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Biologically enhanced degassing and precipitation of magnesium carbonates derived from bicarbonate solutions

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ABSTRACT

This contribution reports the results of batch and semibatch experiments involving bubbling of nitrogen in aqueous solutions of magnesium bicarbonate, with and without the addition of either carbonic anhydrase (CA) or *Scenedesmus alga* to the solution. Precipitation of nesquehonite occurred during both an accelerated degassing of CO_2 induced by sparging small nitrogen bubbles (representative diameter of 20 μm), and during slow degassing engendered by introducing large nitrogen bubbles (representative diameter of 5 mm). The response of the system during low rates of degassing closely approached quasi-thermodynamic predictions, which permitted an estimation of the level of supersaturation of nesquehonite, prior to the onset of precipitation. Small bubbles and CA significantly increased rates of degassing and indirectly the production of nesquehonite, as the rate of degassing can limit the precipitation process. The response of the system during rapid rates of degassing, prior to precipitation, was not entirely consistent with quasi-thermodynamic predictions. During precipitation, higher rates of degassing produced similar alkalisation and precipitation trends to that observed for lower rates of degassing. Our results agree with the formation of travertine deposits in nature, where the degassing of solutions enriched with inorganic carbon, and enhanced alkalisation by microorganisms, have been shown to influence carbonate formation. The results demonstrate a catalytic effect of CA on the rate limiting carbonate reactions, increasing CO_2 exchange between nitrogen and water, and indirectly accelerating the precipitation of carbonates for a system controlled by rate of degassing. The results of this study have applications to large-scale storage of CO_2 by mineralisation.

1. Introduction

The evasion or degassing of carbon dioxide (CO_2) from mineral solutions enriched in inorganic carbon represents a promising approach to mineral carbonation. For a solution rich in mineral ions, degassing causes the solution pH to increase and leads to elevated mineral saturation indices and mineral precipitation. The process of degassing of CO_2 is fundamentally a kinetic phenomenon driven by the difference in chemical potential of CO_2 between the bulk solution and that of the gas–liquid interface. That is, the chemical behaviour of the system depends on the concentration of carbonate species in the bulk solution and on mass transfer of CO_2 across the liquid–gas interface. The concentration of carbon species in the bulk solution decreases as CO_2 degassing of the solution progresses.

Microalgae and in particular carbonic anhydrase (CA), an enzyme produced by microalgae and living organisms more generally, have been implicated in the precipitation of carbonates in nature (Liu, 2001; Liu et al., 2010; Sondi and Mladen, 2010). The precipitation mechanism is controlled kinetically by the rate of CO_2 removal from the system, and thermodynamically by pH; the latter elevated through the cellular consumption, by the microalgae, of aqueous CO_2 and bicarbonate, HCO_3^-. Microalgae extracellular CA is the catalytic component in the carbon concentrating mechanisms (CCM) used to promote uptake of carbon into the cell needed for growth and metabolism of the algae. In instances, for example in the formation of travertine deposits, both microorganisms and degassing of solutions enriched with inorganic carbon, have been shown to influence carbonate formation (Pentecost, 2005). CA has been demonstrated as an activator in the accelerated weathering of carbonate rocks, and the enzyme has been previously shown to increase rates of CO_2 exchange between air and sea water, and intensify rates of precipitation of carbonates by way of catalysing rate limiting carbonate reactions (Berger and Libby, 1969; Liu, 2001; Dreybrodt et al., 1997).

This study investigates the degassing of carbon enriched solutions, in a situation analogous to natural mechanisms, and the enhancement of the degassing and precipitation mechanisms through incorporation of CA and microalgae in the reacting system to increase the rate of production of carbonate. The study explores batch and semibatch operations.

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2. Materials and methods

2.1. Materials

Solutions for batch and semibatch experiments were prepared with ultrapure deionised water with electrical resistivity of 18.2 MΩ/cm and reagent grade magnesium sulfate heptahydrate ($MgSO_4{\cdot}7H_2O$) and sodium bicarbonate ($NaHCO_3$). Glass bottles contained the solutions for batch experiments, and polyethylene bottles for the semibatch experiments. Gaseous nitrogen (N_2) used for aeration was discharged into the reactor through either a 2 μm aperture stainless steel air diffuser or directly through 4 mm ID silicone tubing. A thermostatically controlled water bath (Axyos Technologies, Model w10) housed bottles containing the solutions for batch and semibatch experiments. Mini variable flow peristaltic pumps (VWR and Control Company) fed reagent solutions to the reactor for the semibatch experiments.

Supplements to chemical reagents used in preparing the test solutions included bovine carbonic anhydrase (CA) (Worthington Biochemical, carbonic anhydrase from bovine erythrocytes, dialysed, lyophilised powder) and the green freshwater alga *Scenedesmus* (species 005; Australian Water Quality Centre). Cellulose fibre filter pads (0.2–0.5 μm) served to filter algal solutions. Submersible white LED lights (Nelson Industries, MGL540LED) illuminated algae supplemented solutions. An illuminometer (Kyoritsu, Model 5200) facilitated light intensity measurements. A haemocytometer (Neubauer-improved bright-lined haemocytometer (Superior Marienfeld)) enabled a cell count of algal solutions.

