stems, internal discoloration and brown curds.
Cabbage	Hollow stem, watery areas, heads hollow and stunted plants.
Carrot	Reddening of leaves and root splitting.
Cauliflower	Leaves curled, hollow stems, curds dwarfed and brown.
Celery	Stem crooked, cracked, striped brown and the heart blackened.
Lettuce	Stunted growth, discoloration and brittleness of the leaves.
Potatoes	Black spots in the interior.
Tomato	Thickened leaves, brittle leaves and the fruit fails to set.
Turnip	Hollow center or brown head, and watery areas.
Radish	Pale roots, brittle stems, watery flesh and flecked coloration.

[a] Flannery, 1985; Anon., 1994.

(Rosenfelder, 1978). In animal tissue
be about 1 ppm. Boron is not known t
in humans or animals, although one
body's ability to use calcium (Kistler
content in soils (the solid phase, not
10 ppm to more than 300 ppmB, with
of the boron in the top layers of soil
the total boron is usually not "avail
occurs as very insoluble minerals, and
on, organic material and soil particles
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clays. Adsorption is influenced by th
Thus, with reduced adsorption and i
boron "availability" occurs at pH va
boron content in the soil with plant g

There are two laboratory procedur
soils. A 1 to 2 ratio of soil to water m
and the solution separated and analyz
allowed to equilibrate for 24 hours, an
in both tests is proportional to be
correlated with optimum growth cond
soils that may have a boron deficienc
(light-textured sandy soils low in orga
or a high-organic content, alkaline soi
of boron may occur in soils derived fro
marine sediments, and some arid soils.
the western United States (Anon., 19

9.3.3.2 Application Methods

Broadcast application of boron fert
periods, or after any cutting is genera
best for heavy clay soils, irrigated cro
Sideband rates of 0.25 kgB/hectare (
(2–3 in.) to the side and below the pla
be applied through irrigation water, a
Finally, boron may be foliar applied, w
fungicides, or other nutrients during t
exceed 0.25–0.5 kgB/hectare (Segars,

9.3.3.3 Herbicidal Applications

Because of borax's relative low to
it has phytotoxicity comparable to that

9.3
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(Rosenfelder, 1978). In animal tissues the boron content has been found to be about 1 ppm. Boron is not known to have an essential biochemical function in humans or animals, although one of its functions may be a role in the body's ability to use calcium (Kistler and Helvaci, 1994). The natural boron content in soils (the solid phase, not in solution) varies from approximately 10 ppm to more than 300 ppmB, with the U.S. average at about 30 ppm. Much of the boron in the top layers of soil comes from decayed plant tissue, and the total boron is usually not "available" to the plants. Most of the boron occurs as very insoluble minerals, and boron is also complexed by, or adsorbed on, organic material and soil particles, with much of the adsorption being on fine clay fractions, particularly illite or micaceous high-iron and aluminum clays. Adsorption is influenced by the pH, with the maximum at pH 8.5–9. Thus, with reduced adsorption and increased dissolving power, the greatest boron "availability" occurs at pH values of 5.5–7. The correlation of total boron content in the soil with plant growth is very erratic.

There are two laboratory procedures for extracting "available" boron from soils. A 1 to 2 ratio of soil to water may be boiled for 5 minutes under reflux, and the solution separated and analyzed, or a soil can be saturated with water, allowed to equilibrate for 24 hours, and then filtered. The boron concentration in both tests is proportional to be that of the soil solution, and may be correlated with optimum growth conditions for different plants. Examples of soils that may have a boron deficiency are those formed from igneous rocks (light-textured sandy soils low in organic matter), acidic soils containing peat or a high-organic content, alkaline soils, and heavily irrigated soils. An excess of boron may occur in soils derived from parent rock that is rich in boron, some marine sediments, and some arid soils. Soils in both classes occur frequently in the western United States (Anon., 1980, 1995a).

9.3.3.2 Application Methods

Broadcast application of boron fertilizers before planting, during dormant periods, or after any cutting is generally preferred. Split applications may be best for heavy clay soils, irrigated crops, or for maximum economic efficiency. Sideband rates of 0.25 kgB/hectare (0.2 lbB/acre) should be placed 5–8 cm (2–3 in.) to the side and below the planting level, or 0.25–0.5 kgB/hectare may be applied through irrigation water, alone, or combined with other nutrients. Finally, boron may be foliar applied, with or without a number of insecticides, fungicides, or other nutrients during the growing season, but rates should not exceed 0.25–0.5 kgB/hectare (Segars, 1987).

