

Experimental assessment of the supercritical carbonation of recycled concrete aggregates

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1. Introduction

The cement industry is responsible for 7 % of the global greenhouse gas emissions ¹. Concrete, one of the most commonly used materials in the world, is made by mixing ordinary Portland cement (OPC) with water and aggregates (*e.g.*, sand and crushed stone). OPC is a synthetic material obtained by burning a mixture of limestone, clay or materials of similar composition, in a rotary kiln at a temperature of 1450°C. The manufacture of Portland cement releases considerable amounts of carbon dioxide (CO₂). Most of the emitted CO₂ (64%) by the cement industry comes from the chemical decomposition of limestone according to (Eq. 1).



A promising way to mitigate CO₂ emissions from concrete consists of using its ability to be re-carbonated by contact with gaseous CO₂ and therefore allowing CO₂ sequestration ². This trapping is due to the carbonation process of the main cement hydrates. So this reaction can be used to capture carbon dioxide and “compensate” part of the carbon dioxide emitted during the manufacture of cement by carbonating recycled concrete aggregates. Moreover, unlike conventional recycled aggregates which are known to exhibit poor properties for their re-use in the building industry (due to their porosity and water absorption), it has been shown that carbonated recycled aggregates present better properties ². Considering the exponential increase in the demand for cement ³, their re-use in the building industry could help the cement industry to meet carbon reduction targets and contribute to the transition to net-zero emissions by 2050 ⁴. Since natural carbonation is too slow, there is an incentive to explore accelerated processes and this study proposes the use of supercritical CO₂ to attempt maximizing CO₂ storage and improving reaction kinetics. In this work, we have studied the role of pressure and CO₂ water content on kinetics of the carbonation reaction under different temperatures using dried and wet cement-based mortar powders. Results of these preliminary tests on powder mortars using the supercritical technology are presented here.

2. Materials and Methods

The schematic diagram of the carbonation set-up is presented in **Figure 1**. Runs of supercritical carbonation tests were carried out using a cylindrical reactor (V = 200 mL; height = 280 mm, diameter 30 mm) which can withstand pressures up to 300 bar. The CO₂ was injected into the reactor using a volumetric membrane pump to reach the desired pressure, which took a few minutes. Pressure is kept constant using a CO₂ syringe pump allowing injection of CO₂ to maintain the pressure during the experiment, as CO₂ is consumed by the reaction. The system was operated at a temperature between 40°C and 80°C and pressure between 100 bar and 250 bar and the reaction operated in batch mode. The reaction duration was varied between 2 and 24h.

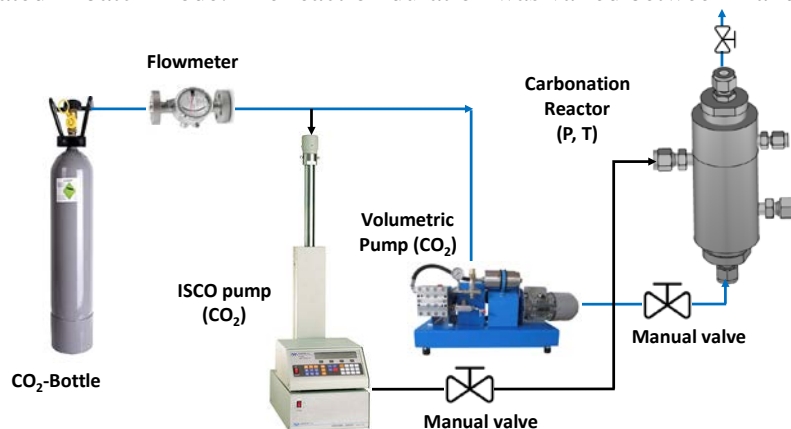


Figure 1 : Overview of the experimental set-up of supercritical carbonation

The treated samples were concrete cylinders (CEM I, 52.5N) and ground cement-based mortar powders with a particle size of approximately ~ 100 microns. The cylinders were crushed and ground using a disc crusher. Before and after reaction, solid samples were weighed and analyzed by X-ray Diffractometer (XRD), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) to investigate the CO_2 content, morphology, size and texture of the carbonated products.

