Towards Robust Models of Well Seals and Plugs in CO_2 Storage Sites

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Underground storage of CO_2, captured at fossil fuel power stations and certain large industrial point sources, is widely proposed as a transitional technology for mitigating climate change due to anthropogenic CO_2 emissions. The greatest long-term risk is often assessed to be potential leakage from abandoned wells. Cement is the most common material used to plug such wells during abandonment. It is therefore necessary to assess how this material will behave in the presence of CO_2 and very saline formation water (brine), which is common in many potential CO_2 storage reservoirs. However, well cement behaviour under such conditions cannot be predicted reliably using conventional geochemical models. The reason is that these models calculate the activity coefficients of aqueous species using equations such as the Davies equation that are inappropriate for brines. To produce a more reliable model of cement well plugs in the presence of CO_2-charged brine, a fully-coupled model was developed that calculated activity coefficients using the "Pitzer" approach, which is appropriate for high ionic strength solutions. The models reproduced the main alteration features of well cement cores that had been in contact with CO_2-charged brine for c.30 years. The models also demonstrated that the cement's porosity would be sealed by amorphous silica and calcite after c.100 years, preventing significant further reaction. The results are consistent with hydrocarbon industry experience that suggests the biggest potential limitation on the effectiveness of any given cement well plug will not be chemical degradation, but rather physical defects associated with its emplacement. However, the geochemical alteration of different cements cannot be assumed to be identical. Specific applications of models like the one presented here are needed to help to support claims of long-term performance of different cement materials that might be used in well seals.

1. Introduction

Underground storage of CO_2, captured at fossil fuel power stations and certain large industrial point sources such as cement works and steel works, is widely proposed as a transitional technology for mitigating climate change due to anthropogenic CO_2 emissions. Frequently, the greatest assessed CO_2 long-term leakage risks from a proposed storage site arise from abandoned wells. At a properly selected and appropriately operated site these risks are low, but nevertheless confidence needs to be built that seals and plugs in wells will not degrade significantly over time. Long-term evolution models of sealing materials are therefore needed. The timescales are not precisely defined, but need to cover the period for which CO_2 must be isolated from the atmosphere to mitigate climate change. This period depends upon the residence time of CO_2 in the atmosphere, which is uncertain; published estimates range from a few years to several hundred years. However, the IPCC 5th Assessment Report (IPCC, 2015) states that between 15% and 40% of anthropogenic CO_2 emissions until 2100 will remain in the atmosphere after 1000 years. Furthermore, the European Commission's Carbon Capture and Storage (CCS) Directive (Council Directive (EC) 2009/31/EC) states that CO_2 must be contained "permanently". Clearly the evolution of well seals and plugs must

be assessed for timescales of thousands of years, much longer than the periods of a few hundred years normally considered by the hydrocarbon industry when abandoning wells. In most well abandonment concepts for CO_2 storage, seals and plugs are composed of cement (usually Class G or H API) and it is necessary to evaluate the evolution of this material in the presence of CO_2-saturated water. However, when doing so a major challenge is that well cement behaviour in the presence of CO_2-charged brines cannot be predicted reliably using conventional geochemical models. The reason is that these models calculate the activity coefficients of aqueous species using equations such as the Davies equation that are appropriate only for low ionic strength solutions and not for brines. The work reported here aimed to address this limitation by developing robust fully-coupled models of reactions between cement and CO_2-charged brine that employ the "Pitzer approach" (Pitzer, 1987) to calculate activity coefficients of aqueous species.

2. Well Plugging and Abandonment Methods

In most concepts for underground storage of CO_2, supercritical dry CO_2 will be injected via one or more wells that are sited and / or orientated to prevent subsequent post-abandonment leakage of CO_2 through them. For example, injection wells may be located down-dip from the high-point of a storage reservoir, so that the injected CO_2 will move laterally away from the injection point, as it ascends due to its buoyancy (Figure 2-1). Thus, in the long-term such injection wells will not contact CO_2 or CO_2-charged water. In many areas that may be considered for a CO_2 store the potential leakage pathways of greatest concern are abandoned wells that may be contacted by the CO_2, after the CO_2 has attained its final location within the reservoir (Figure 2-1). Such wells are likely to be most common where a depleted hydrocarbon reservoir is to be used as the CO_2 store.

