20 MULE TEAM BORAX™

BARITE & OILFIELD MINERALS FORUM 2024
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The Royal Sonesta Hotel Houston Galleria

Borates Market and Application in Oilfield

Presented in Barite and Oilfield Minerals Forum

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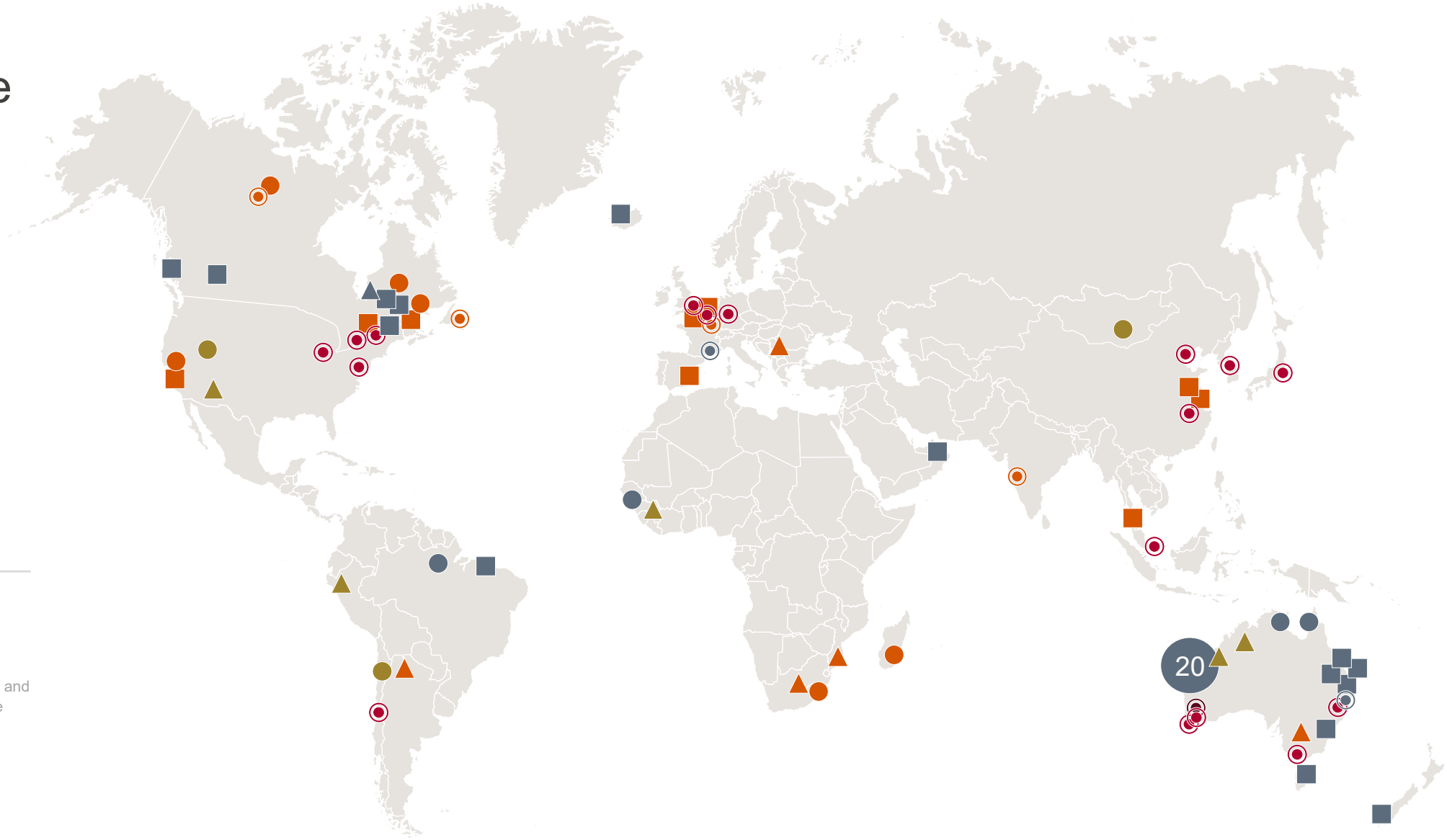
U.S. Borax | Rio Tinto
Overview and Markets



RioTinto

Rio Tinto

54,000 people
35 countries



- Aluminium
- Copper
- Iron Ore
- Minerals
- Commercial and Corporate

Icon key

- Mines
- Smelters, refineries, power facilities and processing plants remote from mine
- Projects
- Operations Centre, Research and Development, Offices, Sales and Marketing

What we do

- Alumina
- Aluminum
- Bauxite
- Borates
- Copper
- Diamonds
- Iron ore
- Lithium
- Salt
- Titanium dioxide



Lithium is an essential ingredient in lithium-ion batteries for hybrid and electric cars.

RioTinto

We were the first to mine borates on a large scale

20 MULE TEAM BORAX™



Our history dates back to 1872

RioTinto

Who we are

~30%
World's refined borates supply

650 customers
90 countries
1,800 locations

Mine
Refine
Ship
6
continents

Corporate and support offices

- Chicago, United States
- Frankfurt, Germany
- New Delhi, India
- Shanghai, China
- Singapore

Refining and shipping facilities

- United States
- Canada
- China
- France
- Malaysia
- Netherlands
- South Korea
- Spain

U.S. Borax is a world leader in the borate business

Developing borates' potential

Most product developments and process improvements are invented under our roof and with our partners.

Customer values

Technical support for customers, product quality, and supply reliability are the pillars of our commercial commitment.

