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COMPLEX TECHNOLOGIES OF BRUCITIC LIMESTONE CAPITALIZATION

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Abstract: *The paper presents a synthesis of the research consisting in a complex capitalization of a brucitic limestone deposit from Romania, in environmental protection, respectively of the complex processing possibilities for using the final products could in a very well defined direction such as: the getting of MgO with 99% purity from a brucitic concentrate with 38-40% MgO content; the getting of a fertilizer containing struvite, limestone and microelements with benefit effects on the acid soils amelioration and on plants growth. The research allowed the establishing of a complex system of three technologies, respectively, one of brucitic limestone processing, the second of magnesia obtaining by brucitic concentrate leaching with carbon dioxide and the third, that of getting a double-role agricultural fertilizer (manure for plants growth and acid soils neutralizer).*

Keywords: *brucitic limestone, limestone processing, brucitic concentrate, struvite*

1. Theory

The ionic salts have a good solubility in polar solvents such is the water. The dissolution process takes place because the solvent's molecules have an attraction force sufficient to get off the ions from the crystalline network. During this process the ions become solvated:

$$MX(s) \xrightarrow{x + y H_2O} M(H_2O)_x^+ + X(H_2O)_y^- \qquad (1)$$

Although the anions and the cations are behaved as solvated ions, the attraction between the water molecules and the metallic ions is weak enough.

Because the water molecules and the ions from solution are in a continuous and rapid movement, the number of water molecules corresponding to one metallic ion, are variable. The average number is known as hydration number. In the hydrated crystals, the water molecules number is fixed. The solubility of the compounds from the brucitic ore is very little. The solubility of $CaCO_3$ decreases with the temperature increasing, while the solubility of $Ca(HCO_3)_2$ increases with the temperature increasing. [1], [2], [3].

The solubility product (K_{ps}) represents the way to deduce the optimal conditions for the formation and the dissolution of precipitations. These conditions consist in: temperature, pH, concentration of precipitation agent, the salt concentration and the solvent composition. In the calcium carbonate case, the equilibrium and the solubility product (K_{ps}) relations are as follows:

$$CaCO_{3(s)} \leftrightarrows Ca^{2+} + CO_3^{2-} \qquad (2)$$

$$K_{ps} = 0{,}99 \cdot 10^{-8} (M)^2 = [Ca^{2+}]\,[CO_3^{2-}] \text{ la } 15°C \qquad (3)$$

$$K_{ps} = 0{,}87 \cdot 10^{-8} (M)^2 = [Ca^{2+}]\,[CO_3^{2-}] \text{ la } 25°C \qquad (4)$$

In the magnesite case, the equilibrium and the solubility product (K_{ps}) relations are:

$$MgCO_{3(s)} \leftrightarrows Mg^{2+} + CO_3^{2-} \qquad (5)$$

$$K_{ps} = 2{,}6 \cdot 10^{-5} (M)^2 = [Mg^{2+}]\,[CO_3^{2-}] \text{ la } 15°C \qquad (6)$$

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If the carbonate ion is added as sodium carbonate in a saturated solution of $CaCO_3$, in the system equilibrium a constraint occurs.

The common ion of carbonate affects the equilibrium system toward the solid $CaCO_3$ formation. The obvious result is a calcium ions decreasing in solution. If Na_2CO_3 is added, the calcium ions concentration decreases in the end. This is an example of the common ion effect and this effect can be calculated through the solubility product. When there is a mixture of $CaCO_3$ and $MgCO_3$, the proportion between solubility is as follows:

$$\frac{P_{CaCO_3}}{P_{MgCO_3}} = \frac{[Ca^{2+}]}{[Mg^{2+}]} = \frac{0.99 \cdot 10^{-8}}{2.6 \cdot 10^{-5}} = 3.8 \cdot 10^{-4} \quad (7)$$

