

Artificial weathering pools of calcium-rich industrial waste for CO₂ sequestration

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Abstract

Processes of carbonation of calcium-rich aqueous industrial wastes from acetylene production were performed mimicking rock weathering, using the atmospheric carbon dioxide as reactant. This residue was carbonated exposing it to the air in artificial pools with controlled solid-to-liquid and surface-to-volume ratios, and the efficiency of this simple mineral carbonation process was maximized. Considering realistic values of just one acetylene production plant, the intelligent handling of the calcium-rich waste would make it possible to counteract the emission of around 800 t of carbon dioxide per year, so the CO₂ emissions of the acetylene production could be completely compensated and its carbon footprint significantly reduced.

X-ray diffraction patterns and thermogravimetric analyses reported the conversion, up to 88%, of the calcium hydroxide into calcium carbonate under atmospheric conditions. So, considering a realistic industrial scale-up, 476 kg of CO₂ could be captured with 1 t of dry waste. The morphology of the grains is resolved by electron microscopy, and can be described as needles 15 nm wide and 200 nm long arranged in grains smaller than 1 micron. We exploit these nanometric textural parameters (nanometric pores and particles having a specific surface area ~50 m²/g) to design an efficient carbon fixation procedure. The aim of this work is to propose this simple carbonation technology, based on aqueous alkaline industrial waste, as a contribution to reducing global CO₂ emissions.

Keywords CO₂; Mineral sequestration; Waste; Portlandite; Weathering

1. Introduction

The increase in the concentration of CO₂ in the atmosphere from the pre-industrial level of 280 to 380 ppm [1] has led to alarm about the likely effects on the earth's climate. The seriousness of the damage caused by climate change to the way of life of the developed countries has forced them to assign enormous resources to mitigate this situation. Nowadays, the challenge is to develop and improve technologies for energy production and to reduce the concentration of greenhouse gases in the atmosphere. In this work, a feasible technology for alkaline industrial residues weathering is proposed. The process mimics the actual geological rock weathering because it only considers the interaction between industrial wastes with greenhouse gases present in the atmosphere, as carbon dioxide. Therefore, the proposed weathering management considers only the industrial waste and the greenhouse gases, and

no extra devices, reactants, additives, or activation heat or pressure are needed. This technology is possible thanks to the properties of the industrial waste, as the composition or the microstructure of the solid phase, namely, grain size, specific surface area and porosity. These structural parameters promote and enhance the reaction rate.

Currently, most of the works about carbon capture and storage (CCS) technologies comprise geological storage and ex situ mineral sequestration, and they work once the CO₂ is separated from the flue gas, mainly to reduce CO₂ emissions from localized industrial sources (large industries). The first one has been considered since decades ago when CO₂ injection-based enhanced oil recovery systems were implemented in mature oil fields [2] and [3]. However, it presents several problems such as the reaction of carbon dioxide with the cementitious seals of the injection wells [4] which can affect the isolation of the reservoirs, or the diffusion of the CO₂ via rock cracks over centuries. The second technology considered is a mineral carbonation process [5]. This process consists in chemically binding the carbon dioxide molecule to a mineral to form carbonates, similar to the weathering process that has regulated the CO₂ concentration of the earth's atmosphere for millions of years. Mineral sequestration allows the removal of CO₂ coming from not only power plants or other localized industrial sources but also diffuse sources (typically transport means) and past CO₂ emissions. In this case, the atmosphere carries the carbon dioxide produced elsewhere above cities or countries, and it can be sequestered thousands of miles away.

The strongest advantage of mineral sequestration [5], [6], [7] and [8] is that the hazardous greenhouse gas is converted into innocuous, stable and environmental benign carbonate mineral, fixing the carbon dioxide definitively. Its weakest points are the low speed of the reaction, the carbonate by-product that is produced and should be managed, and the costs of the process [9] and [10]. Therefore, the carbonation reaction ought to be sped up to become a realistic solution for carbon sequestration, but without penalizing its efficiency due to a high energy consumption or negative net carbon balance. Besides, the by-product has to be innocuous and easy to handle so that hundreds of tons can be managed without complex technologies or extra risks. Moreover, one by-product with an added value will be the most desirable option to support this technology.

The use of industrial alkaline wastes will contribute to reducing the costs of carbon sequestration enormously, besides avoiding the ecological impacts of mineral extraction on a massive scale. Some prototypes based on the absorption of the atmospheric CO₂ have already been presented, and the costs of one sequestered ton of carbon dioxide are estimated to be between 10\$ [11] and 127\$ [12]. In the last decade, several industrial products have been considered for sequestration of carbon dioxide. Cementitious materials were initially considered [13] followed by municipal solid waste incinerator bottom ashes [14], steel slag [15] and [16], paper mill waste [17], coal combustion fly ash [18], air pollution control residues [19] or oil-shale wastes [20]. In summary, the current research focused on portlandite or calcium oxide for mineral sequestration is quite wide, but very few raised and studied the relationship between kinetics and microstructure [21].

