Experimental study of the diffusion-controlled acid degradation of Class H Portland cement

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1. Introduction

1.1. Context of the research

Underground storage of carbon dioxide in geologic formations is widely regarded as a potentially important carbon mitigation option. It is also generally agreed that demonstration of Carbon Capture and Storage (CCS) technology is an important precursor to wide deployment of CCS at the scale necessary for appreciable reduction in CO2 emissions (IEA, 2008; IPCC, 2005; Bachu, 2008). With financial incentives and regulatory pathways both currently in place, CCS in depleted oil reservoirs is an important step in demonstrating the practicality of CCS, especially with respect to ensuring that CO2 remains in the storage formation without leakage for long times (viz., on the order of hundreds of years).

The principle corrosion scenarios are shown schematically in Fig. 1. If the cement used to seal an abandoned well provides a good seal, then corrosion occurs from the bottom of the cement plug (Fig. 1a), and leakage will not occur until the corrosion front passes entirely through the height of the cap rock. As we will show, that would take geological time. On the other hand, if there is an annular gap or crack that extends along the entire interface between the cement and the casing or the formation, then carbonated brine from the formation can flow into the overlying reservoir, bringing fresh acid into contact with the cement. If the rate of flow is slow compared to the rate of reaction between the brine and the cement, then corrosion could occur uniformly along the height of the annulus (Fig. 1b, “Fast flow”). As we will show, the corroded layer contracts, which will increase the width of the gap and allow the flow rate to increase. If the corroded material were to detach, the debris might be carried away, leaving a larger gap, or it might form a plug that would inhibit the flow. If the rate of flow is slow compared to the rate of corrosion, then the acid will be consumed near the entrance of the annulus (Fig. 1b, “Slow flow”), so that neutralized brine rises through the rest of the annulus. In such a case, the annulus would retain its original width above the corroded zone, and the fluid entering the overlying reservoir would be neutral brine until the corroded zone progressed most of the way through the cap rock. The results of the present study suggest that the latter scenario is likely, unless the original gap width is large (in which case, leakage would be rapid even without corrosion). However, detailed modeling is needed to explore these scenarios, particular when multiphase fluids are entering the annulus.

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Fig. 1. Schematic of leakage scenarios: (a) in the absence of an annular gap, attack is from the bottom (reservoir); (b) when a continuous annular gap is present, two limiting cases occur according to whether flow is fast or slow compared to corrosion. If flow is relatively fast, then the annulus widens uniformly; if it is slow, then corrosion is concentrated near the bottom, as explained in the text.

The need to predict the sub-surface storage behavior over a 100+ year time horizon makes computer modeling of the durability and integrity of the wellbore of prime importance. The model will need to predict the response of cement to carbonic acid that forms when stored CO₂ dissolves in sub-surface brine. Variables of interest include the pH, ion concentrations of various chemical species, temperature, pressure, and the flow conditions around the wellbore. There have been several experimental studies that have explored this parameter space (Duguid and Scherer, 2010; Kutchko et al., 2007, 2008; Rimmelé et al., 2008) and simulations have been matched with some of these results (Huet et al., 2010).

In this context, the goal of this paper is to contribute experimental data that systematically extend the range of subsurface conditions simulated. We employ both batch and flow-through experiments to examine differences in attack rates resulting from leached species accumulating at the cement–acid interface.

1.2. Acid attack rates and the potential for well-bore leakage

In addition to the geochemical and geophysical heterogeneity of storage sites, there may also be “anthropogenic” site-specific heterogeneities related to the quality of well completion or cement/wellbore and cement/caprock bonding (Carey et al., 2007; Duckworth, 2009; Watson and Bachu, 2009). The latter defects could result in the situations illustrated in Fig. 1b, which bring a flow of fresh acid to the surface of the cement. Therefore, flow-through experiments were designed primarily to examine the “worst case scenarios”. In such cases, the concentration of leached chemical species (leachate) is held to a low constant value by the continuous flow, rather than accumulating as a function of time. In the field, the flow rate might be slow or even static (as in Fig. 1a), so it is important to compare flow-through experiments with batch (static) corrosion experiments to quantify the effect of the leachate on the rate of attack.
1.3. The relevance of accelerated leaching tests

The fact that rates of carbonic acid attack on cement are relatively slow – not exceeding millimeters per month – is of primary importance with respect to the design of bench-top experiments relevant to CO$_2$ leakage. Several studies have aimed to accelerate the process by using low pH (achieved by HCl addition) (Duguid et al., 2007; Duguid and Scherer, 2010), as well electrical fields (Rimmelé and Barlet-Gouédard, 2010). From the perspective of understanding the larger issue of wellbore leakage, it is essential to establish that the mechanical and transport properties of cement degraded under these types of accelerated conditions are similar in nature to those produced under the milder conditions likely to prevail in the sub-surface. Additionally, it must be shown that such experiments are relevant in determining the in situ rates (i.e., rates of attack on the actual wellbore in the subsurface). The present study provides evidence that the accelerated studies succeed on these counts.

