Slow Release of Boron Micronutrients for Agricultural Fertilizers

H. R. Hores, L. E. Mattenella, C. Gomez Opazo, L. H. Kowk

Instituto de Bénéficie/ de Minérales (INBEMI), Facultad de Ingénieriez, Universidad National de Salta
Avenida Bolivia 5150, (4400) Salta, Argentina

ABSTRACT: The production of slow release boron micronutrients in water for agricultural fertilizers is presented in this paper. Agglomeration, pelletizing and sinterization techniques are appropriate for manufacturing particles whose dissolution rate can be controlled through their size and chemical composition, according to a selected feeding. The results of boron dissolution in water from pellets made by feeding a pelletizer disk with borate concentrates and colemanite ore (scarcely soluble in water) as well as the influence of the chemical composition of the feeding, the size of pellets and the hardening temperature are analyzed. Pellets made from calcinate colemanite and from tyncal-ulexite raw materials offer better properties for slow release boron micronutrients than other kind of feedings, especially the one related to the severe specification regarding agricultural fertilizers which restrict the boron concentration in water up to 30 ppm.

1. INTRODUCTION

Among over 200 boron minerals identified in nature, only few have industrial importance. Some of them are tyncal, colemanite and ulexite (Garrett, 1998). Borates and their derivatives are widely used in the production of borosilicate glass, ceramics, fiber glass for thermal insulation, plastic reinforcement, flame retardants, cleaning compounds and detergents, metallurgy, refractories, abrasives, cosmetics, medicine, wood preservatives, nuclear and many other applications (Hores, 2002). Furthermore, boron is one of the seven basic micronutrients in plants. Its effectiveness is ranged in a relatively narrow concentration boundary; beyond lower and upper boundaries, it is deficient and excessive respectively. So, dosage of boron in plants plays a critical role with growing (Tilsdale and Werner, 1970; Gupta et al, 1985).

Boron is present in soils between 2 and 200 ppm (Villanueva et al., 1998); it is often ranged between 7 and 80 ppm. Generally, less than 5% of boron in soils is available for plants (Sardâ et al., 1997). It is a consequence of both the scarcely soluble boron in soils and the drainage to deep beds.

Naturally or intensively farmed soils deficient in boron require an adequate amount of it and the concentration for every crop should be outfed. Outfeeding ranges approximately between 0.5 and 15 boron kg per hectare (Bohn et al, 1993).

Plants absorb boron from soils as undissociated boric acid. Studies on the rate of uptaking boron in sugar cane tissue reveled a fast absorption in the first 20 minutes due to diffusion in voidage, followed by 4 hours of slow linear intracellular metabolism.

Independent of the initial consumption, it is evident that boron deficiencies in soils have to be outfed in the growing plant season.

Main factors acting on the boron plant uptake are: soil features (Boron concentration in soils, pH, texture, present impurities, hydric state), type of rains (acid or not), temperature, environmental humidity, properties of the micronutrient and the

application methods. Boron may be applied as solid (granular or powder) or liquid (irrigated or sprayed). In the latter form it is applied with highly soluble refined borates (borax, sodium tetraborate pentahydrate, sodium pentaborate).

Boron plant uptake varies widely. Table 1 contains guidelines on the suggested boron dosage along with fertilizers and the recommended range of boron concentration in soil solutions for the best growth (Bohn et al, 1993).

Table 1. Recommended boron dosage for the growing of some plants.

Crop	Dosage kgB/he	Recommended concentration ppmB
Coco	0.5-1	<12
Sunflower	1-3	35-150
Soybean	0.5-1	10-100
Red beet	1-3	<15
Potato	0.5-1	5-70
Carrot	1-2	18-200
Cherry	1-2	20-182
Apple tree	1-2	20-50
Grape	2-6	25-200
Tomato	1-1.5	10-200
Rice	0.5-1	5-40
Corn	0.5-1.5	5-60

By analyzing the above paragraph we can conclude that the appropriate features of a micronutrient are:

a) Higher initial dissolution rate to supply a fast contribution attack
b) Long mean life with constant rate dissolution, enough to supply the required dosage in plants.
c) Boron concentration in soil solutions should be within the plant uptake range to avoid toxicity by boron excess.
d) An appropriate strength to resist mechanical damage produced by loading/unloading, conveyance, transportation, handling and environmental effects (caused by the sun, humidity, thermal changes, etc.) during its mean life in the soil.

