



ABSORPTION OF SULFUR DIOXIDE IN WASTE CALCIUM CARBONATE SLURRY I. PREPARATION AND CHARACTERIZATION OF SLURRY♦

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Abstract: Preparation of relative stable slurries from waste calcium carbonate, resulted from the NPK fertilizers industry, and their testing as buffering agent, are reported. Characterization of the waste calcium carbonate was carried out by IR spectra, chemical analysis and thermal behavior, in comparison with two natural limestones, taken out from two Romanian deposits, i.e. Săndulești and Vața de Jos. In order to establish the main physical properties of the slurries prepared by dry and wet milling, measurements of their particle size composition, settling number and rheology were performed. The buffering capacity against some acid solutions, determined in a batch reactor with stirring and provided with conductometrical sensitive elements was utilized as a measure of their reactivity.

Keywords: *precipitate calcium carbonate waste, wet and dry milling, buffering capacity, settling number, flow rate.*

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INTRODUCTION

The natural calcium carbonate represents one of the most utilized additives in sulfur dioxide capture from gases [1, 2]. It is utilized under milled form or under form of some derivative products, quick lime, hydrated lime and lime milk [3]. During over 50 years of utilization of the natural calcium carbonate and its derivatives in flue gas desulphurization (FGD), two procedures of desulphurization were developed, intra-combustion and post-combustion ones [4-6]. The post-combustion desulphurization is performed in two variants, semi-dry one and wet another. In the wet process, sulfur dioxide is retained by slurry of calcium carbonate leading to formation of sulfite/acid sulfite of calcium in a first step and, then, after oxidation, in gypsum, product than can be transformed in plaster, a marketable hydraulic binder [6, 7].

Being given the existence of some great amounts of waste calcium carbonate produced by NPK fertilizers industry (Norcks-hydro procedures [8]), a study on behavior of this waste product as sulfur dioxide capturing agent is necessary. Because, in majority of the post-combustion desulphurization systems, retention of sulfur dioxide is realized in the column type reactors, in this paper we study the possibilities to obtain a relative stable suspension of waste calcium carbonate, with high buffering capacity.

EXPERIMENTAL

Characterization of waste. In the first step of study, the product sampled from AZOMURES Tg Mureş Co., was characterized chemically and by particle size distribution. Definition nature of the solid was realized by means of IR spectra. The content of calcium carbonate was determined by volumetric, gas-volumetric, gravimetric and complexometric analysis. The particle size distribution was determined by sieve analyzing of the dried sample at 373 K, on a series set TGL 7354, 0.040-6.30 mm in dimension. The IR spectra of the waste and limestone samples were recovered on DIGILAB FTS 2000 Spectrophotometer with 48 scanning resolution.

The calcium carbonate content, listed in table 1, and the IR Spectra points out the fact that the waste, milled at dimension less than 45 µm do not differ significantly from natural limestone. The high calcium carbonate content in terms of calcination losses points out that the waste have another volatile component. This fact is more distinguished in the case of unwashed waste, which, as was evidenced, contains ammonium compounds.

Table 1. Chemical composition of the carbonates (particle size < 0.045 mm)

Choice of carbonate	CaCO ₃ content, %			
	Calcination losses	Gas-volumetric	Balthasov volumetric	Complexometric
Limestone of Sanduleşti	98.34 (43.26)	91.77	97.65	97.35
Limestone of Vata de Jos	98.72 (43.44)	98.77	96.73	98.73
Waste (unwashed sample) April 2005	103.36 (45.47)	96.26	91.51	95.62
Waste (washed sample) April 2005	99.67 (43.85)	99.13	95.33	99.36

The distribution of calcination losses versus particle size of waste, Figure 1, shows that this is situated between the limits 43-44 %, having somewhat greater values in the range of small particle and constant values in the range of large particles.

Particle size analysis of the washed and dried waste points out a shifting of population to the zone of particles with less than 0.05 mm in diameter. The relative large spectrum of particles in population was proved also by wet particle size analysis, when the slurry with 10-20 g waste/100 mL water of dispersant remain turbid even after 8 h of testing. If at unwashed and dried waste, the agglomerates can be seen in a bigger measure, the waste washed till ammonium free in the washing water, exhibits a more uniform spectrum, in spite of here can be seen the presence of agglomerations, especially at sedimentation test.

The reactivity of the waste against different mono, di- and polybasic acids was determined by means of stirred batch reactor technique. As a measure of the reactivity was utilized evolution of the calcium ion content in solution versus time. The obtained results, given in Figure 2, point out the fact that the waste has a similar behavior with fine milled natural carbonates. With the particle size increases, the reactivity lowers much, but not in the same measure as of compact limestone, where the rate constant of the process lowers 6 times for a size increasing from 0.056 to 0.3 mm. At utilization of the particle size fraction less than 0.045 mm, the kinetic curves obtained for limestone and waste are practically superposed.

