

## PHYSICOCHEMICAL PROPERTIES OF BORATES FROM THE SOUTHAMERICAN PUNA

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### ABSTRACT

Since most of the borates produced in Argentina (concentrates and processed products) are exported and the technical marketing regulations have become more severe, producers have to improve competitiveness through technology including some concentration and/or purification stage in the mill circuit. The objective of the separation is a graded product in  $B_2O_3$  and lowered in undesirable impurities (mainly iron, chlorides and sulphates).

Concentration steps usually involved in the borate processing are gravity separation, froth flotation, size classification and magnetic separation, based on the differences of specific weight, superficial energy, hardness and magnetic susceptibility, respectively. Another easy grading method is calcination. This is the conversion to a less hydrated crystalline form. Unfortunately, also impurities are graded.

This paper reports the results obtained of the above mentioned properties for the following industrial interesting South American borates: sodium (tincal), calcium (colemanite and inyoite), sodium and calcium (ulexite) and calcium and magnesium (hydroboracite)

borates. Also, the techniques employed to collect pure samples are commented. This work has been carried out at the INBEMI with financial support of ANPCYT (SECYT), BID 802/OC-AR PICT N° 07-0-02059/07464 projects.

### INTRODUCTION

South American Puna has the world's third largest borate mineral reserves, after United States and Turkey.

Few mineral species are commercially interesting. They are: colemanite, hydroboracite, inyoite, ulexite, and tincal.

Technical marketing regulations require upgraded

concentrates over 75% of purity as it is shown in Table I. The upper limit of impurities depends on the use of the borates. For example: arsenic content may be accepted in the market from 0.05 to 0.10 % as  $As_2O_3$ . Iron as  $Fe_2O_3$ , has to be lower than 0.5 %.

Table I. Commercially interesting boron minerals.

Mineral	Structural formula n= atoms B, Δ=triangle, T = tetrahedro	Molecular weight	B <sub>2</sub> O <sub>3</sub> %		
			Mineral (pure)	Calcinated (pure)	Concentrated
Colemanite	Ca [ B <sub>3</sub> O <sub>4</sub> (OH) <sub>3</sub> ] .H <sub>2</sub> O 3:Δ+2T	411.09	50.84	65.10	39-42
Hydroboracite	Ca Mg [B <sub>3</sub> O <sub>4</sub> (OH) <sub>3</sub> ] <sub>2</sub> .3H <sub>2</sub> O 3:Δ+2T	413.33	50.55	68.45	38-42
Inyoite	Ca [ B <sub>3</sub> O <sub>3</sub> (OH) <sub>5</sub> ] .4H <sub>2</sub> O 3:Δ+2T	555.21	37.62	65.10	
Tincal (borax)	Na <sub>2</sub> [B <sub>4</sub> O <sub>5</sub> (OH) <sub>4</sub> ] .8H <sub>2</sub> O 4:2Δ+2T	381.37	36.52	69.20	28-34
Ulexite	Na Ca [B <sub>5</sub> O <sub>6</sub> (OH) <sub>6</sub> ].5H <sub>2</sub> O 5:2Δ+3T	405.24	42.97	66.69	34-40

Regulations are less severe when borate concentrates are employed as raw material either to the boric acid or borax industries.

Thermal treatments (calcination or melting) used to upgrade the  $B_2O_3$  content, require a previous purification stage to remove impurities (especially iron), because they are also upgraded. Figure 1 shows the

processing methods usually employed to upgrade borate ores in the North-West of Argentina (NOA).