9.3.3.3 Herbicidal Applications

Because of borax's relative low toxicity to man and animals, and because it has phytotoxicity comparable to that of sodium chlorate ($NaClO_3$) or arsenic trioxide (As_2O_3), higher concentrations are used as nonselective herbicides. Combinations with sodium chlorate are even superior to either ingredient alone. The maximum effectiveness, and where the fire or explosion hazard is removed, is at a borate-to-chlorate ratio greater than four. When used alone, the borates are usually applied at rates ranging from 0.24 to 0.49 kgB/m^2 (5 to 10 lbB/100 ft^2) for annuals, and the effects last for one growing season. Borates can also be combined with one or more organic herbicide, supplying a biostatic effect to reduce microbial breakdown (Sprague, 1972).

9.4 CLEANING COMPOUNDS AND BLEACHES

Borax's mild alkalinity allows it to emulsify oil and greases, and to reduce the surface tension of water, which aids in loosening dirt particles. Borax also reacts with some organics to form esters, and has a mild bactericidal action. This combination gives borax a strong but gentle cleansing action for personal use, and on many types of fabrics, surfaces, and contaminants. Borax may be combined with surfactants or abrasives for scouring powders, soap bars, or many other cleaning applications, such as in automotive cooling systems (Oberhofer, Benko and Drozd 1976). Sodium perborates are very popular as a laundry cleanser in countries that employ comparatively hot washing machine water. Either the monohydrate or tetrahydrate is employed in various formulations (Table 9.4A) at the beginning of the wash cycle. It functions both as a mild alkali and a controlled oxidizing agent, loosening dirt and gently removing (oxidizing) stains and chemically reacted contaminants from the cloth. It is more powerful than chlorine-type bleaches at temperatures above 55°C, and is less likely to harm some fabrics. About 790,000 tons/year were used in Europe and Japan in 1985 (Lyday, 1985; Raymond and Butterwick, 1992). Activators have been added, such as tetracetyl-ethylenediamine, alkyloxybenzene sulfonate, or pentaacetylglucose,

Table 9.4
Typical Composition of Several Borate Products[a]

A. Heavy-duty household detergent (wt.%)			
Sodium perborate	20–35	Optical brightner	0.1–0.5
Sodium tripoly phosphate	35–45	Amount used	7–8 g/l
Surfacant	10–15	Liquor ratio	1–5 kg/l
Sodium silicate	3–5		
B. Nickel-plating electrolyte (g/l)			
Nickel sulfate	240		
Nickel chloride	45		
Boric acid	30		

[a] Rosenfelder, 1978.

temperatures (i.e., 40°C), resulting in t
year in the late 1990s. Washing tempe
elsewhere from 60 to 40°C.

Sodium perborate is produced by re
with sodium hydroxide to form sodium
hydrogen peroxide. Stabilizers such a
usually present, and the perborate is n
(Rosenfelder, 1978). The crystals usu
are centrifuged or filtered, making the a
tive. The tetrahydrate ($NaBO_3 \cdot 4H_2O$
monohydrate ($NaBO_3 \cdot H_2O$), usually pr
15.5%. Other methods of producing so
hyperoxide ($NaHO_2$) with boric acid (
a borax solution containing sodium ca

Because the monohydrate has a
increasingly replacing the tetrahydrat
powders. Both hydrates are white cr
good storage stability. They lose o
content in a year's normal storage. T
mill and textile bleaching, as well
laundry bleaches, dishwashing powder
other special-purpose cleaners. The t
is about 2(23 g/liter) at 20°C, 3(37
monohydrate is 15 g/liter at 20°C an
form that is less soluble, but it is rare
solutions is about 10.1–10.4, and is
concentration. The monohydrate ra
tetrahydrate, and the tetrahydrate me
The monohydrate is stable at this t
oxygen is lost, and intermediate com
formed. Perborates are shipped in barr
material), and although not regarde
mixed or heated with combustibles (
and Butterwick, 1992). Other borates
laundry detergents (Anon., 1996c).

9.5 FIBERS AND COMPOSITES O

Composites of boron or boride fibers (
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modulus of elasticity. The initial applic

are used as nonselective herbicides.
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where the fire or explosion hazard is
greater than four. When used alone,
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effects last for one growing season.
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:al Borate Products^a

Optical brightner	0.1–0.5
Amount used	7–8 g/l
Liquor ratio	1–5 kg/l
240	
45	
30	

zene sulfonate, or pentaacetylglucose, to increase its effectiveness at lower temperatures (i.e., 40°C), resulting in the U.S. market growing by about 4%/year in the late 1990s. Washing temperatures are also slowly being reduced elsewhere from 60 to 40°C.