In this work, we have considered the calcium rich waste of the industry of the production of acetylene as a new material for carbon dioxide sequestration. Acetylene produced via calcium carbide generates an aqueous suspension of portlandite (calcium hydroxide, Ca(OH)₂). The experimental conditions to obtain the maximum carbonation efficiency are researched. The carbonation process is carried out under atmospheric conditions, paying special attention to the texture of the samples and to strategies to enhance the reaction speed as well [22], [23] and [24]. The experimental results allowed us to design the weathering pools, a very

simple atmospheric carbon dioxide sequestration process. The reaction by-product obtained is calcium carbonate that is easy to handle and could be disposed of or even commercialized.

2. Materials and methods

The sample is an industrial waste discarded by the acetylene industry, and it was supplied by the AIR LIQUIDE España S.A. acetylene factory located in Seville (Spain). The waste is an inhomogeneous greyish water slurry.

2.1. Characterization of the samples

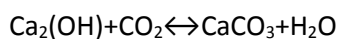
Chemical analyses performed on the original sample, prior to any carbonation experiment, were done by X-ray fluorescence (AXIOS, Panalytical, with an Rh tube) using the semi-quantitative method. Crystalline phases of the samples were identified by X-ray diffraction (XRD) in a Philips X'Pert diffractometer with Cu K α radiation, from 5.00° to 70.00° with a step of 0.05° and counting time of 80 s. The morphology of the waste was characterized by nitrogen physisorption experiments and scanning electron microscopy (SEM). Physisorption experiments were performed in a Micromeritics device model ASAP2010 at a constant temperature of 77.35 K. Samples were milled and degasified at 150 °C under vacuum for 2 h prior to the experiment. In order to keep the original structure before any possible carbonation due to atmospheric CO $_2$, the “original sample” was taken from the wet industrial waste container, dried, and degasified inside the physisorption experimental device. Specific surface area and pore size distribution (PSD) were obtained by analysing the physisorption isotherm using the BET and BJH methods, respectively. SEM was performed in a SEM-FEG Hitachi S480 using an acceleration voltage of 2 kV.

Finally, the carbonation degree of the samples was estimated by thermogravimetric analyses (TGA) in a STD Q600 experimental device. The experiments were carried out under a nitrogen flux of 100.0 ml/min, starting from ambient temperature and increasing by 10 °C/min up to 1000 °C. As a reference, we have born in mind that for a pure calcite sample, the stoichiometric weight loss due to decarbonation is 44% in the range between 550 °C and 900 °C. To compare the experimental results with this theoretical maximum, mass of the samples from TGA experiments was normalized to the weight of the dehydrated sample, that is, the mass at $T = 200$ °C.

2.2. Carbonation process

Calcium hydroxide reacts with CO $_2$ to form calcium carbonate CaCO $_3$ and water:

(1)



The carbonation of this industrial waste was studied using the atmospheric CO $_2$. The weathering pools consist in very shallow flat ponds where the waste is disposed as a film. The carbonation of the waste occurred during drying under atmospheric conditions, typically taking from 3 days to one week. With the uncontrolled disposal of this portlandite-based waste, some carbonate is precipitated on the outer face of the grains due to the drying process, but the core of the sample remains as portlandite. In this research, two parameters were analysed to explore their influence on the efficiency of the carbonation process. The first was the solid-to-liquid ratio of the aqueous system, defined as the ratio between the mass of

the solid phase and the mass of the liquid in which the solid is in suspension. To control and to measure this ratio, an amount of wet paste is weighed and its volume measured. Then a certain volume of supernatant is added up to a defined volume, and then the system is weighed again.

The second studied parameter is the height of the volume that occupies the aqueous system. This parameter is critical as it defines the surface-to-volume ratio of the system, that is, the quotient of the surface in contact with the air by the volume of the system. In other words, it defines the surface in contact with the atmosphere, which controls the kinetics of the drying as well as the dissolution of the CO₂ from the atmosphere into the system. Systems giving two different heights were used: a glass where the system was set to a height of 2.3 cm, and spreading the aqueous sample on a flat surface, giving this system the theoretical height of 0. In this work, the containers will be referred to as “weathering pools”.

Finally, the influence of rewetting daily or stirring was also tested. Rewetting the sample consisted in adding 3 ml of distilled water to 10 g of dry sample on each rewetting. Sampling of each configuration was done until the maximum degree of carbonation was achieved.

3. Results and discussion

3.1. Characterization of the original sample

The original waste was characterized prior to any carbonation process. The results of the chemical analysis by XRF (Table 1) showed a calcination weight loss of 22.45%, a calcium content of 52.41 wt.%, an oxygen content of 23.10 wt.%, and a silicon content of 1.04%. Some traces of Al, S, Fe, Cl, Mg, and Sr were also found. This result matches a mineralogical content of 97.0 wt.% of portlandite and silica content of 2.2 wt.%, where the calcination weight loss matches the release of water due to the conversion of the portlandite into lime (CaO), supporting that the waste is composed of portlandite. This result was confirmed by XRD analysis (Fig. 1). The sound sample was found in the core of large dried pieces of the waste. The core of these grains remained uncarbonated despite the drying process. In the outer face of the grains, calcite and portlandite instead of pure portlandite could be observed by XRD (not shown). Note that spontaneous weathering occurs but only the controlled management and conscious weathering of the waste will mean significant amounts of captured carbon dioxide.

