



ABSORPTION OF SULFUR DIOXIDE IN WASTE CALCIUM CARBONATE SLURRY II. THE INFLUENCE OF THE PARAMETERS ON THE ABSORPTION RATE ♦

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Abstract: Using Lewis’s reactor technique we have studied the influence of the calcium carbonate’s nature and its milling degree on the saturation rate of the slurry with different rations between the solid and the liquid. The evolution of this process has been expressed by variation of the content of sulfur dioxide absorbed, reported to the reaction mass. The result shows the importance of the source of calcium carbonate’s nature and milling degree on the absorption rate. Regardless of the carbonate’s type – natural or waste product – and the s/l ration in the suspension, the sulfur dioxide concentration in the reaction mass is over the value obtained for water. If the dry milling in balls or impact-mills changes in a reduced measure the dissolution rate, the wet milling guarantees an advanced reactivity.

Keywords: *absorption, sulfur dioxide, calcium carbonate waste suspensions, wet desulfurization.*

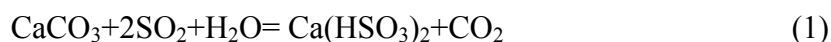
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INTRODUCTION

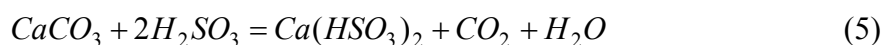
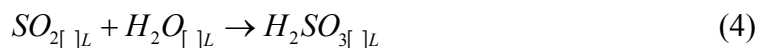
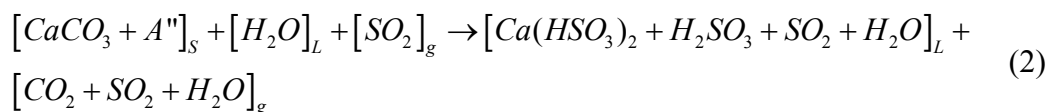
The use of the calcium carbonate for the wet desulphurization is conditioned so much by the relative stability of the suspensions as by their reactivity [1-3]. In the s-g-l systems, the gas restraint, especially of the sulfur dioxide, is conditioned by the contact surface between the condensed phases. The enlargement of the specific initial surface, by milling, could make up a way of increasing the efficiency of the behavior in absorption of NPK's fabrication waste. The positive results of the previous researches concerning the reactive dissolution of the calcium carbonate precipitate in sulfurous acid solutions [4-6] make possible the approach of some experimental studies referring to the influence of the carbonate's nature, of the waste's grinding degree and of the solid/liquid rations on the absorption rate of the sulfur dioxide from gases. Therefore, in this work are presented the results of some laboratory researches, made by using the calcium carbonate waste precipitate from S.C. AZOMURES S.A. Tg. Mures.

THE MECHANISM OF SULFUR DIOXIDE REACTIVE DISSOLUTION IN CALCIUM CARBONATE SUSPENSIONS

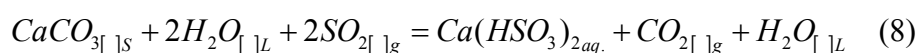
The reactive dissolution of sulfur dioxide is based on the following reaction:



Being known the weak solubility of the calcium sulfite [7], the process will need to be leaded so that the final solution should still contain free sulfur dioxide, able to dissolve the eventually particles of calcium sulfite. Though the sulfur dioxide is a stronger acid than the carbonic one, its restraint in solution, especially in the conditions of an intense agitation, imposed by the hydrodynamic conditions of the homogeneous suspension and by an advanced CO_2 emission is extremely difficult. When the physically dissolved oxygen is absent, the oxidation of sulfite to sulfate can be neglected, fact which makes possible to describe the global process by using the "characteristic equation" (2) and the elementary processes (3) ... (7) [8]:



Neglecting water's vaporization, the real process can be described using the simplified "characteristic equation" (2) and the global reaction s-l-g (8):



