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Experimental analysis of the reaction rate of hydrated Class G cement powder at 11 bar P_{CO2} and ambient temperature

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Abstract

The aim of this work is to study the alteration of class G Cement at ambient temperature under a relatively high CO_2 partial pressure through suitably designed laboratory experiments, in which cement hydration and carbonation are taken into account separately. First, the hydration process was carried out for 28 days to identify and quantify the hydrated solid phases formed. After the completion of hydration, accompanied by partial carbonation under atmospheric conditions, the carbonation process was investigated using a stirred micro-reactor by reacting cement powder with pure $CO_{2(g)}$ (P_{CO2} = 11 bar) and MilliQ water for different reaction times. The reaction time was varied to constrain the reaction kinetics of the carbonation process and to investigate the evolution of primary and secondary solid phases. Mineralogical analyses (X-ray Powder Diffraction and Scanning Electron Microscope) were carried out to this purpose. Water analyses were also performed by ion chromatography at the end of each experimental run to investigate the chemical effects of cement carbonation on the aqueous solution. The carbonation degree was calculated from the results of Thermo-Gravimetric analysis (TGA). The main results of these experiments is the quick conversion of portlandite and $Ca_{1.60}SiO_{3.6} \cdot 2.58H_2O$ (C-S-H) to calcite. In fact, the carbonation degree attains 80 % after 6 hours of reaction time. Experimental outcomes will be simulated by means of the PHREEQC software package to obtain further indications on cement carbonation

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1. Introduction

One of the major risks posed by the geological sequestration of CO_2 and other gases, is the gas leakage from reservoirs in which they have been disposed. This fact is usually related to well integrity issues in a high-pressure environment where gas leakage can be triggered by relatively fast cement corrosion in wells with damaged casing.

Several authors have studied the interactions between cement, rock, steel casing, water and CO_2 by laboratory carbonation experiments of cement and other solids involving CO_2 diffusion through cement cores with suitable openings or fractures[1-3]. In the case of a well with damaged casing it is however likely that advective processes, much faster than diffusion, dominate the alteration of cement and other solids. Thus, in this study, laboratory experiments of cement carbonation were performed using cement powder to obtain the alteration reaction rate of a class G Portland cement under relatively high P_{CO2} conditions. The obtained results are expected to be relevant to understand the comparatively fast cement reactivity in wells with damaged casing.

2. Experiments

After the completion of cement hydration in 28 days, accompanied by partial carbonation under atmospheric conditions, the carbonation process of cement powder was completed in a stirred micro-reactor (Parr instrument) under 11 bar of pure $CO_{2(g)}$ and in the presence of MilliQ water. The micro-reactor was kept at room temperature during the whole duration of the experiments. Different reaction times in hours were adopted in separate experiments for; 1, 3, 6, 21, 67, 97 and 120 hours; to investigate the carbonation rate of cement.

2.1. Crushed hydrated samples

Hydrated cement was prepared by mixing 1 kg of cement and 0.5 kg of water, i.e. cement/water weight ratio of 2:1. After 28 days at atmospheric pressure and room temperature conditions, the cement paste was grinded and sieved. The powder size between 125 and 63 μm was selected for carbonation experiments.

2.2. Carbonation experiments

Before the carbonation, the hydrated cement powder was heated for 2 hours at 40 °C in an oven. In each experiment, the micro-reactor was charged with 1 g of this cement powder and 15 mL of MilliQ water. The micro-reactor was initially flushed with pure $CO_{2(g)}$ to get rid of atmospheric air before setting the P_{CO2} value at 11 bar.

3. Results

Most of the aqueous solution was sampled, just before the end of the laboratory experiment from the micro-reactor into a flask to be filtered through membranes with pore size of 0.45 μm and stored in two 25 ml flasks, one containing 1 mL of HCl (37%). This operation did not allow to collect the whole aqueous solution. Once the micro-reactor was opened the remaining aqueous solution (<10 ml) was sampled, filtered and added to the two different flasks. The reacted cement powder was then dried for two hours into an oven at 40 °C before storage.

The aqueous solution and the reacted cement powder were both analyzed by using different methods.

