Calcium Carbonate Precipitation through Carbon Dioxide Chemisorption from Flue Gas into Lime Suspension

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The carbonation of hydrated lime solutions in order to obtain precipitated calcium carbonate with pure polymorphic phase and small particle sizes was studied. CO_2*-air mixtures with similar composition to flue gases were used and the yield of* CO_2 *removal was also investigated. The experimental results concerning the process evolution, the calcium carbonate characteristics and* CO_2 *chemisorption efficiency recommend this method as an alternative route for* CO_2 *sequestration using alkaline wastes.*

Key words: Calcium carbonate, CO_2 *chemisorption, lime carbonation*

Precipitated calcium carbonate is an extensively studied inorganic product due to its various applications such as fillers in paper, pigments, paints, textiles or plastic industries [1, 2]. Each industrial application requires a certain particle size distribution, morphology and crystal structure to optimally cope with its use [3]. Calcium carbonate has three stable anhydrous polymorphs (calcite, aragonite and vaterite) with different characteristics that can recommend each of them for certain practical applications and market demand. There are two main routes for PCC synthesis: the solution route [4, 5] which consists in the reaction of two solutions containing Ca^{2+} and CO_3^{2-} ions respectively, and the carbonation route [6 - 8]. The carbonation method, the calcium ions are supplied from reagents such aqueous slurry of $Ca(OH)_2$ or slaked lime [9] and the carbonate ions are produced by the injection of carbon dioxide in the gaseous phase [6, 9]. This route is applicable not only on research of calcium carbonate precipitation, but also on methods of carbon removal and sequestration [8, 10]. In the last few decades, the development of different methods to remove the pollutant gases emitted by chemical or power industries has been very important. The remove of carbon dioxide from flue gases in aqueous alkaline solutions or suspensions to obtained useful products is a strategy related to the carbon dioxide sequestration and reusability of the alkaline wastes. One of these directions is the carbonation of lime solutions to obtain precipitated calcium carbonate (PPC) with controlled morphology and particle size distribution as a final useful product.

In several industrial processes gases with low CO_2 content are obtained, and its removal is recommended. This is mainly the case of flue gas resulted from the combustion of solid, liquid or gaseous fuels, but also the fuel gas in biomass gasification [11]. The cost of removing CO_2 from an industrial off-gas represents about 80% of the total cost of carbon removal and sequestration. A good means of reducing these costs is to use CO_2 directly out of the flue gas at low CO_2 partial pressures [12]. The long duration of alkaline waste degradation makes the novel approach for synthesizing PPC using alkaline waste very attractive [4, 13]. Using the flue gas directly as CO_2 source will transform both alkaline waste and flue gas in raw material for a valuable product, such as PCC. The quality of final PCC is a major concern in such processes [13], as well as the yield of CO_2 removal.

The present paper aims to investigate the influence of working conditions on the precipitation process and on the final PCC structure and particle size distribution when carbonation is performed using CO_2-air mixtures and an aqueous suspension of hydrated lime, considering that various industrial wastes contain $Ca(OH)_2$.

The chemical reactions involved in the chemisorption process are well known:

$$Ca(OH)_2\,(s) \leftrightarrow Ca^{2+}\,(l) + 2OH^-\,(l) \tag{1}$$

$$CO_2\,(g) \leftrightarrow CO_2\,(l) \tag{2}$$

$$CO_2\,(l) + OH^-\,(l) \leftrightarrow HCO_3^-\,(l) \tag{3}$$

$$HCO_3^-\,(l) + OH^-\,(l) \rightarrow H_2O + CO_3^{2-}\,(l) \tag{4}$$

$$Ca^{2+}\,(l) + CO_3^{2-}\,(l) \rightarrow CaCO_3\,(s) \tag{5}$$

It is noted that (1), (2) or (3) may be the rate determining step, according to specific operation conditions. Reactions (4) and (5) are considered to be instantaneous.

Experimental part

The experiments were carried out in a glass bubbling column with an internal diameter of 60 mm and a height 800 mm used as reactor. The volume of the liquid phase was 0.6 L. The bubbler diameter was 55 mm. The gas flow rate was established so that, for the highest $Ca(OH)_2$ loads, the suspension to be well entrained. This flow rate, 50 L/h was maintained for all experiments to provide similar hydrodynamic conditions: fictive velocity u_g=0.49 cm/s. The CO_2 concentration in our experiments was set to be similar to that in flue gases, 15% CO_2 corresponding to coal combustion, respectively 7.5% CO_2 in methane combustion. The lime suspension concentration varied in the range 10 – 80 g/L $Ca(OH)_2$ (p.a. Merck).