Differences of physical properties among valuable mineral and gangue particles are the key for those upgrading techniques. The most interesting properties and the corresponding borate processing methods are:

- a) Work index (Kwh/tn) – Molturability: Size reduction followed by size classification is the most used method of beneficiation. The gangue is always concentrated in fine fractions, so it is separated by wet classification (trommels, screw classifiers or hydrocyclones) or dry mechanical classification (screening).
- b) Density ( $\text{g/cm}^3$ ): Gravity concentration is not an usual method of borate processing. An interesting application is the concentration of ulexite either dry way (pneumatic tables) or wet way (hydrocyclones). Washing of colemanite or hydroboracite in trommels and/or screw classifiers is carried out to separate the easily cracked mud (clays).
- c) Zeta potential (mV): Froth flotation method is not used in the NOA even if it can be thought of as an interesting alternative of processing for colemanite and hydroboracite minerals upgraded in arsenic.
- d) Specific magnetic susceptibility ( $\text{m}^3/\text{kg}$ ): Magnetic separation method is used both in concentration (upgrading  $\text{B}_2\text{O}_3$ ) and in purification processes (separation of iron and/or arsenic impurities) in the processing of ulexite, tincal and hydroboracite ores.
- e) Solubility in water ( $\text{g}/100 \text{ ml}$ ): It is used in the hot water leaching of tincal to separate the undissolved gangue. Boric acid manufacture also uses a water washing stage to remove soluble impurities coming from the mother liquor.

- f) Thermal decomposition temperature: High content of hydrous water is a characteristic of borates: 0.43 kg  $\text{H}_2\text{O}/\text{kg B}_2\text{O}_3$  for colemanite, 0.517 for hydroboracite, 0.827 for ulexite and 1.29 for tincal ( $\text{borax} \cdot 10 \text{ H}_2\text{O}$ ). Calcining upgrades up to 14.3 %  $\text{B}_2\text{O}_3$  for ulexite and 32.7 % for tincal can be obtained. So, this property is used as a concentration method producing high-grade calcinates and frits. The decrepitation phenomenon of colemanite and the entrainment of high-grade calcinated ulexite generated during the thermal decomposition are used for the same purpose. High graded  $\text{B}_2\text{O}_3$  fines are recovered by size classification.

The results obtained from the determination of the physical properties mentioned above and the methodologies used are reported in this paper, as well as the techniques to obtain purified samples of every studied borate.

## EXPERIMENTAL

### Obtaining purified samples

**Boric acid and tincal:** By leaching of technical grade boric acid (or borax decahydrate) with hot distilled water ( $90^\circ\text{C}$ ), followed by cool crystallization at  $20^\circ\text{C}$ . The obtained crystals were dried ( $50^\circ\text{C}$ , during 24 hs.) and then powdered in a ring mill.

**Ulexite:** A high-grade pneumatic table concentrate (93 % of purity) was dried ( $60^\circ\text{C}$ , 24 hs.), ground into  $-40 \text{ M}$  ( $0.42 \text{ mm}$ ) and repeatedly washed with distilled water to remove soluble impurities (chlorides and sulphates). The settled mud was dried and then powdered into  $-100 \text{ M}$ .

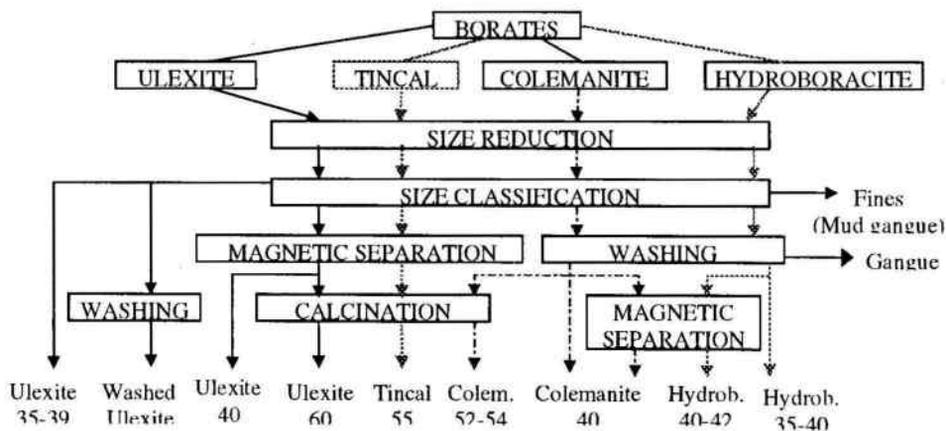


Figure 1. Flowsheet of the South American Puna borate processes.