Sodium perborate is produced by reacting borax (usually the pentahydrate) with sodium hydroxide to form sodium metaborate, heating, and then adding hydrogen peroxide. Stabilizers such as magnesium sulfate and silicates are usually present, and the perborate is next crystallized, centrifuged, and dried (Rosenfelder, 1978). The crystals usually are washed at about O°C as they are centrifuged or filtered, making the active oxygen recovery almost quantitative. The tetrahydrate ($NaBO_3{\cdot}4H_2O$) has 10.5% active oxygen, while the monohydrate ($NaBO_3{\cdot}H_2O$), usually produced by drying the tetrahydrate, has 15.5%. Other methods of producing sodium perborate are by reacting sodium hyperoxide ($NaHO_2$) with boric acid (Lyday, 1985), or by the electrolysis of a borax solution containing sodium carbonate.

Because the monohydrate has a higher active oxygen content, it is increasingly replacing the tetrahydrate, particularly in "compact" washing powders. Both hydrates are white crystalline or powdery materials with a good storage stability. They lose only a few percent of active oxygen content in a year's normal storage. The perborates are also used for pulp-mill and textile bleaching, as well as in dye oxidation, tooth powders, laundry bleaches, dishwashing powder, and household surface, denture, and other special-purpose cleaners. The tetrahydrate solubility (as g/100gH_2O) is about 2(23 g/liter) at 20°C, 3(37 g/liter) at 30°C, and 30 at 60°C; the monohydrate is 15 g/liter at 20°C and 24 g/liter at 30°C. A trihydrate can form that is less soluble, but it is rarely obtained. The pH of the perborate solutions is about 10.1–10.4, and is only slightly affected by changes in concentration. The monohydrate rapidly hydrates with moisture to the tetrahydrate, and the tetrahydrate melts at about 63°C with decomposition. The monohydrate is stable at this temperature. Above 100°C the active oxygen is lost, and intermediate compounds such as the peroxyborates are formed. Perborates are shipped in barrels with an ICC yellow label (oxidizing material), and although not regarded as hazardous, they should not be mixed or heated with combustibles (Edwards and Curci, 1967; Raymond and Butterwick, 1992). Other borates can also stabilize enzymes in liquid laundry detergents (Anon., 1996c).

9.5 FIBERS AND COMPOSITES OF BORON AND BORIDES

Composites of boron or boride fibers (as mats, whiskers, chopped or continuous) in a matrix of plastics, ceramics or metals have great strength and a high modulus of elasticity. The initial applications for these advanced composites were for the military, primarily in air or spacecraft. Boron fibers in plastics offer a stiffness-to-density ratio six times that of aluminum and titanium, and they have been used in jet-engine compressor blades, wing flaps, rudders, floor beams and sheathing. They combine high temperature resistance, flexibility, and light weight with strength and ease of fabrication (Kistler and Helvaci, 1994). A boron–epoxy skin on the horizontal stabilizers of the F-14 Tomcat, F15 Eagle, and B1 bomber decreased the weight of the planes by 91 kg (200 lb) compared with equivalent parts of titanium. About 15.9 metric tons (35,000 lb) of boron filament were used, but later replaced by the less expensive carbon composites. In the space shuttle a weight saving of 137 kg (300 lb) was obtained by using boron–epoxy reinforcement. Other applications include sports equipment such as golf club shafts, tennis rackets, fishing rods and bicycle frames, for which the higher cost can be justified by superior performance.

Boron fibers are made by chemical vapor deposition on a 1-mil tungsten or carbon filament, to become 4–8 mils (100–200 μ) thick. Boron trichloride is deposited on the wire at 1300°C, and reduced by hydrogen: $2BCl_3 + 3H_2 \rightarrow 2B + 6HCl$. The filament, with a density of 2.3 (on carbon) to 2.6 (on tungsten), is processed into a tape held in position by semicured resin. Wide tapes 1.2 m (48 in.) across use a scrim cloth for support. The fibers are compatible with the resin (but not metal matrices), with the amount controlled to 50 vol%. Boron filaments may also be interwoven into fabrics with polyester, glass, graphite, Kevlar, and other reinforcements to provide specific mechanical and physical properties. They can also be bonded at 5000 psi and 500°C to aluminum alloy foils. Strength in several directions is supplied by cross-plies of the filaments. Boron epoxy composites have tensile strengths of up to 230,000 psi, and compressive strengths of 360,000 psi, both superior to those of other materials such as fiber glass, silicon carbide, aluminum oxide, and Aramid fibers. High-strength graphite does have the same tensile strength, but less than 50% of boron's compressive strength (Lyday, 1985).