The morphology of the portlandite grains suspended in the aqueous waste was studied by nitrogen physisorption and electron microscopy. Measured values of the structural parameters are listed in Table 1. The PSD showed two typical pore sizes of 3.7 nm and 16.8 nm and the specific surface area is 47.5 m²/g. The SEM images showed that portlandite precipitates in the form of nanometric needles of around 15 nm wide and 200 nm long (Fig. 2). These needles form aggregates of around 500 nm and these aggregates are agglomerated in larger grains. But the specific surface area is smaller than that corresponding to one single needle of portlandite and larger than that of one grain of portlandite of 500 nm size. In addition, the pore sizes measured correspond to the spaces among the nanometric portlandite needles. Consequently, it can be concluded that the nanometric structural features are still present in the large agglomerates.

Up to now, the main drawback of some of the carbon mineral sequestration technologies was the cost of milling to obtain a small grain size (and large reactive area) from bulk mineral, which is necessary to obtain significant values of carbonation efficiency. In the samples presented in this work, large reactive surface areas are present due to the particular

morphology of the calcium hydroxide rich waste, enhancing the carbonation reaction as the carbonation efficiency is very sensitive to particle size [25] or the porosity of the sorbents [21]. So, the nanostructure of the portlandite allows the CO₂ dissolved into the aqueous system to attack the whole sample before the passivating layer [26] hinders the carbonation of the grains, yielding large carbonation efficiencies.

To avoid the precipitation of some carbonate while handling the sample for thermogravimetry, and to verify the absence of calcite in the original waste, a sample of the original wet paste was taken and quickly submitted to the TGA. The drying process was carried out in an inert atmosphere of nitrogen inside the experimental device. The curve obtained (not shown) presented a first large weight loss at around 100 °C due to the dehydration process. The second weight loss at around 400 °C is associated with the dehydroxylation¹ of the portlandite [27] and [28]. Reported values of dehydroxylation of portlandite are slight larger than the 400 °C found for these samples (450 °C and 467 °C in the referred papers, respectively). It is well known that experimental conditions as well as sample size and morphology can affect greatly the rate of thermal dehydroxylation [28], so this decrease in the dehydroxylation temperature can be obtained due to the high reactive area of the sample.

3.2. Ambient carbonation

The carbonation of the samples due to the atmospheric carbon dioxide, the so-called weathering, was studied by measuring the degree of carbonation for different experimental configurations. First of all, the carbonation reaction was verified by the appearance of different calcium carbonate polymorphs (calcite, vaterite, and aragonite) in the samples, as revealed by XRD. In Fig. 1, the XRD pattern of a carbonated sample (P0, regarding to labels in Table 2) is shown. Total carbonation is not present as portlandite is still observed. Once the samples were completely dry, no more carbonation was observed, as expected. The influence of the solid-to-liquid ratios and the height of the aqueous system were studied to control and to maximize the weathering process. Both parameters are directly related to the kinetics of the drying process of the sample, and both were revealed to be critical to the degree of carbonation.

Firstly, the influence of the surface-to-volume ratio was studied. Two different samples were considered. Details of their configuration and carbonation efficiency are listed in Table 2 and the TGA curves of samples P4 and P5 are plotted in Fig. 3. It can be seen how decreasing the height of the system from 2.23 cm (P4) to 0 cm (P5) increases the efficiency of the carbonation from 15% to 65%. If the aqueous system is not shallow enough, one layer of floating calcite will precipitate in the interphase liquid/air slowing down the carbonation. The high carbonation efficiency obtained in such a simple system as this shallow weathering pool P5 makes this waste a very promising carbon dioxide sequester for industrial implementation. In Fig. 4, the morphology of the precipitated calcite floating layer is shown. Nanometric spheres of calcite (confirmed by SEM and XRD, not shown) precipitated and clumped together to form large arrays and clusters (branched bottom of the precipitated phase) where the calcite rhombohedrals appeared later.

Secondly, the influence of the solid-to-liquid ratio of the wet paste was researched. The considered values of the ratio and the carbonation results are listed in Table 2 (P3–P4–P6 series). These results are shown in Fig. 5. Again, it can be stated that complete carbonation was not achieved in any case. Nevertheless, the higher the solid-to-liquid ratio is, the higher is the carbonation efficiency. Then, this ratio is found to be critical given that, for a similar geometry, it controls the appearance of the calcite floating layer which hinders the CO₂ flux to the solution and eventually the carbonation of the sample. It is worth mentioning that the

original waste has a solid-to-liquid ratio close to 0.33, the maximum value considered in this work. So, the addition of water to the system will result in a delay in the drying process and impede the carbonation process.