Better quality, better results

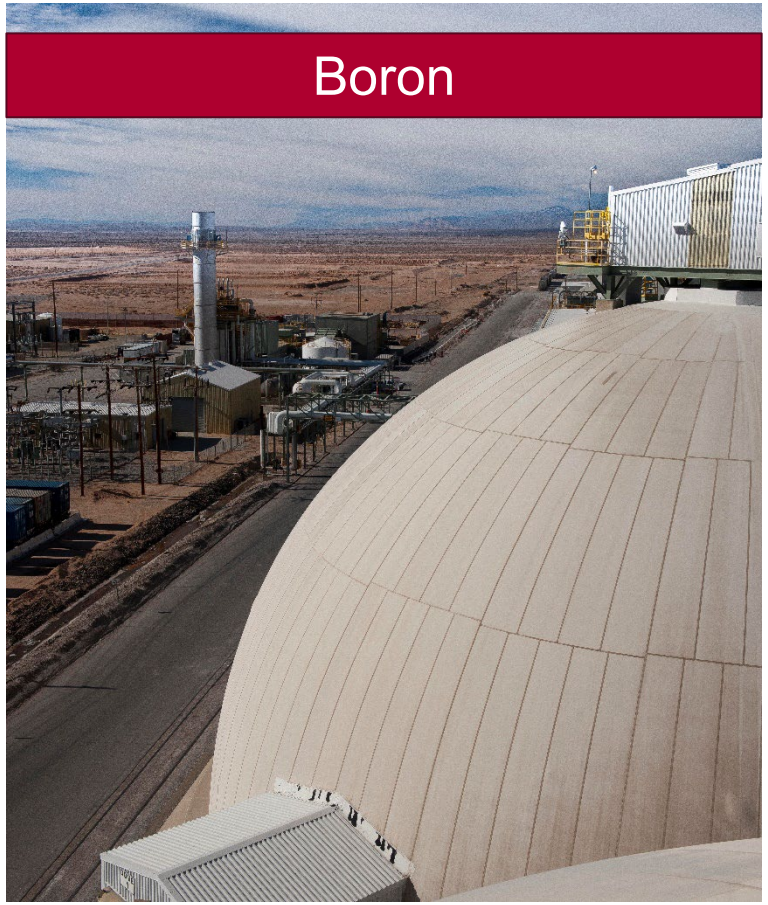
We continually monitor and improve product quality at every stage, from our exacting refinement process to product finishing, packaging, and shipping.

RioTinto



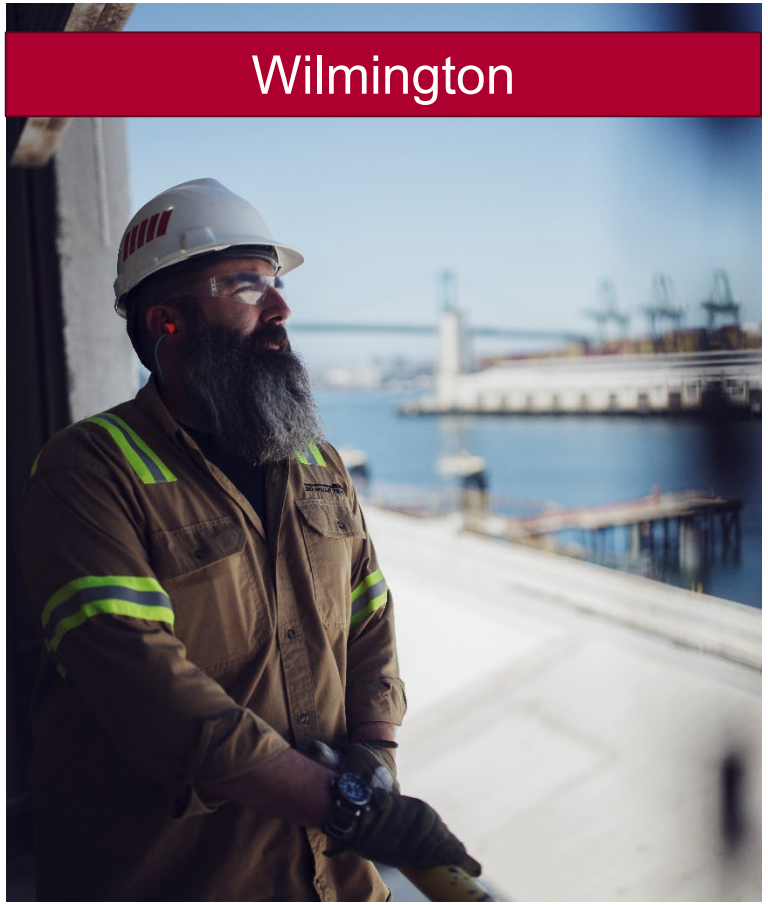
Overview of our California operations today

