Research article

Dissolution kinetics of clinoptilolite and heulandite in alkaline conditions

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Temperature and pH-dependent dissolution kinetics of natural clinoptilolite and a ‘pure’ heulandite phase have been determined and compared. Si dissolution rates increased with increasing temperature and pH. Heulandite has a slightly higher dissolution rate than clinoptilolite in the pH range 8–10. Measured reaction order was 0.23 and 0.14 for clinoptilolite and heulandite, respectively. This is slightly lower than for other aluminosilicate phases at comparable temperatures. The measured dissolution rates indicate a 1 mm spherical crystal would dissolve in 38 848 years and 17 301 years for clinoptilolite and heulandite, respectively. If solution composition is maintained, and remains unsaturated with respect to Si, Al, etc., the presence of zeolites in the vicinity of an underground nuclear waste repository would be beneficial as a sorption barrier.

Key words: dissolution kinetics, clinoptilolite, heulandite.

Introduction

Deep geological disposal (DGD) is the main viable option for disposal of high level nuclear waste as proposed by the UK government.1 DGD repository designs propose the use of a bentonite backfill with concrete, to act as a chemical barrier. Bentonite swells on contact with groundwater, and therefore act to prevent radionuclides leaching away from the repository, should steel waste canisters fail. Reaction of the low-solubility cement-based backfill with slow-flowing groundwater is likely to produce a plume of long-lasting highly alkaline conditions (approximately pH 13) as a result of the formation of calcium silicate hydrate and calcium hydroxide;2, 3

\[
2\text{Ca}_3\text{SiO}_3(s) + 6\text{H}_2\text{O}_{(aq)} = 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}_{(s)} + 3\text{Ca(OH)}_2_{(aq)}
\]

Alkaline conditions are thought to be beneficial in the repository environment, not only because radionuclides are likely to have reduced mobility at high pH, but also because research has shown that alkaline conditions, along with high temperatures caused by decaying radioactive waste, are thought to encourage formation of zeolites.4 Zeolites are expected to form within crystalline bedrock surrounding a repository, as bedrock will be the principal source of Si and Al for their formation. As the alkaline plume migrates throughout the repository, Si and Al will be dissolved. Edges of the plume are likely to contain the greatest amounts of Si and Al as there the plume would have reacted with the most rock, and also have the lowest pH (Fig. 1).

It is under these conditions that zeolites, along with other mineral phases, are likely to form. The potential for zeolites to sorb selected radionuclides arises due to the mechanisms of ion-exchange and co-precipitation, and their structure.6 Zeolites are formed from SiO₄ tetrahedra, with isomorphic substitution of Al, giving rise to a negative charge within the structure which is balanced by alkali or alkaline earth cations present within the framework channels.

Radionuclides which pose a long-term threat to the safety of human health and the environment include plutonium, uranium, neptunium, caesium and strontium. Oxidation state, pH and speciation of these radionuclides are important factors in determining their mobility and potential for zeolitic sorption.7, 8

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Materials and methods

A natural clinoptilolite ([Na_{4.5} K_{5.6} Ca_{0.4} Mg_{1.4}] [Al_{16.2} Si_{27.3} O_{72}]·H_2O) and a ‘pure’ heulandite ([Na_{2.0} K_{1.7} Ca_{3.6}] [Al_{17.1} Si_{27.3} O_{72}]·H_2O), both from Poona, India, were used in this study to investigate dissolution rates, and stability under varying pH and temperature conditions. Experiments were performed in solutions with pH ranging from 7.90 to 12.97. The compositions of the pH buffers used are listed in Table 1.

Minerals were broken up using a geological hammer and then a ball mill, before sieving to a size fraction of 212–300 μm and 125–250 μm for clinoptilolite and heulandite, respectively. Samples were rinsed with deionized water to remove any fines, and dried overnight in an oven at 30°C. Surface areas of the samples were calculated assuming a spherical particle of average diameter, giving values of 109 cm² and 145 cm² for clinoptilolite and heulandite, respectively. Acid digestion of the clinoptilolite phase was undertaken to establish the levels of impurities present.

Approximately 1 g of clinoptilolite and 0.5 g of heulandite were added to labelled 100 ml polyethylene reactors. A 100 ml aliquot of an appropriate buffer solution was added to each reactor, sealed to reduce evaporation and the sample shaken to ensure mixing. Reactors were then placed in a shaking water bath and gently agitated at 30°C or 60°C. Temperature was monitored using an alcohol thermometer which was checked daily. Samples were taken at intervals, ranging from a minimum of 2 h, to a maximum of 48-h intervals as the experiment progressed and steady-state dissolution was approached. Each sample of 4–5 ml of solution was removed using a pipette. It has been previously demonstrated that filtration was not necessary. Samples were stored in polypropylene sample tubes and acidified prior to analysis. Dissolution rate calculations were corrected for evaporative and sampling losses.

