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A reactive transport model for geochemical mitigation of CO₂ leaking into a confined aquifer

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Abstract

Long-term storage of anthropogenic CO₂ in the subsurface generally assumes that caprock formations will serve as physical barriers to upward migration of CO₂. However, as a precaution and to provide assurances to regulators and the public, monitoring is used to detect any unexpected leakage from the storage reservoir. If a leak is found, the ability to rapidly deploy mitigation measures is needed. Here we use the TOUGHREACT code to develop a series of two-dimensional reactive transport simulations of the hydrogeochemical characteristics of a newly formed CO₂ leak into an overlying aquifer. Using this model, we consider: (1) geochemical shifts in formation water indicative of a leak; (2) hydrodynamics of pumping wells in the vicinity of a leak; and (3) delivery of a sealant to a leak through an adjacent well bore. Our results demonstrate that characteristic shifts in pH and dissolved inorganic carbon can be detected in the aquifer prior to the breakthrough of supercritical CO₂, and could offer a potential means of identifying small and newly formed leaks. Pumping water into the aquifer in the vicinity of the leak provides a hydrodynamic control that can temporarily mitigate the flux rate of CO₂ and facilitate delivery of a sealant to the location of the caprock defect. Injection of a fluid-phase sealant through the pumping well is demonstrated by introduction of a silica-bearing alkaline flood, resulting in precipitation of amorphous silica in areas of neutral to acidic pH. Results show that a decrease in permeability of several orders of magnitude can be achieved with a high molar volume sealant, such that CO₂ flux rate is decreased. However, individual simulation results are highly contingent upon both the properties of the sealant, the porosity-permeability relationship employed in the model, and the relative flux rates of CO₂ and alkaline flood introduced into the aquifer. These conclusions highlight the need for both experimental data and controlled field tests to constrain modelling predictions.

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1. Introduction

Physical and chemical trapping mechanisms are both associated with long-term storage of CO₂. Initially, structural and hydrodynamic trapping dominates, requiring low permeability units, or caprocks, to act as seals above the injection reservoir. Efficient physical trapping will lead to chemical trapping processes over longer periods of time, including dissolution, sorption and mineralization [1]. The time period over which chemical processes become dominant is long enough that physical trapping offers the first defence against CO₂ migration and loss.

Although tens to thousands of years may be required for chemical trapping to become a substantial contribution to CO₂ sequestration [2], perturbations to the geochemical composition of formation water in response to the introduction of concentrated CO₂ can be rapid. As a result, if CO₂ migrates into an overlying reservoir due to a defect in the caprock structure, this migration could be associated with abrupt chemical changes [3]. Furthermore, the response of the formation water to CO₂ intrusion (*e.g.*, decreased pH) may be leveraged for engineered intervention strategies.

Remediation strategies for leakage scenarios commonly require discontinuation of injection into the primary reservoir, but from an operations standpoint, such disruption to a full-scale project may be costly and prohibitively difficult. Here we evaluate a chemical mitigation strategy requiring continuous injection of CO₂ to establish a reactive mixing zone with a chemical sealant.

1.1. Geochemistry of a CO₂ leak

Solubility trapping involves the dissolution of CO₂ into the aqueous phase and is thus a function of pressure, temperature and ionic strength of the fluid [2]. While the majority of total DIC in solution exists as CO_{2(aq)}, the dissociation of carbonic acid governs the shift in pH and the stability of solid phases. The composition and mineralogy of the reservoir thus exert a principle control on the geochemical response of the system to a CO₂ leak [4]. Initial pore water acidification after introduction of CO₂ results in dissolution of readily soluble minerals, such as calcite, dolomite, siderite, iron (oxy)hydroxides and even the cement and steel comprising installed well casings [5,6]. This enhanced dissolution increases the concentration of cations, carbonate and bicarbonate ions and thus subsequently increases pH [3,7], and potentially trace metal concentrations [8]. During the initial phases of a leak, the abundance of carbonate minerals in the upper reservoir influences both the magnitude of the pH decrease and the increase in cation and trace element concentrations in the vicinity of this pH drop.

The combined effect of the processes described above leads to a general expectation that the pore water immediately adjacent to a newly formed CO₂ leak will exhibit an initial drop in pH and increase in DIC. This chemical shift is significant because it may precede the breakthrough of a supercritical CO₂ plume in a down-gradient monitoring well. Such pH and DIC shifts prior to the arrival of CO₂ were observed in the primary injection reservoir during the Frio Carbon Capture and Storage (CCS) project [5]. Detecting such a shift requires that the chemical and hydrodynamic conditions allow for pore water in contact with the leak to subsequently mix into the surrounding fluid and advect down-gradient in advance of the CO₂ plume. In total, pH and DIC responses associated with a CO₂ leak into an upper reservoir are predictive, but the magnitude of the observed response will also depend on the timing and location of the leak relative to monitoring well observations, the hydrodynamics of the system and the host rock mineralogy.