All the experiments were carried out at room temperature, 25±2°C, under the atmospheric pressure. In some experiments, the influence of additives on final solid phase characteristics was investigated; the concentration of additive was set to 38, AD1, and 75 µM/L $Na_3P_3O_{10}$ (p.a. Merck), AD2 respectively.

The experimental set-up is presented in figure 1. The gas mixture was realized using air supplied by the

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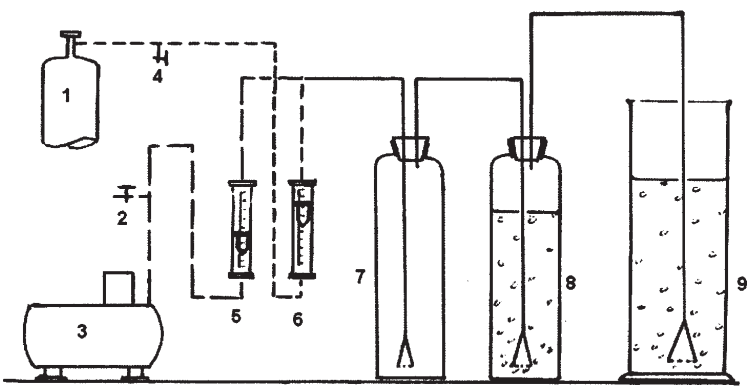

Fig. 1. Experimental set-up: 1-CO_2 cylinder; 2, 4-screw valve for fine adjustment of gas flow; 3-air compressor; 5-air rotameter; 6-CO_2rotameter; 7-air/CO_2expansion vessel; 8-humidifier, 9-bubbling column reactor

compressor (3) and CO_2 from the cylinder (1). The composition was adjusted by means of the valves 2 and 4. The gas flow rates were measured be means of the rotameters 5 and 6. To homogenized the gas composition and avoid gas flow rate fluctuations the expansion vessel (7) was introduced in the system. After saturation with distilled water in the humidifier (8), the gas mixture was introduced into the column (9) by a G_0 frit. The gas was passed through humidifier to prevent equimolecular counter-diffusion. The operation regime was continuous in relation with the gas phase and batch for the suspension. Aqueous suspension of calcium hydroxide was prepared in the stirred vessel under an inert atmosphere to prevent the possible reaction between the solute and the carbon dioxide present in the laboratory air. The gas phase, at constant flow rate, was fed to the bubbling column reactor after the aqueous suspension was homogenized. The total liquid volume was kept constant during all experimental runs.

Time variation of ionic concentrations in the liquid phase were measured by taking sample from the solid–liquid suspension in the bubbling column and filtered on a G_4 funnel. For the clear filtrate, the method used to analyze the concentration of calcium hydroxide and calcium carbonate was into two steps [14]. This method basically consists in finding the volume of HCl 0.1 N (Merck) at the first titration end-point using phenolphthalein as indicator, and a second volume for methyl orange endpoint, similar to the method used in water alkalinity determination. The carbonation process is completed when the concentration of calcium hydroxide in the solution, titrated in the presence of phenolphthalein, is practically zero. As in our experimental runs, the *p*H values are generally maintained at high values: starting from about *p*H=12.4 down to *p*H=10.5, the bicarbonate ions concentration may be neglected. From the titration results, the concentration of Ca^{2+}, OH^- and CO_3^{2-} ions were computed. At the end of each experimental set, the suspension was transferred to settle in a graduated cylinder with a diameter of 5.0 cm. After 24 h the volumes of liquid phase and of precipitate were measured. After settling, the precipitated calcium carbonate was dried at 105 ^{0}C. The final PCC was analysed by IR spectroscopy (Perkin-Elmer spectrophotometer) to determine the polymorphic phase. The particle and aggregates morphology was examined by SEM photographs using electron microscope JEOL TEMSCAN 200CX. The particle size distribution (PSD) of $Ca(OH)_2$ and final PCC were measured by microscopic investigation using the optical trinocular microscope MOTIC1000 and a specialized software that provides characteristic particle size (Ferret diameter), shape factor and specific area which enables a rapid number based PSD evaluation, as the frequency of each size class defined by the user.