3.3. Assisted ambient carbonation

Some additional technical measures were considered to improve the efficiency of carbonation. Firstly, stirring the sample was tested to avoid the appearance of the calcite floating layer. It was observed that the floating layer appeared even under vigorous stirring. Stirring yields small increases in the carbonation efficiency from 10% up to 15% for the pool P3_S and from 15% to 18% in the case of pool P4_S. Details of the pools and carbonation efficiencies are listed in Table 2.

Rewetting the sample was also considered to achieve higher carbonation efficiency. In Fig. 3, TGA curves of the rewetted samples in pools P4_w2 and P5_w are also plotted and their carbonation efficiencies are compared in Table 2. Results reveal the enhancement of the carbonation efficiency with the rewetting of the pools. Thus, pool P4_w rewetted once with distilled water increases its carbonation efficiency up to 41%, almost three times the efficiency of the non-assisted pool P4. Rewetting the pool again (sample P4_w2) reveals that the carbonation reaction can continue up to 58%. But again, the geometrical configuration was essential to obtain carbonation efficiencies close to 100%. Rewetting the sample in pool P5_w, with a height equal to zero (spread on a flat surface), gave an increase in the efficiency from 65% to 81%. This improvement of the efficiency was found to saturate in pool P0, which was rewetted and slightly stirred daily for 7 days. This sample showed an efficiency of 88%, but then it was not possible to improve it further. So, by rewetting these samples, carbonation efficiency close to 90% can be obtained.

SEM images have revealed some steps of the structural evolution of the carbonation of the fibrous clusters of portlandite to calcium carbonate crystals. In Fig. 6, top, it can be seen how the calcium carbonate precipitated on the surface of the clusters of portlandite fibrous grains as a layer (indicated by the arrow), but this sort of passivating layer [26] does not prevent high carbonation efficiencies thanks to the small size of the portlandite grains. In Fig. 6, bottom, wheat-sheaf-like bundles of calcium carbonate can be seen. It has been reported that the precipitation of the calcium carbonate in these morphologies is caused by the presence of impurities of Mg [29] and [30]. The existing impurities of Mg among others in our system (Table 1) cause the precipitation of the calcite into these morphologies of bundles. SEM imaging also confirms the precipitation of the calcium carbonate into rhombohedral morphologies (not shown), together the wheat-sheaf-like bundles.

3.4. Industrial scale-up

Firstly, considering an acetylene industrial plant of 80 kW with a potential production of 50 t/month of acetylene [31], 1707 t/year of $\text{Ca}(\text{OH})_2$ are produced (6800 t/year of aqueous waste, considering a solid-to-liquid ratio close to 0.33), so thanks to this technology, around 800 t of CO_2 could be captured each year directly from the atmosphere. Thus, the fixation power of the carbonation pools could be established at 7%, or 47.6% considering the dry waste (476 kg of captured CO_2 per ton of $\text{Ca}(\text{OH})_2$) much higher than that from municipal solid waste bottom-ash (2.3%), carbon fly ash (2.6%) or even paper mill waste (21.8%) [17]. Although acetylene synthesis does not produce carbon dioxide directly, indirect CO_2 emissions produced by the energy consumed (estimated at 288 t CO_2 /year) could be completely mitigated by a weathering pool of 3000 m^2 . So, the carbon footprint of the acetylene plant could be reduced.

But, considering the 1 ha weathering pool set-up, it would be possible to capture not only the carbon dioxide indirectly emitted by the acetylene production but also some of the CO₂ emitted during the synthesis of the calcium carbide (CaC₂), the precursor of the acetylene. The calcium carbide is obtained by burning coke and lime in electric furnaces, with high energy consumption. The energetic requirement to obtain 1 t of CaC₂ at 80% purity is around 3300 kWh [32]. Thus, 1.55 t of CO₂ is indirectly emitted to the atmosphere for each ton of calcium carbide. Consequently, 1 day's production of acetylene yields total indirect carbon dioxide emissions of 7.3 t of CO₂, whereas one weathering pool will capture 2.3 t (Table 3). So, 30% of total indirect emissions of CO₂ could be mitigated. Finally, it must be remarked that the carbon sequestration by-product is calcite, a valuable product that can be simply disposed of, used in different industries or commercialized as precipitated calcium carbonate [33].

Secondly, regarding to the assisted carbonation procedures, the experimental set-up with maximum carbonation efficiency was considered, that is, rewetting the weathering pool with minimum height. Water consumption was estimated by Dunne and Leopold [34] and Meyer [35] empirical equations and the costs of the rewetting process have been evaluated. Using the local mean weather and solar radiation data of the area of Seville (where the acetylene plant is located) for a 1 ha weathering pool, 41.15 m³/day will be consumed. Rewetting will cost 45.68 €/day so it will not be a major drawback of this technology. But, given that carbonation efficiency will be increased by only 15%, the rewetting process, water pipes, and logistics could not be interesting at an industrial scale. Consequently, this should be considered and evaluated for each particular case.