Solution samples were analysed using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS), for elements including Si, Al, Mg, Ca and Sr. pH was measured on Day 9 of the experiment after solutions had cooled to room temperature, to see if any changes had occurred.

Results

Rates of dissolution were calculated from linear regions of concentration vs. time plots, after a volume correction had been applied (Fig. 2). The stoichiometries of heulandite and clinoptilolite were taken into account in order to allow a direct comparison of the Si release rate of the phases.

An initial period of rapid Si release was observed during the first 72 h, and then dissolution slowed as steady state was approached between the sample and the solution. This pattern was observed for all ions analysed and at all solution pHs. These two different periods have been described as

| Table 1. Dissolution rates of natural clinoptilolite and heulandite. |
|------------------|------------------|------------------|
| pH Buffer | Si Release Rate (μg/g/day) | Ca Release Rate (μg/g/day) | Al Release Rate (μg/g/day) |
| pH 7.9 | 0.5 | 0.3 | 0.1 |
| pH 10.0 | 1.0 | 0.5 | 0.2 |
| pH 12.0 | 2.0 | 1.0 | 0.5 |

Mineral dissolution rates are typically fastest at higher temperatures, due to an increase in energy available for reactions to take place, and at higher pH due to an increased concentration of OH⁻ ions, which react to destabilize the structure. Natural clinoptilolite is likely to have faster dissolution rates than heulandite, as the presence of impurities causing structural instability is likely.
short-term dissolution and long-term steady-state dissolution, respectively.

The initial linear gradient of each graph of concentration vs. time was divided by the calculated surface area of the reacted zeolite and converted into a dissolution rate in mols cm\(^{-2}\)s\(^{-1}\). The effect of pH on dissolution rate is shown in Fig. 3.

Si dissolution rates increased with both pH and temperature for both phases (Figs 3 and 4). Si dissolution was faster for heulandite at both temperatures which given the structural similarity of the phases, is strange as impurities present in clinoptilolite would cause structural instability resulting in faster breakdown. The reaction order determined at 30°C from the slope of a plot of Log Si release rate vs. pH is 0.23, increasing to 0.47 as temperature increases to 60°C (Fig. 5).

**Effect of pH on dissolution**

Si dissolution approached steady state after approximately 120 h (as shown in Fig. 1), whereas release of Al and Ca did not achieve steady state during the experiment.

**Zeolite lifetimes**

Near neutral pH (8) and 30°C dissolution rates for clinoptilolite and heulandite were applied to assess the time taken to dissolve a hypothetical 1 mm spherical crystal using the equation:

\[
r_{\text{g}} = r_{0}^{\star} - k_{b}V_{0}t
\]

where \(r_{\text{g}}\) is effective radius, \(r_{0}^{\star}\) is initial radius, \(k_{b}\) is dissolution rate, \(V_{0}\) is molar volume and \(t\) is time. Results suggest that clinoptilolite and heulandite would dissolve completely in 38 848 years and 17 301 years, respectively. These values are within the large range of those given in the literature, which show values ranging from several hundred years to several millions of years. If a N\(_2\)-BET measured value of heulandite surface area of 1.63 \(\times\) 10\(^{-1}\) m\(^{2}\)g\(^{-1}\) is used instead of the geometric value used in this study to calculate dissolution rates at pH 8 and 303 K, the equation given by Lasaga gives a lifetime value of 245 137 years for a hypothetical 1 mm spherical crystal of heulandite. Forsterite and heulandite have lifetime values of 600 000 and 300 000 years, respectively, as determined by Lasaga (1984) and Ragnarsdottir. The difference between rates calculated based upon geometric and measured surface areas is problematic. A true lifetime is difficult to ascertain as measured zeolite surface areas do not include the surface areas of internal channels.

**Effect of temperature on dissolution**

The effect of temperature on dissolution rate was found by estimating the activation energy. Activation energy (E\(a\))

![Figure 2. Si dissolution rate as a function of volume corrected time for clinoptilolite at 60°C, pH 12 showing an initial increase in dissolution with time up until approximately 120 h of dissolution, after which steady state was approached.](#)

![Figure 3. Si release rate as a function of pH for Clinoptilolite at 60°C and 30°C showing an increase in dissolution rate as pH increases.](#)
was calculated from the Arrhenius equation, \( k = A e^{-\frac{E_a}{R T}} \), and a graph of \( \ln k \) against \( \frac{1}{T} \) used to find the gradient of the graph, from which \( E_a \) and the pre-exponential factor, \( A \), were calculated (Fig. 6).