Results and discussions

The experimental results obtained during the carbonation process are synthesized in terms of time variation of *p*H, calcium ions concentration and supersaturation. The supersaturation is the driving force in the crystallization process and is calculated with the relation:

$$S = \sqrt{\frac{\left[Ca^{2+}\right] \cdot \left[CO_3^{2-}\right]}{K_{sp}}} \qquad (6)$$

where: K_{sp} is the solubility product (for calcite, K_{sp} is 3.3 . 10^{-9} $[mol/L]^2$)

The dynamics of *p*H values is a current way to characterize the evolution of lime carbonation [3, 14] and, on the other hand, *p*H is also a means of controlling the PCC polymorphic phase composition [7]. During carbonation, two processes are competing: the hydrated-lime dissolution and calcium carbonate precipitation. In the first period, the CO_2 dissolution and CO_3^{2-} ion formation are rate controlling as the concentration of $Ca(OH)_2$ in the solution corresponds to saturation conditions and as a consequence the *p*H value remains practically constant. In the last part of the process the hydrated-lime dissolution becomes rate determining. In this period the total hydrated-lime particles surface decreases and the dissolution rate also decreases. The *p*H time variation (fig. 2 and fig. 3) proves that for lime carbonation the *p*H is high and almost constant for about 80% of total process duration. When the hydrated lime dissolution rate decreases, the *p*H value drastically falls. This point corresponds to the depletion of Ca^{2+} ions concentration (fig. 4). At this moment, the CO_2 addition is stopped. If further CO_2 is added, the process will shift towards the dissolution of PPC due to HCO_3^- «CO_3^{2-} equilibrium that would mainly be shifted to HCO_3^- formation [15].

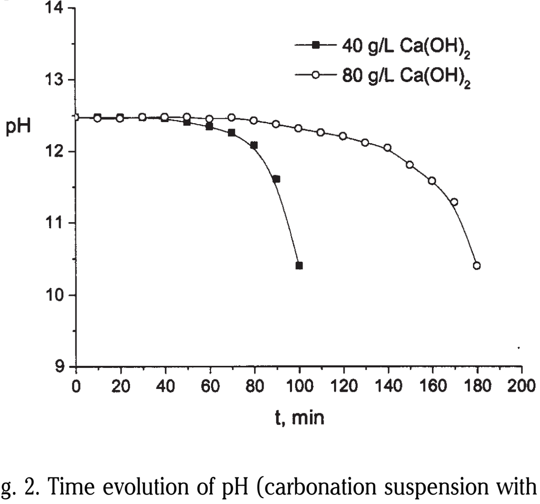

Fig. 2. Time evolution of pH (carbonation suspension with 7.5% CO_2 in gaseous phase)

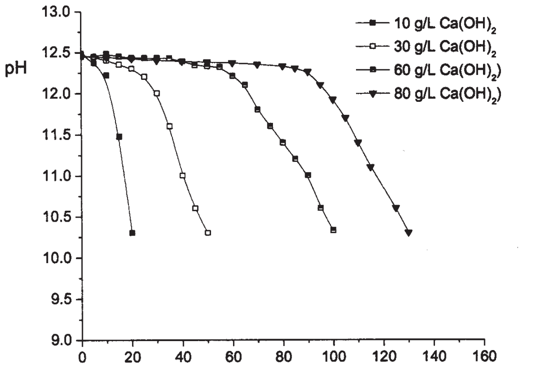

Fig. 3. Time evolution of *p*H (carbonation of suspension with different load and 15% CO_2 in gaseous phase).

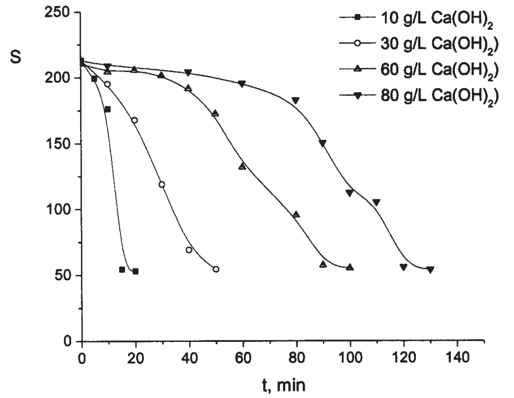

Fig. 5. Time evolution of supersaturation (carbonation of suspension with different load and 15% CO_2 in gaseous phase)

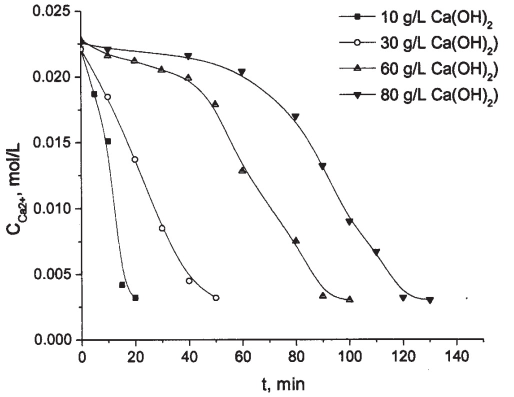

Fig. 4. Time evolution of the Ca^{2+} ions concentration (carbonation of suspension with different load and 15% CO_2 in gaseous phase).