4. Conclusions

This research work has proven that the management of aqueous industrial alkaline wastes can be an effective strategy for carbon dioxide mineral sequestration. Carbonation efficiencies up to 88% were achieved using just carbonation pools where the aqueous residue is disposed and let to dry, under atmospheric conditions. Actually, this work is proposing a change in the waste management pointing to CO₂ sequestration. In the studied case, the calcium-rich acetylene industry wastes have been shown to be a promising material for atmospheric CO₂ sequestration. It is possible to sequester up to 800 t per year of carbon dioxide just considering the wastes of one simple acetylene plant, reducing the carbon footprint of the acetylene production. Knowing that this amount is not a huge CO₂ removal, the most important point to remark is the change of the philosophy on the waste management. For any other industry producing alkaline wastes, the amount of carbon dioxide that could be captured will depend on the amount of waste and its composition. Up to now, several solid industrial residues were considered for CO₂ sequestration, but in this work it has been shown that it is technologically simpler and more efficient to capture CO₂ using the aqueous alkaline industrial wastes, as those coming from the acetylene industry.

Acknowledgements

The authors would like to acknowledge the research services of the ICMSE (CSIC-US), Air Liquide España S.A. for supplying the samples and especially Mr. Miguel Bermejo from Trenzamet for taking the initiative. The authors are grateful to the Consejería de Innovación Ciencia y Empresa of the Junta de Andalucía (Spain) for supporting this work with the annual Grant TEP115 and to the Ministerio de Ciencia e Innovación of the Spanish Government for the Grant PIA42008-31. V.M.F. thanks the CSIC for financial support through the JAE programme.

References

[1] Intergovernmental Panel on Climate Change, Special Report: Carbon Dioxide Capture and Storage, Cambridge University Press, Cambridge, 2005.

[2] J.W. Carey, M. Wigand, S.J. Chipera, G. Woldegabriel, R. Pawar, P.C. Lichtner, S.C. Wehner, M.A. Raines, G.D. Guthrie Jr.

Analysis and performance of oil well cement with 30 years of CO₂ exposure from the SACROC Unit, West Texas, USA

Int. J. Greenhouse Gas Control, 1 (2007), pp. 75–85

[3] P. Jaramillo, W.M. Griffin, S.T. MCCoy

Life cycle inventory of CO₂ in an enhanced oil recovery system

Environ. Sci. Technol., 43 (2009), pp. 8027–8032

[4] A. Fabbri, J. Corvisier, A. Schubnel, F. Brunet, B. Goffé, V. Barlet-Gouédard, G. Rimmele

Effect of carbonation on the hydro-mechanical properties of Portland cements

Cement Concrete Res., 39 (12) (2009), pp. 1156–1163

[5] W. Seifritz

CO₂ disposal by means of silicates

Nature, 345 (1990), p. 486

[6] T. Kojima, A. Nagamine, N. Ueno, S. Uemiy

Absorption and fixation of carbon dioxide by rock weathering

Energy Convers. Manage., 38 (Suppl.) (1997), pp. S461–S466

[7] J.C.S. Wu, J.D. Sheen, S.Y. Chen, Y.Ch. Fan

Feasibility of CO₂ fixation via artificial rock weathering

Ind. Eng. Chem. Res., 40 (2001), pp. 3902–3905

[8] W.J.J. Huijgen, G.J. Witkamp, R.N.J. Comans

Mechanisms of aqueous wollastonite carbonation as a possible CO₂ sequestration process

Chem. Eng. Sci., 61 (13) (2006), pp. 4242–4251

[9] W.J.J. Huijgen, R.N.J. Comans, G.J. Witkamp

Cost evaluation of CO₂ sequestration by aqueous mineral carbonation

Energy Convers. Manage., 48 (2007), pp. 1923–1935

[10] J. Sipila, S. Teir, R. Zevenhoven, Carbon dioxide sequestration by mineral carbonation, Review update 2005–2007, Report 2008-1, Heat Engineering Laboratory, Faculty of Technology, Abo Akademi University, Finland, 2008.

[11] K.S. Lackner, P. Grimes, H.J. Ziock

Capturing carbon dioxide from air

Proceedings of the 2nd US–China symposium on CO₂ emissions control science and technology, 28–30 May, Hangzhou, China (2008)

[12] J.K. Stolaroff, W.D. Keith, G.V. Lowry

Carbon dioxide capture from atmospheric air using sodium hydroxide spray

Environ. Sci. Technol., 42 (2008), pp. 2728–2735

[13] Y. Shao, X. Zhou, S. Monkman, A new CO₂ sequestration process via concrete products production, EIC Climate Change Technology 2006 IEEE, 10–12 may 2006, Ottawa, 2006.