3.1. Aqueous solution

The aqueous solution was analyzed by ion chromatography for $Ca^{2+,}$ Mg^{2+}, K^+, Na^+ and Cl^-, F^-, SO_4^-, and NO_3^-. Alkalinity (HCO_3^-) was measured by acidimetric titration using methylorange as indicator. The initial pH of the aqueous solution (not measured, as the micro-reactor is not equipped with a pH electrode) can be reasonably assumed to be fixed by P_{CO2} and alkalinity.

Temperature, P_{CO2}, the total concentration of main solutes and alkalinity will be used as input data for speciation-saturation calculations and reaction path modeling of cement carbonation.

3.2. Solid phases

The mineral species present at the end of hydration and carbonation experiments were characterized by X-ray powder diffraction (Figure 1a) and SEM analysis. Calcite was identified upon both hydration and carbonation, whereas portlandite was identified upon hydration. The C-S-H phases (e.g. $Ca_{1.60}SiO_{3.6} \cdot 2.58H_2O$) were also identified by SEM and TGA analysis.
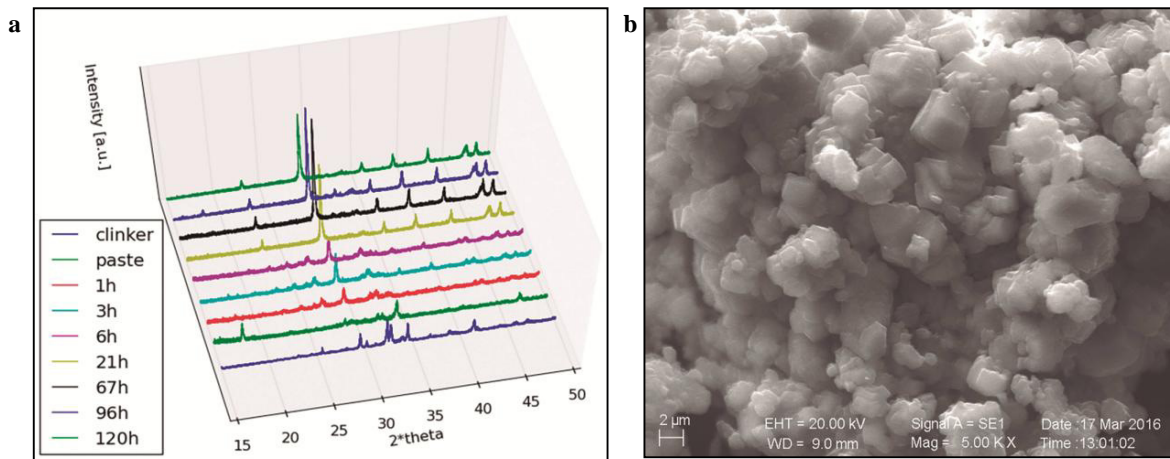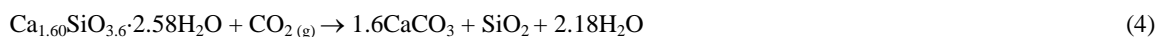
Fig. 1 (a) X-ray powder diffraction for the initial Clinker, the hydrated cement paste and all the carbonation experiments at different reaction times as indicated; (b) SEM image showing calcite crystals upon 96 hours of cement carbonation.

As shown by the multiple XRD diagram of Fig. 1, portlandite is only present in the hydrated cement paste (main diffraction peaks of portlandite at 2Theta 18.09, 34.08, 47.12) and converted into calcite after one hour of carbonation. The intensity of the calcite peaks (located at 2Theta 29.4, 39.4, 43.14) increases with the carbonation reaction time as expected.

