# BORON

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Boron compounds are used in a variety of products and manufacturing processes. Borax is a white crystalline substance chemically known as sodium tetraborate deca-hydrate ($Na_2B_4O_7 \cdot 10H_2O$). Boric acid ($B_2O_3$) is a white, colourless, crystalline solid sold in technical national formulary and special quality grades as granules or powder. Boron oxide is a hard, brittle, colourless solid resembling glass that is ground and marketed most often under the name anhydrous boric acid. Elemental boron is a dark brown powder in the amorphous form and a yellowish-brown, hard, brittle solid in the monoclinic crystalline form. Boron is marketed in grades from 90% to 99% purity.

Ferroboron is a name given to a variety of boron-iron alloys containing 0.2% to 24% boron used primarily to introduce small quantities of boron into specialty steels. In the boron hydride series are diborane, a gas; pentaborane, a liquid; and decaborane, a solid.

Boron nitride, a soft, white, highly refractory solid resembling graphite, can withstand significant oxidation to temperature up to 650°C. Boron nitride produced in fibrous form are equivalent to glass fibres in strength and modules of elasticity, but is lighter in weight and more resistant to high temperature. When subjected to extremely high pressure and temperature, boron nitride forms cubic crystals that rival the hardness of diamond.

Boron carbide, produced by reacting carbon and boric acid at 2,300ºC, is a highly refractory material and one of the hardest substances known. Most commonly used for both abrasive and abrasion-resistant applications as well as nuclear shielding, boron carbide is marketed in technical and high-purity grades.

Only a few of the many minerals that contain boron are commercially valuable. Substances containing boron oxide are commonly known as borates. The major borate minerals being produced are borax, colemanite, datolite, kernite, probertite, szaibelyite, tincal and ulexite. A list of the common minerals and compounds of boron are included in Table 1. The largest deposits being mined are sedimentary rocks formed during the Cenozoic Era as a result of evaporation of geothermal springs. Major deposits occur in the South America, Turkey and the US in the form of ores and brines.

At the Kramer deposit in California, US, and the Kirka deposit in Ankara, Turkey, open-pit mining methods are used to exploit two very large deposits of high-grade beds of tincal. South American borates are primarily ulexite but deposits of tincal and howlite also are mined. In Russia, datolite, a calcium borosilicate and szaibelyite, a magnesium borate, are mined in low-grade deposits. China also produces borates from low-grade deposits of brines and szaibelyite (ascharite). A list of producing countries and production are included in Table 2.

**Consumption and uses**

Fibre-glass insulation and glass fibre primarily used as reinforcement for plastics were the largest consuming industries. Glass fibre for thermal insulation, primarily used in new construction, was the largest area of demand for borates. Cellulosic insulation continued to be used in new homes and weather-proofing older homes from the cold. Manufacturing high-tensile-strength glass fibre material continued to have strong demand. The nonconductive and low dielectric properties of high-strength glass reinforced materials make them transparent to radar and valuable for 'stealth' applications in the military.

Carbon-fibre-reinforced resins can be stronger than metals and, with higher modulus, more stable. Although composites can be 10 times more expensive than typical aerospace-grade aluminium, the flexibility they offer in design and consolidation of parts allows large, complex structures to withstand high temperatures, and have made them the material of choice for a variety of aerospace applications. A list of end uses and reported consumption in the US for 2002 is included in Table 3.

Consumption of borates in borosilicate glasses remained a major end use in 2003. Boron added to glass in amounts of between 4% and 15%, reduces the viscosity of the melt, assists with fibre formation during processing, allows for improved specific optical properties, increases resistance to aqueous or chemical attack, enhances certain mechanical properties, and reduces the thermal-expansion coefficient and thermal-shock resistance of the product. Boron oxide provides a range of favourable benefits to the melting of final glass properties. Addition of 1% of boron oxides reduces the melting temperature of the glass by 20ºC.

Special glass can be divided into five types, as follows: borosilicate glass (10% to 13% boron oxide); opal glasses (0% to 13% boron oxide); potassium glasses (0% boron oxide); glass ceramics (0% boron oxide), and fibreglass for reinforcing (0% to 9% boron oxide). Alumina contained in glass contact refractories can have a positive effect to prevent corrosion, but in speciality glasses can generate bubbles. The use of zircon refractories can present an alternative in the manufacturing process if crystallographic stability is considered.