[14] E. Rendek, G. Ducom, P. Germain

Carbon dioxide sequestration in municipal solid waste incinerator (MSWI) bottom ash

J. Hazard. Mater., B128 (2006), pp. 73–79

[15] W.J. Huijgen, R.N.J. Comans

Carbonation of steel slag for CO₂ sequestration: leaching of products and reaction mechanisms

Environ. Sci. Technol., 40 (2006), pp. 2790–2796

[16] D. Bonenfant, L. Kharoune, S. Dauvé, R. Hausler, P. Niquette, M. Mimeault, M. Kharoune

CO₂ sequestration potential of steel slags at ambient pressure and temperature

Ind. Eng. Chem. Res., 47 (2008), pp. 7610–7616

[17] R. Pérez-López, G. Montes-Hernandez, J.M. Nieto, F. Renard, L. Charlet

Carbonation of alkaline paper mill waste to reduce CO₂ greenhouse gas emissions into the atmosphere

Appl. Geochem., 23 (2008), pp. 2292–2300

[18] G. Montes-Hernandez, R. Pérez-López, F. Renard, J.M. Nieto, L. Charlet

Mineral sequestration of CO₂ by aqueous carbonation of coal combustion fly-ash

J. Hazard. Mater., 161 (2009), pp. 1347–1354

[19] V. Prigiobbe, A. Polettini, R. Baciocchi

Gas–solid carbonation kinetics of air pollution control residues for CO₂ storage

Chem. Eng. J., 148 (2009), pp. 270–278

[20] M. Uibu, M. Uus, R. Kuusik

CO₂ mineral sequestration in oil shale wastes from Estonian power production

J. Environ. Manage., 90 (2009), pp. 1253–1260

[21] H. Gupta, L.S. Fan

Carbonation–calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas

Ind. Eng. Chem. Res., 41 (2002), pp. 4035–4042

[22] A. Santos, J.A. Toledo-Fernández, R. Mendoza-Serna, L. Gago-Duport, N. De la Rosa-Fox, M. Piñero, L. Esquivias

Chemically active silica aerogel–wollastonite composites for CO₂ fixation by carbonation reactions

Ind. Eng. Chem. Res., 46 (2007), pp. 103–107

[23] C.H. Huang, K.P. Chang, C.T. Yu, P.C. Chiang, C.F. Wang

Development of high-temperature CO₂ sorbents made of CaO-based mesoporous silica

Chem. Eng. J., 161 (2010), pp. 129–135

[24] A. Santos, M. Ajbary, V. Morales-Flórez, A. Kherbeche, M. Piñero, L. Esquivias

Larnite powders and larnite/silica aerogel composites as effective agents for CO₂ sequestration by carbonation

J. Hazard. Mater., 168 (2–3) (2009), pp. 1397–1403

[25] G. Montes-Hernandez, A. Pommerlon, F. Renard, P. Beck, E. Quirico, O. Brissaud

In situ kinetic measurements of gas–solid carbonation of Ca(OH)₂ by using an infrared microscope coupled to a reaction cell

Chem. Eng. J., 161 (2010), pp. 250–256

[26] H. Béarat, M.J. McKelvy, A.V.G. Chizmeshya, D. Gormley, R. Nunez, R.W. Carpenter, K. Squires, G.H. Wolf

Carbon sequestration via aqueous olivine mineral carbonation: role of passivating layer formation

Environ. Sci. Technol., 40 (2006), pp. 4802–4808

[27] M. Arandigoyen, J.L. Pérez Bernal, M.A. Bello López, J.I. Alvarez

Lime-pastes with different kneading water: pore structure and capillary porosity

Appl. Surf. Sci., 252 (2005), pp. 1449–1459

[28] J. Zelic, D. Rusic, R. Krstulovic

Kinetic analysis of thermal decomposition of $\text{Ca}(\text{OH})_2$ formed during hydration of commercial Portland cement by DSC

J. Therm. Anal. Calorim., 67 (2002), pp. 613–622

[29] L. Fernandez-Diaz, A. Putnis, M. Prieto, C.V. Putnis

The role of magnesium in the crystallization of calcite and aragonite in a porous medium

J. Sediment. Res., 66 (3) (1996), pp. 482–491

[30] Y. Nishino, Y. Oaki, H. Imai

Magnesium-mediated nanocrystalline mosaics of calcite

Cryst. Growth Des., 9 (1) (2009), pp. 223–226

[31] <http://www.rexarc.com>. Last visit: 5th July 2010.

[32] Kirik-Othmer, Encyclopedia of Chemical Technology, fifth ed., Wiley, Hoboken, NJ, 2007.

[33] Y. Katsuyama, A. Yamasaki, A. Iizuka, M. Fujii, K. Kumagai, Y. Yanagisawa

Development of a process for producing high-purity calcium carbonate (CaCO_3) from waste cement using pressurized CO_2

Environ. Prog., 24 (2) (2005), pp. 162–170

[34] T. Dunne, L.B. Leopold

Water in Environmental Planning

W.H. Freeman and Company, San Francisco, USA (1978)

[35] A.F. Meyer

Evaporation from Lakes and Reservoirs

Minnesota Resources Commission, Minnesota (1942)

Figure captions

Figure 1. XRD pattern of the original and carbonated samples. The letters “P”, “C”, “V”, and “A” indicate portlandite, calcite, vaterite, and aragonite peaks, respectively.