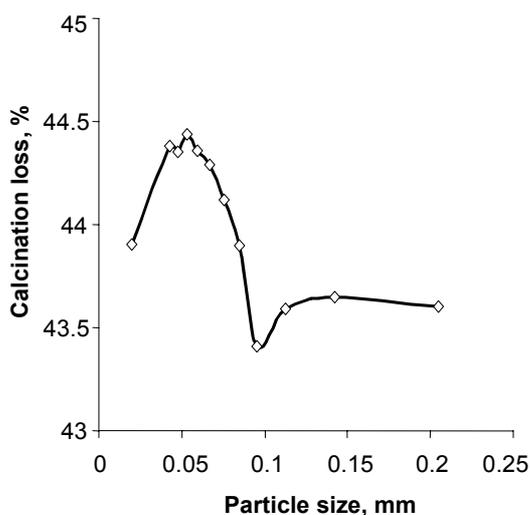


Figure 1. Evolution of the calcination loss versus granule size of unwashed waste with 0.38 % moisture

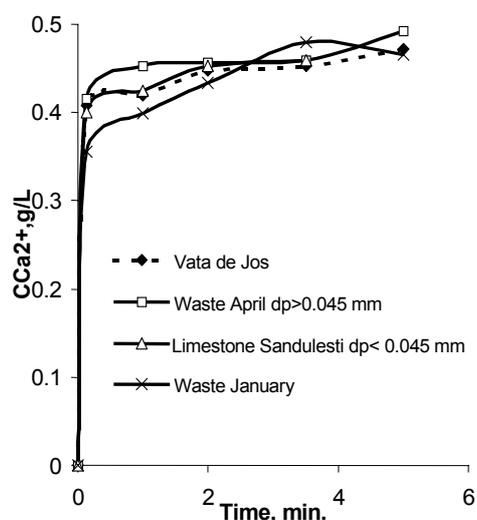


Figure 2. Influence of the nature of carbonate over the reactive dissolution in hydrochloric acid

Preparation and characterization of the waste calcium carbonate slurry. Taking into account how important is the particle size over the reactive dissolution rate in mono-, di- and polybasic acids, fact proved by own previously experiments [9-11], those of Fellner [12], and Allbeck [13], we proposed an improvement of behavior of waste by lowering its particle size. To lower the particle size of waste, the milling was utilized. It was studied in ball-mill and in impact mill as well as wet milling in ball mills. The milling efficiency was controlled by the following indicators: granule size distribution, hydrodynamic stability of slurry, buffering capacity.

RESULTS AND DISCUSSION

The curves of cumulative oversize reject, determined by wet particle size analysis, represented in Figure 3, show that duration of wet milling of waste, feed in a waste/ball ratio 1.3/2.7, assures a shift of curves to the little granule size range.

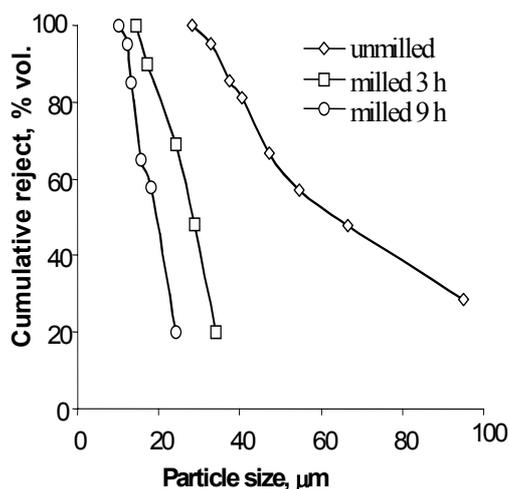


Figure 3. Dependence of the cumulative oversize reject on the wet milling duration of the waste

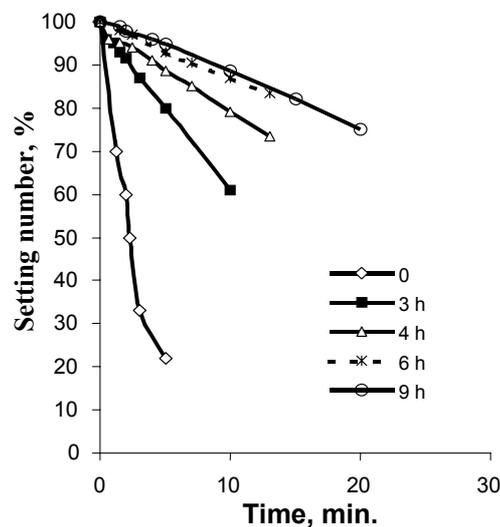


Figure 4. Dependence of the settling number on time for the milled paste with 20% consistency, obtained at different milling times

In order to define the main characteristics of the solids resulted by milling, we used the settling number, whose meaning is found in Romanian Standard 1083/81 (SR 1083/81), quantity completed with flowing duration of a constant volume of slurry (100 mL) through a calibrated orifice (4.62 mm). In this context, samples with 10, 20, 30 and 40 % milled waste were tested for settling number, measuring in time evolution of the suspension level. The obtained results, plotted in Figures 4 and 5, show a significant influence of the milling period of the wet milling and type of milling. It can be seen that the slurry resulted after 9 h of wet milling exhibit a higher stability than those obtained by mixing water and powder resulted by dry milling. The increase of the waste content of slurry increases significantly its stability.