**Hydroboracite:** A preconcentrated sample coming from washing in trommels (particle size  $\frac{3}{4}$ " –  $\frac{1}{4}$ ", 70 %  $B_2O_3$ ) was ground into -100 M in a hammer mill, and then deslimed in a hydrocyclone. The underflow was dried in a kiln and screened into 100, 140, 200, 270 and 400 M (ASTM). Every narrow sample size was fed to a Frantz Barrier Magnetic Separator, under electric current (i), longitudinal angle ( $\alpha$ ), cross angle ( $\beta$ ) selected to obtain the

following products:

- Magnetic:  $\alpha = 15^\circ$ ,  $\beta = 15^\circ$ ,  $i = 0.5$  amp.
- Paramagnetic:  $\alpha = 15^\circ$ ,  $\beta = 5^\circ$ ,  $i = 1$  amp.
- Non magnetic:  $\alpha = 15^\circ$ ,  $\beta = -1^\circ$ ,  $i = 1$  amp.
- Diamagnetic:  $\alpha = 15^\circ$ ,  $\beta = -5^\circ$ ,  $i = 1.5$  amp., recycled three times.

Major mineral constituents in every product have been identified by X-ray diffraction (Ridak-Denki D/Max II-C diffractometer) in order to determinate the abundance range of the main species. The obtained results are reported in Table II. It was determinated that hydroboracite and a little colemanite are concentrated in the diamagnetic fraction. This mixture could not be separated, neither by magnetic separation (Frantz Barrier Separator) nor by heavy media (tetrabromoethane and/or carbon tetrachloride blends,  $2.52 > \rho_{\text{medium}} > 2.30$ , which made necessary hand

sorting under microscope in order to obtain a hydroboracite sample over 95% of purity.

**Colemanite:** The separation of purified samples has the same difficulties as hydroboracite.

### Techniques used in the measurement of physical and physicochemical properties

**Density** ( $\rho_s$ , g/cm<sup>3</sup>): Measured in a 25 ml appraised flask containing a well-known weighted powdered sample (about 5 to 10 g). It has been evened with a well-known liquid density ( $\rho_L$ ). Turpentine ( $\rho_L = 0.77$  g/cm<sup>3</sup> at 20°C) has been the liquid employed in this work because of the characteristic of wetting the solid surface (including inner surface of pores) without dissolving it. The density of the solid sample has been calculated from the weights of solid sample ( $P_s$ ) and the liquid ( $P_L$ ):  $\rho_s = P_s / [25 - (P_L / P_L)]$

**Specific magnetic susceptibility** ( $K_e$ , m<sup>3</sup>/kg): Measured by the force method with a Gouy Balance (Flores and Redondo, 1990). The magnetic force ( $F_m$ ) acting on a weighted sample ( $P_s$ ) of known density ( $\rho_s$ ) and length (L)

placed in a magnetic field of intensity H has been measured. Then, the magnetic force may be approach by:

$$F_m = (\mu_0/2) K_s H_x^2 P_s / (L g_c) \quad (1)$$

Table II – Major mineral species found in a hydroboracite concentrated sample.