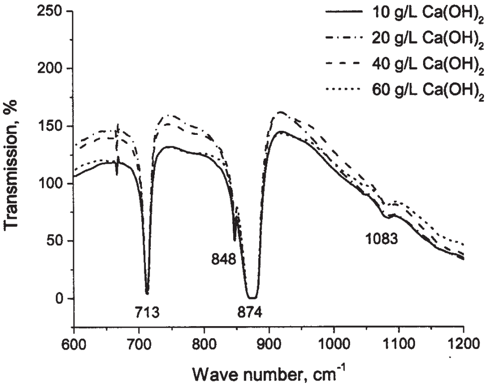

Fig. 6. FT-IR spectra of PCC (suspension with different load and 15% CO_2 in gaseous phase)

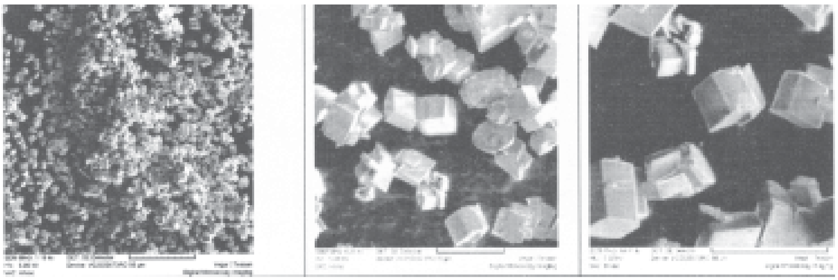

Fig 7. SEM images for PCC (at the end of the carbonation process at 60 g/L $Ca(OH)_2$ and 15% CO_2 in the gaseous mixture)

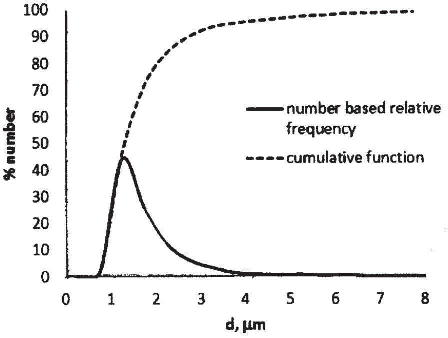

Fig. 8. PCC particle size distrubution (suspension with 10g/L $Ca(OH)_2$ and 15% CO_2 in the gaseous mixture)

The high values of supersaturation (fig. 5) explain the fast $CaCO_3$ precipitation, with dominant nucleation process and growth. As the carbonation experiments have longer duration for higher $Ca(OH)_2$ load, the agglomeration may also contribute to the final particle sizes.

As it is well known, by carbonation route at room temperature, the steps in PCC formation are defined by the precipitation of an unstable amorphous calcium carbonate which is transformed into vaterite and calcite [7]. As in our working conditions, the *p*H level was over 10, during the reactive crystallization process, the vaterite phase is transformed into calcite by dissolution and recrystallization.

The FT-IR analysis of the final PCC revealed a pure polymorphic phase, calcite. An example of the FT-IR spectra is shown in figure 6, where the characteristic calcite peaks at 713 and 874 cm^{-1} are present. The SEM images (fig. 7) show well crystallised cubic particles, specific for calcite polymorphic phase.

As the PSD was measured by a microscopic method, the number base distribution is used. The experimental frequencies, exemplified in figures 8 and 9 show dominant particle sizes, in the range of 1.5-2.5µm.

The particle size distribution of final PCC was analyzed in terms of mean size and variance for all experimental runs. The mean particle diameter in number based distribution d_n was calculated using the experimental frequencies. The mass mean particle size, d_m was evaluated using the mass distribution obtained by classical transformation of the number based PSD. For both cases the standard deviation in number and mass base respectively (σ_n and σ_m) were also calculated. The computed values of mean sizes and standard deviations are presented in table 1.