Pelletizing, which is the agglomeration method chosen, holds enough versatility to confer the final product the desirable features which can be reached controlling the dissolution rate by:

• The choice of raw materials on the basis of their solubilities
• The choice of a suitable pellet size
• The choice of hardening kiln temperatures, which allow (or not) changes in the structure, strength and chemical composition of the pellets

2. EXPERIMENTAL WORK

2.1 Mineral characterization

Selected raw materials were chemically analyzed. They were chosen on the basis of their solubilities in water (high, medium, low) among calcinate colemanite (C), calcinate ulexite (U), natural mixtures of tyncal-ulexite and calcinate colemanite-calcinate ulexite mixtures (CU). Chemical composition and solubility in water are summarized in Table 2.

Table 2. Raw materials. Chemical composition and range of solubility in water at 20 °C.

Raw material	Solubility range gB/l,20°C	Chemical composition (%)			
		B	CaO	Na$_2$0	Ins.
TU	5.0-1.2	11.3	7.1	11.4	9.9
C	0.2-0.8	14.7	27.2	0	13.6
U	0.5-2.0	16.8	14.8	10.9	11.2
CU	0.2-2.0	15.7	21.2	5.33	14.3

2.2 Pelletization

Pellets were made by rolling in an inclined disk, which was built at the INBEMI workshop. It is a rotating disk of 775 mm in diameter, provided with two baffles and a spray feeder for liquid (water or borate solution). The spray allows the addition of a suitable liquid for the agglomeration of mineral particles. Suitable binders may also be added to confer adequate strength to the pellets to avoid breakdown while being transported and loaded to the hardening kiln. Clays (bentonite) or a solution of some refined borate acting as binder may be added for such purpose.

A frequency controller for an asynchronic motor was also provided to change the rotation speed. It was 29 rpm in this study.

Pellet formation involves nucleation and growth by picking small particles up. Suitable large particles were taken off the disk. Moisture content was between 25 and 35%.
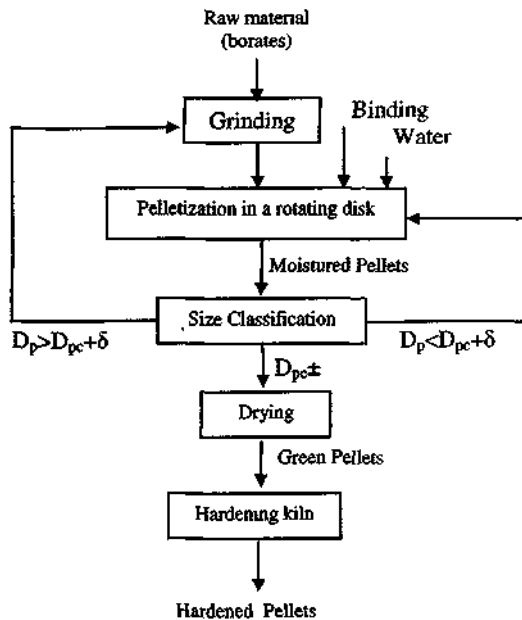
Every sample was identified by means of 2 letters, according to the selected raw material, followed by a number meaning the hardening temperature (°C) and a second number meaning the mean size of pellets (Dpc, mm). E. g. TU500, 7.14 is a pellet made of tyncal-ulexite at 500°C and 7.14 mm mean size.

Figure 1. Flowsheet of the pelletizing process.

Chemical reactions occurring when borates are exposed upon increasing environmental temperatures are: drying (s), calcination, partial vitrification (v) or sintering and total smelting. The consequences of those processes are summarized in Table 3.

Table 3. Chemical reactions and physical state of the products.

T(°C)	Reaction	Consequence
50 <, Ts S105	Drying	Loss of moisture
Ts<TST$_c$	Calcination	Loss of crystallization water molecules. Colemanite décrépites. Tyncal swells.
Tc<TST$_v$	Partial vitrification	Hardening of pellets. Agglomeration by partial smelting.
Tv<T<T$_f$	Total smelting	Unique smelted phase: Homogeneous chemical composition glass. Total smelting.

2.3 Pellet drying/Hardening

Pellet hardening was carried out in a laboratory kiln at a given temperature. Pellets were uniformly spread on a tray to reach homogenous heating. Hardening temperature assays were carried out within the range 50 °C < T < 800 °C

After firing, hardened pellets were naturally air-cooled at room temperature, and then size classified to take samples for physical and mechanical characterization and leaching assays. Pellets that disintegrated as a consequence of firing temperatures lower than hardening temperatures, were taken away. Size distribution of selected pellets was in the range of 7.4 mm to 5.5 mm, and also 13 kg compression strength and 8 m fall resistance.

2.4 Pellet leaching

Water leaching of pellets at room temperature was carried out only with those pellets mechanically resistant. It was simulated the natural boron dissolution in soils for plants.