Initially, stored CO_2 can interact only with the lower end of the deepest cement plug in a well, unless there are permeable pathways such as fractures that conduct CO_2 or CO_2-charged brine through the cement (Figure 2-1).
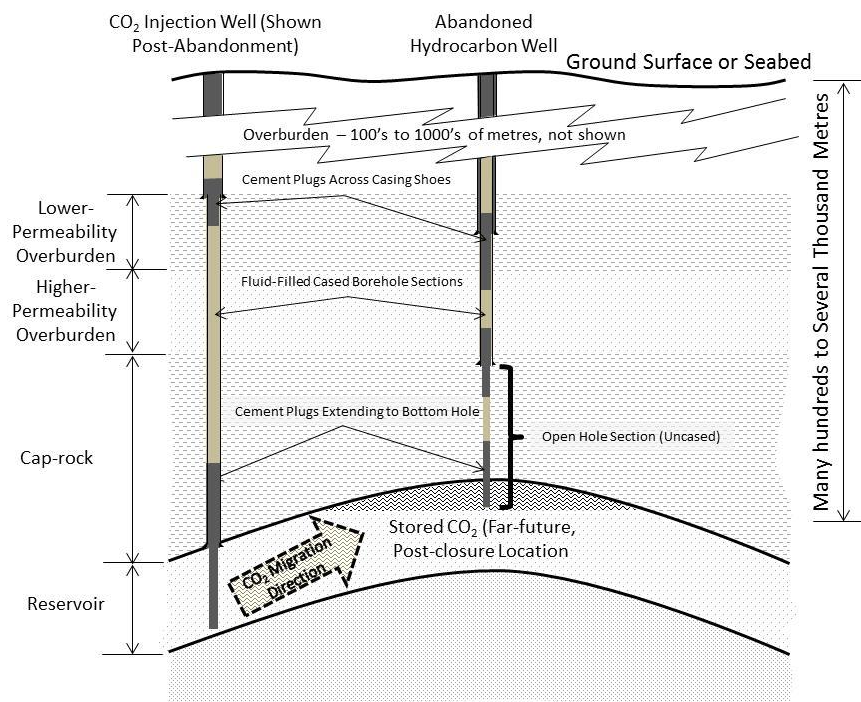

Figure 2-1. Schematic illustration of a CO_2 storage site showing two wells with different plug/seal designs.

3. Modelling Approach

Quintessa's QPAC software (Quintessa, 2013) was used to develop fully coupled 1-D chemical-transport models in which cement was exposed to CO_2-charged water. Alternative model cases were designed to determine the significance of uncertainties in thermodynamic and kinetic data.

Cement evolution was simulated using an ideal solid-solution model for C-S-H gel described by Kulik and Kersten (2001). Equilibrium constants were calculated for hydrolysis reactions involving the C-S-H gel over temperatures between 0°C and 100 °C. These calculations assumed that the gel is a solid solution of jennite-like and tobermorite-like end-members with compositions $(CaO)_{1.67}(SiO_2)(H_2O)_{2.1}$ and $(CaO)_{0.83}(SiO_2)(H_2O)_{1.3}$ respectively. Solid phase data were taken from Lothenbach et al (2008) and aqueous species data were taken from SUPCRT92 (dprons96.dat; Johnson et al., 1992). Equilibrium constants for other solid phase hydrolysis reactions were taken from the Geochemist's Workbench database "thermo.com.v8.r6+.dat" (Bethke, 2008).

Transition State Theory (Aagaard and Helgeson,1982; Palandri and Kharaka 2004) was used to model solid phase dissolution/precipitation kinetics, according to:

$$\frac{ds}{dt} = \left(k.A(H^+)^{n_1} + k.A + k.A(OH^-)^{n_2} + k.A(P_{CO_2})^{n_3} \right) \left(1 - \frac{Q}{K} \right)$$

where: s (mol) is the quantity of a solid, t is time (s), k is the rate constant (mol m^{-2} s^{-1}), A is the evolving reactive surface area of the solid (m^2 – calculated from the mineral abundance and its specific surface area), $n_{1,2,3}$ are dimensionless constants that determine the dependence of the reaction rate on the acidity/alkalinity/carbonate content of the fluid, Q is the ion activity product and K is the equilibrium constant for mineral dissolution (Q and K both being dimensionless). For calcite, kinetic data were taken from Palandri and Kharaka (2004). SiO_2(am) was assigned a fixed "rapid rate" k value of 10^{-3} mol m^{-2} s^{-1}. As no reliable published dissolution rates exist for C-S-H gel and $Ca(OH)_2$, these were determined by calibration against laboratory data, as described below.

