CO_2-mineral dissolution experiments using a rocking autoclave and a novel titanium reaction cell

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Abstract

A novel titanium reaction cell has been constructed for the study of water-rock-CO_2 reactions. The reaction cell has been used within a direct-sampling rocking autoclave and offers certain advantages over traditional 'flexible gold/titanium cell' approaches. The main advantage is robustness, as flexible cells are prone to rupture on depressurisation during gas-rich experiments. The reaction cell was tested in experiments during an inter-laboratory comparison study, in which mineral kinetic data were determined. The cell performed well during experiments up to 130°C and 300 bar pressure. The data obtained were similar to those of other laboratories participating in the study, and also to previously published data.

Introduction

The long-term trapping of carbon dioxide (CO_2) within deep geological storage schemes will be modified by CO_2-water-rock reactions.[1] A key factor in this trapping will be the rates at which reactive minerals dissolve, as they will provide divalent metal ions with which to make secondary carbonate phases, and will also buffer pH towards more neutral values.[2] Well-controlled laboratory experiments can be used to simulate *in-situ* storage conditions and study the direction, rate and magnitude of these reactions. It is essential that models predicting the future evolution of the stored CO_2 use reaction rate parameters which are realistic and in which there is a high degree of confidence

We describe a novel reaction cell used to obtain kinetic data from mineral dissolution experiments conducted under *in-situ* pressures and temperatures relevant to CO_2 storage.[3] This work formed part of the "GaMin '11" inter-laboratory study which aimed to compare the results of mineral dissolution experiments from laboratories utilizing a range of experimental techniques.[4] The reaction cell was used within direct sampling rocking autoclaves and was used as it offered certain advantages over more traditional 'flexible cell' approaches when conducting gas-rich experiments.

Using CO_2 in experimental studies

Although dry CO_2 is relatively inert, it is considerably more reactive in the presence of water, and especially saline water. Laboratory experimental equipment must therefore be able to withstand high pressures and temperatures and be resistant to corrosion. Previous investigations of CO_2-water-rock reaction have used a variety of equipment, often made from inert metals (e.g. gold or titanium), or conventional vessels with non-reactive liners (e.g. Teflon^{TM}).

Unfortunately, no one technique is perfect for all studies, and many have specific limitations. For example, simple fixed volume batch systems may not be able to withstand higher temperatures and pressures, while flexible gold or titanium cells may be ruptured during depressurisation of CO_2-rich experiments. The approach adopted here aims to

minimize such problems and to provide another technique for experimentalists to use.

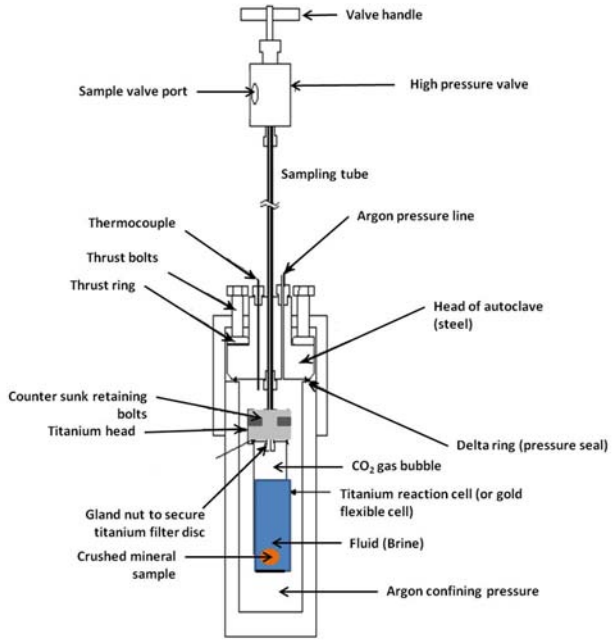

FIG. 1. Diagram showing the titanium cell secured inside the autoclave vessel (modified from Seyfried et al.[5]).

A new titanium reaction cell

'Dickson-type', direct-sampling rocking auto-claves (Fig. 1) have been used for many years for the study of reactions at high temperatures and pressures.[5,6] Typically all parts in contact with the fluid are made of gold or titanium, which are virtually inert to all but the most aggressive fluids. The experimental charge is placed within a flexible gold or titanium cell, which is surrounded by a confining gas. The confining pressure causes the reaction cell to contract/expand on fluid removal or addition, making this a constant pressure/variable volume system.

While the conventional reaction cells have performed well in many types of experiments, it has been our experience that the flexible gold cells are delicate, being especially prone to over-inflation or even rupture during depressurisation at the end of gas-rich experiments. This may lead to loss of solid reaction products into the body of the autoclave and hence possible contamination, and it is also costly in terms of damaged gold components. We have therefore designed a new titanium reaction cell[7] (a schematic is given in Figure 2) to directly replace the conventional flexible reaction cell. It aims to combine the positive aspects of flexible reaction cells (variable volume, low corrosion and chemical inertness) with the robustness of floating piston samplers. Like the gold cells, the new piston-type cell is not itself a strong pressure vessel, but it is designed to withstand a higher pressure-differential, and it can vent overpressure.