Figure 2. SEM image of the original sample.

Figure 3. Comparison of the geometrical effect on the TGA of carbonated samples. The weight loss $\Delta m(\text{CO}_2)$ represents the weight loss due to the release of CO_2 from the calcium carbonate.

Figure 4. SEM image of the floating calcite layer. Submicrometric spheres of precipitated calcium carbonate formed branched film and turned into calcite crystals.

Figure 5. Comparison of the solid-to-liquid ratio in the TGA of carbonated samples.

Figure 6. SEM image of the calcium carbonate layer precipitating on the portlandite clusters, indicated by the arrow (top) and bunches of calcium carbonate grains piled up (bottom).

Table 1. Chemical composition (XRF) and structural features of the original sample.

Chemical composition (%)	
Calcination weight loss	22.45%
Major elements	Ca: 52.41%; O: 23.09%; Si: 1.04%
	Normalized to the calcined mass: CaO: 94.56%; SiO ₂ : 2.88%
Traces (<0.6%)	Al; S; Fe; Cl; Mg; Sr
Structural data	
Specific surface area	47.5 m ² /g
Pore mean size	3.7 nm and 16.8 nm
Particle shape and size	Nanometric needles of 15 nm × 200 nm arranged in clusters of 500 nm

Table 2. Different configurations considered for ambient carbonation and their carbonation efficiencies.

		<u>Carbonation efficiency (%)</u>
Surface-to-volume ratio (height)		
P4	Sol/liq = 0.24; height = 2.3 cm	15
P5	Sol/liq = 0.24; height = 0	65
Solido-to-liquid ratio (sol/liq)		
P3	Sol/liq = 0.07; height = 2.3 cm	10
P4	Sol/liq = 0.24; height = 2.3 cm	15
P6	Sol/liq = 0.33; height = 2.3 cm	38
Stirring		
P3_S	Stirred, sol/liq = 0.07; height = 2.3 cm	15
P4_S	Stirred, sol/liq = 0.24; height = 2.3 cm	18
Rewetted samples		
P4_w	P4, rewetted once	41
P4_w2	P4, rewetted (after 4 days)	58
P5_w	P5, rewetted once	81
P0	Height = 0	88

Rewetted and stirred for 7 days

a Carbonation efficiency is the ratio between the sample weight loss between 550 °C and 750 °C measured in the TGA analyses and the theoretical maximum for calcium carbonate of 44%.

Table 3. Daily production of one acetylene plant, alkaline waste (portlandite) and different elements of the acetylene carbon footprint. The mitigation power of this technology is evaluated for 1 ha weathering pool.

Acetylene production	1.67 t
Portlandite production	4.74 t
Maximum stoichiometric theoretical CO ₂ absorption	2.82 t
Indirect CO ₂ emissions (energy consumption)	0.96 t
CO ₂ sequestered (80% efficiency considered)	2.28 t
CO ₂ balance	-1.94 t (total mitigation)
Calcium carbide consumption	4.10 t
Indirect CO ₂ emissions	6.35 t
CO ₂ balance	5.03 t (31% reduction)

