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Minerals Engineering xxx (2005) xxx–xxx
MINERALS ENGINEERING
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Technical note

Slow release boron micronutrients from pelletized borates of the northwest of Argentina

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Received 5 July 2005; accepted 11 September 2005

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 calcinate colemanite, natural mixtures of tyncal–ulexite, mixtures of calcinate colemanite–calcinate ulexite to a pelletizer disk, as well as the size of pellets and the hardening temperature are analyzed.

Pellets made up on feeding calcinate colemanite (700 °C) and calcinate tyncal–ulexite perform better properties for slow release boron micronutrients, restricting the concentration in water around 30 ppm.

Keywords: Industrial minerals; Non-metallic ores; Oxide ores; Agglomeration

1. Introduction

The Puna region in South America is one of the few areas of the world with large borate reserves.

Over 200 boron minerals were identified in nature, but only few have industrial importance (Garret, 1998). Among them the sodium (tyncal and kernite), the calcium (colemanite, inyoite and priceite), the sodium–calcium (ulexite and probertite), the magnesium–calcium (hydroboracite).

Borates and their derivatives are widely used in industry (Flores, 2004).

Boron is one of the seven basic micronutrients in plants. It is present in soils between 2 and 100 ppm (Villanueva et al., 1998). However, the presence of enough micronutrient does not mean its availability. Generally, less than 5% of boron in soils is available for plants due to the scarcely soluble boron in soils water and the drainage to deep beds.

Naturally boron deficient soils or those intensively farmed should be outfed supplying between 0.5 and 15 boron kg per hectare during the plant growth.

Main factors acting on the boron plant uptake are: soil features, kind of rains (acid or not), temperature, environmental humidity, properties of the micronutrient and the application methods. Boron may be supplied as solid (granulated or powdered) or liquid (irrigated or sprayed). In the latter form, it is supplied as highly soluble refined borates (borax, sodium tetraborate pentahydrate, sodium pentaborate).

All borates contain combinations of three- (triangular) or four-bond (tetragonal) B–O structures. Upper part of Table 1 shows the structural formula and some properties. Solubility in water is the most important property for the use of borates in agriculture. Variables such as temperature, pH, the solution concentration, cations in solution,

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doi:10.1016/j.mineng.2005.09.034

Table 1
Solubility of agricultural interesting borates in water (25 °C), chemical reactions and physical state of the products according to the pyrometallurgical treatment

Mineral	Structural formula	Molecular weight	% B_2O_3	Solubility (ppm) B	% B anion	Nat. pH
Colemanite	$Ca[B_3O_4(OH)_3] \cdot H_2O$ $3\infty{:}\Delta + 2$	411.09	50.84	253	22.01	8.6
Hydroboracite	$CaMg[B_3O_4(OH)_3]_2 \cdot 3H_2O$ $3{:}\Delta + 2$	413.33	50.55	314	22.01	8.7
Tyncal	$Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ $4{:}2\Delta + 2$	381.37	36.52	7157	22.63	9.3
Ulexite	$NaCa[B_5O_6(OH)_6] \cdot 5H_2O$ $5{:}2\Delta + 3$	405.24	42.97	560	21.46	8.8
Boric acid	$H_3[BO_3]$	61.84	56.31	8819	95.15	3.7
Turmaline	$NaMgAl_6B_3Si_6O_{27}(OH)_4$	909.95	11.48	<0.1		
T (°C)	Reaction	Consequence				
$50 \leqslant T \leqslant 105$	Drying	Loss of moisture. Borax and ulexite start dehydration				
$T_d \leqslant T \leqslant T_c$	Calcination	Loss of crystallization water molecules. Colemanite decrepites. Tyncal swells. Ulexite crumbles				
$T_c \leqslant T \leqslant T_v$	Partial vitrification	Hardening of pellets. Agglomeration by partial smelting				
$T_v \leqslant T \leqslant T_s$	Full smelting	Unique smelted phase: Glass of homogeneous chemical composition				

and other factors can significantly change the borate's structure and influence the anions in the solution.

The appropriate features of a micronutrient are:

(a) Higher initial dissolution rate.
(b) Long mean life with constant rate dissolution.
(c) Boron concentration in underground water in the plant uptaking range.
(d) An appropriate strength to resist mechanical damage during its mean life in the soil.

Pelletizing 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.
- The chemical reactions occurring when borates are exposed upon increasing hardening temperatures. The consequences (d: drying, c: calcination, v: partial vitrification or sintering, s: full smelting) are summarized in lower part of Table 1.

Use of boron as an agriculture fertilizer is an interesting option for the commercialization of concentrates which do not fulfill the standard borate specifications.

Particularly, middlings and concentrates graded in iron could be commercialized in the market of fertilizers and micronutrients.

2. Experimental work

2.1. Mineral characterization

Selected raw materials were chosen under 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

Raw material	Solubility range g B/l, 20 °C	Chemical composition (%)			
		B	CaO	Na_2O	Insoluble
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

Chemical composition and water solubility range at 20 °C.