The data shown in table 1 indicate that the carbonation process led to a narrow distribution (small values for the standard deviation). The micron and submicron sized particles have a high contribution resulting in mean number

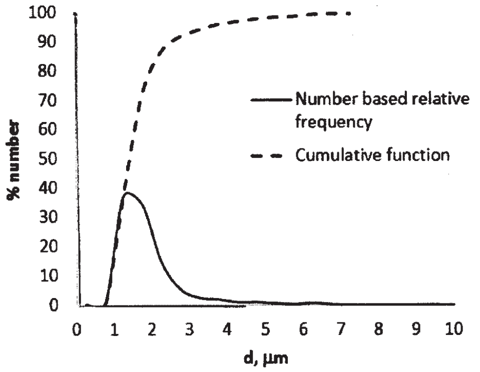

Fig. 9. PCC particle size distribution (suspension with 60g/L $Ca(OH)_2$ and 15% CO_2 in the gaseous mixture)

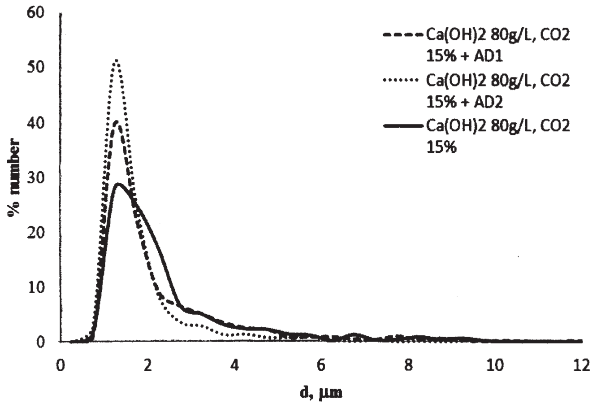

Fig. 10. PCC particle size distribution (with and without additives)

Table 1
MAIN PSD CHARACTERISTICS OF PCC

$C_{Ca(OH)_2}$, g/L	d_n, μm	σ_n, μm	d_m, μm	σ_m, μm
CO_2 15%				
10	1.82	1.00	4.37	2.97
20	2.10	1.41	5.90	3.00
30	2.25	1.50	6.73	3.58
40	1.82	1.12	9.57	1.95
60	1.92	1.05	10.08	2.15
80	2.40	1.05	10.05	1.80
80+AD1	2.25	1.57	9.20	1.85
80+AD2	1.75	1.00	7.57	1.50
CO_2 7.5 %				
40	2.00	1.25	8.15	1.78
80	1.75	0.98 (0.56)	8.00	1.60

Table 2
YIELD OF CO_2 REMOVAL IN THE CARBONATION PROCESS

Suspension load, g/L	Process duration, min	CO_2 chemisorption yield
10	20	0.81
20	40	0.81
30	50	0.97
40	65	0.99
60	100	0.97
80	130	0.99

based diameter about 2μm. If we compare the d_m values corresponding to 10 g/L $Ca(OH)_2$ and 40 g/L $Ca(OH)_2$ respectively, we can notice that even if the number based mean diameters, d_n have the same value (1.82 μm), the mass based diameter, d_m is larger in the case of higher hydrated-lime load (9.57mm and 4.57μm), standing for the assumption that some larger particles are formed by agglomeration and their mass contribution is important. This may be a consequence of longer carbonation time and higher solid phase concentration that increases the chance of PCC particle to collide and finally to form agglomerates. The influence of natrium-tripolyphosphate additive decreases the mean particle size for the same $Ca(OH)_2$ initial concentration (from 2.40 to 1.75μm). This decrease can be appreciated also by examining the PSD in figure 10, where the relative contribution of small particles is greater in the case of additives added to the reaction medium. This may be considered as a consequence of modifying the surface particle growth mechanism [16] and preventing agglomeration [17]. When the bubbling column was fed with a 7.5% CO_2-air mixture, despite the longer reaction duration of the process compared with more concentrated gases (15% CO_2), a final product with comparable main characteristics of PSD is obtained. This result is in good agreement with the assumption that the mass transfer in the gaseous phase is less important in the carbonation process and calcium carbonate crystallization [3, 7].

Referring to the carbonation process as a means of CO_2 removal from flue gases, the yields of CO_2 removal was also estimated (table 2).

The yield obtained is almost 100% in the case of high hydrated-lime load, but is still acceptable for lower $Ca(OH)_2$ initial concentration. This result is encouraging to promote the carbonation method both for alkaline waste treatment and CO_2 sequestration.

Conclusions

The hydrated lime carbonation was experimentally investigated to evaluate the quality of PCC and the efficiency of CO_2 removal from air-CO_2 mixture with similar composition as in flue gases. The results proved that both 15% and 7.5% CO_2 mixtures led to fine calcite particles which may have various applications. The results obtained for different hydrated-lime load show that at higher $Ca(OH)_2$ concentration the yield of CO_2 removal is grater, but in these conditions the contribution of larger PCC particles size is more important, due to the increase of the agglomeration mechanism. The PSD can be controlled by additives addition that reduce the mean particle sizes. The present results can be easily extended to the carbonation of other industrial hazardous wastes containing $Ca(OH)_2$.

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