The model was used initially to simulate published results from 9-day long laboratory experiments that investigated reactions between CO_2-charged water and cement (Kutchko et al., 2007). These experiments used water with an ionic strength of c.0.2 and hence activity coefficients could be calculated using the Davies equation, which is considered reliable to ionic strengths of c. 0.5 (Bethke, 2008). The models employed the "llnl.dat" thermodynamic database, which is distributed with PHREEQC (Parkhurst et al., 1999) and is derived from the Geochemist's Workbench database ""thermo.com.v8.r6+.dat". The CO_2-rich water composition used by the QPAC model was calculated using PHREEQC (Parkhurst and Appelo, 1999), taking as input the water composition reported by Kutchko et al. (2007) , the CO_2 concentration being fixed by its solubility, as determined using the equations of Duan and Sun (2003) and Duan et al. (2006). The water was calculated to have a dissolved C concentration of 1.357 mol kg^{-1}, ionic strength of 0.17 and pH of 3. Diffusion coefficients and kinetic parameters were adjusted until the model outputs matched the experimental observations closely, gaving an effective diffusion coefficient of 1.35 x 10^{-12} ms^{-2} for the cement and a reaction rate constant of 1 x 10^{-9} mol m^{-2} s^{-1} for C-S-H gel and portlandite.

After values for diffusion coefficients and kinetic parameters had been established, the model was used to simulate observed cement alteration in a well that had been used for CO_2-enhanced oil recovery (CO_2-EOR) in Scurry Area Canyon Reef Operators (SACROC) oilfield in Texas (Carey et al., 2007; Figure 3-1). Here, well casing cement (thought to be API Class A), had been exposed to CO_2-rich brine during EOR for >30 years, at a temperature of c.50 °C. Carey et al. (2007) reported

observations on steel casing, cement and shale wall rock samples from between 4 m and 6 m above the contact of the limestone oil reservoir with the shale caprock. They found that the cement was carbonated for between 1 mm and 10 mm from both the casing-cement contact and the wallrock-cement contact (Along section A-B in Figure 3-1). These observations imply an alteration rate of up to 0.33 mm yr^{-1}.
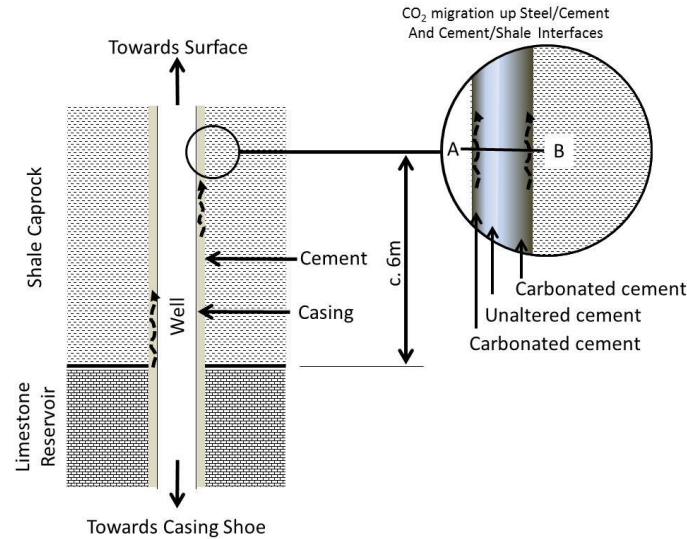

Figure 3-1. Schematic illustration of the SACROC situation, as described in Carey et al. (2007).

Again the CO_2-rich water composition used by the QPAC model was calculated using PHREEQC (Parkhurst and Appelo, 1999) and the water compositions given by Carey et al. (2007), the CO_2 concentration being solubility-limited, as determined using the equations of Duan and Sun (2003) and Duan et al. (2006). The water was calculated to contain 0.9 mol kg^{-1} dissolved C and to have ionic strength of 1.87 and pH of 4.5. Aqueous activity coefficients were calculated by the "Pitzer" approach, using the thermodynamic database "data0.ypf.R2" developed by Sandia National Laboratories, which is reliable for Na-Cl dominated water to ionic strengths >10 (USDOE, 2007).