Boron



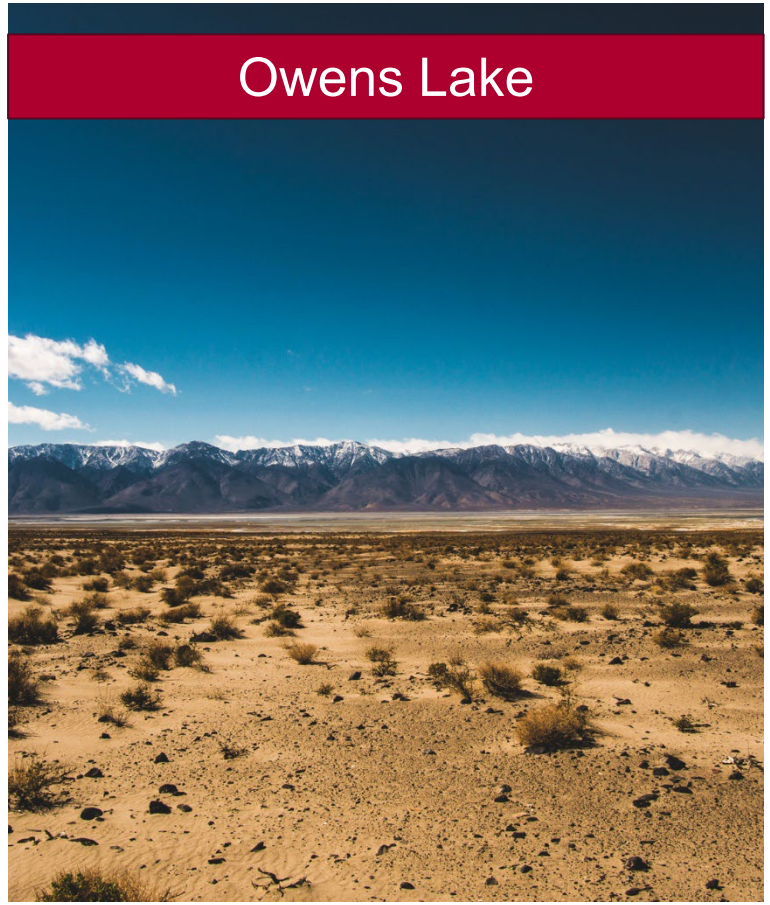
- Mine operations
- Primary process and refining facilities: Boric acid, sodium borates, boric oxide
- Packaging and shipping

Wilmington



- Port shipping facility
- Refining: Zinc borate, DOT

Owens Lake



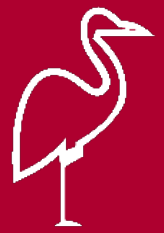
- Trona production for borate refining

Environmental responsibility at Boron

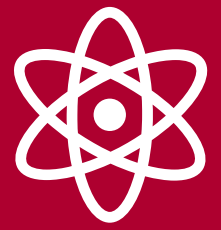
First open pit mine to transition heavy machinery to renewable diesel



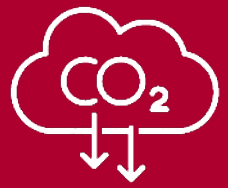
Federally-sanctioned Wildlife Rescue Center



Generating carbon-free energy



Lowered greenhouse gas emissions by more than 5% per ton of product



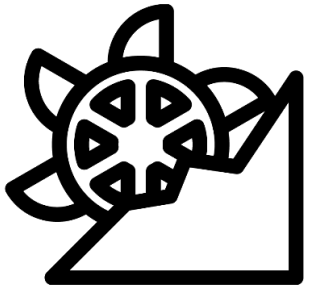
Produce certified organic fertilizer products



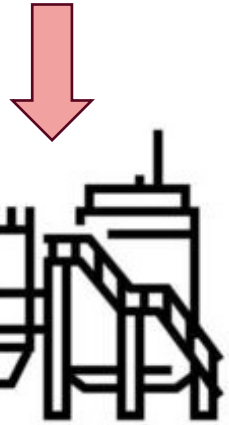
Donated the land that is now Death Valley National Park



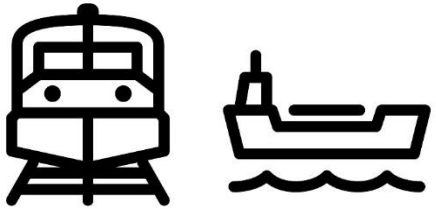
Borates: Mine to market



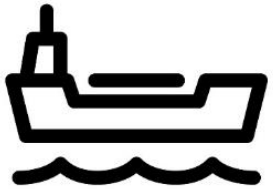
Mined from Boron, CA



Refined in California



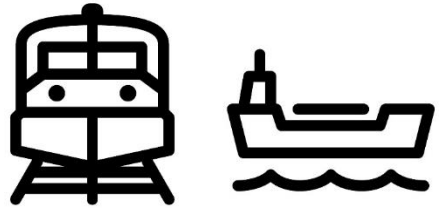
Products shipped to global customers



Product shipped to Coudekerque



Further refined, developed and packed in Europe



Specialty products shipped to customers

The U.S. Borax refining process involves several important steps:

1. We mine high-quality sodium-borate ore that is naturally low in calcium and other contaminants
2. We dissolve the ore in water
3. We settle the dissolved borate liquor to remove impurities
4. We cool the liquor and then further wash and filter the resulting crystal slurry
5. We dry the refined slurry to produce dry borate crystals
6. We check our products for purity, solubility, consistency, and optimal granulation
7. Our specialty borates undergo a secondary refining process to increase purity and produce high value specialty borates

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U.S. Borax process flow: Industrial products

U.S. Borax Mine



Tincal ore



- Crush ore
- Dissolve in hot water
- Concentrate (thicken)
- Crystalize
- Filter
- Dry product

Dehydrate

Anhydrous borax ← Borax pentahydrate

Crystalize → Filter → Dry product

Borax decahydrate

Kernite ore



- Crush ore
- Dissolve in sulfuric acid
- Concentrate (thicken)
- Crystalize
- Filter
- Dry product

Dehydrate

Boric oxide ← Boric acid

Dehybor®

Neobor®

Borax Decahydrate

Boric Oxide

Optibor®

Our diverse product catalog supports a variety of end uses

Major Industrial Products

Optibor®
Industrial optimization powerhouse

Boric Oxide
Increases yield and strength in glass and ceramics

Borax Decahydrate
Mild alkaline salt used as a buffering and fluxing agent

Neobor®
Concentrated sodium borate and easy conveyance

Dehybor®
Increases yield and reduces energy consumption when forming flux or glass