Plants receive repeated washing cycles (due to rain and/or irrigation) followed by natural environmental drying until the boron in the pellet is exhausted.
A known weight of boron pellets was introduced in a leaching device at a ratio 1:1 weight of pellets to water volume during 10 minutes, and then it was filtered. The remaining moistured pellets were dried at room temperature and saved for the next simulation step of the assay. Boron in solution was chemically analyzed.

The sequence was repeated up to six times, feeding the pellets recovered in the previous step of washing. Results are shown as ratio of cumulative leached boron (XB) and partial boron concentration in the liquid phase versus the cumulative volume of washing water used (V) per pellet kg.

The independent variable V is directly related to the volume of water supplied to the plant (by rain and by irrigation).

3. RESULTS AND DISCUSSION

Dissolution rate data must be evaluated on the basis of their application: It is a boron micronutrient in agriculture. Boron dissolution rate in "grams of boron dissolved per minute" is not useful for agriculture. The variable "time" would be useful only if the useful life of pellets were determined which could also be determined by the curves plotted in Figure 2. In such a Figure the cumulative boron dissolved ratio (X) as a function of cumulative washing water flow per mass unit of pellets (V) is plotted for every raw material, every hardening temperature and every pellet size. The value $V|_{x=i}$ matches the volume of washing water necessary to take out the whole boron content from the pellet. Time necessary to supply such a volume of water, coming from rains and/or by irrigation, is the useful time of the pellets.

Another interesting result from the agricultural point of view is shown in Figure 3, in which the concentration of boron in the filtered liquid (C) after each addition of washing water is plotted. Such a concentration must be ranged between the low and upper boundary concentration recommended for plants in Table 1. The application range of boron for plants is taken between 5 and 200 ppm B, matching 0.005 and 0.2 g B/ 1, respectively. Only colemanite and tyncal-ulexite pellets hardened at 700 °C fulfill that condition. Groups of curves in that condition overlap in the lower part of Figure 3.

Maximum concentration of boron in decreasing order and hardening temperature for every raw material fed to pelletization are presented in Table 4. Each one of them for the lowest pellet size obtained.

It is possible to make difference ranges of concentration differences among:

• 1-10 g B/l for hardened TU pellets at 600 °C
• 0.1-1 g   B/l for hardened CU pellets at 100 and 300 °C, and
• g B/l for C and TU pellets, both of them hardened at 700°C

Table 4. Maximum concentration of boron in washing water of pellets.

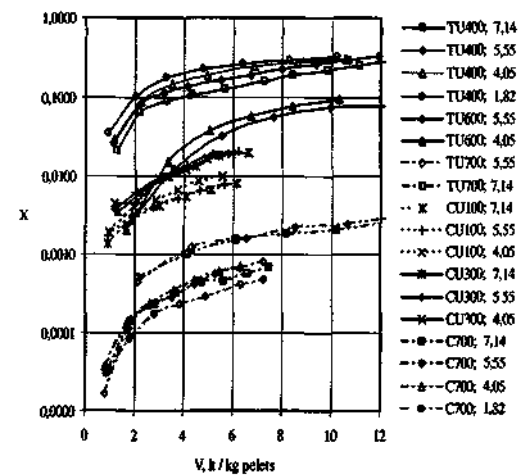| Nomenclature	Pellet raw material	Hardening temperature °C	B,g/1
TU400	Tyncal-ulexite	400	6.44
TU500	Tyncal-ulexite	500	6.52
TU600	Tyncal-ulexite	600	1.87
CU300	Colemanite - ulexite	300	0.86
CU100	Colemanite - ulexite	100	0.36
TU700	Tyncal-ulexite	700	0.032
C700	Colemanite	700	0.030

Figure 2. Cumulative ratio of boron dissolved as a function of washing water: X vs. V.
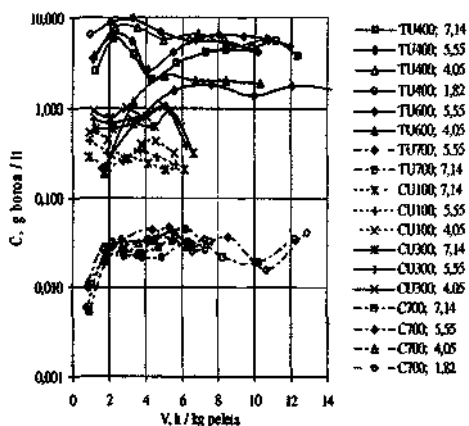
Figure 3. Boron concentration in liquid as a function of washing water: C vs. V

4. CONCLUSIONS

Pelletization is an adequate method to produce slow release of boron micronutrients on the basis of a suitable selection of raw materials, hardening temperature and size of pellets. Colemanite pellets, 7.14 mm in diameter, hardened at 700 °C, gives 0.030 g BA, which is the lowest boron concentration found in liquid phase.

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