Boron was used in the manufacture of frits and glazes on ceramic tiles and cast iron fixtures to increase their strength, scratch resistance, and chemical resistance. These products can be found in wall and floor tiles, tableware, and porcelain and enameled appliances.

Boron compounds continue to find applications in the manufacture of biological growth control chemicals for use in water treatment, algaecide, fertilisers, herbicides, and insecticides. Boron can be applied as a spray or incorporated in herbicides, fertilisers and irrigation water. Boron is an essential plant micronutrient and, for certain crops such as corn, boron fertilisers can quadruple corn yields.

A growing and important use of zinc borate, ammonium pentaborate, and boric oxide is as fire retardants in the plastics industry. Zinc borate is of commercial importance because it is water insoluble and does not release water until heated to 290ºC. There are advantages in partially replacing alumina trihydrate (ATH), used as a halogen-free fire retardant in ethylene-vinyl acetate polymers, with zinc borate. Partial replacement of ATH with zinc borate results in a tenfold increase of char and changeover from the glowing to smoldering combustion mode.

Detergent bleaching systems are used primarily in Western Europe and use sodium perborate as an oxygen-carrier. A detergent is a synthetic cleansing agent resembling soap in its ability to emulsify oil and hold dirt. It contains surfactants, which do not precipitate in hard water, and may also contain protease enzymes and whitening agents. About 75% of sodium borate consumption in Europe is in the detergent market. Stricter regulations for boron levels in drinking water in the European Union are to take effect by 2013 and are expected to decrease the consumption of boron in detergents. Consumption of sodium borate in the US is about 10% of European usage and therefore does not contribute significantly to water quality.

**New applications**

Millennium Cell has developed a proprietary process called Hydrogen on Demand™ using water and sodium borohydride. Hydrogen from the system can be used in a fuel cell or fed directly to an internal combustion engine. The car would have advantages to gasoline engines in that the fuel is emission-free, can be easily stored and transported in lightweight plastic tanks at normal temperatures and pressures, and is neither poisonous, flammable, nor explosive. Millennium also has designed a boron-based longer-life battery.

Boron-doped diamond, which is normally a semiconductor, turns into a superconductor at low temperatures. The synthetic diamond containing about 3% boron becomes a superconductor at 4 K. Because it can carry electricity without resistance, superconducting diamond might be useful for making improved power storage devices or electrical motors.

**Production**

The US was the largest producer of boron compounds. US Borax Inc, a wholly- owned subsidiary of UK-based, Rio Tinto plc, mines borate ores at Boron, CA. The Miocene Age ore is processed into sodium borate or boric-acid products in the refinery complex adjacent to the mine. Primary boric acid production is about 260,000 t/y.

Additional engineering and equipment upgrades are planned to increase annual capacity by 80,000 t by 2004. An onsite plant also produces anhydrous sodium borate and boric oxide. Refinery products are shipped by railcar or truck to North American customers, or the US Borax Wilmington, CA facility at the Port of Los Angeles for international distribution. In addition to its refinery and shipping terminal in Wilmington, US Borax has its global headquarters in Valencia, CA, and its Owens Lake trona mine supplies raw material to the Boron, Ca, refinery. The Owens Lake operations enable the company to ensure control of the trona supply which is used to reduce scaling in the processing of borates.

IMC Chemicals, a subsidiary of IMC Global Inc, produced borax, soda ash and related products from Federal and private land from Searles Lake, CA. Searles Lake is a closed structural basin filled with alluvium and lacustrine evaporites of Quaternary age. The flat area overlies two separate salt structures that contain borates and other salts in the form of brines. In March 2004, IMC Global sold IMC Chemicals. Sun Capital Partners Inc, of Boca Raton, Florida, purchased the soda ash and boron chemicals operations in Searles Valley. As a result of the sale, the company's name changed to Searles Valley Minerals Inc. A specialty borates plant in Lardellero, Italy, was purchased by Tuscan Stars GSA, LLC and certain of its affiliates. IMC Global retained a 19.9% equity interest in the IMC Chemical entities.