9.6 FLAME RETARDANTS

Boric acid, borax and pentahydrate have been used to make inexpensive cellulose insulation material. Shredded newspaper can be used as blown-in insulation for attics and walls, but has a lower insulation value than fiberglass, and in time compresses to lose much of this effect. However, if the cellulose is treated with a borate solution (primarily boric acid) and then well dried before it is installed, this problem is considerably reduced, and it becomes reasonably fire resistant, toxic to bacteria (anticomposting), and unpalatable for rats, mice, and insects. The borates react with the hydroxyl groups of the cellulose to form a very thin but unifor
most insulations of this type, however,
mixed with the newspapers (i.e., 40-wt
3% boric acid) as they are shredded i
Its insulating effectiveness is thus sor
flammability properties, since the bor
which absorbs heat and lowers the tem
a glassy substrate that inhibits burning

Wood particle chips also may be m
formaldehyde resin is added to form fl
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flameproof cotton mattresses. In man
($2ZnO{\cdot}3B_2O_3{\cdot}15H_2O$) has a greater fla
To produce it, zinc oxide is reacted w
form a paste, and then dewatered by c
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formation of char and inhibits the rel
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9.7 FUELS

Boron and its hydrides have the highe
of all the elements, 25,120 compared w
causing it to be considered as a fuel
cost and harmful end products have p
(B_2H_6, a gas), pentaborane (B_5H_9, a liq
were all considered. As a totally differe
ophenathrene is a highly effective anti
and sodium borohydride has been use
fuel by the U.S. Navy. As little as 1
compounds is used in sterilizing hydro
corrosion and prevent microorganis
(Anon., 1996a). Other fuel-related use
as catalysts in petroleum refining, an
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averages about 75 ppmB, and 10,500 m
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spacecraft. Boron fibers in plastics
that of aluminum and titanium, and
ressor blades, wing flaps, rudders,
high temperature resistance, flexi-
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por deposition on a 1-mil tungsten
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ily boric acid) and then well dried
siderably reduced, and it becomes
(anticomposting), and unpalatable
act with the hydroxyl groups of the

cellulose to form a very thin but uniform borate film that is quite stable. With most insulations of this type, however, the boric acid or pentahydrate is dry-mixed with the newspapers (i.e., 40-wt% paper, 7% borax pentahydrate, and 3% boric acid) as they are shredded in a hammermill (Rosenfelder, 1978). Its insulating effectiveness is thus somewhat reduced, but it retains its low flammability properties, since the borates promote the formation of water, which absorbs heat and lowers the temperature during heating. It later forms a glassy substrate that inhibits burning.

Wood particle chips also may be mixed with boric acid before the urea–formaldehyde resin is added to form flame-resistant particleboard. The particle- or pressboard will give off little smoke or flame when heated, and "afterglow" is prevented. Similarly, boric acid can be milled with cotton to flameproof cotton mattresses. In many fireproofing applications zinc borate ($2ZnO \cdot 3B_2O_3 \cdot 15H_2O$) has a greater flame retardancy than borates used alone. To produce it, zinc oxide is reacted with just enough boric acid solution to form a paste, and then dewatered by centrifuging, dried in a gas furnace, and ground. The zinc borate does not affect the color of plastics, and is only slowly affected by high temperatures. When heated, zinc borate promotes the formation of char and inhibits the release of combustible material (Lyday, 1985). The addition of aluminum trihydrate to the zinc borate forms a synergistic mixture more effective than either material alone, particularly in reducing the fire's smoke.

9.7 FUELS

Boron and its hydrides have the highest heat of combustion per unit weight of all the elements, 25,120 compared with 18,500 Btu/lb for aviation gasoline, causing it to be considered as a fuel for space or aircraft. However, their cost and harmful end products have prevented commercialization. Diborane (B_2H_6, a gas), pentaborane (B_5H_9, a liquid), and decaborane ($B_{10}H_{14}$, a solid) were all considered. As a totally different application, 10-hydroxy-9,10-boroarophenathrene is a highly effective antioxidant additive for hydrocarbon fuels, and sodium borohydride has been used for the same purpose in jet bomber fuel by the U.S. Navy. As little as 1 gal/5000 gal of certain organoboron compounds is used in sterilizing hydrocarbon fuel storage systems to reduce corrosion and prevent microorganisms from growing and clogging filters (Anon., 1996a). Other fuel-related uses are boron trichloride or fluoride used as catalysts in petroleum refining, and boron–nickel catalysts (resistant to sulfur poisoning) used in converting carbon monoxide to fuels. Finally, coal averages about 75 ppmB, and 10,500 metric tons/year of boron ends up in fly ash or enters the atmosphere (Lyday, 1985).