Agricultural Products

ANHYBOR®
Designed for fertilizer manufacturers

FERTIBOR®
Optimum for suspensions

GRANUBOR®
Made especially for bulk blenders

LIQUIBOR®
Liquid boron from boric acid

SOLUBOR®
For foliar applications

SOLUBOR® FLOW
For fertigation or hydroponic growing

ZINCUBOR®
Perfect combination of zinc and boron

Specialty Products

Ammonium Pentaborate
Heat, flame, and corrosion inhibitor

Borogard® ZB
Preservative for wood and wood composites

Firebrake® ZB
Zinc borate protection for polymers

Firebrake® 500
Polymer protection for high processing temperatures

Polybor®
Multi-function cleaning and protection

Other Products

Potassium Pentaborate
Strength and versatility

Potassium Tetraborate
Superb buffering agent

Sodium Metaborate
Essential buffering agent

Sodium Pentaborate
Customized lubricator

Tim-bor®
Industrial wood protection

Borate functions

- Bio-essential effects
- Biocidal or biostatic effects
- Buffering effects
- Cross-linking effects
- Anti-corrosion effects
- Detergency and cleaning effects
- Fire-retarding effects
- Glass-forming effects
- Metallurgical effects
- Powder processing and physical effects
- Nuclear and spectroscopic effects

Also used in the manufacture of advanced materials and specialty chemicals and reagents.



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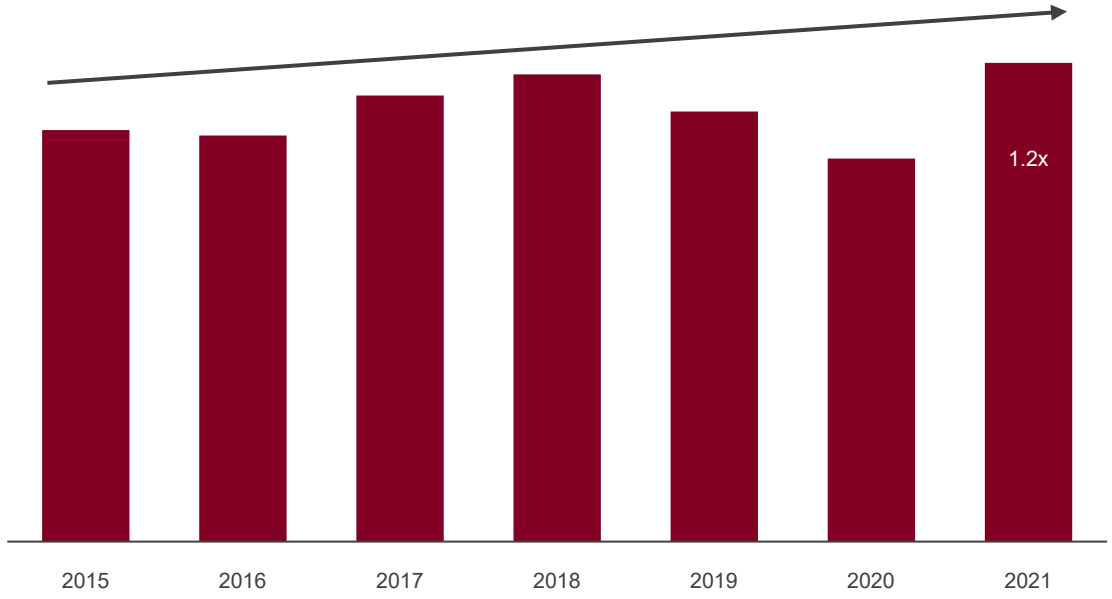
General list of borate applications

- Adhesives
- Agriculture
- Antifreeze
- Boron hydrides and carbides
- Brake fluids
- Cement
- Ceramic frits
- Corrosion inhibitors
- Detergents and cleaners
- Electrolytic capacitors
- Fire retardants
- Fuel additives
- Glass
- Gypsum board
- Industrial chemicals
- Iron and steel
- Leather tanning
- Lubricants
- Metal refining
- Metalworking fluids
- Nuclear power plants
- Nylon
- Oil field chemicals
- Personal care
- Photography
- Pool treatment
- Rare earth magnets
- Solders and welding
- Textiles
- Waxes and polishes
- Water treatment
- Wire drawing
- Wood treatment