1.4. Summary of relevant boundary conditions

There are several boundary conditions that have significant impact on the rate of acid attack on cement: (1) leachate concentrations in the acid, (2) temperature and pressure of the reactor, (3) pH and CO$_2$ concentration of the acid, and (4) flow velocity. The accumulation of leached species in the acid will inhibit dissolution; for example, raising the concentration of calcium by pre-equilibrating the brine with limestone causes a drastic reduction in the rate of corrosion of cement (Duguid and Scherer, 2010). While it is known that high pressure (≈10 MPa) will have a significant impact on the CO$_2$ concentration and/or pH of the acid reservoir (Duan and Sun, 2003), it has not been demonstrated that it otherwise affects degradation rates. It has been shown that lower pH, higher temperature, and higher concentrations of CO$_2$ also increase the rates of cement degradation (Duguid and Scherer, 2010; Rimmelé et al., 2008). Limited discussion in the literature has been devoted to the effects of flow rate on the overall rates of cement degradation. In the present study, we investigate all of these variables, except pressure.

2. Methods and materials

2.1. Cement preparation

Samples of Class H Portland cement were prepared according to API 10B standards. The mix water was prepared as 0.5 M sodium chloride (NaCl) solution (see preparation details below). In increments of 6–7 mL, the mixed paste was transferred to 15 mL polypropylene centrifuge tubes that were used both as the sample mold and ultimately as the reaction vessel for bench-top acid experiments. Just after filling, the tubes were placed on a vibration table (FMC Tech Syntron) for 5 min at a rate of 60 Hz to ensure that all air voids were removed from the paste. The samples were cured at room temperature for 8–12 h before the centrifuge tube was topped off with ∼7.5 mL of 0.5 M NaCl solution. Samples were cured at room temperature for a minimum of 6 months prior to exposure to the acidic solution.

2.2. Acid and brine solutions preparation

Brines at a concentration of 0.5 M NaCl were prepared from USP/FCC grade sodium chloride acquired from Fisher Scientific (#5640) and deionized water (DI). All acidic solutions were prepared by mixing HCl and/or CO$_2$ with 0.5 M NaCl brine and deionized water solutions. Hydrochloric acid (HCl) mixtures were prepared by mixing ACS grade 12.1 N HCl solution with 0.5 M NaCl brine.

Carbonic acid solutions were prepared by continuously sparging gaseous CO$_2$ through 0.5 M brine solution. Industrial grade carbon dioxide cylinders were obtained from Air gas. Non-metallic sparging fixtures were used to prevent the introduction of additional metal ions into the reaction vessels.

2.3. Uniaxial acid attack of cement samples

Several cement-mold materials were tested for good sealing between cement and the cement mold wall, so that acid attack would proceed uniaxially, normal to the cement/acid interface. Polypropylene centrifuge tubes proved to be suitable not only for producing uniaxial leaching fronts, but also for their relative transparency, which allowed time-lapse videos to be taken of the cement samples during the acid front ingress.

2.4. Batch 1 M HCl experiments

When using concentrated HCl (1 M) in accelerated corrosion tests, it was possible to conduct short (24–55 h) batch experiments without significant change in pH. However, for higher pH, batch-type experiments, the pH would rise, primarily owing to neutralization of the acid by reaction with Portlandite (Ca(OH)$_2$), and thus stop reacting in a few hours, or tens of minutes.

Batch experiments using 1 M HCl were performed in two orientations, upright and inverted. For the inverted orientation, special measures needed to be taken to remove air bubbles from the acid/cement interface. Flexible inlet tubing was inserted into the centrifuge caps such that the capped centrifuge tube remained airtight and leak-proof. After the acid-filled tube was inverted, syringes were used to inject acid to top-off the reservoir and to provide a vacuum to vent the air bubbles collected at the acid/cement interface. Inverted batch experiments were used to determine attack rates in 1 M HCl for temperatures, $T$, in the range $30 \leq T \leq 80$. An incubator (Fisher Scientific Isotemp) was used for $30 \leq T \leq 60$, and a convection oven was used for $50 \leq T \leq 80$.

2.5. Measuring leaching front via time-lapse video

A USB microscope (Celestron Handheld Digital Microscope model #44300/44302) was used in conjunction with commercially available time-lapse software (HandyAvi, Version 4.3) to create time-lapse movies of the cement/acid interface over the course of the experiment. The video data were analyzed using Screen Calipers ProScope Edition 3.2 to measure the growth of the degradation front over time. The volume graduation marks on the centrifuge tube were included in each frame and were used as calibration marks when making screen caliper measurements. Fig. 2 shows a typical frame taken from a time-lapse video, as well as the digital screen calipers used to measure the reaction front.

2.6. Acid/brine flow-through apparatus

For flow-through experiments, a peristaltic pump (Cole-Parmer Masterflex L/S) was used to feed acidic solutions at rates varying from 7.5 to 300 mL/h into the reaction vessel. The outlet stream was actively pumped out of the reactor vessel through the peristaltic pump at the same flow rate. The inlet and outlet tubes were passed through the centrifuge caps, the lengths being trimmed such that the inlet tubing was deeper in the vessel (i.e., closer to the cement surface). This tubing arrangement, along with the active pumping, ensures that the volume of acid above the sample is constant (at ∼5 mL) throughout the experiment, and that the acid is continuously well mixed in the reactor. Fig. 3 shows a schematic of the centrifuge tube used as a reactor for the acid/brine experiments.
Fig. 2. Time-lapse video is used to record the growth of the degradation reaction front and digital calipers are used to measure layer thickness at a magnification of \(30 \times\). The space between the top caliper and the cement surface reflects the surface recession over the course of the experiment, i.e., the caliper is placed at the location of the original cement surface at the start of the experiment. The calibration marks are \(\sim 3\) mm apart (from the top of one mark to the top of the adjacent mark).