As a measure of the process's evolution we can choose the variation of concentration in the solution, either of the calcium ion or of the total sulfur dioxide of the reaction mass. The transformation degree of the calcium carbonate, defined by relation (9), may also be a measure of the process's evolution:

$$\eta = \frac{n_{CaCO_3}^0 - n_{CaCO_3}}{n_{CaCO_3}^0} = \frac{V_{[L]} \cdot C_{Ca^{2+}}}{m_p^0 \cdot X_{CaCO_3}^0} \cdot \frac{M_{CaCO_3}}{M_{CaCO_3}} \quad (9)$$

where: $V_{[L]}$ - liquid phase's volume at a certain moment, L, $C_{Ca^{2+}}$ - calcium's concentration, mole/L, m_p^0 - mass of the solid sample used, g, $X_{CaCO_3}^0$ - calcium carbonate waste's mass fraction [9], M_{CaCO_3} - calcium carbonate's molar mass, g/mole, n_{CaCO_3} , $n_{CaCO_3}^0$ - the number of calcium carbonate moles at a certain moment, respectively at the initial moment, mole.

EXPERIMENTAL

The kinetic study of the sulfur dioxide's chemisorption in calcium carbonate suspensions has been achieved according to Lewis's reactor technique, using the installation depicted in Figure1.

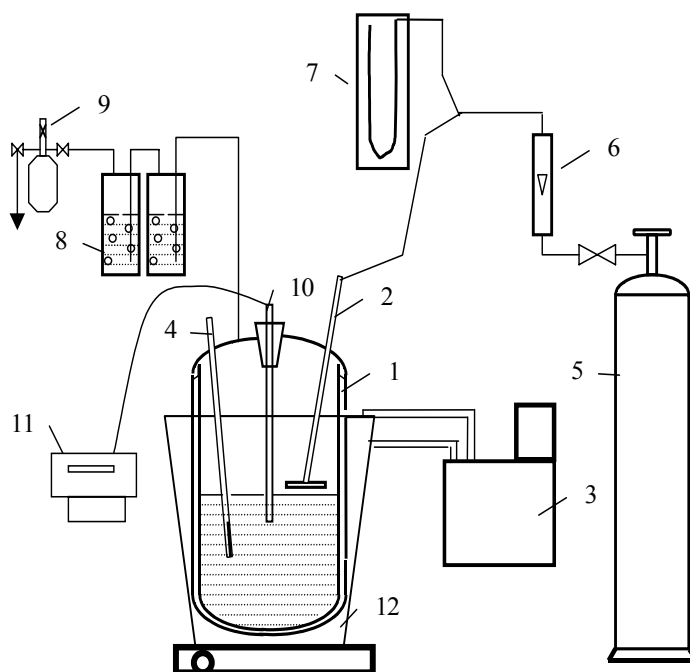


Figure 1. Experimental installation used for the chemisorption study

1 – discontinuous reactor with magnetic stirrer, 2 – gas distributor, 3 – U15 thermostat, 4 – thermometer, 5 – sulfur dioxide cylinder, 6 – rotameter, 7 – manometer, 8 – bubbling recipients, 9 – vacuuming installation, 10 – conductometric cell, 11 – conductometer, 12 – thermostat casing.

To eliminate the possibility that the sulfur dioxide's transfer through the gas phase become limitative stage of rate, we have worked with technical sulfur dioxide (99% SO_2), introduced in the reactor at about 5 mm above the suspension, at a constant flow and at an overpressure of 7-8 mm water column. The maintenance of the particles in suspension has been done by magnetic agitation of the reaction mass. The agitating device's rotation was adjusted so that the separating surface of the gas suspension should be smooth, without waves generated by the moving reaction mass. The unabsorbed gas was continuously exhausted, being absorbed in the distilled water. The temperature, the same for all the samples, has been controlled using the U15 thermostat. The evolution of the process has been monitored both by a continuous measuring of solution's conductivity and by determining the total content of sulfur dioxide in the samples taken at different spells. The analysis of the total sulfur dioxide's concentration in the weighted samples has been made by the indirect iodometrical method, titrating the iodine excess with thiosulfate solutions, in the presence of starch as indicator.