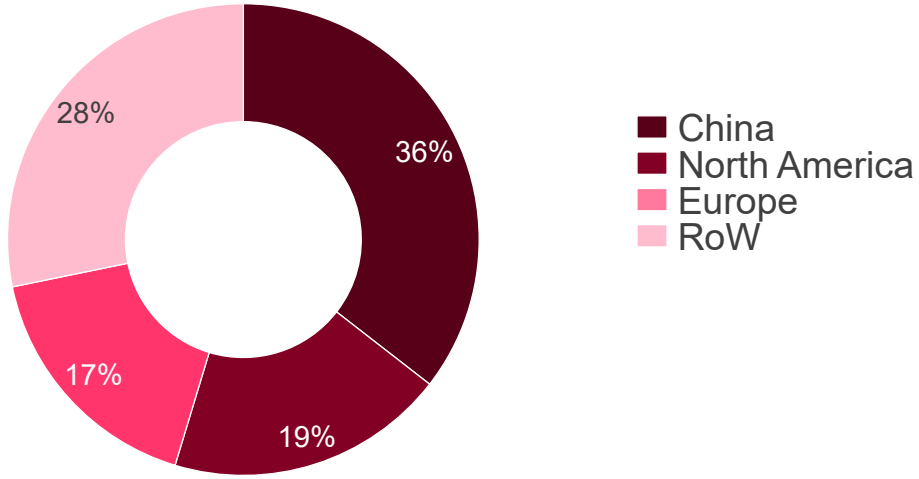
Borates market

Global borates demand

2015=100



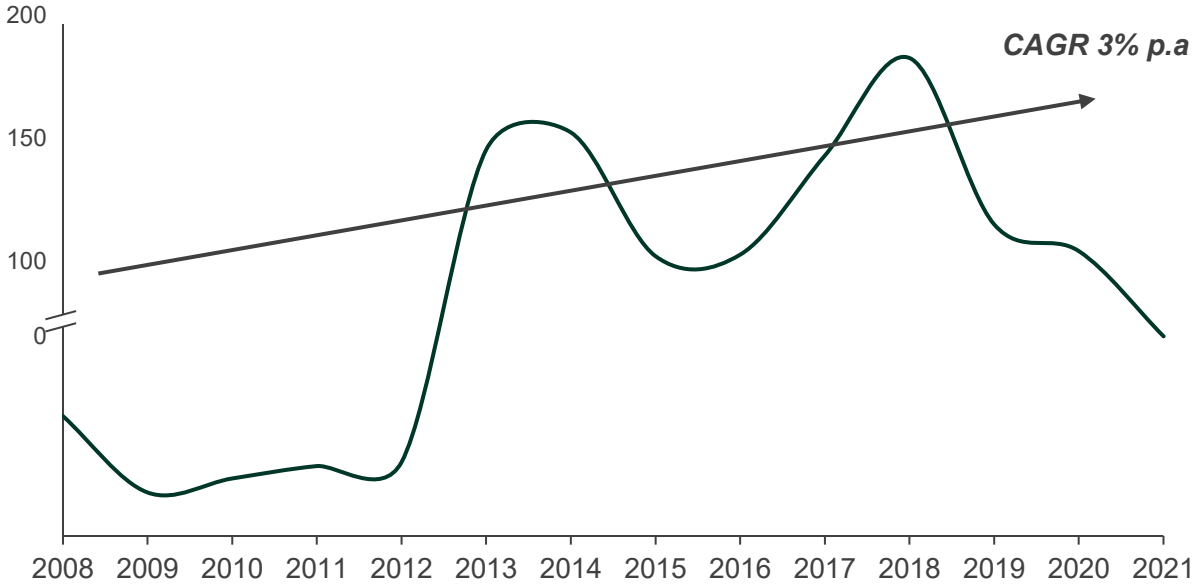
Borates demand by region



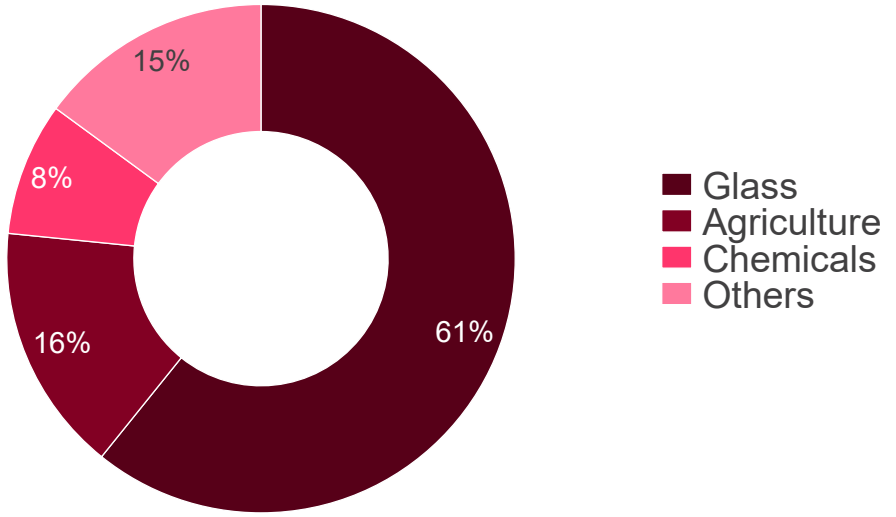
Source: Rio Tinto Market Analysis

Borates market

Borates demand for chemical application 2008=100



Borates demand by end-use



RioTinto Source: Rio Tinto Market Analysis

Borates Application in Oilfield



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Borates used in oil and gas

Refined borates	Formula	$\%B_2O_3$	pH of 1% solution
Sodium metaborate	$NaBO_2 \cdot 4H_2O$	25	11.0
Borax pentahydrate	$Na_2B_4O_7 \cdot 5H_2O$	48	9.2
Borax decahydrate	$Na_2B_4O_7 \cdot 10H_2O$	36	9.2
Potassium tetraborate	$KB_5O_7 \cdot 4H_2O$	46	9.2
Disodium octaborate	$Na_2B_8O_{13} \cdot 4H_2O$	68	8.5
Sodium pentaborate	$NaB_5O_8 \cdot 5H_2O$	59	8.4
Potassium pentaborate	$KB_5O_8 \cdot 4H_2O$	59	8.4
Boric acid	$B(OH)_3$	56	5.0
Mineral borates			
Ulexite	$NaCaB_5O_9 \cdot 8H_2O$	sparingly soluble	
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$	"	"

Borate functions useful in the oilfield

Borates provide a variety of useful functions in oilfield applications

- Polymer crosslinking
- Lubricant effects
- Corrosion inhibition
- Wide ranging water solubility and dissolution rates
- pH buffering
- Oxidizing agent
- Neutron absorption
- Cement set retarding