A pH glass electrode (Hanna HI 1131) recorded proton activity in the experimental solutions, with the electrode calibrated at working temperature with commercial buffer solutions. Measurements were logged with 'DataTaker' (505 Series 2 Data Logger) data acquisition hardware. Solutions at the end of each experiment were filtered using Whatman Grade 1 paper filters and then using Millex GP 0.22 μm syringe driven filters. A Varian 715-ES inductively coupled plasma–optical emission spectrometer (ICP-OES) provided the elemental analysis of magnesium (Mg) present in filtered samples (0.22 μm) of the test solutions. X-ray powder diffraction (XRPD) with a Philips X'Pert Pro multipurpose diffractometer using Cu Kα radiation in the range of 5° to 90° 2θ, with a step size of 0.008° and collection time of 42 s $step^{-1}$, were deployed for the identification of the mineral phase in precipitates. The gaseous vent stream from the solution passed through a membrane separator (Genie Model 170–005-SS) prior to its CO_2 concentration being measured with a micro gas chromatograph (Varian 4900 micro GC with PoraPLOT Q column with column temperatures of 60 °C and injection time of 40 ms). Initial volumes of the vented N_2 stream from the experiments were collected using sample bags (SKC FlexFoil PLUS) for subsequent analysis using the micro GC.

2.2. Methods

Batch and semibatch experiments involved bubbling of N_2 in aqueous solutions of magnesium sulfate ($MgSO_4$) and sodium bicarbonate ($NaHCO_3$). The preparation of the $MgSO_4$ solutions using magnesium sulfate heptahydrate ($MgSO_4{\cdot}7H_2O$) accounted for the hydrated nature of this compound in establishing molar concentrations of the $MgSO_4$ solutions; typically 0.1 M $MgSO_4$ and 0.1 M $NaHCO_3$. The temperature of the thermostatically controlled water bath housing the bottle reactors was set to 30 °C for all batch and semibatch experiments. Gaseous N_2 at a preset rate flowed to the reactor containing the test solutions with N_2 discharged into the solution at the base of the reactor through an air diffuser or directly through tubing. The period for all batch experiments was 24 h and for semibatch experiments 4 h.

Table 1 provides a summary of experimental conditions for the batch experiments. Prior investigations, during which reported trends were clearly evident, permitted establishment of appropriate experimental conditions for the batch reactor.

Two of the batch and one of the semibatch experiments exploited CA at a concentration of 0.5 μM and 0.25 μM, respectively. The selection of a 0.5 μM CA concentration corresponded to that used in previous research (Dreybrodt et al., 1997), and the application of a 0.25 μM strength CA solution for semibatch experiments allowed for a prefatory assessment of the effect of varying CA concentration. Semibatch experiments comprised the continual addition of reagent solutions (0.5 M $MgSO_4$ and 0.34 M $NaHCO_3$ to result in molar dosing rates of 1.1×10^{-5} mol s^{-1} and 2.3×10^{-5} mol s^{-1}, respectively) as separate streams into the reactor. The reagent streams entered into an initial batch solution of the same chemical composition as that deployed for the batch experiments.

We also completed a batch experiment using *S. alga*. The growth medium for the alga comprised demineralised water supplemented with soluble plant nutrient. Cultures grew at air-equilibrated levels of CO_2 at ambient laboratory conditions under a lighting level of 1000 lux. Filtration of aliquots of culture through cellulose fibre filter pads, and rinsed with ultrapure deionised water prior to harvest, provided a concentrated algal inoculum. The filtered and rinsed microalgae of paste-like consistency were then added to a solution that comprised only $MgSO_4{\cdot}7H_2O$ reagent. Submersible lighting illuminated the test solution at a level of 10,000 lux. A diluted sample (5:1) of the test solution allowed for an algal cell count. The inoculated solution was then bubbled with CO_2 and subsequently purged with gaseous N_2 under ambient conditions in order to promote CA production by the microalgae. Finally, the addition of $NaHCO_3$ reagent resulted in a solution of chemical composition of 0.1 M $MgSO_4$ and 0.1 M $NaHCO_3$. Aeration of the prepared solution using N_2 followed.

Gaseous N_2 at a preset rate flowed to the reactor containing the test solutions, discharging into the solution at the base of the reactor through either the air diffuser or directly through tubing. The former generated small bubbles giving rapid bubbling and an accelerated rate of mass transfer through its large interfacial area, and the latter formed large bubbles resulting in slow bubbling and a diminished rate of mass transfer through reduced interfacial area. Bubbles were photographed and empirically sized and bubble travel times estimated using a digital camera with video capture. Bubble coalescence was evident for N_2 aeration generated by tubing. Fluid depth (bubble travel distance) was approximately 50 mm for the batch experiments and initially 30 mm increasing to 120 mm for the semibatch experiments. Representative bubble diameter, time to traverse 50 mm of fluid depth and rise velocity corresponded to 5 mm, 0.22 s and 0.23 m s^{-1} respectively for tubing, and 20 μm, 0.15 s and 0.33 m s^{-1} respectively for the air diffuser. At the conclusion of each experiment involving the diffuser, we recorded a value of the decreased flow rate of N_2, as a consequence of carbonate build-up in the pores of the diffuser.

We sampled the test solutions at the commencement and conclusion of each experiment, decanting and then filtering them for subsequent analysis. Potentiometric titration of 5 cm^3 or 10 cm^3 aliquots of 0.22 μm filtered samples against standardised 0.01 M sulfuric acid (H_2SO_4) enabled the determination of alkalinity of the samples. ICP-OES analysis afforded determination of Mg balance. Sample bags accumulated the vented gas stream for the first 2 min of degassing, in duplicated experiments, for subsequent analysis using the micro GC. All precipitate, including that which was retained within the reactor, underwent drying under ambient conditions open to atmosphere until attaining stable mass measurements. Mineral phase identification utilised the dried precipitates.