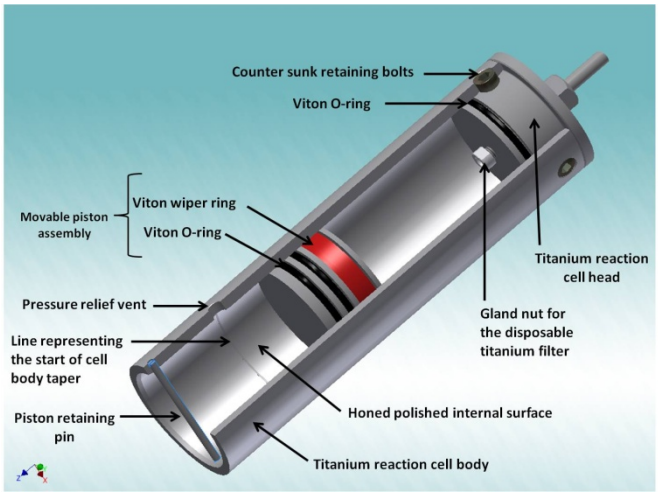

FIG. 2. Titanium reaction cell showing key features of the design.

The equipment consists of three main parts:

1) A titanium head that fixes onto a conventional titanium high pressure sampling tube via a ¼ inch HP fitting. A small disposable titanium filter is fitted to the inner surface of this to prevent particulates migrating along the sample tube.

2) A tubular titanium body with an external diameter of 60 mm, 200 mm in length and a wall thickness of 4.8 mm. The central part of this has been polished to achieve a smooth internal surface. The head seals into the body with the help of a Viton O-ring and three countersunk retaining bolts. The useable volume of this is just in excess of 200 ml – similar to that of a flexible gold/titanium reaction cell.

3) A titanium piston fitted with two Viton O-rings, and a Viton 'wiper ring' to prevent particulates damaging the O-rings.

The bottom of the body section is designed to prevent over-pressurisation. A pressure relief vent allows excess gas pressure to dissipate if the piston is pushed backwards towards a retaining pin which prevents the piston from coming out of the body. Associated with the vent is a slight taper on the inner surface out towards to the retaining pin of the

titanium cell, which also helps vent excess pressure when the piston passes it. Over-pressurisation is prevented and importantly the solid reaction products are still contained within the reaction cell when fluid pressure is released.

Experiment

Mineral dissolution experiments were conducted using 10g of mineral separate and 200g of 150g L^{-1} NaCl solution to give a fluid:rock ratio of 20:1. The cell was filled with the piston placed just in front of the vent hole and taper, and the titanium head securely attached. The head of the cell was fitted to a titanium sample tube, and this assembly placed into a large steel rocking autoclave (Fig. 2). The autoclave was heated to either 80 °C or 130 °C in a horizontally-mounted heating jacket and high-pressure argon gas was fed into the autoclave to a pressure of either 200 bar or 300 bar. Pressure was transmitted directly to the experimental fluid through movement of the titanium floating-piston. Sample agitation was achieved by the rocking motion of the autoclave. Once the experiment had been left to stabilise for several days, an excess of CO_2 was introduced into the titanium cell via the sampling tube, producing a CO_2 saturated solution.

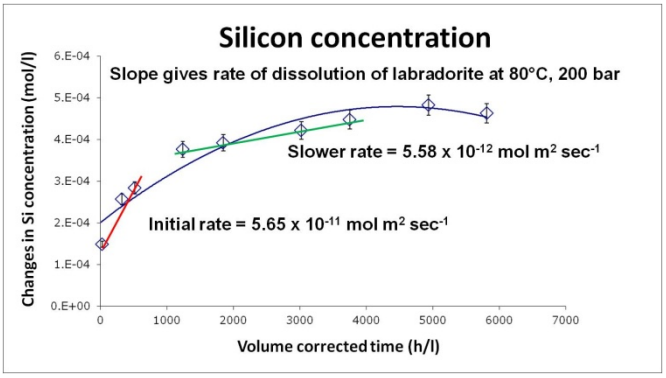

FIG. 3. Variation in Si concentration with time used to determine dissolution rate of labradorite at 80°C and 200 bar in 150 g L^{-1} NaCl solution.

Mineral dissolution rates were calculated based on the analysis of approximately 10 extracted fluid samples which showed increasing concentrations of released elements over time (Fig. 3). Reacted mineral sample was recovered successfully at the end of the experiments. The titanium cell performed well in its application with no corrosion or fluid loss at the end of the experiments. The experimental data gained was broadly comparable to that obtained within GaMin '11 study[4] which incorporated a large range of experimental techniques, including flexible gold cells.

Conclusions

A novel reaction cell has been constructed to aid in the laboratory study of water-mineral-CO_2 reactions. The 200 ml reaction cell is designed for use within direct sampling rocking autoclaves and is a direct replacement for flexible bag reaction cells. It offers greater robustness than traditional 'flexible cell' approaches, because it is not prone to rupture on depressurisation of gas-rich experiments.

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[7]See supplementary material at [URL will be inserted by AIP] for technical drawing of titanium reaction cell.