2.7. Sampling and analytical techniques

Leached cement samples were prepared for SEM and BSE analysis, first by exchanging the pore solution to isopropyl alcohol, and then drying under a flow of nitrogen for a minimum of 1 week. Imaging and analysis were executed at the Imaging and Analysis Center at Princeton University, using a FEI Quanta 200F Environmental Scanning Electron Microscope. Compositional analysis of the leachate solution was performed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). These measurements were performed at the Rutgers Inorganic Analytical Laboratory.

3. Results

3.1. Accelerated batch experiments

Accelerated acid-leaching experiments were performed by exposing cement samples to 1 M HCl at room temperature and atmospheric pressure. Two orientations, upright and inverted, were tested under these conditions and the results are shown in Fig. 4. The degradation front of the inverted sample penetrates to twice the depth of the upright sample over an equivalent time interval. The same results are plotted as a function of the square root of time in Fig. 5.

Fig. 3. Schematic of the centrifuge tube used as both cement mold and reactor vessels. For flow-through experiments, acid is pumped in from a peristaltic pump, while effluent is pumped out of the reactor vessel at the same rate as the inflow. Batch experiments were conducted in the same setup minus the influx and efflux.

3.2. Accelerated flow-through experiments

Flow-through experiments were performed using 1 M HCl over a range of flow rates from 7.5 to 300 mL/h to produce acid replenishment and mixing conditions similar to those of the inverted samples. The data are summarized in Fig. 4. Flow rates \(\geq 75\) mL/h provided a constant boundary condition and so represent the worst-case scenario for the rate of acid attack on cement. Inductively Coupled Plasma (ICP) analyses for both orientations are shown in Fig. 6, plotted as a function of the square root of time. The cumulative cation mass loss also varies linearly with \(t^{1/2}\). Fig. 7 shows the cumulative cation mass loss plotted as a function of acid attack depth, for both the inverted and upright experiments. The linearity of this graphs shows that cation mass loss in the leached region is not only linear with respect to leaching depth, but that it is invariant with respect to rate of attack.

Fig. 4. Acid attack depth vs time for batch and flow-through experiments, under accelerated leaching conditions with an acid solution at pH 0.

Fig. 5. Plot of corrosion depth vs square root of time (h) for a variety of flow rates. “Upright” and “Inverted” are batch experiments.
3.3. Determining the activation energy for the cement degradation front

Using the same procedure as described for the inverted batch experiments, cement samples were tested at 30–80 °C to determine the temperature dependence of the degradation reaction rate. The penetration depths are plotted as function of $t^{1/2}$ in Fig. 8.

Suppose for the moment that the corrosion process is a simple case of diffusion into a semi-infinite medium, where the initial concentration of acid in the cement is zero and the surface concentration, $C_0$, is held constant. In that case, the concentration profile in the cement is described by the complementary error function (Crank, 1975):

$$\frac{C(x, t)}{C_0} = \text{erfc}\left(\frac{x}{2\sqrt{D}t}\right)$$  \hspace{1cm} (1)

where $x$ is the distance from the solution/cement interface, $D$ is the diffusion coefficient of the corrosion front, and $t$ is time. Assuming that the degradation front depth, $x_D$, corresponds to a particular acid concentration, $C_D$, the measured depth should be proportional to $t^{1/2}$:

$$x_D = 2\sqrt{D} t \text{erfc}^{-1}\left(\frac{C_D}{C_0}\right) \equiv S\sqrt{t}$$ \hspace{1cm} (2)

where $S$ is the slope of a plot of corrosion depth vs $t^{1/2}$. It is shown in Appendix A that a similar expression is obtained if we assume that corrosion involves diffusion plus reaction (as it must), the only difference being the strength of the dependence of $S$ on $C_0$.

The temperature dependence of the diffusion coefficient is given by the Arrhenius equation:

$$D = D_0 \exp\left(-\frac{\Delta E}{RT}\right)$$ \hspace{1cm} (3)

where $R$ is the ideal gas constant, $T$ is the absolute temperature, and $\Delta E$ is the activation energy. Since $D$ is proportional to $S^2$, according to Eq. (2), the activation energy for the cement degradation rate is found by plotting the natural log of $S^2$ vs $1/T$. This plot is shown in Fig. 9 and the linear fit yields $\Delta E \approx 39.6$ kJ/mol (9.3 kcal/mol), which falls within the range of values (viz., 4–11 kcal/mol) reported in the literature for leaching of Portland cement (Matsumuru et al., 1979; Fuhrmann et al., 1990; Goñi et al., 1996). The fit also provides an expression for $S$ as a function of temperature, the usefulness of which will be illustrated in the following section.

3.4. Flow-through experiments at constant pH

Experiments were performed with a flow rate of 75 mL/h over a range of pH values from 0 to 3.7. Experiments were conducted at pH 0, pH 2, and pH 3 at two distinct CO$_2$ concentration levels. Samples labeled “No CO$_2$” were equilibrated with the atmosphere, which is expected to result in a total dissolved CO$_2$ concentration of $\sim$0.01 mM (CHESS, 2002); those labeled “1 Bar CO$_2$” were equilibrated with one atmosphere of pure CO$_2$ to produce $\sim$34 mM total
dissolved CO₂ (Duan and Sun, 2003; CHESS, 2002). Degradation fronts were measured as described in Section 2. These measurements were plotted as a function of the square root of time and are summarized in Fig. 10.