Borates: Multifunctional additives for oil and gas

Borates can be used in many stages of oilfield operations:

Drilling and completion

- Drilling fluids
- Oil well cement set retardant
- Well and reservoir logging
- Sour gas scavenging

Stimulation

- Hydraulic fracking fluids

Enhance oil recovery

- Water flooding profile control
- Alkaline surfactant flooding

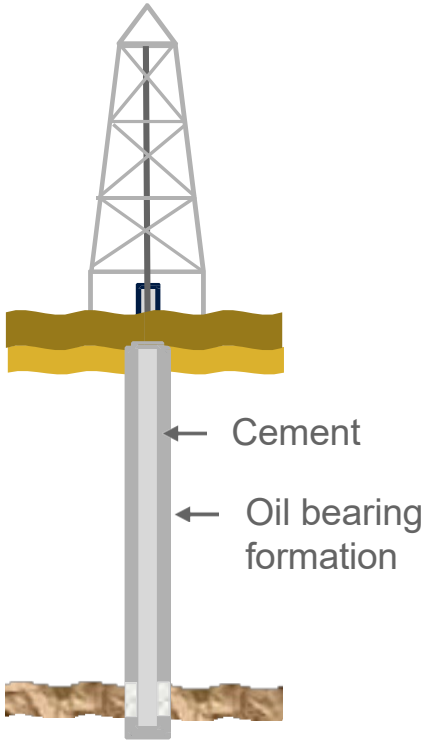
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Oil well cement set retardant

Drilled well bores are stabilized with steel casings reinforced with cement

- Cement setting rates must be controlled to ensure they can be pumped into the well and only set once in place. High well temperatures accelerate cement setting.
- Borates are widely used as set retardants for oil well and other cements
- Borates typically used with Portland cements (eg API class G and H). Borates can also retard setting of other cements, eg phosphate and aluminate types.



Mechanism:

Borate adsorbs onto cement grain surfaces initially forming amorphous calcium borates that act as a temporary barrier to cementious calcium silicate formation.

Borax Decahydrate

Neobor®

Polybor®

Optibor®

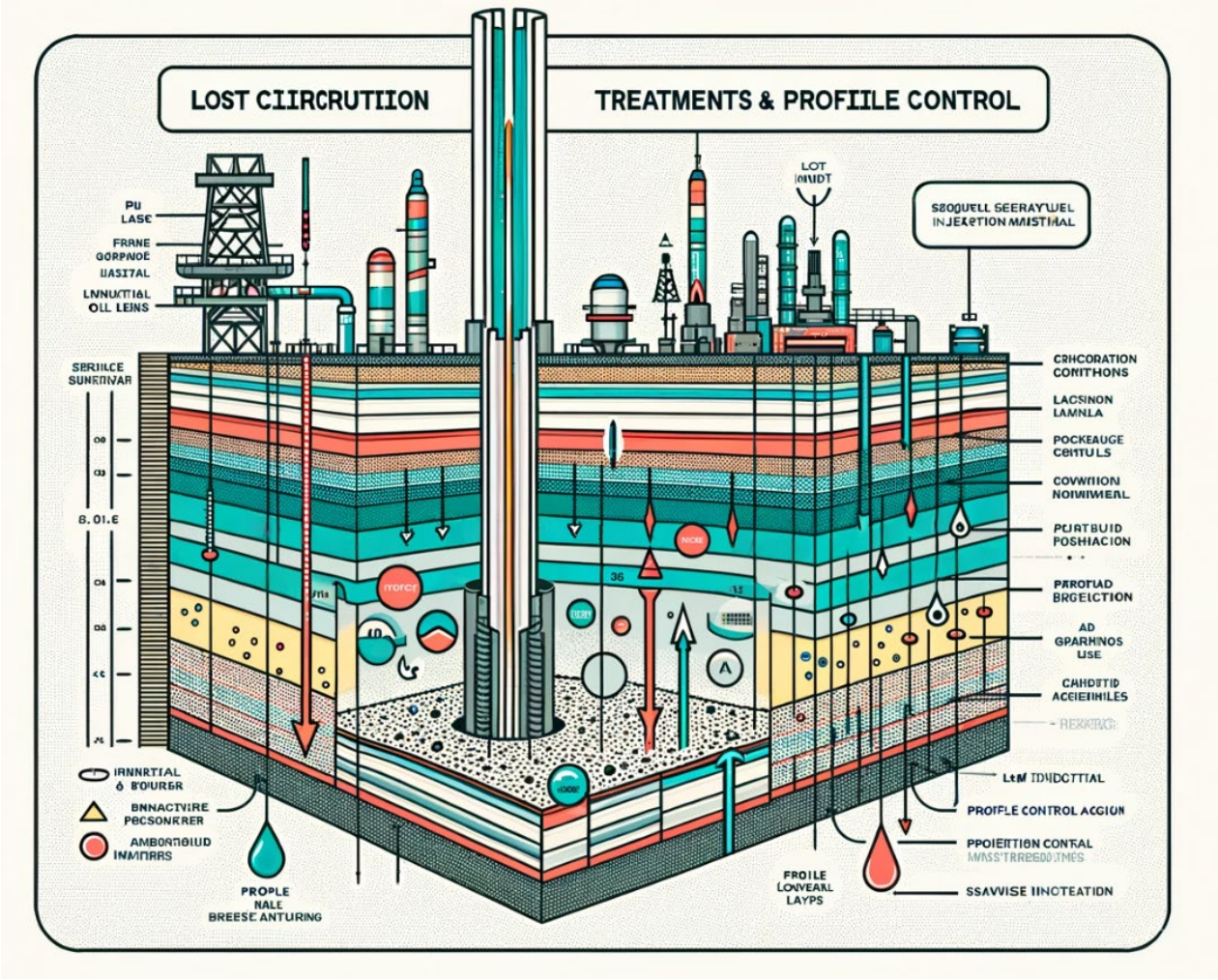
Lost circulation treatments and profile control

