

Determination of Critical Parameters for Mineral Carbonation Kinetics

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Summary

A specifically adapted apparatus has been designed to study the passive and spontaneous carbonation of Mg-rich silicates. This device allows continuous observation of CO₂ uptake over long periods of time. The effect of different parameters on the total CO₂ uptake and on the reaction kinetics has been examined. The grain size of the reactive material appears to be a crucial property, as the finely powdered serpentinites can incorporate up to 8-9 wt% CO₂ while the coarser samples barely reach 1.5 wt% CO₂. The fine grained samples also display a higher reaction rate. Though the presence of water is necessary for the reaction to occur, the reaction rate slows down when the sample is totally submerged. Under the experimental conditions, the CO₂ content in the gas mixture appeared as an important limiting factor only for concentrations below 1 vol%

Introduction

The estimation of CO₂ uptake by analysis of the carbonated product after reaction gives no insight about the evolution of the reaction rate throughout the experiment. In order to obtain this information, the Laval Eudiometer, a modified eudiometer from Landriani (1775) has been developed that allows real time monitoring of gas volume variations inside the apparatus over several weeks.

Analytical method

The main component of the eudiometer is a ca 500 mL graduated container whose bottom opening is dipped in a cylinder filled with glycerol (Figure 1). A beaker containing the sample is kept in an atmosphere composed of N₂, O₂ and CO₂ in known proportions. All the glassware is made of PYREX glass. As the device is airtight, the sample is left to react at constant

temperature as long as necessary. The level of glycerol varies according to the changes of gas volume inside the eudiometer. A bend glass tube connected to a gas cylinder can be used to replenish the air mixture in CO₂.

Because the reactions are monitored for periods as long as three weeks, each series of experiments, involving several eudiometers, includes a control apparatus loaded with non reactive material (quartz) set in the same gas mixture as the samples in order to correct for the effect of phenomena other than CO₂ consumption. Fluctuation of atmospheric pressure is the main interfering parameter.

Volume changes of 2 mL can be detected with the ca 500 mL device, which corresponds to 3.6 mg or 82 μmole of CO₂. If this amount of CO₂ was absorbed by a 2 g sample, it would provoke a weight increase of 0.18%. The method allows then determining precisely the CO₂ uptake by the sample. The final carbon content of the reacted samples has been measured by combustion and IR analysis and the results show good agreement with the total CO₂ consumption observed in eudiometers.

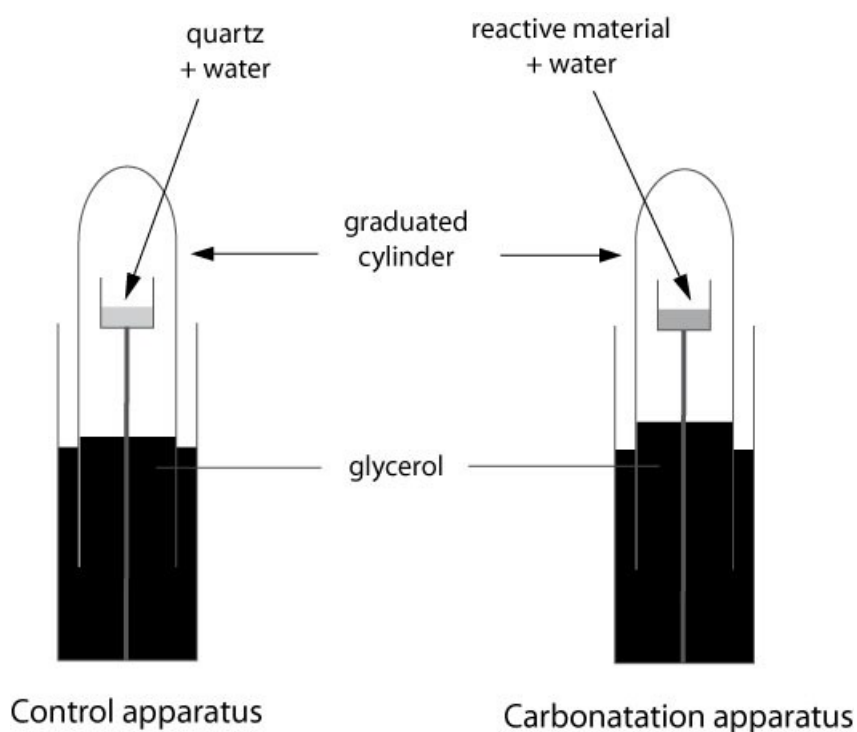


Figure 1: Schematic representation of the experimental device. The level of glycerol in the graduated tube of the control apparatus varies according to external parameters only (mainly atmospheric pressure), which allows to correct the variations observed in the experimental apparatus and then to determine the effect of CO₂ uptake only.