American Borate Co continued to produce from the Billie mine, an underground operation in Death Valley National Park. The deposit is located in thick Furnace Creek Formation of Pliocene Epoch age, and contains colemanite, probertite and ulexite. The ore was processed by flotation and calcining at a plant in Amargosa, Nevada. Production was shipped overseas, primarily to Asia.

About 50% of US production of boron compounds is exported. The value of boric oxide contained in minerals and compounds for 2003 was estimated by the USGS at US$475 million.

In Turkey, government-owned Eti Bor (a subsidiary of Eti Holding, Inc, formerly known as Eti Bank) announced that a 100,000 t/y boric-acid plant is being constructed at Emet and is expected to be operational in 2004. Production capacity of refined borates was reported as 560,000 t/y in 2001. Eti Holding operated processing plants at Bandirma and Kirka. Borate ores in Turkey occur in a series of upper Pliocene lacustrine sediments. Boron mineralisation consists of colemanite, colemanite-ulexite, and tincal in deposits of Tertiary age. Deposits of colemanite are found in Oligocene deposits of western Kütahya, Bigadiç-Balikesir, and Mustafa Kemalpa-Bursa. Ulexite is produced in the Bigadiç region of Balikesir. Tincal is produced in Eskisehir, Kirka region. In Emet, colemanite is ground, washed, and transported by truck to loading facilities at the port of Bandirma on the Sea of Marmara. A large tincal deposit at Kirka is the only commercial sodium-borate deposit known in Turkey. The ore occurs in a Tertiary cyclic sequence of carbonate to borate to carbonate.

The ore is processed at the mine site then transported by truck and rail to shipping facilities at Izmir. Turkey was the world's largest producer of boron ore in 2003, with a reported capacity of 1.8 Mt/y. Down-stream derivatives are produced and sold internationally from a plant at Bandirma. Most of the products are exported, only about 7% being consumed in Turkey. Exports are mainly to Europe (40%) and North America (25%).

The world supply of borates is dominated by Rio Tinto Borax and Eti Holdings. Together, they provide over half of the world's supply. Under Turkish law, all existing mining titles are owned by Etibank. However, newly discovered deposits of boron minerals can be operated by new title holders. The Turkish Government plans to establish a Boron Research Institute to develop Turkey's exports of processed boron. At present, about 11% of waste is boron oxide. Improved technology could recover the borate and protect the environment from the toxicity of the boron waste to plants and fish.

The borates from South America are primarily ulexite and are mined at altitudes of about 4,600 m between latitudes 15° and 18° south. Some 35 playas are known to contain borates in Argentina, Peru, Bolivia and Chile.

Borax Argentina SA (a subsidiary of Rio Tinto plc) was the country's leading producer of borates and exported large quantities to the US. Borax Argentina mined borates at three deposits—Tincalayu and Sijes in Salta Province and Porvenir in Jujuy Province. The Tincalayu mine is Argentina's largest open-pit operation. About 100,000 t/y of ore is trucked from the mine to a rail terminal at Pocitos, 120 km north of Tincalayu, and loaded on trains of 11 cars, each with a 30-t capacity. A drilling and expansion programme has verified a new borate resource.

In Chile, Química del Bórax (Quiborax), Rio Grande, produces about 25,000 t/y of ulexite at the Capina Mine. Quiborax also has a 35,000 t/y boric acid plant at El Aguila, 60 km from Arica and intended to invest US$7 million between 2003 and 2008 in modern technology and plant automation. Quiborax also owns the Surire ulexite deposit in northern Chile. Production capacity is 2,000 t/d, or 350,000 t/y during the 7-month production period.

In China, boron deposits of szaibelyite, a magnesium borate, are located in the provinces of Hunan, Jilin, and Liaoning. Total capacity is estimated at 870,000 t/y. Most of the ore is refined into boron derivatives, primarily borax decahydrate for sale on the domestic market. Production capacity of decahydrate is estimated at 350,000 t/y.