The depth of attack decreases as a function of increasing pH, as expected. By looking at the data for “No CO₂” and “1 Bar CO₂” for both pH 2 and pH 3, it is clear that the rates for the CO₂-saturated solutions are faster. This comparison also shows that the difference in rates between “No CO₂” and “1 Bar CO₂” is greater at pH 3 than at pH 2. For the “1 Bar CO₂” case, the slope of a linear fit in Fig. 10 is 0.081 mm/h1/2 for pH 2 and 0.034 mm/h1/2 for pH 3, which represents a decrease by a factor of 2.4. For the “No CO₂” case, the decrease is by a factor of 10; the slope for pH 2 is 0.066 mm/h1/2 and for pH 3 it is 0.006 mm/h1/2.

The slope, S, for each boundary condition in Fig. 11 can be obtained from a linear fit to the data, and these slopes can, in turn, be plotted as a function of pH. Fig. 11 shows the experiments under 1 Bar CO₂ plotted in this manner, and it indicates that these data exhibit a close fit to an exponential function:

\[ S (\text{mm/h}^{1/2}) = 0.38 \exp(-0.8 \ \text{pH}), \quad T = 22°C = 295 \text{K} \quad (4) \]

Recognizing that the rate of attack is temperature dependent, we can write Eq. (4) more generally as

\[ S = \alpha(T) \exp(-0.8 \ \text{pH}) = \alpha(T)[H^+]^{0.35} \quad (5) \]

where the second equality, in terms of the molar concentration of H⁺, follows from the definition of pH. This dependence on concentration is somewhat weaker than that predicted for a process involving a first-order reaction, as shown in Appendix A. Assuming that the reaction proceeds according to Eq. (2), and using the activation energy from Fig. 9, we obtain:

\[ \alpha = 1305 \exp \left(-\frac{2383}{T} \right) \quad (6) \]

Inserting \( T = 293.15 \text{ K} \) into Eq. (6) yields \( \alpha = 0.385 \), which agrees well with the value in Eq. (4) derived from the fit to the flow-through data in Fig. 10. The corrosion rates predicted by Eqs. (5) and (6) compare favorably with rates reported in the literature, as shown in Fig. 12.

3.5. Shrinkage of corrosion product

The position of the exposed surface of the sample changes as the corrosion layer thickens, indicating that the corrosion products

\[ \text{Fig. 9. Arrhenius plot using the slopes (m/s}^{1/2}\text{) from the linear of depth vs h}^{1/2}\text{. The cement was exposed to pH 0 acid solution at temperatures between 30°C and 80°C.} \]

\[ \text{Fig. 10. Plot of corrosion depth vs square-root of time for flow-through experiments ranging from pH 0 to pH 3.7 and for both the 1 Bar CO₂ case and for the “No CO₂” case (acid in equilibrium with atmospheric level of CO₂).} \]

\[ \text{Fig. 11. Fit of the slope of plots of depth vs square root of time for flow-through experiments with acid solutions over a range of pH. All acid solutions were equilibrated with 1 Bar CO₂.} \]

\[ \text{Fig. 12. Comparison of corrosion rates from Eqs. (5) and (6) with values reported in the literature.} \]
occupy less volume than the original cement. This could result from syneresis in the gel layer (Brinker and Scherer, 1990) or it might mean that the gel is formed by dissolution and re-precipitation, rather than being a relict of the silicate framework of the original cement. As shown in Fig. 13a, the shrinkage is linearly proportional to the depth of corrosion for samples corroded at pH 0. The shrinkage is greater in the flow-through experiments, so there is apparently a contribution from surface loss by erosion. At the slowest flow rate (7.5 mL/h), the shrinkage rate lies between the static and fast-flow results.

When enhanced pressure of CO2 is applied, the shrinkage rates are similar, but the behavior is more complex (Fig. 13b). At pH ≥ 3, there is a thin layer of calcium hydroxide on the surface of the sample following curing in brine, and the contraction does not begin until that layer dissolves. At pH 3, this happens when the corrosion depth reaches about 0.9 mm; at pH 3.7, that layer had not disappeared at the end of the experiment. At pH 2, the dissolution of that layer is very rapid, so the contraction begins immediately and at a rate somewhat higher than in the absence of CO2. Under 0.3 mbars of CO2, the rate eventually becomes equal to that seen in the flow-through experiments at pH 0; at 1 Bar CO2, the rate of contraction begins to decline when bands resembling Liesegang rings appear in the gel (see Appendix B).