Fraction		Decreasing abundance sorting					Nomenclature
Size	Magnetic property	1	2	3	4	5	
100 - 140 M $Dp_m = 127 \mu m$	Magnetic	Bi, A/M	Hb/Col				Bi : biotite A/M : clays / mica
	Paramagnetic	Bi	Hb/Col	Fel			
	Not-magnetic	Hb	Col	Fel			
	Diamagnetic	Hb	Fel				
140 - 200 M $Dp_m = 89.5 \mu m$	Magnetic	Bi, A/M	Hb	Col	In		Col : colemanite Cal : calcite
	Paramagnetic	Bi	A/M				
	Not-magnetic	Col	Hb	Bi			
	Diamagnetic	Hb	Col	Qz	In	Cal	
200 - 270 M $Dp_m = 63.5 \mu m$	Magnetic	A/M					Fel : feldspar Hb : hydroboracite
	Paramagnetic	Qz	Hb/In	A/M			
	Not-magnetic	A/M					
	Diamagnetic	Hb	Col	Fel			
270 - 400 M $Dp_m = 45 \mu m$	Magnetic	A/M, Fe <sub>3</sub> O <sub>4</sub>	Col	In			In : inyoite Qz : quartz
	Paramagnetic	A/M	Qz	Hb/Col			
	Not-magnetic	Col	Hb	Qz	Bi		
	Diamagnetic	Hb	Col	M			

where  $K_s$  is the specific magnetic susceptibility (cgs) and  $\mu_0 = 1$  (magnetic susceptibility in a vacuum, cgs).

Afterwards,

$$K_e \text{ (SI)} = 4 \pi 10^{-3} K_s \text{ (cgs)} \quad (2)$$

$$K_e \text{ (SI)} = 24.66 \text{ Fm L} / (P_s H^2) \quad (3)$$

Fm [=] gr, L[=] cm,  $P_s$  [=] gr and H [=] Gauss

**Zeta-Potential:** It has been calculated by the Smoluchowski's equation from electrophoretic velocity measurements,  $u_E$  [=] ( $\mu\text{m}/\text{sec}$ )/(V/cm).

$$Z(\text{mV}) = u_E 4\pi \eta / \epsilon \quad (4)$$

where  $\epsilon$  is the dielectric constant of the medium (water) and  $\eta$  is the dynamic viscosity. pH at which the charge on the surface is zero is the zero point of charge. Conditions under which Zeta-Potential is zero is called the iso-electric point.

**Work Index** (Kwh/tn): Molturability M (g/rev) has been determined by the Bond's technique in a standard ball mill, simulating a continuous operation with 250% circulating load. Work Index has been calculated by the following equation:

$$Wi = 44,5 / [P_1^{0,23} M^{0,82} (10/P^{0,5} - 10/F^{0,5})] \quad (5)$$

where  $P_1$  is the separating size, and F and P are the sizes ( $\mu\text{m}$ ) corresponding to the 80% passing size of the feeding to, and the discharge from the standard mill, respectively.

**Solubility in water** (g/100 ml  $\text{H}_2\text{O}$ , 20°C): It has been carried out by mixing 200 g powdered mineral (previously washed) and 1000 ml distilled water in an agitated tank until constant electric conductivity, measured with an Antares III conductimeter. Afterwards, the solution has been vacuum filtered and the concentration of  $\text{B}_2\text{O}_3$  analyzed. The results have been reported in grams of dissolved mineral / 100 ml water.

**Decomposition temperature** (°C): It has been determined through thermogravimetric curves and differential thermal analysis (TG and DTA) on approximately 100 mg sample in a Neztch STA thermobalance, with slow ramped heating (2-5°C/min) until constant weight. TG curves corresponding to borax, boric acid and ulexite show loss of crystallization water in a wide range of temperature, which starts under

100°C. For this reason, the decomposition temperature of the studied borates have also been determined by measuring the dissociation pressure ( $P_d$ ) over a wide range of temperature. A well-known amount of sample was placed in a sample holder, which is provided with temperature and pressure measurement devices, then was under vacuum and finally introduced in a tubular furnace with controlled temperature, measuring the equilibrium pressure at every temperature. The temperature at which  $P_d = 1$  atm corresponds to the thermal decomposition of the ore analyzed.