9.8 GLAZES, FRITS, AND ENAMELS

One of the earliest uses of borates, and one that is still important even though it does not consume much borax, is the production of glazes and frits to impart color and texture, as well as heat, chemical, or wear resistance to appliances, ceramics, and tile. Borax assists in the production of smooth, hard, resistant, blemishless, and craze-free ceramic surfaces. Early in the eighteenth century ceramic enamels consisting of a low-melting borax glass to which pigments were added began to be used, and ceramic painting techniques became quite sophisticated. With pigmented enamels, variations in tint could be achieved by laying on the color more or less thickly (impasto technique), and the style of overglaze enamels came to resemble oil painting. New colors were developed, and new flux compositions for enamels that contained bismuth oxide and borax additions to the basic lead or lead alkali silicates evolved, causing the decorating process to become increasingly complex. One of the earliest pigments was "Egyptian blue," a copper–calcium silicate manufactured by grinding together quartz, malachite, lime and borax (as a "flux"). This technique is still in use today, with the ingredients intimately mixed and then heated to form a liquid. After the melt is cooled the excess borate is dissolved in acid, and the frit is milled to obtain the fine particles required for effective light scattering (Kingery and Vandiver, 1986).

Most boron compounds are soluble to some extent, so the 3–15% B_2O_3 desired in most glazes (Table 9.5) normally is used in this insoluble glass, or fritted form. The frits melt easily, and the boron intensifies the coloring effect.

Table 9.5

Examples of Borate-Containing Ceramic Frits (wt%)

	Typical 1000–1020°C M.P.[a]	Leadless tile frit[b]	Lead borosilicate[b]	Corrosion-resistent glaze[c]
B_2O_3	10.8	13	21	3.7–7.3
SiO_2	39.5	63	12	1–5 (spodumene)
Al_2O_3	19.8	8	—	—
CaO	17.9	8.3	—	5–15
Na_2O	10.5	6.6	—	11.7–17.6
K_2O	1.5	—	—	5–15 (Mo ore)
ZnO	—	1.1	—	0.5–2 (Co_2O_3)
Pb	—	—	67	0.5–2 (NiO)

[a] Fournier, 1977.
[b] Rosenfelder, 1978.
[c] Wang and Shao, 1990.

Very soft (low melting point) borax frits
of 3% bentonite for raku ceramics. Bor
in salt-glazing, although it will slightly
property of boric oxide that makes it ve
in amounts less than 10% it has a neg
helps with craze resistance (Fournier, 19
glazes heal over and melt more smooth
Commercial tableware formerly was gla
because of their smoothness, freedom fr
range, and good wearing properties (R
being replaced by high-borate, no-lea
problems.

Vitreous (porcelain) enamel is made
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products a glass-like surface with excel
resistance. Wall and floor tile also may
that allows a wide range of decoration
containing glazes ("glass") are employ
for corrosion protection (Wang and Sh

9.9 MEDICINE

Boric acid and sodium borate are mild
bacteria, and boric acid has long been us
boron compounds inhibit tumor growth,
highly effective in killing parasites such
compounds such as the closo icosahedral
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Fairchild and Brugger, 1992).

In other medical applications, some b
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lly is used in this insoluble glass, or
boron intensifies the coloring effect.

5
ıg Ceramic Frits (wt%)

d borosilicate[b]	Corrosion-resistent glaze[c]
21	3.7–7.3
12	1–5 (spodumene)
—	—
—	5–15
—	11.7–17.6
—	5–15 (Mo ore)
—	0.5–2 (Co_2O_3)
67	0.5–2 (NiO)

Very soft (low melting point) borax frits (850°C) can be used with the addition of 3% bentonite for raku ceramics. Borax also can be added to salt to assist in salt-glazing, although it will slightly change the glaze characteristics. A property of boric oxide that makes it very useful in earthenware glazes is that in amounts less than 10% it has a negative coefficient of expansion, which helps with craze resistance (Fournier, 1977). Small amounts also help in making glazes heal over and melt more smoothly, and in forming a tougher surface. Commercial tableware formerly was glazed with lead oxide–boric oxide frits because of their smoothness, freedom from pits or other blemishes, long firing range, and good wearing properties (Rhodes, 1975). However, they are now being replaced by high-borate, no-lead mixtures because of lead's toxicity problems.

Vitreous (porcelain) enamel is made by a single or two-coat dipping, spraying, or electrostatic process with a borate glaze to give appliances and other products a glass-like surface with excellent thermal, corrosion, and abrasion resistance. Wall and floor tile also may use a highly reactive borosilicate glaze that allows a wide range of decorations (Rosenfelder, 1978). Molten borax-containing glazes ("glass") are employed in coating metal vessels and pipes for corrosion protection (Wang and Shao, 1992).