4. Discussion

Fig. 5 shows that the depth of corrosion is strictly proportional to the square root of time, indicating that the reaction is diffusion-controlled, when the flow rate is sufficient to flush away the leachate. The depth of the corrosion front, $x_D$, is related to temperature and the concentration of acid at the surface, $C_0$, by

$$S = \frac{dx_D}{dt^{1/2}} = \alpha(T)C_0^m$$

(7)

where $\alpha$ is given by Eq. (6) and $m \approx 0.35$ for the cement paste used in these experiments. In the batch experiment where the sample was inverted, the initial rate of corrosion was identical to that in the fast flow-through case, but the rate decreased and eventually the depth of corrosion reached a constant value as the acid was neutralized by reaction with the cement paste. The reaction zone varies in composition, with the outer region being nearly pure silica gel, followed by zones in which sequential attack on calcium–silicate–hydrate, calcium hydroxide, and other phases predominates (Duguid, 2006). Nevertheless, the images show an abrupt transition from a light-colored corroded layer to a gray zone in which the attack is limited to partial dissolution of calcium hydroxide. Therefore, we can assume that most of the neutralization occurs in the silica-rich outer zone, whose thickness is plotted in Fig. 5. The corrosion in the inverted case ends when the corrosion depth is 1.5 mm over an area of 177 mm², so $2.65 \times 10^{-4}$ L of cement paste were fully reacted; the volume of acid was 9.85 mL at pH 0, so the solution originally contained 0.00985 mol of H⁺. Thus, we find that the neutralization capacity is $C_N = 37.2$ mol of acid per liter of cement.

In the batch reaction, the concentration of acid in the solution at any time is given by

$$C_0(t) = C_0(0) - \frac{C_N x_D}{h}$$

(8)

where $A$ is the cross-sectional area of the tube and $h$ is the depth of the pool of acid. To estimate the effect of the changing acid concentration on the rate of corrosion, we will assume a pseudo-steady-state, which means that the concentration distribution within the corroded zone adjusts to the changing boundary concentration. In that case, we can use Eq. (8) in Eq. (7) to solve for $x_D$:

$$\frac{dx_D}{dt^{1/2}} = \alpha(T)\left[C_0(0) - \frac{x_D C_N}{h}\right]^m$$

(9)

which leads to

$$x_D(t) = \frac{h C_N(0)}{C_N} \left[1 - \left(1 - \frac{C_N(1-m)}{h C_N(0)} \alpha(T)C_0(0)^m \sqrt{t}\right)^{1/(1-m)}\right]$$

(10)

Substituting the known values for each of the parameters ($h = 55.7$ mm, $C_0(0) = 1.0$ M, $C_N = 37.2$ M, $m = 0.35$, $\alpha = 0.38$), Eq. (10) can be used to predict the depth of corrosion in the inverted batch experiment; for the upright sample, we have seen that $\alpha$ is lower by a factor of 2.7 (owing to the effect of leachate on the diffusivity, as explained below). Using those values in Eq. (10), the calculated curves are in very good agreement with the data, as shown in Fig. 14.

To analyze the flow-through experiments, we allow for acid flowing into the sample tube at concentration $C_i$ and flowing out at $C_o$; the acid is consumed by reaction with the cement. If the mixing is good, then the concentration in the tube is given by

$$\frac{\partial C_o}{\partial t} = \frac{1}{V} \left[F(C_i - C_o) - C_N A \frac{dx_D}{dt}\right]$$

(11)

where $A$ is the surface of the cement/acid interface, $V$ is the volume of solution in the reactor, and $F$ is the flow rate of leachant.
into the reactor (volume per unit time). From Eq. (7), subject to the assumption of a pseudo-steady-state in the corroded zone,

\[ \frac{d\alpha}{dt} = \frac{\alpha(T)C_m^m}{2\pi^2} \]

The result is a nonlinear equation that must be solved numerically. Using the dimensions of the sample tube, with \( C_0 = 1.0 \text{ M}, C_R = 37.2 \text{ M}, \) and \( \alpha = 0.38 \text{ mm/h}^{1/2} \), the calculated curve for a flow rate of 75 mL/h is in excellent agreement with the data, as shown in Fig. 14.

Comparing the slopes in Fig. 6, we find that the corrosion rate is 2.7 times faster in the inverted tube than in the upright one. Nevertheless, Fig. 7 shows that the total ion loss depends on corrosion depth in the same way for both orientations, so the same phases are being dissolved. The difference in rate can be attributed to the presence of a gelatinous leachate (hereafter called sludge) that accumulates near the surface of the cement when the tube is upright, but which is seen to settle away from the surface when the tube is inverted, and which apparently slows the transport into the cement. In the flow-through experiments, when the flow rate is \( \geq 75 \text{ mL/h} \), the corrosion rate is the same as the initial rate seen in the inverted sample, and such samples show no evidence of sludge.

At a flow rate of \( 7.5 \text{ mL/h} \), the corrosion rate is initially similar to that of the upright sample, and it suddenly rises after about 9 h and becomes similar to that of the inverted sample. The video shows that sludge is present early, but is flushed away after about 9–10 h. We can simulate this by solving Eq. (11) with \( \alpha = 0.38 \text{ mm/h}^{1/2} \) after 9 h, but \( \alpha = 0.14 \text{ mm/h}^{1/2} \) before that (to account for the reduced diffusivity caused by the sludge). The result, shown in Fig. 15, agrees well with the data.

Evidently, the sludge forms from leachate that accumulates near the surface, unless it is removed by settling (in the inverted case) or flushing (in the flow-through experiments). The flow rate needed to dislodge the sludge must be close to that in the 7.5 mL/h run; given the cross-sectional area of 1.77 cm², this corresponds to a flow velocity of \( \sim 4.2 \text{ cm/h} \).