The experiments have been performed at a 293-296 K temperature, at a constant rotation of the magnetic agitator, using more carbonate types – milled limestone from Vata de Jos, unmilled waste, dry milled waste in balls-mill, in impact-mill and wet milled waste in balls-mill with a proportion balls/material/water of 2.7/1.0/0.7. The carbonate content from the suspension has been varied between 0 g/100 g of water to 20 g/100 g of water.

RESULTS AND DISCUSSIONS

Analyzing the results we got by using different carbonate types we found that the unmilled waste has the same behavior as the limestone from Vata de Jos, with an advanced grinding degree (dimensions under 0.045 mm). Instead, the wet milled waste presents a much higher reactivity than the unmilled one, fact which can be seen from the dependences in Figure 2. In all the cases the growth of the total sulfur dioxide content is much over the one we get when we use water as absorbent.

Comparing the reactive solubility of different unmilled waste, it can be seen from the Figure 3, that the drying, washing and drying of the waste assures a little influence over the concentration of total sulfur dioxide in the reaction mass. If the wet milling of the waste guarantees a growth of

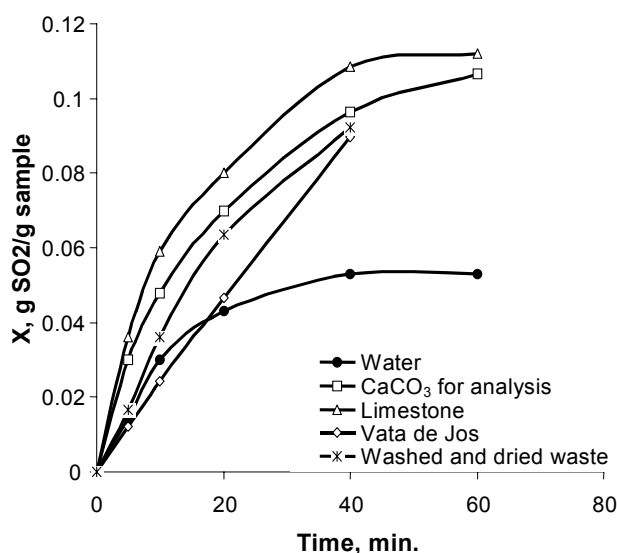


Figure 2. Kinetic curves resulted at the sulfur dioxide absorption in suspensions with different carbonate types

the capacity of retaining sulfur dioxide, the dry milling in balls-mills or in impact mills modifies the waste's reactivity in a smaller measure. This fact can be distinguished from the dependences in Figure 4, where we can observe that grinding the waste during 3 or 9 hours increases the sulfur dioxide's capacity of absorption, but in a measure comparable to the one obtained by using waste milled in impact-mills.

As we expected, the growth of the waste content in the suspension insures a substantial increase of the sulfur dioxide absorption capacity. As the dependences in Figure 5 show, the growth of the waste content from 5 to 15 g/100 g of water has about the same effect like passing from water to a suspension with 5 g of waste content for 100 g of water. The growth of the waste content in the suspension substantially diminishes the time needed for reaching a certain concentration of total sulfur dioxide.