The addition of Mg^{2+} ions will have as a result a decreasing of calcium ion concentration. Another theoretical aspect consists in the effect of magnesia addition in the domestic residual waters cleaning. The magnesia can remove efficiently the nutritious (the phosphate and the nitrate ions) as “struvite”. Struvite (magnesium ammonium phosphate hexahydrate) with the chemical formula $(NH_4)Mg(PO_4)\cdot 6(H_2O)$, is a colorless crystal, with rhombohedra lattice type. Struvite has a low solubility in water (about 0.02 g/100 ml water), is highly soluble in diluted acidic solutions and highly insoluble in alkaline solutions. His specific density is 1.7 kg/dm^3 and the molecular weight is 245.41 g [4]. The precipitation reaction is:

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} = MgNH_4PO_4 \quad (8)$$

In the precipitation process a lot of chemical elements such as: Hg, Ag, Pb, Al, Fe, Mn, Zn are also removed from waste waters. Under the same conditions, arsenic ions precipitate as AsO_4^{3-}. The magnesium necessary for precipitation must not be added as precipitation reagent. The magnesium dissolution is, in a low measure, the consequence of its solubility:

$$Ps = [Mg^{2+}]\cdot[CO_3^{+2}] = 2,6\cdot 10^{-5} \quad (9)$$

The solubility product allows a solubility of magnesium of 0.005 mol/l.

A better solubility of magnesium is in the carbon dioxide presence:

$$Mg(CO_3) + CO_2 + H_2O = Mg(HCO_3)_2 \quad (10)$$

The struvite, as result of these reactions, when it is not contaminated with low metals, can be used as agricultural fertilizer with phosphorous and ammonium. The chemical composition of the pure struvite is: NH_3 - 23,29%; PO_4^{3-}- 69,34%; Mg^{2+}- 7,37%.

2. Experimental research

2.1. The characteristics of mineral sample

The chemical results of the mineral sample are presented in Table 1.

Table 1 The chemical results of the mineral sample

Component	UM	Contents
SiO_2	%	0.42
TiO_2	%	0.01
Al_2O_3	%	0.03
MnO	%	0.02
Fe_2O_3	%	0.13
MgO	**%**	**23.18**
CaO	**%**	**33.12**
Na_2O	%	0.09
K_2O	%	0.06
P_2O_5	%	0.18
P.C.	%	42.28

The brucitic limestone processed has a wetness of around 3% and contains: 23.18%MgO, 33.12% CaO, 0.42% SiO_2 ; 0.01% TiO_2 ; 0.03% Al_2O_3 ; 0.02% MnO; 0.13% Fe_2O_3 ; 0.09%Na_2O; 0.06% K_2O; 0.18% P_2O_5, and 42.28%, calcination loss.

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2.2. Processing technology of brucitic limestone

Concentration tests applying diferrent conventional methods, predominantly hydrogravitational, but also through flotation, were carried out after a global technological scheme presented in figure 1.

The figure also renders the main products and their features.

The best results for coarse or grinded material were obtained with Mozley concentrator. The concentrate has 37-39% MgO and the weight recoveries were 12-15%. In figure 2 is presented the technological flow sheet for brucitic limestone processing, in order to obtain magnesia with purity around 98% and two secondary products rich in calcium carbonate as final products too [5].

The proposed technology assures a total capitalization of the rough material, without tailings and without negative effects on environment. The physical and thermo-chemical operations assure a global efficiency of 85% and a low energetically consumption due to an efficient calcinations and solubilization circuit [6].

The technical solution is available for the processing of a brucitic limestone with 22-25% MgO. The first part of the technology allows to get a concentrate with 35-40% MgO after two grinding stage and a pneumatic concentration. The concentrate is calcinated at 500-600 ^{o}C, when the brucite are decomposed to magnesia, very reactive in regard with the carbon dioxide.

The brucitic concentrate calcined, so called “activated concentrate” is solubilized with carbon dioxide at 2-5 atm pressure. The solubilisation result is the magnesium bicarbonate. After a filtration, results a rich solution in magnesium bicarbonate and a secondary product rich in limestone.

The solution of magnesium bicarbonate is boiled 20-30 minutes for the precipitation of magnezite. The suspension is filtered at 80^{o}C, resulting a magnesium concentrate with a purity of 98%.

The main advantages of this technology are:
- an energy consumption reducing;
- a high efficiency of the magnesia recovery;
- a decreasing of ratio solubility by addition the magnesium ions in excess through the time of reaction reducing.