3. Results and discussion

Thermograms and XRD analyses are presented in **Figure 2**. Both evidence the formation of calcium carbonates (CaCO_3). First, a succession of mass losses is observed from 500°C in the thermograms, corresponding to the decomposition of calcite. Also, the diffractograms of the carbonated samples show the presence of peaks, characteristic of the calcite (position $2\theta = 29$), and the reduction in the intensity of the peaks related to portlandite ($\text{Ca}(\text{OH})_2$).

Initial runs carried out on concrete cylinders show a relatively low carbonation rate (CO_2 uptake of 24.1 g/kg). Indeed, specimens were well carbonated on the surface and not at the core. Different factors such as the short reaction duration, the low temperature and the CO_2 which cannot enter inside the material, can explain this low carbonation degree of the cylinders. Moreover, a parametric study was performed, using powder cement-based mortar, to determine the influence of pressure, water content, temperature and duration on the reaction. The results show that kinetics of the carbonation reaction is favored by the water content of the initial solid sample, the temperature, the pressure and the duration. Also, kinetics are faster with the wet powder than with the dried powder. The carbonation yields at different pressures and water contents were calculated and it was shown that more than 90% of carbonation ratio is reached in less than 2 hours, using powder mortar.

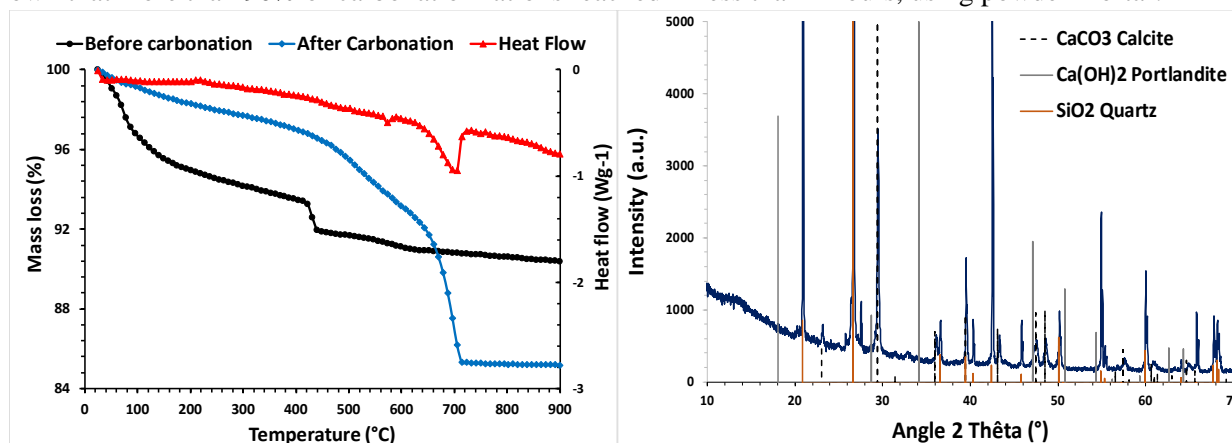


Figure 2 : Thermograms (TGA) and XRD patterns of powder mortar after supercritical carbonation

4. Conclusions

The purpose of this work was to study accelerated carbonation reaction of cement-based mortar powders using supercritical CO_2 . The aim was to understand the role of pressure and water content in the carbonation reaction and to improve kinetics. XRD, SEM and TGA analyses showed the formation of calcium carbonate in the final products with carbonation yields higher than 90%. We mainly demonstrated that high initial water content in the material plays a beneficial role in the carbonation reaction, which is faster in the case of the wet solid. The influence of water-saturated CO_2 and dry CO_2 on carbonation reaction kinetics has not yet been clearly established and will be the subject of further targeted experimental tests.

References

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