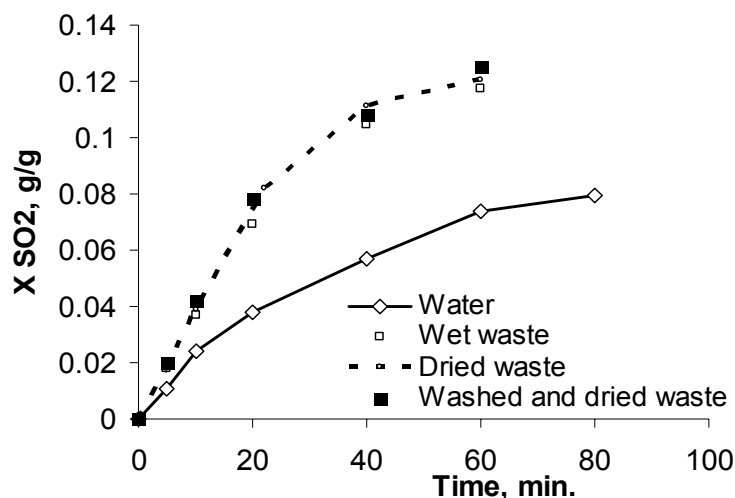


Figure 3. Kinetic curves obtained by using unwashed, washed and dried, and dried waste (solid/liquid ration: 10 g/100 g water)

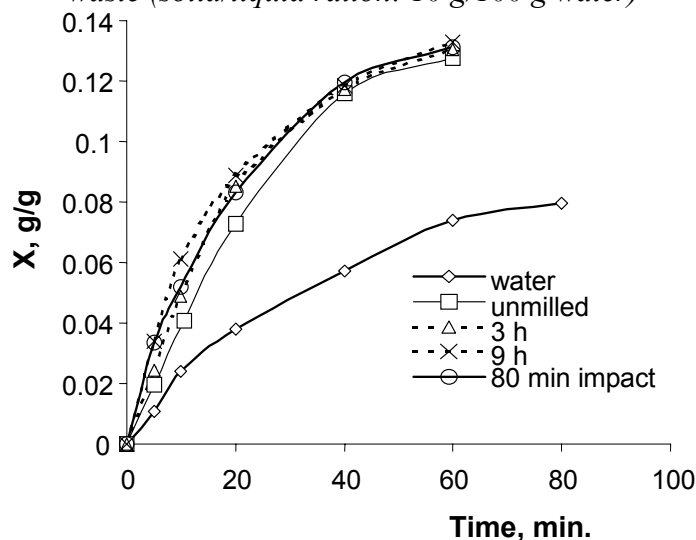


Figure 4. Kinetic curves obtained by using dry milled waste for different periods (solid/liquid ration: 10 g/100 g water).

Based on the primary dependences in Figure 5 we have established, using the data in Figure 6, the calculus relation of the necessary time to guarantee a certain concentration, respectively:

$$\tau = (1.694 - 27.284 \cdot X_{SO_2T}) \cdot x_{[s]} + 673.01 \cdot X_{SO_2T} - 38.505; \text{min} \quad (10)$$

where: $x_{[s]}$ - the solid/liquid ration of the initial suspension, g/100 g of water.

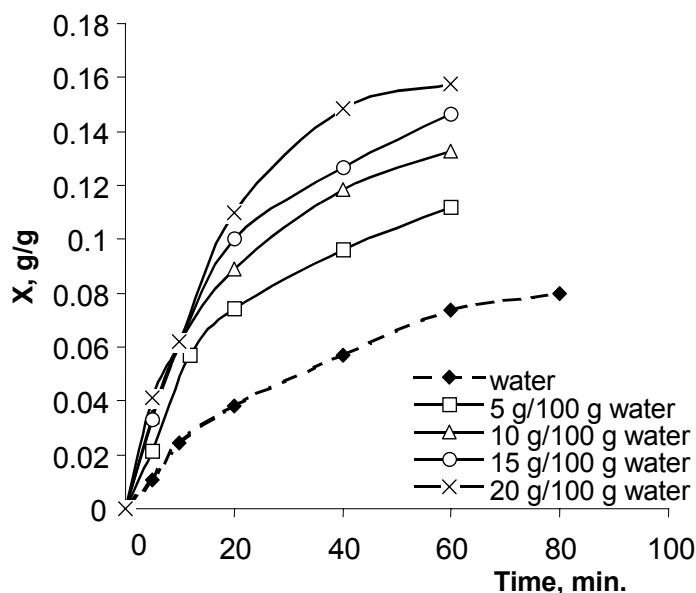


Figure 5. Kinetic curves obtained for different solid/liquid ratios by using dry milled waste during 9 hours