Fig. 10 shows clearly that the rates are, at equivalent pH, enhanced by saturation with CO₂. The effect is more obvious at pH 3 than at pH 2. At pH < 3, the effect of dissolved CO₂ is less significant, probably owing to the high solubility of calcium carbonate at pH values below this range. As the pH rises, precipitation of the carbonate is expected, and it can affect the transport kinetics, as well as the phase distribution (Huet et al., 2010). This could explain why the rate for “pH 3 No CO₂” falls off so dramatically. This is discussed in forthcoming publications (Huet et al., in preparation; Matteo et al., in preparation).

Fig. 12 compares the corrosion rates calculated from Eqs. (5) and (6) with values reported in the literature. The rates are sensitive to the concentrations of calcium and other solutes, which are not explicitly included in the equations; however, those concentrations are directly related to the amount of acid consumed, so they are implicitly (but very approximately) taken into account. The predicted rates match well with those reported by Duguid and Scherer (2010); given the constant flow and ambient pressure used in those experiments, this correspondence is expected. The agreement with the data of Rimmelé and Barlet-Gouédard (2010) and Kutchko et al. (2007, 2008) is remarkable, as those were batch experiments conducted at high pressure; nevertheless, the rates are within a factor of 2 for both cases. The predicted rate for pH 2.9 and \( T = 50 \text{ °C} \) is 0.076 mm/h\(^{1/2} \), while that reported by Kutchko et al. (2007) is 0.040 mm/h\(^{1/2} \). Given that the prediction is based on zero accumulation of leachate in the reactor at ambient pressure, and the experiment pertains to a closed batch reactor at high pressure, the agreement is satisfactory. Pressures on the order of tens of MPa appear to have a modest effect on the corrosion rate of cement in carbonic acid, even though a pressure of 10 MPa raises the total dissolved CO₂ content of the brine to about 1.4 M (Duan and Sun, 2003); that is, the impact of dissolved CO₂ seems to have saturated when the atmosphere contains \( \geq 1 \text{ bar} \) of CO₂.

The ability of Eqs. (5) and (6) to account for the present data and that of other workers encourages us to explore its implications for practical applications. First, we can estimate the time needed for geosequestered CO₂ to escape from a reservoir by dissolution of a sound plug of cement, as in Fig. 1a. If the thickness of the caprock is \( h \), then the time needed for the acid to eat through the cement and enter the overlying reservoir is \( t \approx (h/S)^2 \). For a reservoir at a depth of 1 km, the temperature would be \( \sim 50 \text{ °C} \) and the pressure would be \( \sim 10 \text{ MPa} \), resulting in carbonic acid with a pH of \( \sim 3 \) (Duguid and Scherer, 2010). This pH represents the “worst-case” condition for CO₂-saturation of brine, likely to occur only in a formation with a low capacity for acid buffering. Under those conditions, it would require about 2 million years to escape through a caprock only 10 m thick. Therefore, corrosion of cement presents no risk of leakage, if the well is properly sealed. If there is an annular gap that only
extends part way through the caprock, the situation is the same: to extend the annulus upward by corrosion would take geological time.

The situations depicted in Fig. 1b might be of greater concern. In the event that there is a gap extending along the entire surface of the cement plug, carbonate acid would be driven upward by the overpressure $\Delta p$, in the reservoir. As a worst-case illustration, suppose that there is an annulus with width $a$ around a cement plug with radius $R \gg a$, so that the area of the annulus is $A_D = 2\pi Ra$. The flow velocity, $f$, of brine in the annulus would be (Bird et al., 1960) 

$$f = \frac{a^2 \Delta p}{12\eta h}$$  \hspace{1cm} (13)

where $h$ is the height of the caprock and $\eta$ is the viscosity of the carbonated brine. Assuming that the viscosity of the brine is similar to that of water ($-5.5 \times 10^{-4}$ Pa s at 50 °C), and that the overpressure is 1 MPa, the time for the brine to flow from the bottom to the top of a caprock with $h = 10$ m would be about 8 days if $a = 1$ mm, but only about one minute if $a = 100$ mm. We found that the flow velocity required to flush the debris from the corroded surface was about 4.2 cm/h. Under the conditions just stated, that rate would be achieved in an annulus with $a > 1$ mm, so it is reasonable to assume that the relevant rates are those obtained from the faster flow-through experiments. Of course, the corrosion rate would only be about 3 times slower, if we assumed that the debris was not flushed away.

To decide whether the “Fast flow” or “Slow flow” scenario (Fig. 1b) is more realistic, we must take account of the rate at which acid in the rising fluid is neutralized by reaction with the cement. First, consider the time, $t_D$, that it would take for the acid in a gap of width $a$ to diffuse into contact with the cement. Assuming that the acid concentration at the cement surface is held at zero, and there is no flux of acid across the formation/fringe boundary, solution of Fick’s law shows that the diffusive flux to the cement is completed in a time interval of about $t_D = 1.5 a^2/\mathcal{D}$, where $\mathcal{D}$ is the diffusion coefficient of acid in the brine. Approximating $\mathcal{D}$ by the self-diffusion coefficient in water, we estimate $\mathcal{D} = 4.6 \times 10^{-9}$ m$^2$/s at 50 °C (Kisel’nik et al., 1974). If the gap width is $a = 100$ mm, then $t_D \approx 3.3$ s, which is about 5% of the time for the acid to rise through the caprock. In that case, it is necessary to take account of diffusion in the solution and the cement, as well as the vertical flow rate, to analyze the corrosion. However, such a large gap would constitute a significant leak without corrosion. We are more interested in the risk of an insignificant leak growing substantially as a result of corrosion. If we consider a gap with $a = 10$ mm, then $t_D = 0.03$ s, whereas it would take about 1.8 h to rise through 10 m of caprock in such a gap with $\Delta p = 1$ MPa. Therefore, in gaps with $a \leq 10$ mm, we are justified in ignoring the time for diffusion to occur within the gap, and the analysis presented in Appendix C provides a useful approximation.