9.9 MEDICINE

Boric acid and sodium borate are mild antiseptics that inhibit gram-negative bacteria, and boric acid has long been used as an eye wash. Some heterocyclic boron compounds inhibit tumor growth, while borax and some of its ores are highly effective in killing parasites such as oncomelania (Xu, 1990). Organic compounds such as the closo icosahedral anion $[^{10}B_{12}H_{11}SH]^{2-}$ (that can attach to tumorous tissue, and with a high ^{10}B content) are injected into cancer patients and then exposed to a high-neutron source. This generates intense energy in a very localized area, destroying the tumor (Greenwood, 1991). In one study 5 years after the boron treatment 33% of the patients were alive, which is an improvement over other therapy (Lyday, 1985). The short-range alpha particles from the ^{10}B and low-energy neutrons have also been used for microsurgery in previously inoperable areas of the brain (Barth, Soloway, Fairchild and Brugger, 1992).

In other medical applications, some boron compounds reduce serum cholesterol and other harmful proteins. Potassium borohydride (KBH_4) has been used to manufacture hydrocortisone, prednisone, and prednisoliene (corticosteroids used in arthritis therapy), and in the synthesis of vitamin A. Sodium borohydride ($NaBH_4$) assists in the manufacture of hormones. Sodium and potassium borates are frequently used in face creams, lotions, dusting powder, ointments, hair preparations, mouth washes, and emulsifiers in medical or cosmetic formulations (Kistler and Helvaci, 1994).

9.10 METALLURGY

The addition of 0.001% to 0.003% boron to steel reduces the amount of nickel, chromium, or molybdenum required in many alloys. The boron is added in the form of 10–17% B ferroboron pellets produced by the aluminothermic reduction of a borate compound (Zambrano, 1985). Because boron is rapidly oxidized it is the last material added to the molten steel, and usually aluminum is also added to react with the steel's oxygen instead of the boron. Boron strengthens high-performance, low-alloy steels by precipitating certain carbides, and by its effect on crystal structure. Being small, boron tends to locate in the interstitial space between the metal atoms of the alloy, causing it to be harder and stronger than the parent metal. It is most effective in low-carbon and fine-grained steels. About 1,000,000 tons/year of boron-containing carbon steels and 300,000 tons/year of boron alloy steels were produced in United States in 1980. The largest tonnage was in Cr and Cr-Mo types (90,000 tons/year each) and carbon steel plate (200,000 tpy). A typical application was with cold-forged parts that subsequently were to be heat treated, since they do not require all of the heat-treating steps needed by other alloys, and develop better machining characteristics. Steels containing less than 4.75% B can be forged, and steels with up to 6% B can be cast. In some cases, however, boron causes poorer surface characteristics, less tolerance to heat treating, loss of hardening ability during carburizing, and in excess, brittleness (Porter, 1980).

Boron master alloys (0.1–2.5% B) are also used in aluminum and titanium smelting as grain refiners (crystal nucleating agents to form a fine, uniform structure; Sussman and Evans, 1985). An iron–boron–silicon alloy sprayed on a cold object, or a rapidly cooled melt produces an amorphous glass–metal (Metglas) coating superior to sprayed metals in strength (up to 600,000 psi), magnetism (low-magnetic hysteresis), and corrosion resistance. It is also 85% more efficient in energy transformers than stainless steel. An iron–boron–rare earth (neodymium and praseodymium) alloy is an excellent magnet for automobile starter motors, stereo speakers, computer disk drives, and telecommunication printers. Boron can also be sprayed or diffused onto metals (boronizing) to produce a tough corrosion- and abrasion-resistant surface coating. Boron alloy journal pins used in oil-drilling bits have a 15% increased weight-bearing capacity, and can remain in the drill hole up to three times longer, thereby reducing round-trip time for bit replacement. Many electroplating-bath compositions include boron chemicals as buffers, cleansers, and agents to reduce the deposit's pitting and porosity (Table 9.4B). There are a wide

variety of other metallurgical applicati
the References.

9.11 NUCLEAR APPLICATIONS

In nuclear reactors the fission of radic
variety of alpha and beta particles, g
effective materials for shielding the neut
gen, lithium, polyethylene and water. M
secondary gamma rays, which then requi
Boron is unique in its ability to absorb
soft gamma ray and an easily absorbec
effectively absorbed by dense materials
the alpha and beta particles are stopped l
has most of the desired neutron-captur
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dimethyl ether complex $[(CH_3)_2O\cdot BF_3]$
was 45 m (148 ft) tall, metal-packed, a
Boron trifluoride–dimethyl ether enrich
of the column, and >90% ^{10}B collected at
as potassium fluoborate and convertec
elemental boron.

Boron carbide also is a widely used
as pellets encapsulated in stainless stee
bricks or a core between cast aluminu
ability and high melting point makes the
of spent fuel elements possible. Other
steel containing a minimum of 2% B, a
slabs that can be machined) is used as
colemanite) can also be added to concr
their ability to absorb neutrons (Tarase
vist, 1990; Yarar and Bayuelken, 1994).