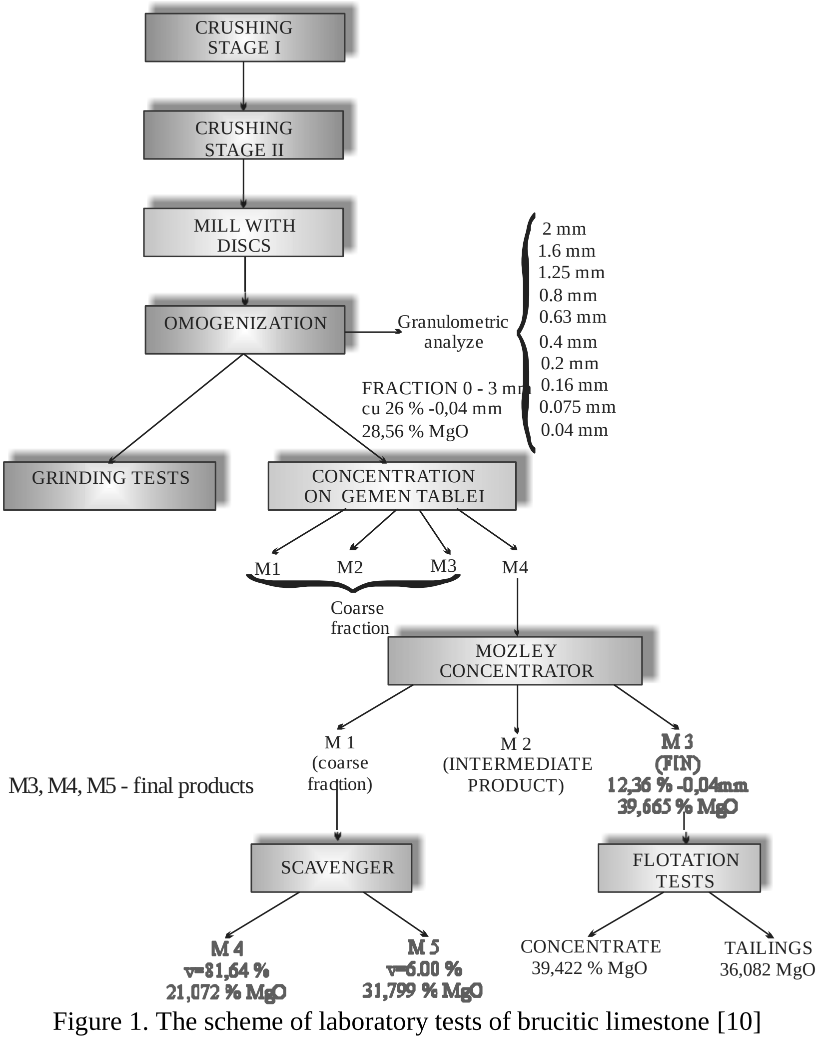

Figure 1. The scheme of laboratory tests of brucitic limestone [10]