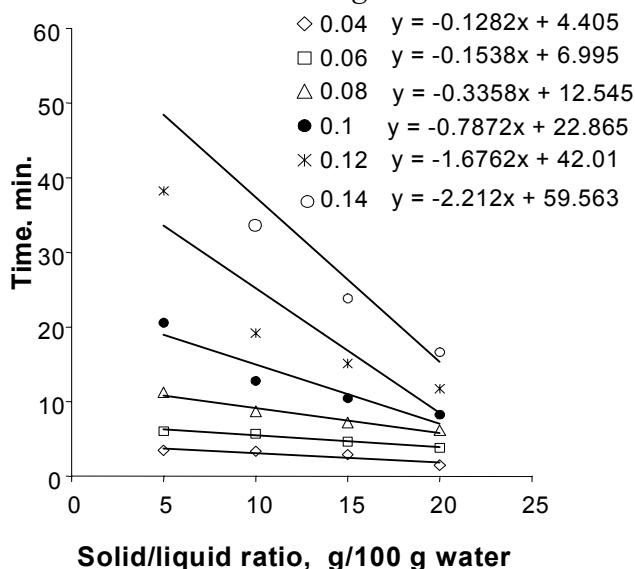


Figure 6. The influence of the solid/liquid ratio on the period of reaching the sulfur dioxide's concentration from the reaction mass

CONCLUSIONS

The experimental study shows that the waste from NPK fertilizers has a similar behavior in the retaining of the sulfur dioxide from gases to the natural, finely milled limestone. The dimensions diminution by dry milling in balls-mills, though it guarantees an enlargement of the specific surface, it doesn't lead to the expected leap regarding the sulfur dioxide adaptation capacity. Instead, the growth of the waste content in the suspension leads to a substantial diminution of the time needed for reaching a certain concentration of sulfur dioxide connected to the reaction mass.

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REFERENCES

1. Miller, M.: Lime, *US Geological Survey Minerals Yearbook*, September, **2004** (www.lime.org)
2. Fellner, P., Khandl, V.: Characterisation of Limestone Reactivity for Absorption of Sulfur Dioxide from Fume Gases, *Chemical Papers*, **1999**, 53(4), 238-241.
3. Ahlbeck, J.: Measuring the Reactivity of Limestone for Wet Flue Gas Desulfurization, *Chemical Engineering Science*, **1995**, 50(7), 1081–1089.
4. Szép, Al., Mihăilă, Gh., Bartha, S., Câșu, M.I.: Kinetic Study of the Reactive Dissolution of Marble into Sulfur Dioxide Solution, *Analele Științifice ale Universității „A.I. Cuza” Iasi*, **2003**, XI, Ser. Chimie, 167-176.
5. Szép, Al., Bartha, S., Tanczos, Sz.: *A nedves kéntelenítés kinetikai vizsgálata. II. A hulladék kalcium-karbonát reaktív oldódása kéndioxid oldatba*, IX. Nemzetközi Vegyészkonferencia Kolozsvár, **2003**, Nov, 14-15, Kolozsvár - Cluj-Napoca, 213-219.
6. Szép, Al., *Varul. Tehnologie si utilizări*. Ed. Ceram, Iasi, **2005**.
7. Szép, Al.: *Cristalizarea sărurilor din soluții apoase*, Ed. Ceram, Iași, **2002**.
8. Ifrim, L., Calistru, C.: *Procesul chimic unitar adsorbție reacție formare si creștere de germeni*, I.P. Iași, **1979**.
9. * * * SR-1083/76/81, *Carbonat de calciu*.