It was assumed that Si release was first order as not enough data was available to calculate \( k \) directly. Graphs of \( E_a \) against pH were then plotted for both heulandite and clinoptilolite to see the effect of temperature and pH on dissolution rate (Fig. 7). \( E_a \) values for both zeolites increased as pH increased from pH 8 to pH 13.

Discussion

pH dependence of dissolution

Si dissolution rate pH dependence of clinoptilolite and heulandite appears to be related to the density of >Si-O<sub>2</sub>.<sup>14</sup>

As pH increases, OH<sup>-</sup> ion concentration in solution increases, thereby increasing the number of OH<sup>-</sup> ions that can be adsorbed into the 8/10-member ring channels and also onto surface functional species, leading to the formation of Si-O<sup>-</sup>,<sup>15</sup> via OH<sup>-</sup> attacking neutral silanol groups.<sup>16</sup> This is ‘surface controlled’ dissolution, where detachment of metal cations from the surface is the rate-limiting step, as suggested by Carroll-Webb and Walther,<sup>12</sup> Lasaga,<sup>13</sup> Wieland, Wehrli and Stumm<sup>17</sup> and Ragnarsdottir.<sup>14</sup> The equation for Si-O<sup>-</sup> formation is:

\[
\text{Si-OH} + \text{OH}^- \rightarrow \text{Si-O}^- + \text{H}_2\text{O}
\]

Hydrolysis by OH<sup>-</sup> weakens the Si-O-Si and Al-O-Si bonds in the surface lattice and causes the detachment of Si-OH and Al-OH by formation of Si-O<sup>-</sup> and Al-O<sup>-</sup>. When a certain number of bonds are hydrolysed, that portion of the framework becomes unstable and detaches into solution.
Al initial dissolution rates are typically faster than Si for zeolites having Si/Al > 1,18 suggesting formation of a Si-rich layer and incongruent dissolution taking place.14 Faster Al dissolution goes against the theory that under alkaline conditions, dissolution rate of aluminosilicate minerals is dependent upon surface charge at Si sites.2 Tetrahedral Al has a smaller charge than Si, so it would be expected that Al would be less likely to be polarized, so would have a lower detachment and hence dissolution rate, compared to Si. However, Si detachment would expose more Al sites and lower the activation energy by ‘decreasing increasing coordination of the Al site’.19 Although this suggests that Al detachment would be dictated by the rate at which Si-O− bonds were polarized, it may be that the exposed Al was able to detach more easily than a Si atom with several bonds, and therefore have a faster dissolution rate than Si. It may also be the case that a negatively charged Al-complex exists under alkaline conditions, allowing preferential release of Al.2 This too has been proposed by Wilkin and Barnes (1998)20 whose research has shown that in alkaline solutions, soluble Al can exist as Al(OH)4−, and in NaOH solutions at high temperatures, the sodium aluminate ion, NaAl(OH)4 may also be present. Unfortunately the Al concentrations determined in this study were unreliable. Typically Al concentrations decreased with time to values below detection limits. An explanation for this decrease in Al concentration may be the formation of an aluminium oxy-hydroxide precipitate, removing Al from solution, as suggested by Savage et al.2 Acid digestion of the natural clinoptilolite phase indicated that sufficient levels of Mn, Cu, Fe and Al were present that formation of an Al–Mn/Cu precipitate or oxyhydroxide was highly feasible.2,21 Without reliable Al results it is difficult to ascertain whether dissolution was congruent or incongruent.