9.12 MISCELLANEOUS

There is a very wide range of other ap
boron compounds are useful in organic
to control the oxidation of cyclohexane
and is a buffer during the dyeing of ny
in the production of photopolymer-cove
of printed circuits, and boron trifluoric

ashes, and emulsifiers in medical or
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oxygen instead of the boron. Boron
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sity (Table 9.4B). There are a wide

variety of other metallurgical applications for boron and borates, as seen in the References.

9.11 NUCLEAR APPLICATIONS

In nuclear reactors the fission of radioactive material produces heat and a variety of alpha and beta particles, gamma rays and neutrons. The most effective materials for shielding the neutrons are boron (especially ^{10}B), hydrogen, lithium, polyethylene and water. Most of the shielding materials produce secondary gamma rays, which then require heat removal and further shielding. Boron is unique in its ability to absorb thermal neutrons and produce only a soft gamma ray and an easily absorbed alpha particle. The gamma rays are effectively absorbed by dense materials such as lead, steel or concrete, while the alpha and beta particles are stopped by thin sheets of metal. The ^{10}B isotope has most of the desired neutron-capture capability, and may be separated by ion exchange or the fractional distillation of boron trifluoride (BF_3) or its dimethyl ether complex [$(CH_3)_2O{\cdot}BF_3$]. The distillation column in one plant was 45 m (148 ft) tall, metal-packed, and operated under a partial vacuum. Boron trifluoride–dimethyl ether enriched in ^{11}B was obtained at the bottom of the column, and >90% ^{10}B collected at the top. The ^{10}B was then precipitated as potassium fluoborate and converted to B_2O_3, boric acid, ferroboron or elemental boron.

Boron carbide also is a widely used neutron-absorbing material available as pellets encapsulated in stainless steel tubes for use in control rods, or as bricks or a core between cast aluminum for shielding. Its neutron-shielding ability and high melting point makes the handling, transportation, and storage of spent fuel elements possible. Other reactor control rods are made from steel containing a minimum of 2% B, and 1% B polyethylene (as bricks and slabs that can be machined) is used as a shielding material. Borates (such as colemanite) can also be added to concrete or structural ceramics to increase their ability to absorb neutrons (Tarasevich, Isaeva, Kuznetsov and Zhenzhivist, 1990; Yarar and Bayuelken, 1994).

9.12 MISCELLANEOUS

There is a very wide range of other applications for borate products. Many boron compounds are useful in organic synthesis. Boric acid is used in nylon to control the oxidation of cyclohexane to cyclohexanol and cyclohexanone, and is a buffer during the dyeing of nylon carpet. Boron tribromide is used in the production of photopolymer-covered silicon chips for the manufacture of printed circuits, and boron trifluoride is used in the production of butyl

Table 9.6
A Partial List of Borate Uses[a]

Abrasives
Adhesives
Alloys
Antiseptics
Bactericide
Bleaches
Boron filaments
Buffering
Catalysts
Cement
Ceramics
Cleaning compounds
Corrosion inhibitor
Cosmetics
Detergents
Disinfectants
Dystuffs
Electrical insulation
Electrolytic refining
Electronic components
Electroplating
Enamels
Enzyme stabilization
Eye wash
Fertilizer
Fiber optics
Fiber glass
  Textiles
  Insulation
  Composites
  Structures
Fire, flame retardants
Fluxes
Frits
Fuel additives
Fuel (high energy)
Fungicides
Glass
Glazes
Goldsmithing
Hair creams
Herbicides
Hydraulic fluids
Insecticides
Leather tanning
Lubricating oil additives
Magnets
Medical applications
Metallurgical applications
Metal hardening
Nuclear applications
Nylon
Organic synthesis
Paints and pigments
Pharmaceuticals
Photography
Plastics
Plating solutions
Polymer stablisers
Pulp bleaching
Purifying speciality chemicals
Pyrotechnics
Refractories
Shampoos
Soil sterilant
Swimming pool sanitizer
Taxidermy
Textile finishing
Textile dyes
Transformers
Waste treatment
Wax emulsifier
Wire drawing
Wood preservative

[a] Anon., 1996c; numerous others.

rubber from isobutene. Boron tribromide and trichloride are used as catalysts in literally dozens of other organic reactions. Boron tetrahydrofuran and borane-methyl sulfide can reduce amides to amines, and carboxylic acids, aldehydes, and ketones to alcohols. Boric acid is used in the production of quinizarin by the reaction of phthalic anhydride and chlorophenol, and in the separation of terpene alcohols. Boric acid reacted with phenol, and the resulting ester treated with paraformaldeh
fumery chemical salicylaldehyde. Sodium
agent, such as with carboxylic acids, in o