Water crystallization loss at relatively low temperatures (<100°C) is characteristic of ulexite, tincal and boric acid. Frequently it is a source of error in the expression of chemical analysis results as well as in the determination of their physical properties

## RESULTS

Table III summarizes the values of density, hardness, specific magnetic susceptibility, solubility in water at room temperature, dissociation temperature and the data obtained from thermograms and differential thermal analysis, corresponding to the studied borates.

In a comparative way, some values of these properties found in the scarcely specific literature have been considered: [(1) Garret-1998; (2) Kirk and Othmer-1964; (3) Kubaschewski and Alcock-1979; (4) Perry and Hilton-1974; (5) Smykatz and Kloss-1974; (6) Weiss-1985; (7) Linke-1958; (8) Dana-1985; (9) Taggart-1976; (10) Lardarello, (11) Celik and Buluk-1996; (12) Klassen-1963; (13) Karazhanov-1963; (14) Yarzhemskii-1968; (15) Ozkan and Veasey; (16) Gulensoy and Kocakerim-1978].

Differences between bibliography and experimental values of a property in Table III are the consequence of the use of ores coming from different deposits, impurities in the analyzed sample, or the use of pure species chemically precipitated (not minerals).

Table III. Physical properties of commercially interesting purified borates.

Property	Tincal	Ulexite	Hydroboracite	Colemanite	Boric acid
Density, gr/cm <sup>3</sup> - Experimental - Reference	1.72 (1,2,6) 1.70 (8,9)	2.03 1.96 (1,6,8) 1.65 (9)	2.29 2.17 (1)	2.41 2.42 (1,8,9) 2.96 (6)	1.51 (2,10) 1.43 (4)
Hardness, Mohs (reference) Work index, Kwh/T	2- 2.5(1,8,10)	1**(8),2,5(1,8) 7	2 – 3 (1) 12.5	4-4.5 (1,8) 9	1(1), 3 (10)
Specific magnetic susceptibility - Experimental, m <sup>3</sup> /kg - Reference, m <sup>3</sup> /kg	-0.80 10 <sup>-8</sup> without data	12.5 10 <sup>-8</sup> without data	-0.83 10 <sup>-8</sup> without data	-1.28 10 <sup>-8</sup> without data	-1.06 10 <sup>-8</sup> without data
Solubility in water at 20°C - Experimental, gr/100ml - Reference, gr/100 ml	2.54 (1) 2.77 (2) 2.65 (7)	0.42 1,09 (7) 0,46 (11) 0,47 (13)	0,20 0,47 (7) 0,21 (13), 0,45 (14)	0,16 0,08 (11, 15) 0,06 (16)	4.72 (1) 5,04 (2,7) 4.88 (7,10)
Iso-electric point - Experimental - Reference		No Z<0 in 7≤pH≤11 (11)	No Z>0 in 3≤pH≤11,8 2≤pH≤12 (12)	pH=10,5 (11)	
Thermogram: (experimental) Max. weight lost, ΔWmax,% Temperature (°C), related to a loss of: 0,1 ΔWmax 0,5 ΔWmax 0,9 ΔWmax ΔWmax	47,22 <100 138 279 575	35,56 <100 170 320 520	26,14 232 295 470 600	21,9 366 395 480 605	43,69 <100 138 288 420
DTA. Endot. peaks, T(°C) - Experimental - Reference, (5)	65 - 90 - 130 270 – 540 100-155- 190	94 – 141 – 170 145 – 182	235 - 285	340-370-390 315 – 405	70-145-170
Dissoc. temp. exptal., °C	645	577	634	652	
Melting point (Reference)	741 (4) 630 (5) 742(10)			485 – 550 (1) 646 (5) ≅ 1070# (3)	450* (3,10) 577* (4) 563 (3)

\* B<sub>2</sub>O<sub>3</sub> melting point (from BO<sub>3</sub>H<sub>3</sub> calcinated).# Calculated for OCa/B<sub>2</sub>O<sub>3</sub> = 0.66

\*\*Agglomerated (cotton ball)

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