Lost circulation is a costly drilling problem

- Borate-crosslinked polymer gels that rely on similar chemistry to fracturing fluids can be used to plug lost circulation zones
- Delayed borate crosslinkers can also be used to allow time to pump fluids into place before gelling *(Dehybor®)*

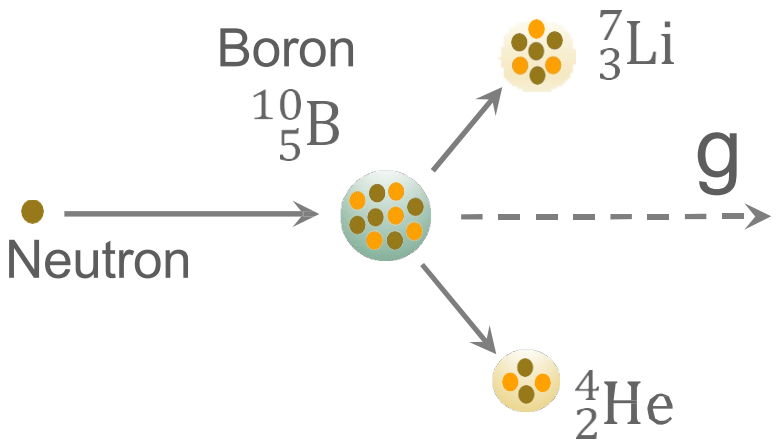
Profile control in water flooding

- Use of borate crosslinked polymers is reported to improve water flood sweep efficiencies by providing higher viscosity



RioTinto Borax Decahydrate Neobor® Polybor® Optibor® Dehybor®

Pulsed neutron well logging



Natural abundance		Neutron capture units
^{1}H	99.99	0.0032
^{12}C	98.89	0.0034
^{24}Mg	78.70	0.052
^{23}Na	200	0.400
^{40}Ca	96.95	0.430
^{35}Cl	75.53	44
^{10}B	19.78	3836

- Boron is unique among the light elements in having a very high neutron capture cross-section.
- The ^{10}B isotope absorbs thermal neutrons giving rise to ^{7}Li and alpha particles accompanied by a gamma emission.
- Too weak to pose danger, the gamma emission can be detected to track the movement of borate-containing fluids underground and measure reservoir porosity.

Borax Decahydrate

Neobor®

Drilling fluids

Borates fulfill several functions in drilling muds and completion fluids:

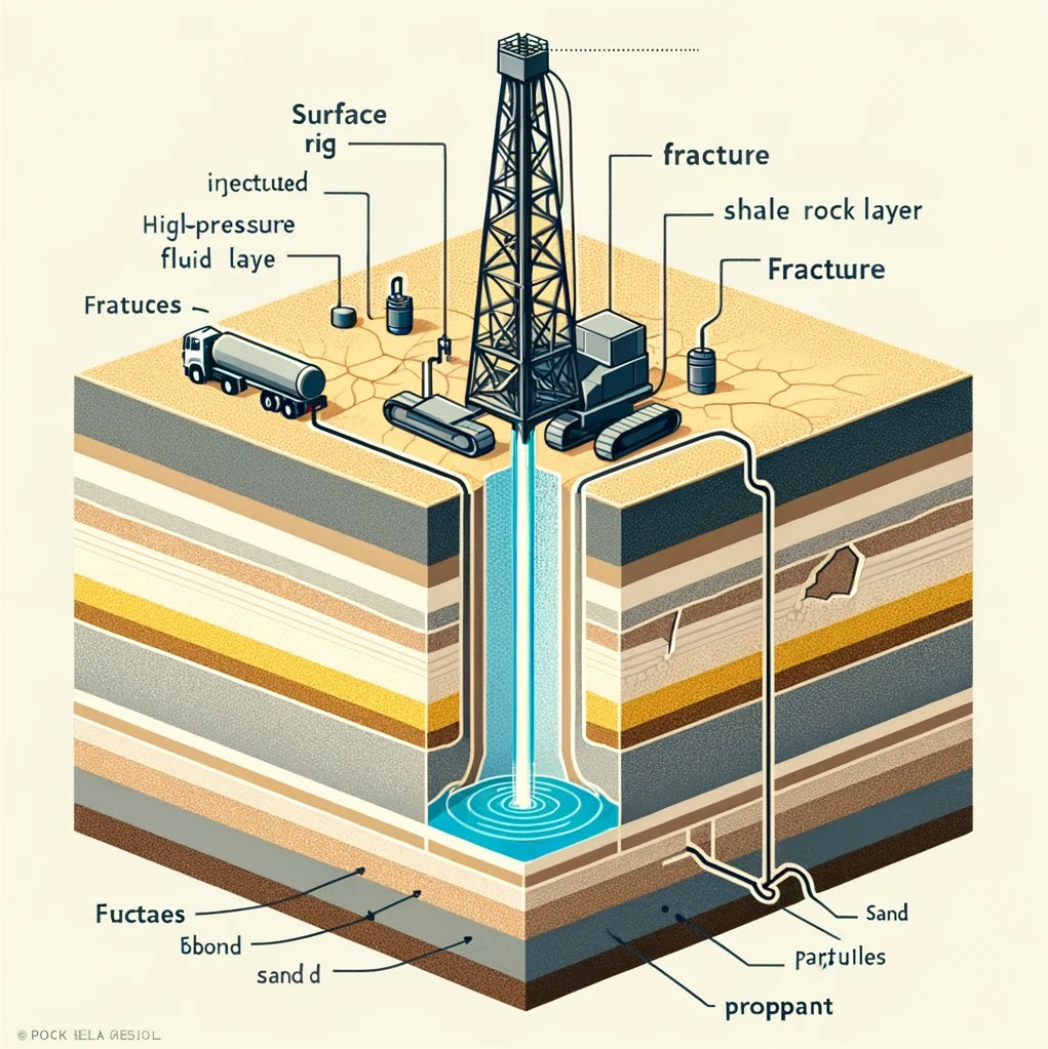
- **Fluid loss additive:** Completion fluids use additives to form impervious filter cake on well bore walls preventing fluid loss into formation. Borates provide shale stabilization and enhance performance of some polymeric fluid loss additives, eg starch.
- **Lubricant:** Borates and borate esters can be used to improve the lubricating properties of drilling muds.
- **pH control:** Borates are excellent buffers for mildly alkaline pH typical of water- based drilling muds.
- **Corrosion control:** Borates act as corrosion inhibitors in drilling fluids to protect steel casings and pipework. Borates often used in water-based muds in combination with other corrosion inhibitors.