Zinc borate and disodium octaborate t
preservatives because of their antimicrobi
1996b). The treatment is by a brief immers
aqueous borate solutions. The borates d
and subsequent seasoning, leaving the wc
tains its original color and odor, and th
animals. The two borate compounds m
before the addition of the resin and w
composites (Laks, 1995). An unusual ap
periodic spraying of an octaborate solut
sunken ships being raised and reconstruct
by the wharf-borer beetle (Greenwood,

Borax is highly soluble in ethylene g
formulations, brake fluids, and hydraulic
ferrous metals. Aqueous solutions have
other diesel coolants. Boron-doped silico
transistors, and microcircuitry. A boron
erbium dodecaboride is used to trap sol
use boron as a bond coat. Borates may alsc
of chlorine as a swimming pool sanitizer (
uses for borates, some of which are indica

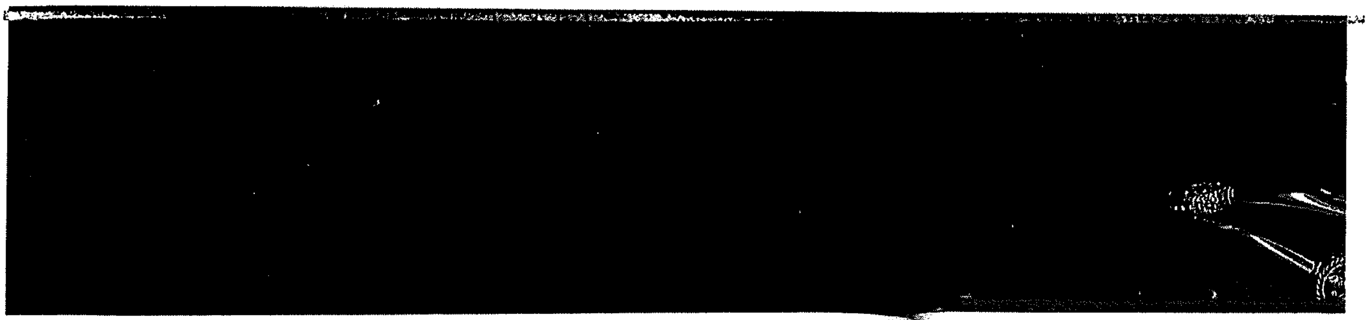
9.6
Borate Uses[a]

- Glass
- Glazes
- Goldsmithing
- Hair creams
- Herbicides
- Hydraulic fluids
- Insecticides
- Leather tanning
- Lubricating oil additives
- Magnets
- Medical applications
- Metallurgical applications
- Metal hardening
- Nuclear applications
- Nylon
- Organic synthesis
- Paints and pigments
- Pharmaceuticals
- Photography
- Plastics
- Plating solutions
- Polymer stablisers
- Pulp bleaching
- Purifying speciality chemicals
- Pyrotechnics
- Refractories
- Shampoos
- Soil sterilant
- Swimming pool sanitizer
- Taxidermy
- Textile finishing
- Textile dyes
- Transformers
- Waste treatment
- Wax emulsifier
- Wire drawing
- Wood preservative

e and trichloride are used as catalysts
actions. Boron tetrahydrofuran and
les to amines, and carboxylic acids,
ric acid is used in the production of
hydride and chlorophenol, and in the
cid reacted with phenol, and the resulting ester treated with paraformaldehyde is used to manufacture the perfumery chemical salicylaldehyde. Sodium borohydride is a powerful reducing agent, such as with carboxylic acids, in organic synthesis (Gribble, 1996).

Zinc borate and disodium octaborate tetrahydrate are widely used as wood preservatives because of their antimicrobial and insecticidal properties (Anon., 1996b). The treatment is by a brief immersion of the timber in hot concentrated aqueous borate solutions. The borates diffuse into the wood during the dip and subsequent seasoning, leaving the wood fully preserved. The wood maintains its original color and odor, and there is no toxicity hazard to man or animals. The two borate compounds may also be mixed with wood chips before the addition of the resin and wax for hot pressing to form wood composites (Laks, 1995). An unusual application of this treatment is in the periodic spraying of an octaborate solution on the water-logged timbers of sunken ships being raised and reconstructed to prevent the wood's destruction by the wharf-borer beetle (Greenwood, 1991).

Borax is highly soluble in ethylene glycol and is useful in car antifreeze formulations, brake fluids, and hydraulic systems as a corrosion inhibitor for ferrous metals. Aqueous solutions have replaced chromates in railroad and other diesel coolants. Boron-doped silicon is used in diodes, semiconductors, transistors, and microcircuitry. A boron coating of yttrium hexaboride and erbium dodecaboride is used to trap solar radiation. Teflon cooking utensils use boron as a bond coat. Borates may also be used to improve the performance of chlorine as a swimming pool sanitizer (Anon., 1995b). There are many other uses for borates, some of which are indicated in Table 9.6 and the References.



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