**Outlook**

Increases in energy costs have decreased expectations of a strong global economy. As a result of the weak economy, low interest rates have increased demand in the housing market. Historically, the housing market has been a large user of boron minerals, notably for fibreglass insulation. Increased usage of ceramic tiles in kitchens and bathroom will keep consumption in the enamels, frits, and glazes end use high.

Demand as a fertiliser will remain high, whereas usage in soaps and detergents will decrease as concern for water quality limits usage. Some cars have been replacing metal parts with reinforced fibreglass plastic parts to reduce weight and increase the efficiency of gasoline consumption. The demand for energy-efficient non-polluting cars could cause increased demand for borates in fuel cells. A prototype car using a sodium borohydride fuel cell was displayed during 2003. The vehicle had a range of 480 km and a top speed of 130 km/h. A prototype battery for titanium diboride has potential to be better than traditional zinc batteries. Titanium diboride batteries could last twice as long as traditional carbon-zinc batteries.

**Table 1**
**Boron minerals of commercial importance**

| | Boron oxide ($B_2O_3$) | |
|---|---|---|
| Mineral[1] | Chemical composition | Weight % age |
| Boracite (stassfurite) | $Mg_6B_{14}O_{26}C_{12}$ | 62.2 |
| Colemanite | $Ca_2B_6O_{11}{\cdot}5H_2O$ | 50.8 |
| Datolite | $CaBSiO_4OH$ | 24.9 |
| Howlite | $Ca_2B_5SiO_9(OH)_5$ | 44.5 |
| Hydroboracite | $CaMgB_6O_{11}{\cdot}6H_2O$ | 50.5 |
| Kernite (rasortie) | $Na_2B_4O_7{\cdot}4H_2O$ | 51.0 |
| Priceite (pandermite) | $CaB_{10}O_{19}{\cdot}7H_2O$ | 49.8 |
| Probertite (kramerite) | $NaCaB_3O_9{\cdot}5H_2O$ | 49.6 |
| Sassolite (natural boric acid) | $H_3BO_3$ | 56.3 |
| Szaibelyite (ascharite) | $MgBO_2OH$ | 41.4 |
| Tincal (natural borax) | $Na_2B_4O_7{\cdot}10H_2O$ | 36.5 |
| Tincalconite (mohavite) | $Na_2B_4O_7{\cdot}5H_2O$ | 47.8 |
| Ulexite (boronatrocalcite) | $NaCaB_5O_9{\cdot}8H_2O$ | 43.0 |

[1]Parentheses indicate common names.

**Table 2**

**Boron minerals: world production, by country[1, 2]**

**('000 t)**

| **Country** | **2003** |
|---|---|
| Argentina | 170[3] |
| Bolivia, ulexite | 33 |
| Chile, ulexite | 430 |
| China[e, 4] | 140 |
| Iran, borax[5] | 4 |
| Kazakhstan[e] | 30 |
| Peru | 9 |
| Russia[e, 6] | 1,000 |
| Turkey[e, 7] | 1,500 |
| US[8] | 1,060[3] |
| **Total** | **4,400** |

[1]World totals, U.S. data, and estimated data are rounded to no more than three significant digits; may not add to totals shown.

[2]Table includes data available through May 20, 2004.

[3]Reported figure.

[4]Boron oxide ($B_2O_3$) equvalent.

[5]Data are for years beginning March 21 of that stated.

[6]Blended Russian datolite ore that reportedly grades 8.6% $B_2O_3$.

[7]Concentrates from ore.

[8]Minerals and compounds sold or used by producers, including both actual mine production and marketable products.

**Table 3**

**US consumption of boron minerals and compounds, by end use[1, 2,]**

**(tonnes of boron oxide content)**

| **End use** | **2003** |
|---|---|
| Agriculture | 12,864 |
| Borosilicate glasses | 19,333 |
| Enamels, frits, glazes | 12,692 |
| Fire retardants: | 11,274 |
| Insulation-grade glass fibres | 177,658 |
| Other | 6,045 |
| Soaps and detergents | 20,865 |
| Sold to distributors, end use unknown | 29,095 |
| Textile-grade glass fibres | 69,298 |
| **Total** | **359,124** |

[1]Data are rounded to no more than three significant digits; may not add to total shown.

[2]Includes imports of borax, boric acid, colemanite and ulexite.