2.2. Pelletization

Pellets were made by rolling in an inclined disk of 775 mm in diameter, supplied with two baffles and a spray feeder (water or borate solution). The rotating speed was settled on 29 rpm.

Moisture content was between 25 and 35%.

The influence of raw material and hardening temperatures of pellets on the water dissolution rate were studied.

2.3. Pellet drying/hardening

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

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. Those ranging size distribution between 7.4 mm and 5.5 mm, compression strength upper than 13 kg and fall resistance upper 8 m were taken away for the assays.

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 (D_{pc}, mm). For example TU500, 7.14 are pellets made up of calcinate tyncal–ulexite at 500 °C and mean size 7.14 mm.

2.4. Pellet leaching

Water leaching of pellets at room temperature was carried simulating the natural boron dissolution in soils. Plants receive repeated washing cycles (due to rain and/or irrigation) followed by natural drying until boron in the pellet is exhausted.

A known weight of boron pellets was immersed in a beaker at a ratio 1:1 weight of pellets to water volume during 10 min, and then drained. Moisturized pellets were dried at room temperature and saved for the next simulation step. Boron in solution was chemically analyzed.

Results are shown as ratio of cumulative leached boron (X_B) versus the cumulative volume of washing water used (V) per kg of pellets.

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 the application of boron as micronutrient in agriculture. The cumulative boron dissolved ratio (X) as a function of cumulative washing water volume per mass unit of pellets (V) is plotted for every raw material, every hardening temperature and every pellet size is shown in Fig. 1. The value $V|_{X=1}$ matches the volume of washing water necessary to eliminate all the boron 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.

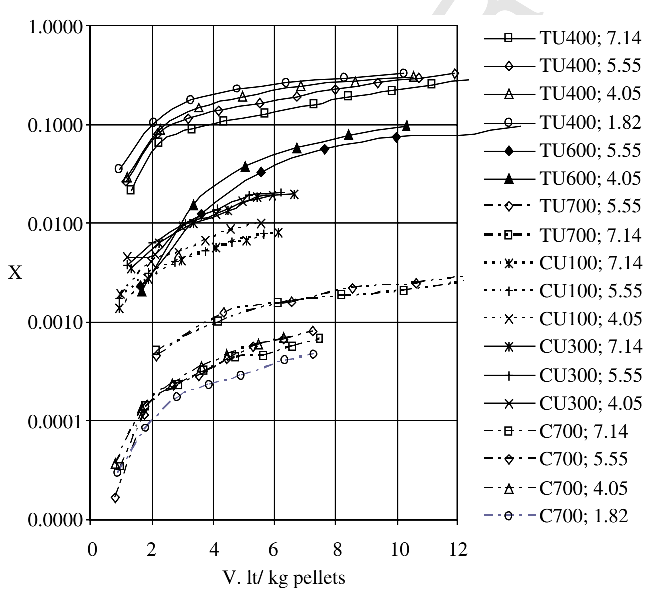

Fig. 1. Cumulative released boron as a function of washing water volume: X (g B/l) vs. V (l).

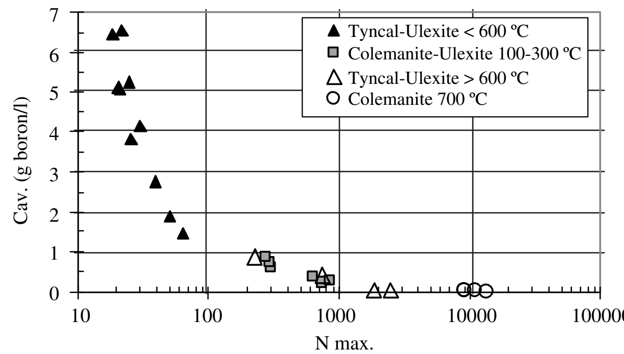

Fig. 2. Maximum number of washing steps.

It is possible to classify the studied raw materials into ranges according to the amount of boron dissolved in water, as follows:

- 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
- <0.1 g B/l for C and TU pellets, both of them hardened at 700 °C

Only colemanite and tyncal–ulexite pellets hardened at 700 °C fulfill the condition of releasing boron under 0.2 g B/l.

Fig. 2 shows the cumulative boron released, C_{av} (average of the six last washing steps for every assay) as a function of the inverted partial fraction of boron dissolved. The last value is approximately the necessary number of washing steps, N_{max}, to become the boron in the pellets exhausted, if it would dissolve at the same rate during its useful life.

The methodology applied to evaluate some borates as an outfeeding source of boron for agricultural micronutrient and the estimation of the mean life of pellets cannot be applied just under the rain regime. Release of boron from the pellets depends on many environmental factors not considered in this study, such as water pH in soil, chemical composition, temperature, slope of the country field, period of rains, etc.

4. Conclusions

Pelletization is an adequate method to produce slow release boron micronutrients on the basis of a suitable selection of raw materials, hardening temperature and size of pellets. Colemanite pellets hardened at 700 °C fulfill the recommended concentration of boron in soil solution for plants ranging between 0.005 and 0.020 g B/l.

Simulation of washing cycles under lab operating conditions, allows an estimation of the mean life of colemanite pellets as boron micronutrient for most of plants.

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