If the carbonated brine is rising through the annulus by laminar flow and the acid is lost by diffusion into the cement, then there will be a height $z_0$ at which the acid content drops effectively to zero. According to the analysis in Appendix C, that height can be estimated to be

$$z_0 \approx \frac{2C_0 a f \mathcal{T}}{(1 - m) \mathcal{C}_N S} \hspace{1cm} (14)$$

For an annulus with $a = 10$ mm and $h = 10$ m, subjected to $\Delta p = 1$ MPa and $T = 50 ^\circ C$, if the acid enters with pH 3 ($C_0 = 0.001$ M), then $S = 0.074$ mm/h$^{1/2}$ and $\eta = 5.5 \times 10^{-4}$ Pa s, so the corroded zone is predicted to reach the top of the caprock (i.e., $z_0 = h$) at $t = 3$ million years. That is an over-estimate, because the bottom of the cement plug would be completely consumed long before that, so it would not contribute to neutralizing the acid. A more conservative estimate is obtained by using Eq. (26) of Appendix C to find the time at which the cement at the bottom is completely consumed. The annular cement sheath around the casing in a well is typically about 3 cm thick, and that much cement would be completely corroded in about 20 years, under the conditions described above. At that time, the corroded zone would only have progressed about 2.5 cm up the annulus; each successive interval of 2.5 cm would take longer, and some neutralization would be contributed by the cement remaining below, so the corrosion front would propagate upwards at a rate on the order of one meter per millennium. These remarkable results reflect the very small acid content of the brine and the huge neutralization capacity of the cement. Therefore, the “Slow-flow” scenario is correct, and the attack by carbonated brine is not expected to cause rapid opening of small annuli into large leaks. Of course, the carbonated brine is being pushed away from the injection site by a two-phase zone of supercritical CO$_2$ mixed with brine, and that fluid has a lower viscosity and a higher acid content, so the damage might be greater after the single-phase brine passes the abandoned well. That problem will be the subject of a future paper.

5. Conclusions

The empirical expression for the corrosion rate of cement expressed in Eqs. (5) and (6) permits estimation of the rate of attack over a wide range of pH and temperature values. The physical basis for the concentration dependence of $S$ is being explored through the use of a comprehensive reactive transport model (Huet et al., 2010), and results will be presented in a forthcoming paper (Huet et al., in preparation).

The batch experiments show that the build-up of leached species can have a significant effect on the degradation kinetics, but the flow rate required to remove the sludge is low ($\sim 4$ cm/h), so the results of the flow-through experiments provide a realistic indication of the reaction rates to be expected in the field.

Estimates of the corrosion rate during flow of carbonated brine in an annulus suggest that the huge neutralization capacity of cement will prevent the acid from causing rapid expansion of small pre-existing leaks. Even if an annular gap of 10 mm diameter extends along the whole plug of cement, the corroded zone is predicted to advance only a matter of centimeters in a century. However, it remains to be seen whether worse damage might result from two-phase flow of brine plus supercritical CO$_2$.

Predicting rates and understanding mechanisms of attack are important steps in addressing the leakage potential in the wellbore, but the mechanical and transport properties of degraded material also figure into this problem. The results of investigation into mechanical and transport properties of corroded cement will be presented in a forthcoming paper (Matteo and Scherer, in preparation).

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Appendix A. Diffusion with reaction

If corrosion is modeled as a diffusion process in which a chemical reaction removes the diffusing species (acid), then the governing equation is (Crank, 1975)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial C_R}{\partial t}$$  \hspace{1cm} (15)
where $C_R$ is the concentration of diffusing species removed by reaction, and the reaction kinetics are described by

$$\frac{\partial C_R}{\partial t} = \lambda C^n - \mu C_R$$ (16)

where the parameters $\lambda$ and $\mu$ control the rates of the forward and reverse reactions. If the exponent $n = 1$, the reaction is first-order; that is the case we will consider now. That is obviously an oversimplification, but the goal is to obtain a qualitative indication of the effect of the reaction on the slope, $S$, of the corrosion plot. There is a finite capacity in the cement for neutralization of acid, $C_N$, which must be approached by $C_R$ at long times, $C_R(x, \infty) = C_N$, at which point the concentration of solution in the pores of the degraded cement approaches the boundary concentration, $C(x, \infty) = C_0$. It can be shown that this imposes the following condition on the reaction parameters: $\mu = \lambda C_0/C_N$. Applying the Laplace transform with respect to time to Eqs. (15) and (16), we find that the transformed concentration is given by

$$\mathcal{L}[C(x, t)] = \frac{C_0}{s} \exp \left[ -\frac{x}{\sqrt{sD}} \sqrt{\frac{(s + \lambda + \mu)}{s + \mu}} \right]$$ (17)

where $s$ is the transform parameter (Hildebrand, 1962). Inverting this is difficult, but we can easily find the long-term solution by considering only the range of small $s$ (viz., $s \ll \lambda, \mu$). In that limit, the solution reduces to