Results

The working material consists of ultramafic crushed serpentinite. Several series of experiments have been carried out in order to determine the relative importance of different experimental parameters. Three grain size fractions split, from a heterogeneous sample of milling residue with gravels up to 5 mm in diameter to a very finely powdered residue, have been tested (Figure 2). As seen in Figure 3, the relative humidity of the samples affects the carbonation rate. It should be noted that totally dry samples as well as water do not consume any measurable amount of CO₂. When CO₂ is almost exhausted from the gas mixture, the reaction rate decreases. Figure 4 illustrates the case of samples that have reached near saturation of reaction sites after three CO₂ gas replenishments.

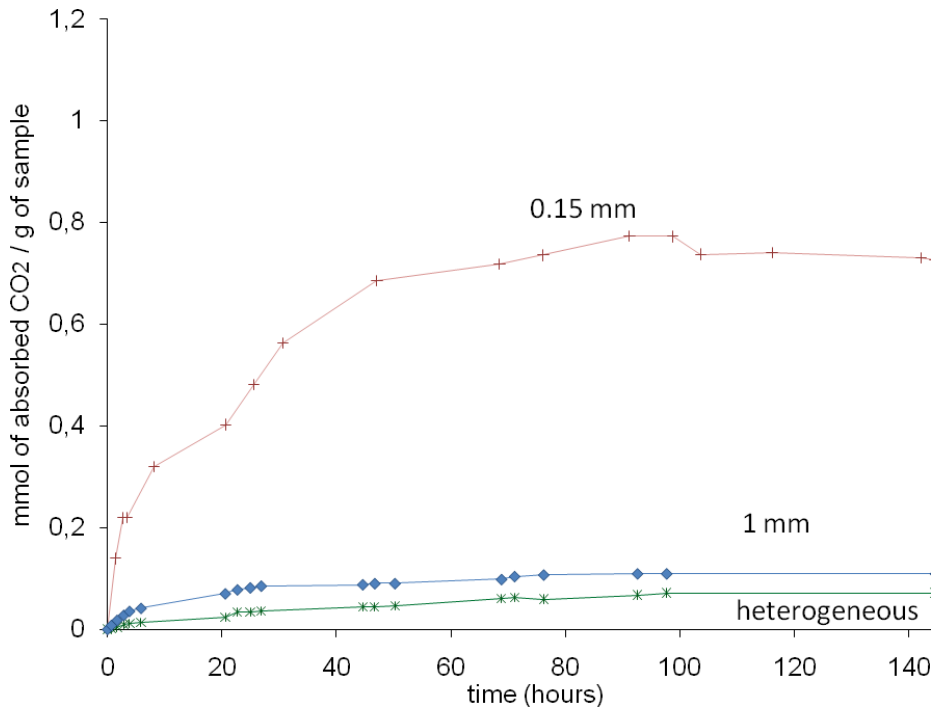


Figure 2: Quantity of absorbed CO₂ (mmol) per weight of sample (g) over the course of a carbonatation experiment for three samples with different grain size set in similar condition (20-30 wt% H₂O and initial CO₂ content of 10 vol%).