Figure 1

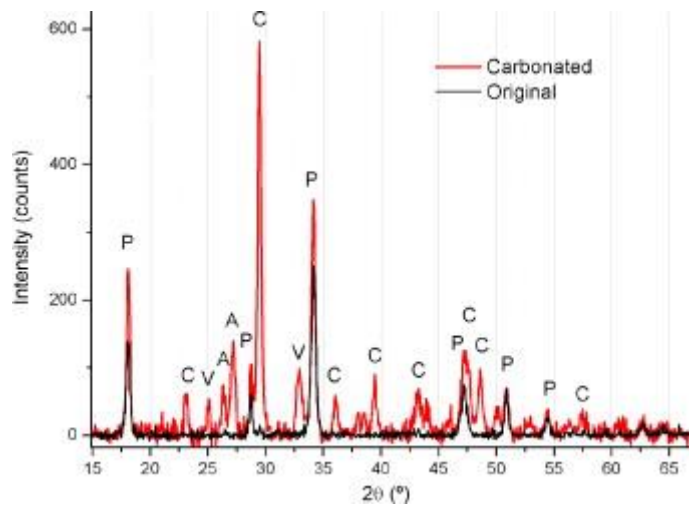


Figure 2

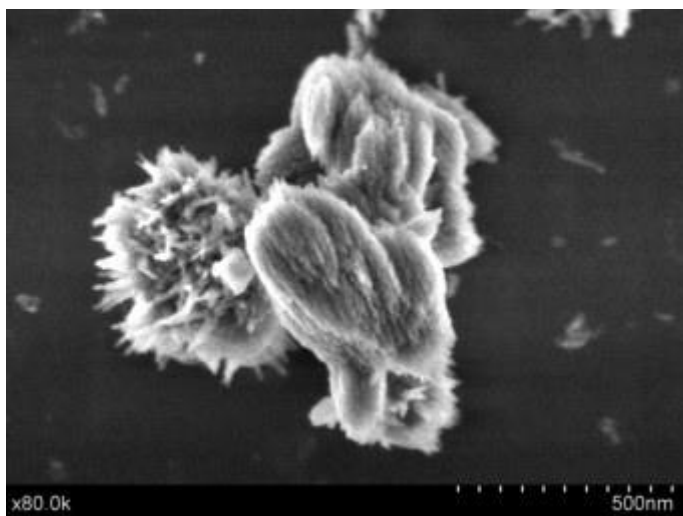


Figure 3

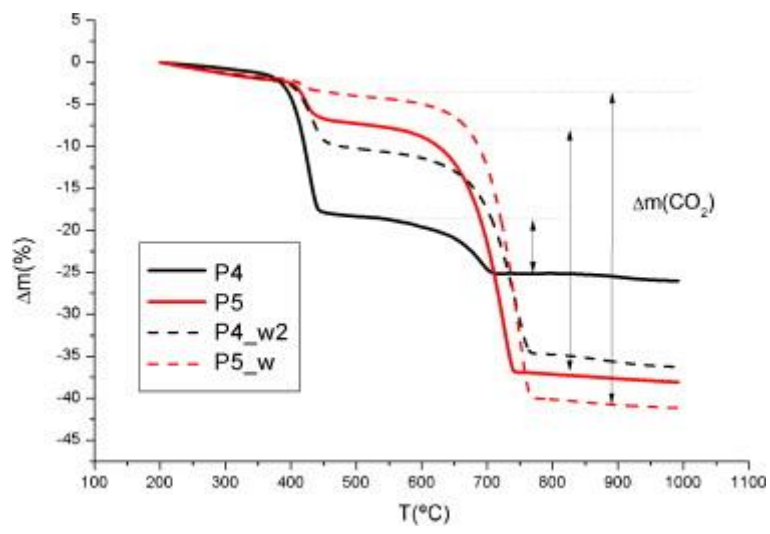


Figure 4

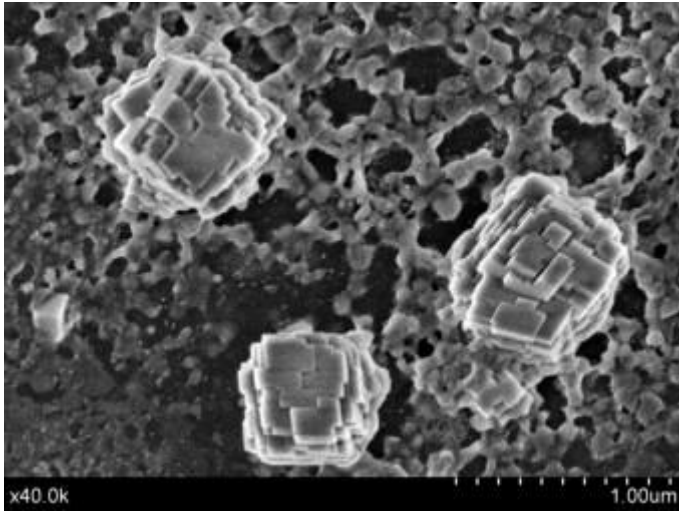


Figure 5

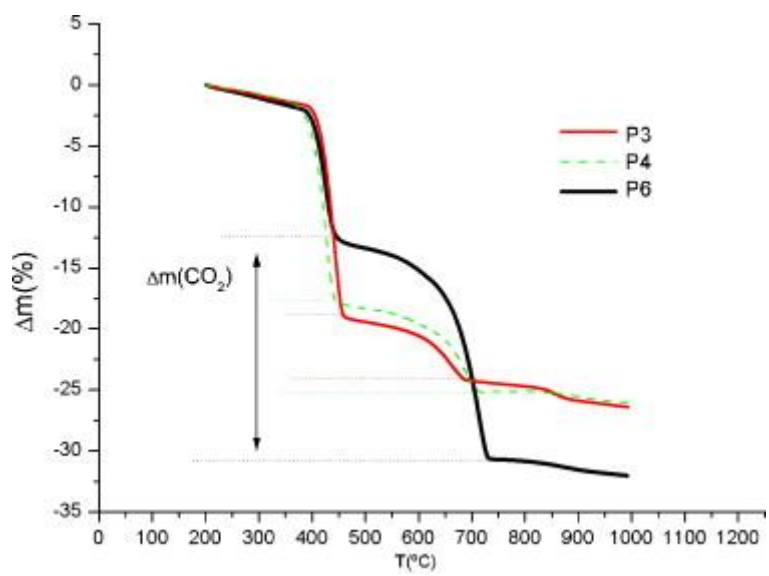


Figure 6