The TGA analysis was carried out for all samples, both hydrated and carbonated, to calculate the progress of the carbonation reaction, which is indicated by the amounts of portlandite, C-S-H and calcite present in the samples. The amounts of portlandite and calcite present in the cement paste at the end of hydration are constrained by reactions (1) and (2), respectively:

$$Ca(OH)_2 \rightarrow CaO + H_2O \tag{1}$$

$$CaCO_3 \rightarrow CaO + CO_{2\,(g)} \tag{2}$$

The amounts of CO_2 fixed in the carbonated cement as calcite through conversion of both portlandite and C-S-H are fixed by reactions (3) and (4), respectively:

$$Ca(OH)_2 + CO_{2\,(g)} \rightarrow CaCO_3 + H_2O \tag{3}$$

$$Ca_{1.60}SiO_{3.6} \cdot 2.58H_2O + CO_{2\,(g)} \rightarrow 1.6CaCO_3 + SiO_2 + 2.18H_2O \tag{4}$$

In addition, the total mass gain (fixed CO_2 and H_2O) from the initial state (Clinker) to the final state (carbonated cement) was calculated. The extent of cement carbonation at 11 bar P_{CO2} and room temperature (Fig. 2) attains 80 % after 6 hours. This value is due to 100 % conversion of portlandite to calcite and 60 % conversion of C-S-H phases (e.g., $Ca_{1.60}SiO_{3.6} \cdot 2.58H_2O$) to calcite.
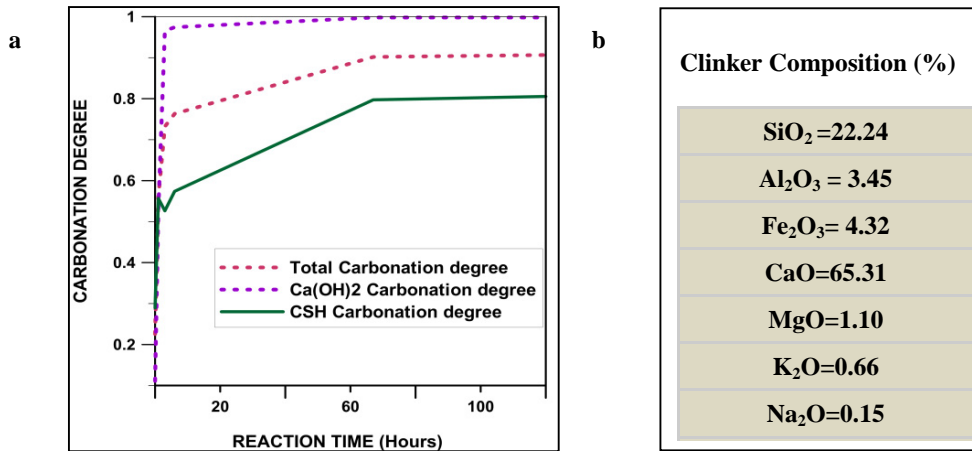
Fig.2. (a) Evolution of the total carbonation extent of class G Cement with time at 11 bar CO_2 and ambient temperature. The carbonation extent is also shown for Portlandite and C-S-H phases; (b) Composition of the clinker used to calculate the carbonation degrees.

The amount of portlandite and C-S-H phases in the cement paste were calculated by PHREEQC from the initial composition of the cement paste (Fig. 2) and represents the 33.84 % and the 72.65 %, respectively. These values were used also to calculate the carbonation degree.

4. Conclusions

A Portland cement G-class of known composition was first hydrated under atmospheric conditions for 28 days. After the completion of hydration, accompanied by partial carbonation, the carbonation process was investigated in a stirred micro-reactor (Parr instrument) by reacting the cement powder with pure $CO_{2(g)}$ (P_{CO2} = 11 bar) and MilliQ water for different reaction times, from 1 hour to 120 hours. The reaction time was varied to constrain the reaction kinetics of the carbonation process and to investigate the evolution of primary and secondary solid phases with time. Minerals were characterized by X-ray Powder Diffraction and Scanning Electron Microscope.

Portlandite was only present in the hydrated cement paste and it was converted to calcite just after one hour of carbonation as expected. The results of thermogravimetric analysis (TGA) indicated that total carbonation attains 80% after 6 hours due to 90% conversion of portlandite to calcite and 60% conversion of C-S-H to calcite.

The chemical results of the aqueous solution will be used to obtain further indications on cement carbonation, through speciation-saturation calculations and reaction path modelling by means of PHREEQC (work in progress).

5. Acknowledgements

References

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