Borax Decahydrate

Neobor®

Polybor®

Hydraulic fracturing fluids

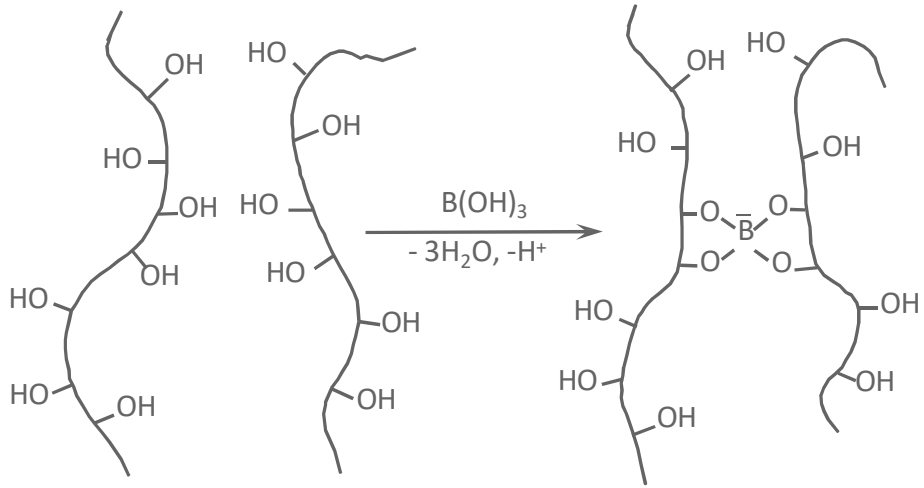


Instant crosslinkers

Borax pentahydrate	$Na_2B_4O_7 \cdot 5H_2O$
Borax decahydrate	$Na_2B_4O_7 \cdot 10H_2O$

Delayed crosslinkers

Dehybor®	$Na_2B_4O_7$
Certain boric acid esters	$B(OR)_3$



Borates are used as crosslinking agents guar or guar-derivative gels to produce rheological fluids

Borates form “self-healing gels” that recover viscosity after high shear

RioTinto Borax Decahydrate Neobor® Polybor® Optibor® Dehybor®

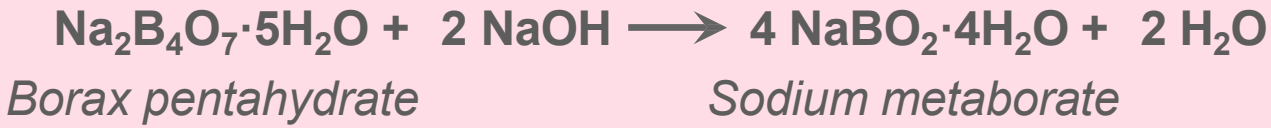
Alkaline surfactant flooding

Traditionally ASP flooding for enhance oil recovery (EOR) employs alkaline agents such as sodium carbonate.

Use of sodium metaborate as alternative alkaline agent:

- Reduces interface surface tension to mobilize oil struck in rock and can substantially improve oil recovery.
- Reduces polymer absorption.
- More compatible in anhydritic and dolomitic formations compared to sodium carbonate.

Most economical method is to prepare sodium metaborate in solution from borax pentahydrate near wellhead



Borax Decahydrate

Neobor®

Sodium Metaborate

RioTinto

Hydrogen sulfide scavenger

- H_2S gas in reservoirs can be a problem during drilling and production when H_2S-rich strata are encountered (sour gas kicks). H_2S is toxic and can cause corrosion of steel drill casings and pipelines.

  Origins: Sulfate present in seawater, pyrite rock and sulfur compounds in crude oil provide nourishment for H_2S producing bacteria.

- H_2S persists under acidic conditions and converts to non-volatile sulfides at high pH. Alkaline borate are particularly suitable for H_2S control.

Borate used

Sodium metaborate (pH11) is shown to be effective for scavenging H_2S.

Sodium Metaborate

Alternatively

Sodium perborate, an oxidizing agent, can also be used to control H_2S.

Summary

Borates can be used in many aspects of oil and gas recovery including drilling, completion, stimulation, and EOR.

- Oil well cements
- Hydraulic fracturing fluids
- Lost circulation treatments
- Pulsed-neutron well logging
- Drilling fluids
- H_2S scavenger
- Surfactant alkaline flooding

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