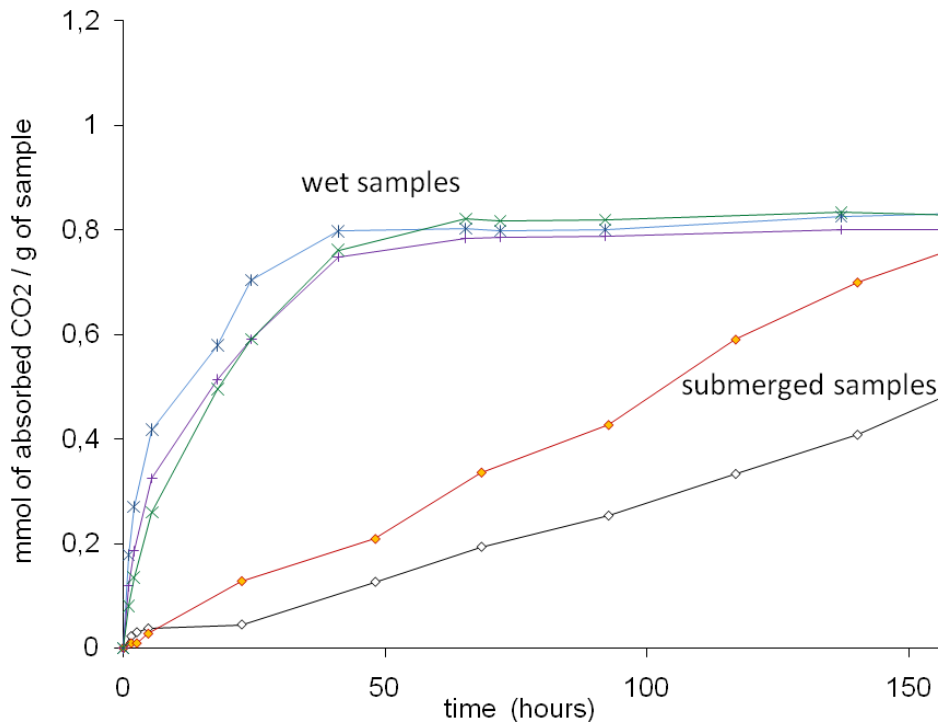


Figure 3: Quantity of absorbed CO₂ (mmol) per weight of sample (g) over the course of a carbonatation experiment for five fine grained samples set in a gas mixture with an initial content of 30 vol% CO₂. Three of the samples contain 30 wt% H₂O while the two others are totally submerged.

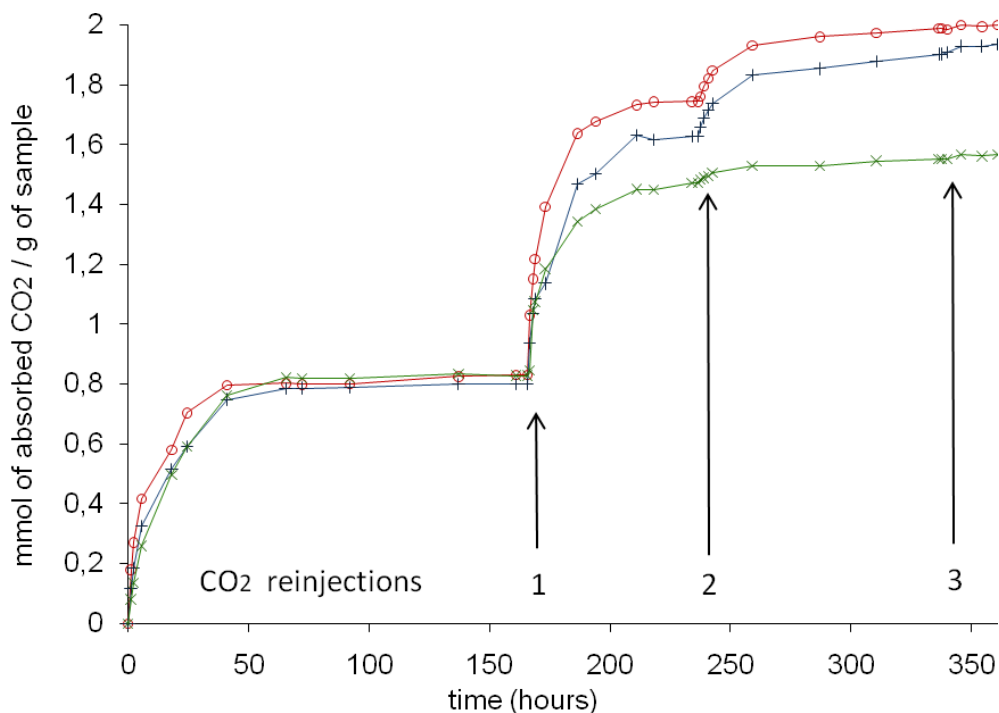


Figure 4: Quantity of absorbed CO₂ (mmol) per weight of sample (g) over the course of a carbonatation experiment for three fine grained samples set in similar conditions (35 wt% H₂O and initial CO₂ content of 30 vol%). After exhaustion of the initial CO₂, the reaction is reactivated by injection of new CO₂ until saturation of the powdered material is reached.

Conclusions

The grain size, that determines the specific surface area, exerts a strong control on both reaction rate and total CO₂ uptake. The finer grained material can fix 5-6 times the amount of CO₂ consumed by the coarser samples and the maximum reaction rate is up to 4 times higher. The CO₂ uptake kinetics is markedly slower for submerged samples compared to wet samples: dissolution and/or diffusion of CO₂ in water is rate limiting in this case. Variations in CO₂ concentration have a small effect in the range 30 to 1 vol% CO₂ but the reaction becomes markedly slower for lower CO₂ contents. Determining the parameters that favor a complete and fast reaction for each type of reactant is a necessary stage for spontaneous carbonation optimization.

Acknowledgements

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References

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