4. Results

The results from the simulations of the SACROC site are summarized in Figure 4-1 and Figure 4-2.
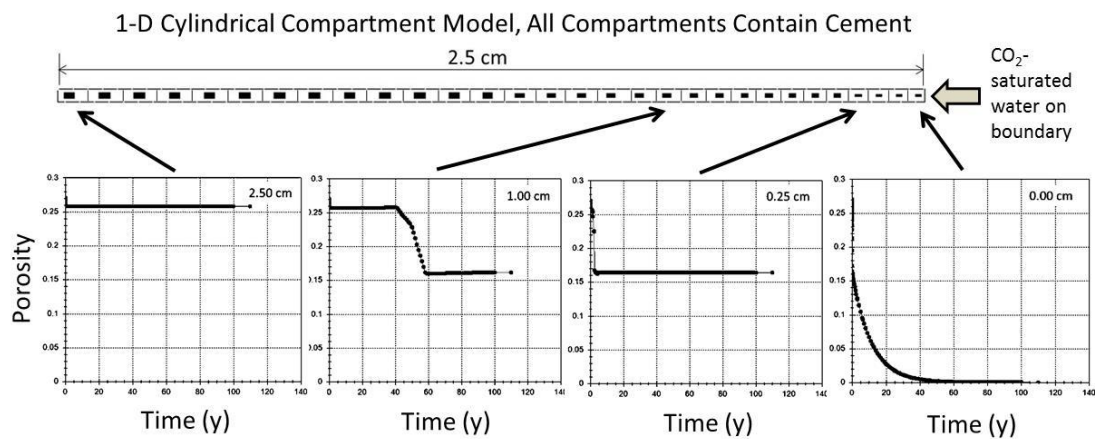

Figure 4-1. Model geometry (above) and output temporal variations in cement porosity(below).
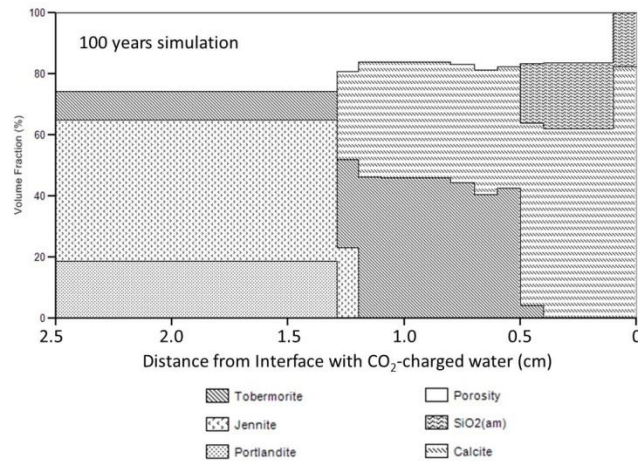
Figure 4-2. Modelled spatial distribution of primary and secondary phases in the cement after 100 years of exposure to CO$_2$-saturated brine at 50 °C.

Cement porosity was completely sealed near the interface between the cement and the CO$_2$-charged brine after 100 years, isolating the remaining cement and causing reactions in it to effectively cease. After 30 years of simulation (not illustrated), 0.9 cm of cement had been carbonated. This alteration rate is 0.3 mm y^{-1} and is comparable to the observed rate of up to 0.33 mm y^{-1} (Carey et al., 2007). After 100 years of reaction the depth of simulated cement carbonation was about 1.25 cm (Figure 4-2), giving an average alteration rate of 0.125 mm y^{-1}. Thus, the results show a gradual slowing of the cement carbonation rate over 100 years due to pore space clogging during progressive reaction.

5. Discussion and Conclusions

On theoretical grounds robust models of long-term cement evolution in the presence of brines should use the "Pitzer" approach for calculating the activity coefficients of aqueous species, rather than the "conventional" Davies equation or similar equations. However, available thermodynamic databases to support the "Pitzer" approach are more limited, in terms of both numbers of species and applicable temperature range, than thermodynamic databases that support the "conventional" approaches. Nevertheless, by simplifying the modelled representation of a real system it has been possible to develop a fully-coupled model of interactions between cement and CO$_2$-saturated brine that can match the main features of experimental and field observations.

The model has been used to predict cement behaviour in the presence of CO$_2$-charged brine over longer timescales (to c. 100 years) than those of laboratory experiments or field experience. This prediction suggests that the extent of cement alteration by CO$_2$-charged brine would be spatially limited to within a few centimetres of the cement-brine contact because the reactions that occur seal the cement's porosity. Due to this sealing the reaction rate becomes very small after about 100 years. The location of cement alteration several metres above the reservoir-caprock contact at the SACROC site (Carey et al., 2007; Figure 4-1) therefore implies that CO$_2$-charged brine ascended along physical defects in the cement, rather than through the cement's matrix. Possibly these defects occurred between the cement and the casing and between the cement and the shale wallrock.

The simulated temperatures were much lower than those of many reservoirs that might be considered in future for CO$_2$ storage; temperatures of over 100 °C are likely to be common. There are uncertainties about the physico-chemical evolution of cements in the presence of CO$_2$ at these high temperatures and in the presence of brines. Chemical processes alone will probably not

compromise the sealing performance of cement plugs, but if there is brittle deformation of the plug, flow pathways for CO_2 might be created. The coupling between physical and chemical properties of cementitious plugs therefore requires further investigation.

6. References

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