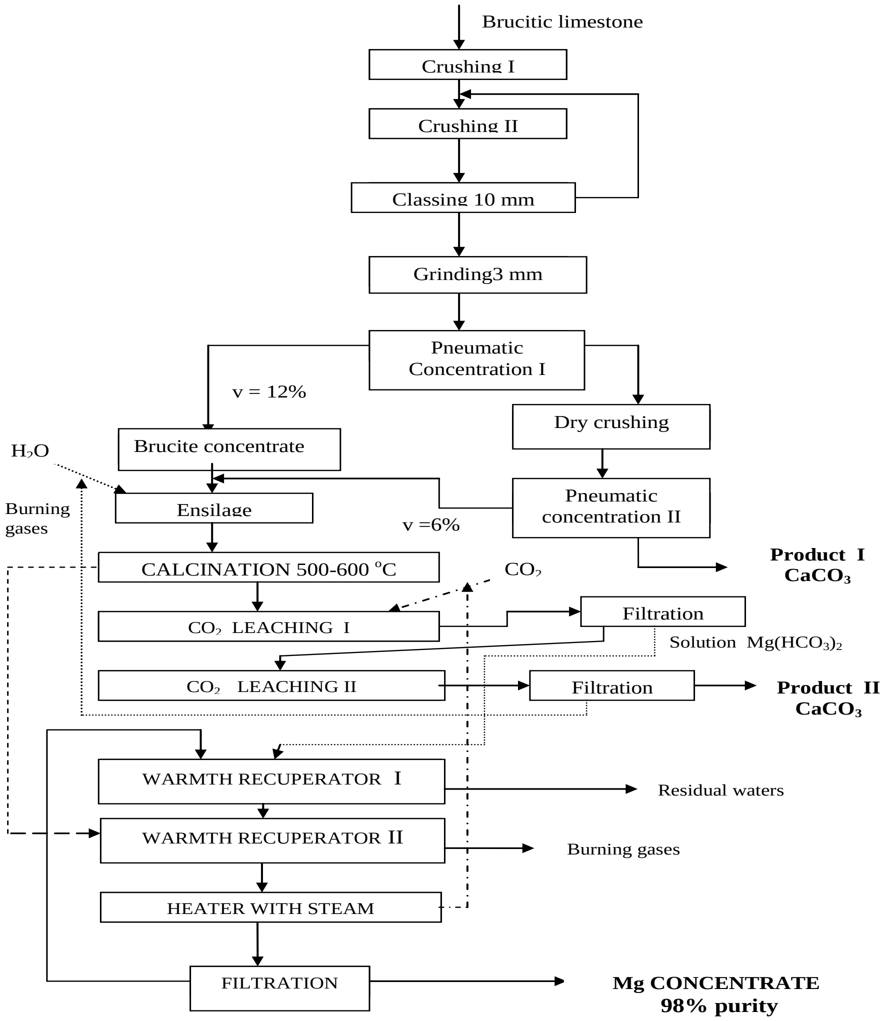

Figure 2. Technology for magnesia getting

2.3. Technology for a complex agricultural fertilizer getting

There are a lot of products as soils fertilizer as results of domestic residual waters processing. This kind of product is the precipitation result of the nutritious (the phosphate and the nitrate ions) precipitation with magnesium salts addition [7]. The final product familiar as struvite is a granular product with particles between 0,5-1 mm and can be used as complex fertilizer in agriculture for soils remediation [8], [9].

The technology presented in figure 3 is the result of our research and allows a total capitalization of the brucitic limestone. From installation don't results tailings, whole feeding quantity becoming an active substance with complex fertilizer role. The product can be used also as neutralizer of acid soils, after nutritious recovery.

The research steps point out highly processing efficiencies concomitant with a better waste waters cleaning with, abating costs.

The processing flow sheet is simple, containing in the first stage two crushing operations followed by material calcinations. After calcinations results a mixture of magnesia, calcium oxide, microelements and another metallic oxides with an important role in the plants culture.

The laboratory tests emphasize that by treating residual waters with nutritious concentrations of 100-150 mg/l PO_4^{3-} and 100-110 mg/l NH_4, it will be recovered 90% from nutritious ions.

The main advantages of this technology are:

- assures the getting of a complex product with fertilizer role, containing natural quantities of microelements and metallic oxides indispensable to the plants metabolism;

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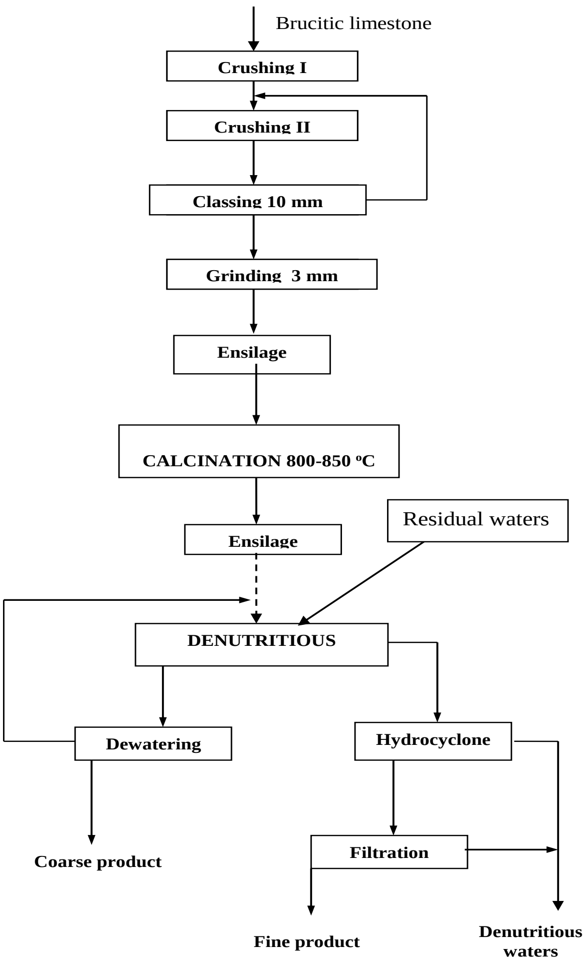