$$C(x, t) \approx C_0 \exp \left[ \frac{x}{2\sqrt{sD}} \right]$$ (18)

where

$$\delta = \frac{\mu D}{\lambda + \mu} = \frac{DC_0}{C_0 + C_N} \approx \frac{DC_0}{C_N}$$ (19)

where the final approximation takes account of the high neutralization capacity of the cement paste (i.e., $C_N \gg C_0$). Now if we assume that the depth of degradation, $x_D$, corresponds to a particular acid concentration, $C_D$, Eq. (18) indicates that

$$x_D = 2\sqrt{\delta Er fc^{-1} \left( \frac{C_D}{C_0} \right)} \approx \sqrt{D} \left[ \frac{C_D}{C_0} \exp \left( -\frac{C_D}{C_0} \right) \right]$$ (20)

Comparing this to Eq. (2) of the text, we see that $S$ is still proportional to the square root of $D$, but the constant of proportionality has a stronger dependence on $C_0$. The coefficient of $\sqrt{D}$ in Eq. (20) is very well fit by a power law in $C_0$ with an exponent of 0.56, whereas the experimental data indicate an exponent of 0.35. Therefore, this simple analytical treatment yields a form that is equivalent to Eq. (7) and has a similar concentration dependence.

**Appendix B. Liesegang rings**

As shown in Fig. 16a, in the sample exposed to pH 2 under 1 bar of CO$_2$, the gel layer developed distinct bands that resemble Liesegang rings (Antal et al., 1998). According to the EDX results shown in Table 1, the compositions of the layers differ primarily in iron content. This type of pattern is associated with a moving reaction front, where an invading species reacts with a resident species; when the concentration of the product exceeds a nucleation threshold, a precipitate forms. This depletes the local concentration of product, but does not stop the diffusion of the invading species, so the reaction continues to advance, and another zone of precipitation occurs when the nucleation threshold is again surpassed. The spacing of Liesegang rings is known to follow the scaling law, $x_{n+1} = P x_n$, where $x_n$ is the distance of the $n$th precipitation band from the gel surface, and the constant $P$ is the spacing coefficient; typically, $1.05 \leq P \leq 1.4$. This means that the depth of band $n+1$ is given by

$$x_{n+1} = P^n x_1$$ (21)

The widths of the bands increase with a similar scaling law. The form of this equation and the value of the exponent can be rationalized in terms of several types of reaction-diffusion theories (Antal et al., 1998). Fig. 16b shows a fit of Eq. (21) to the measured width and depth (measured at the center of the band) of the light-colored bands in the gel. The rings closest to the surface are too thin and crowded to measure accurately, but those farther from the surface are well spaced and of sufficient thickness to be accurately measured. The fits are seen to be quite good, and both yield $P = 1.1$, which is in the expected range.

**Appendix C. Corrosion in an annulus**

We need to write an equation for the conservation of acid as acidified brine flows upward in an annular gap and reacts with the cement that forms one of the boundaries of the gap. The contributions include laminar flow of the brine, described by Eq. (13), reaction of the brine with the cement, at a rate described by Eqs.
and of acid in the brine. Transport by vertical diffusion will be negligible compared to that from flow, unless the gap width or the pressure difference is very small, and in that case, the leakage will be negligible. Therefore, we can neglect vertical diffusion. Diffusion perpendicular to the surface of the cement will control the rate of acid neutralization in larger gaps, but those cause significant leakage without corrosion. As shown in the text, diffusion across the gap is fast compared to vertical flow in narrow gaps (on the order of 10 μm), so we limit our consideration to such cases. Therefore, the concentration of acid in the brine in the annular gap is described by

$$\frac{\partial C}{\partial t} = -f \frac{\partial C}{\partial z} - \frac{C_n \rho C_m}{2a\sqrt{f}}$$

(22)

where the first term represents advective transport and the second accounts for neutralization of acid by reaction with the cement when the rate of attack is given by Eq. (7). This means that we are assuming a pseudo-steady state in which the concentration distribution inside the corroded zone adjusts as fast as the boundary condition changes. The good fits in Fig. 14 indicate that this approximation works well until the corrosion depth is at least a couple of millimeters, but we cannot prove that it works beyond

$$h \gg \left(\frac{f}{1 - m}\right)^{1/2}$$

(23)

where \( \phi \) is a dimensionless parameter defined by

$$\phi = \frac{C_n \rho C_m}{2aC_0} \sqrt{\frac{f}{f}}$$

(24)

The concentration drops to zero at height \( z_0 \) above the reservoir as the acid is consumed by the cement. The result given by Eq. (14) is found by setting Eq. (23) equal to zero, and simplifying the result by recognizing that \( \phi \approx 1 \), owing to the large ratio of \( C_n \) to \( C_0 \):

$$z_0 = \frac{4(1 - m)\sqrt{\phi} - 1}{4(1 - m)^2 \phi^2} \approx \frac{\sqrt{\phi}}{(1 - m)^2}$$

(25)

The depth of corrosion at any height \( z < z_0 \) is found by integrating Eq. (12), with \( C \) given by Eq. (23):

$$x_{0}(z, t) = \frac{\alpha(T)}{2} \int_{0}^{h} \frac{C_m(z, u)}{\sqrt{u}} du, \quad \{t > \frac{h}{f}, \quad z \leq z_0\}$$

(26)

References


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