**pH dependency**

pH dependencies of log rate on pH appear to be 0.14 for heulandite and 0.23 for clinoptilolite, which can otherwise be described as

\[
R = k \left( > \text{Si-O}^- \right) \text{mol cm}^{-2} \text{s}^{-1} \\
R = k \left( > \text{Si-O}^- \right) \text{mol cm}^{-2} \text{s}^{-1}
\]

for heulandite and clinoptilolite, respectively, at 30°C. Where \( R = \text{mol cm}^{-2} \text{s}^{-1} \), \( k \) and \( k' \) = appropriate rate constants, \( > \text{Si-O}^- \) = concentration of metal surface species.19

A pH dependency of 0.14 for heulandite is slightly lower than that measured by Brady and Walther,19 Ragnarssottir,14 Blum and Lasaga (1988)22 and Chou and Wollast23 for alkaline dissolution rates on a range of aluminosilicates. Although slightly higher than heulandite, a value of 0.23 for clinoptilolite at 30°C is broadly in line with values for other aluminosilicates in alkaline pH conditions.12

**Effect of pH\text{pzc}\text{.}\text{pzc}**

The point of zero charge is the pH at which there are equal numbers of cations and anions present so that the surface has effectively no charge. The dissolution rate should be lowest at pH\text{pzc}\text{.}\text{pzc} because both H+ and OH− are absorbed, and hence fewer bonds are polarized and weakened.14 pH\text{pzc}\text{.}\text{pzc} for SiO2 is 2.4, a much lower value than that of MgO (pH 12). Typical values for Al(V)O4 are pH 5–7 and Al(VI)O4 pH 8 (where IV and VI represent tetrahedrally and octahedrally co-ordinated Al, respectively) thereby suggesting that silica is most likely to be a source of negative charge at higher pH.19 For clinoptilolite, the pH\text{pzc}\text{.}\text{pzc} is ~3,24 so higher Si dissolution rates would be expected with increasing pH, as shown in the results. Heulandite is likely to have a similar pH\text{pzc}\text{.}\text{pzc} to clinoptilolite and exhibit similar behaviour. Titrations may have proved useful in determining the pH\text{pzc}\text{.}\text{pzc} of the phases in this experiment, but were not carried out due to time limitations.

**Temperature dependence of dissolution**

Higher activation energies were expected for heulandite rather than clinoptilolite, due to the presence of impurities causing structural defects in the clinoptilolite. This was not observed and may be a result of the higher Si/Al ratio, meaning a greater number of Si-O bonds must be broken, requiring more energy. It may also be due to low bond strength in one direction within heulandite thus reducing thermal stability.10 Due to rates being measured at only two temperatures 30°C and 60°C, the graph of ln K against 1/T was a straight line, and therefore the Ea values are not as accurate as if there had been more than two values.

**Zeolite lifetime values**

Temperatures are likely to be approximately 30°C in a repository after just several years.25 Lasaga13 used Eq to estimate the effect of depth on reaction rate. Using a geothermal gradient of 30 °C/km, rates of reaction will increase by 10 km−1, which is important to consider when determining lifetimes. The lifetime values of clinoptilolite and heulandite at 30°C were of the same order of magnitude, with approximately 21 500 years difference, although it should be stressed that these values are subject to error mainly as a result of the surface area calculation. Heulandite had a faster dissolution rate at 30°C at lower pH thus partially explaining the longer lifetime of clinoptilolite. The presence of other ‘impure’ elements within clinoptilolite may aid the formation of other minerals such as analcime on dissolution,26 and thus prolong its lifetime. SEM analysis of the samples would have been useful to determine if secondary minerals had formed, but this was impossible due to time limitations. Assuming reaction rates increase by a factor of 10,13 and lifetime values decrease by the same factor, total dissolution times may only take 103 years, which is important to consider when determining repository depth.
Conclusions

This study shows that the effect of pH on zeolite dissolution is strong. Dissolution in alkaline solution most likely occurs as a result of polarization and hence de-protonation of Si-OH, forming Si-O⁻ which in turn detaches into solution.

The effect of temperature on zeolite dissolution is important, as increasing temperatures increased dissolution rates. There is little difference between clinoptilolite and heulandite Ea values, suggesting both would be ideal within a repository.

The reaction order for heulandite and clinoptilolite were 0.14 and 0.23, respectively, slightly lower than previously determined for a range of aluminosilicate phases at similar temperatures. Clinoptilolite showed a faster dissolution rate than heulandite at higher temperatures and pH, probably due to the presence of impurities in the natural sample. In terms of their use in a repository, the clinoptilolite sample is most similar to that that would be expected to form, as a natural sample is likely to have impurities present. Further work needs to be carried out to see the effects that impurities may have on dissolution rates. Dissolution rates obtained here, applied to a hypothetical 1 mm spherical crystal show that both zeolites would dissolve in $10^4$ years, once surface area uncertainties had been accounted for. Clinoptilolite had a longer calculated lifetime due to slower dissolution at 30°C at which lifetimes were calculated. A lifetime in the region of $10^4$ years that under high pH and moderate temperatures in a repository environment, indicates that zeolites may prove a useful sorption barrier.

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