Figure 3. Technology for struvite getting

- reduces processing costs because it is not necessary to add regulation substances of pH in the crystallization process of struvite and it is not necessary to add chemical microelements to reach the acid soils;
- allows a continuous treatment of the water flows containing the phosphate and the nitrate ions;
- assures an increasing of the process efficiency of brucitic limestone processing by a sequential stages, with benefit role in the waste waters treatment and to the agricultural fertilization of the acid soils which in Romania becomes at 2 millions hectares.

The recovery of nutritious is one of the most important operations from the technological sheet and it comes off in a special new device, a kind of reactor in fluidized bed, presented in figure 4.

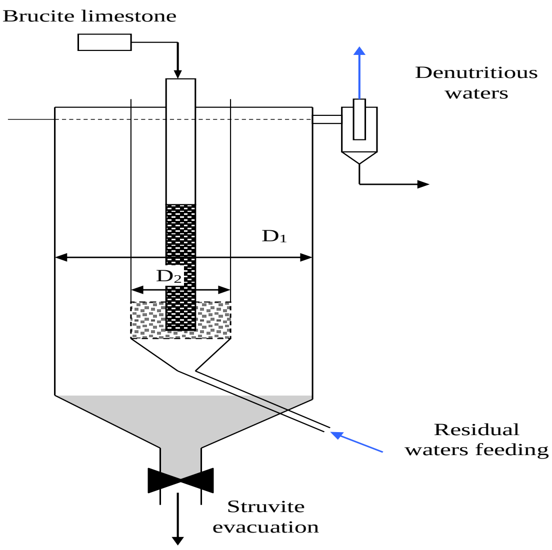

Figure 4. Reactor in fluidized bed

This phase consists in struvite formation by starting to react the very fine particles of magnesia (under 40 microns) which represents 5-7% from the brucitic limestone, with the phosphate and the nitrate ions.

The struvite particles smaller than 0,3 mm are trained to the upper level of reactor and after a hydrocycloning operation, results the fine struvite and the cleaned water. The struvite with granules greater than 0,3 mm are ejected from device to the bottom part.

3. Conclusions

The research results lead to the elaboration of the processing technology of brucitic limestone with an average content of 22-25%, MgO. Through two stages of grinding and pneumatic concentration, results a brucitic concentrate with 35-40% MgO content.

After calcinations at 500-600 ^{o}C, the brucitic concentrate becomes a mixture of calcium oxide with magnesia which reacts easily with carbon dioxide at the pressure of 2-5 atm with formation of magnesium bicarbonate.

The second technology proposed has the aim to get a fertilizer with double role: as neutralizer of acid soils and as fertilizer for plants culture. The fertilizer contains 20-25% struvite after the reaction between the magnesia and the phosphate and nitrate ions from the domestic waste waters. The time of reaction is around 60 minutes and the final product consists of 30-35% calcium oxide, 1,5-2% microelements e.g. cobalt, copper, nickel, zinc, boron and metallic oxides.

The second technology presented includes devices and installations which assure a complex capitalization of the rough material consisting of brucitic limestone. It is important to know that it is a clean technology, without tailings and without negative impact on environment. Whole rough material becomes active mixture made up from calcium oxide and magnesia. Another novelty of this technology consists of the reactor type with fluidized bed where takes place the domestic residual waters cleaning with high treatment efficiency and a high degree of recovering the phosphorous and nitrate ions. [3].

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