The effect of aqueous sulphate on basaltic glass dissolution rates

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ABSTRACT

Steady-state dissolution rates of basaltic glass were measured in mixed-flow reactors at 50°C at pH 3 and 4 as a function of aqueous sulphate concentration. Dissolution rates in the presence of 0.1 moles/kg SO42− were found to be ~3 times greater than those in corresponding SO42− free solutions. This rate increase is found to be approximately consistent with that calculated using a rate equation previously proposed by Gislason and Oelkers (2003). These results suggest that the addition of sulphate to injected CO2 may facilitate CO2 sequestration in basalts by accelerating basaltic glass dissolution rates thus more rapidly releasing aqueous Ca and Mg to solution.

Keywords: basaltic glass, dissolution rates, CO2 sequestration, kinetics, aqueous sulphate.

Introduction

INCREASED CO2 concentration in the atmosphere is thought to provoke climate change. To reduce the emission of this greenhouse gas to the atmosphere, the possibility of sequestering CO2 in basaltic rocks is being investigated (McGrail et al., 2006; Gislason et al., 2007; Matter et al., 2007). This process involves dissolution of the basaltic rock and release of divalent metallic cations such as Ca2+. The Ca2+ ions then react with dissolved CO2 and precipitate as carbonate minerals. One way to enhance the amount of CO2 that can be sequestered in this process is to increase the amount of Ca2+ ions available for carbonate precipitation. The dissolution rate of basaltic glass decreases with increased activity of Al3+ (Oelkers and Gislason, 2001; Gislason and Oelkers, 2001). By adding an aqueous species that leads to Al-complex formation, the dissolution rate of basaltic glass will increase (Wolff-Boenisch et al., 2004).

One other implication of this work is that power plants emitting CO2 often produce sulphuric gases as a bi-product. The high reactivity and oxidation capacity of sulphuric species make them difficult to store on land. By adding sulphate to the injected CO2 solution, it may be possible to store the sulphate safely underground. The purpose of this study was to investigate how much sulphate enhances the dissolution rate of basaltic glass.

Materials and methods

The dissolution-rate experiments were performed with Stapafell basaltic glass in titanium and polypropylene mixed-flow reactor systems at different pH and with solutions containing different amounts of sulphate (Oelkers and Gislason, 2001). The grain size was 125–250 μm and the BET surface area was measured at 1.524 m²/g. The geometric surface area was estimated to be 120 cm²/g assuming that the glass powder used consisted of identical 187.5 μm cubes. This method of estimating the geometric surface area was used in the work of Gislason and Oelkers (2003). The experiments were all performed at 50±2°C. Information about flow rates and the composition of the various inlet solutions used in this study is given in Table 1.

The dissolution rate of basaltic glass was described by Gislason and Oelkers (2003) and can be written:
\[ r_{+geo} = A_A \exp \left( -\frac{E_A}{RT} \right) \left( \frac{a_{H^+}}{a_{Al^{3+}}} \right)^{1/3} \]  

(1)

where \( r_{+geo} \) signifies the geometric surface area normalized steady-state basaltic glass dissolution rate at far-from-equilibrium conditions, \( A_A \) refers to a constant equal to \( 10^{-5.8} \) (mol of Si) cm\(^3\)/s, \( E_A \), designates a pH independent activation energy equal to 25.5 kJ/mol, \( R \) stands for the gas constant, \( T \) signifies temperature in K and \( a_i \) represents the activity of the subscripted aqueous species. By decreasing the activity of Al\(^{3+}\), the dissolution rate increases. A study performed by Wolff-Boenisch et al. (2004) showed that by complexing Al\(^{3+}\) ions with fluorine, they could increase the dissolution rate of the basaltic glass by an order of magnitude or more.

Results

Surface-reaction controlled, far-from-equilibrium basaltic glass dissolution rates as a function of aqueous solution composition at 50ºC can be predicted using equation 1. Figure 1 shows the dissolution rates of basaltic glass with different amounts of sulphate. The curves in the figure were generated using aqueous activities computed with PHREEQC 2.12.5 (Parkhurst and Appelo, 1999) at a total Al concentration of \( 10^{-6} \) moles/kg. The basaltic glass dissolution rate increases by increased concentration of aqueous sulphate at acid to neutral conditions. Basaltic glass is calculated to dissolve 5.5 times faster in a 0.1 moles/kg SO\(_4\) solution than in a SO\(_4\)-free solution at \( pH = 4 \). In contrast, there is no predicted effect of sulphate on basaltic glass dissolution rates at \( pH > 7.5 \). The lack of effect at basic conditions can be explained by the lack of Al-SO\(_4\) complexation at these pH values.