This fact is also seen by rheological measurements. The relative flowing time through calibrated orifice [14] of slurries of different concentrations, obtained by diverse milling durations, varies significantly with milling duration and with their consistency. This dependence is described for slurry with 10-60 % milled waste by the relation:

$$\ln\left(\ln \frac{\tau}{\tau_{water}}\right) = (0.0099 \cdot \tau_{mill} + 0.282)(\% DS) - 0.2132 \cdot \tau_{mill} - 2.48$$

where: τ - flowing through time for slurry, s, τ_{water} - flowing through time for water, s, τ_{mill} - duration of milling, s, %DS - dry substance content of slurry, %.

The buffering capacity of some acid solution was chosen as a measure of the cumulative reactivity of the milled waste. The experiments carried out in the magnetic stirred batch reactor with conductometrical probe point out an increase of the buffering power direct proportional with increase of the milling duration.

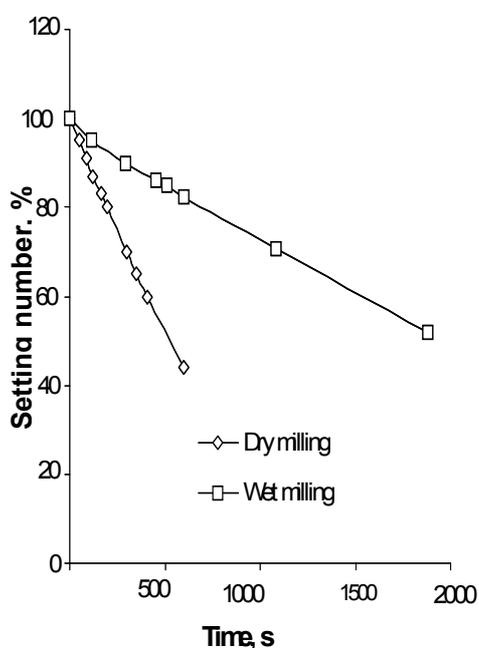


Figure 5. Dependence of the setting number on milling procedure and time for a consistency of 10 %

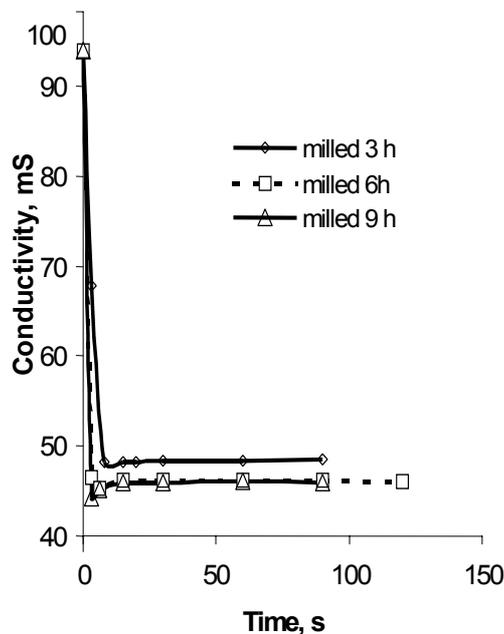


Figure 6. Influence of the milling duration of waste over buffering capacity of 0.5 M monobasic acids

A comparison between slurries of 30 % resulted at different milling periods, point out that, the two final curves, i.e. at 6 and 9 hours, practically are superimposed (see Figure 6). This fact shows that the reactivity and the stability of slurries do not modify in the same measure.

CONCLUSIONS

The results reported here indicate the possibility of using the waste calcium carbonate from the NPK fertilizer manufacture in production of relative stable slurries efficient in capture of sulfur dioxide from flue gases. The crystalline structure and chemical reactivity of calcium carbonate as well as its content in slurries allow their utilization for neutralization of any acid effluents. Using the wet milling, the water-waste slurry with adequate rheological properties required for columns for gases washing can be obtained. The wet milling improves in a much more measure the stability of the slurries and buffering power than the dry milling. Also, by wet milling, the reactivity of the slurries against sulfur dioxide is higher than in the case of unmilled samples.

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