To further investigate the effect of sulphate on the dissolution rate of basaltic glass at far-from-equilibrium conditions, experiments using mixed-flow reactors were performed at \( pH 3 \) and \( 4 \). As shown in Fig. 2, a solution with 0.001 moles/kg sulphate almost doubles the dissolution rate while 0.1 moles/kg of sulphate triples the dissolution rate of basaltic glass. Calculations generated using equation 1 (Fig. 1) suggests that basaltic glass dissolution rates increase by a factor of 1.5 and 5.5 in 0.001 moles/kg and 0.1 moles/kg aqueous sulphate solutions, respectively, compared to that in sulphate-free solutions.

Table 1. The composition of the solutions and flow rates used in the experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>pH (25ºC)</th>
<th>HCl (moles/kg)</th>
<th>NaCl (moles/kg)</th>
<th>Na(_2)SO(_4) (moles/kg)</th>
<th>Ionic strength (moles/kg)</th>
<th>Flow rate (g/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BG6 D</td>
<td>3.05</td>
<td>0.00110</td>
<td>0.009</td>
<td>–</td>
<td>0.010</td>
<td>0.424</td>
</tr>
<tr>
<td>BG7 A</td>
<td>3.02</td>
<td>0.00132</td>
<td>0.008</td>
<td>0.001</td>
<td>0.012</td>
<td>0.401</td>
</tr>
<tr>
<td>BG7 B</td>
<td>3.02</td>
<td>0.00142</td>
<td>–</td>
<td>0.010</td>
<td>0.030</td>
<td>0.343</td>
</tr>
<tr>
<td>BG7 C</td>
<td>3.01</td>
<td>0.00245</td>
<td>–</td>
<td>0.050</td>
<td>0.136</td>
<td>0.371</td>
</tr>
<tr>
<td>BG7 D</td>
<td>3.03</td>
<td>0.00332</td>
<td>–</td>
<td>0.100</td>
<td>0.261</td>
<td>0.384</td>
</tr>
<tr>
<td>BG6 A</td>
<td>3.97</td>
<td>0.00009</td>
<td>0.010</td>
<td>–</td>
<td>0.010</td>
<td>0.382</td>
</tr>
<tr>
<td>BG6 B</td>
<td>3.96</td>
<td>0.00010</td>
<td>0.008</td>
<td>0.001</td>
<td>0.011</td>
<td>0.406</td>
</tr>
<tr>
<td>BG6 C</td>
<td>3.99</td>
<td>0.00014</td>
<td>–</td>
<td>0.010</td>
<td>0.029</td>
<td>0.402</td>
</tr>
<tr>
<td>BG6 E</td>
<td>4.01</td>
<td>0.00024</td>
<td>–</td>
<td>0.050</td>
<td>0.135</td>
<td>0.356</td>
</tr>
<tr>
<td>BG6 F</td>
<td>3.96</td>
<td>0.00042</td>
<td>–</td>
<td>0.100</td>
<td>0.259</td>
<td>0.408</td>
</tr>
</tbody>
</table>

FIG. 1. The logarithm of the dissolution rate vs. pH for basaltic glass at 50ºC. The aqueous activities were computed using PHREEQC 2.12.5 and equation 1. The total Al concentration was \( 10^{-6} \) moles/kg and the sulphate concentration is given in the legend.
Discussion and conclusions

(1) Preliminary results show that the effect of aqueous sulphate on basaltic glass dissolution rates calculated using equation 1 is approximately consistent with their experimentally measured counterparts. This approximate coherence provides support for using this equation for the prediction of the reactive behaviour of basaltic glass in complex natural systems.

(2) Aqueous sulphate is found to increase basaltic glass dissolution rates. As such, the addition of sulphate to injected CO₂ may enhance carbonate mineral sequestration during carbon sequestration in basaltic rocks. Such co-injection may prove to be an effective method for the safe storage of sulphur emissions from power plants.

Acknowledgements

We are grateful to Oleg Pokrovsky, Jacques Schott, Per Aagaard and Guðmundur B. Ingvarsson for helpful discussions during the course of this study. Support from Reykjavík Energy and the European Community through the MIN-GRO Research and Training Network (MRTN-CT-2006-035488) is gratefully acknowledged.

References