Observations from natural [9,10,11] and anthropogenic [5,12-19] examples of subsurface CO₂ infiltration highlight two important points. First, characteristic responses in pore water chemistry, namely decreasing pH and elevated alkalinity, may be detected before the breakthrough of CO₂. These indicators may offer a means of advanced warning where measurements are feasible. Second, these shifts distinguish the geochemical signature of the CO₂ leak from the undisturbed reservoir and thus allow for engineered interventions, such as the introduction of a sealant with pH- or CO₂- dependent solubility.

1.2. Properties of chemical sealants

Creating a seal is a matter of preventing fluid flow through a specified volume by emplacement of a permeability or pressure barrier [20]. Current research is underway to develop CO₂ resistant cements to seal potential leaks in existing wellbores, as well as to improve resistance of new wells to acidic fluids [21, 22]. In contrast, remediation of CO₂ leakage through fault or fracture systems presents a more substantial technological challenge and has received comparatively less attention [e.g. 20].

One of the key issues in mitigating extended leakage zones (e.g., fractured systems in connected wells or in fault/damage zone systems) with current sealant technology is that the initial viscosity and setting time of most sealants will not allow sufficient lateral penetration across a fracture system. For example, hydraulic cements have high viscosity (up to 1000's of cP) and a short setting time of a few hours [22,23,24]. Resins offer somewhat better parameters, with typical initial viscosities on the order of several 10's of cP and setting times of about 10 hours, though this still results in complete polymerization within a few meters of the injection well [22]. Currently only a few sealants reported in the literature have an initial viscosity low enough to support delivery to large damage zones. These include *in situ* generated polymer (IGP) with an initial viscosity similar to water [25,26] and a CO₂ activated silicate polymer initiator (SPI-CO₂) [DOE project DE-FE0005958]. The IGP phase change is temperature dependent, resulting in a maximum gelation time on the order of 10 hours [26,27,28]. The SPI-CO₂ gelation time is highly dependent upon the pH of the solvent, but can remain in solution for up to several days [29,30]. The high pH required to maintain SPI in solution reflects the pH dependence of silica saturation. This pH dependence suggests the potential development of sealants that are not dictated by a setting time, but rather remain in solution until an acidic CO₂ plume is contacted.

In general, effective sealant delivery to a CO₂ leakage zone requires extensive study. Conformance issues present a significant challenge because a comprehensive rock/fluid property database and operational experience are still lacking [20,31], and rock formations are heterogeneous at all scales and cannot be fully characterized with enough resolution to detect small fractures in the caprock by geophysical techniques. An additional limitation is that current reactive transport simulators, which should be used to guide intervention strategies, do not yet have capabilities for accurately modeling the chemical and transport properties of many sealant classes, and for many of these sealants the properties required to develop even basic simulations are currently unavailable. The purpose of the present chapter is to initiate this effort by demonstrating the current capabilities and limitations of a reactive transport modeling approach to describe emplacement of a reactive barrier to mitigate a CO₂ leak. Here we present a conceptual model of CO₂ infiltrating into a confined aquifer above the primary storage reservoir and examine the delivery of a hypothetical SiO₂-based sealant to the damage zone through a nearby injection well.

2. Model Development

Simulations are conducted using the TOUGHREACT nonisothermal multicomponent reactive transport code [32,33,34,35] with the ECO2N thermophysical property module for H₂O-NaCl-CO₂ mixtures in the range of temperatures and pressures appropriate for CO₂ sequestration [36]. Mathematical formulations for the sequential iteration approach [37] utilized in TOUGHREACT to solve the basic mass and energy conservation equations are described in detail elsewhere [34,35,38]. The TOUGHREACT code has been used previously to simulate the hydrogeochemistry of CO₂ storage in saline aquifers [39,40,41,42], and more recently to consider both the geochemical behaviour of a CO₂ leak into an overlying aquifer [43,44,45] and the associated consequences for drinking water quality [46,47,48]. To the authors' knowledge, the current study is the first to report the application of a reactive transport code to the simulation of sealant delivery for remediation of a CO₂ leak into an overlying aquifer.

2.1. Model domain and thermophysical conditions

The current study focuses on the immediate geochemical response to a newly formed CO₂ leak into an overlying aquifer. As a result, the model domain is restricted to the area immediately adjacent to the leak, comprising a 50 m vertical and 2 km lateral extent and simplified to two dimensions (2-D). The upper boundary of the domain is held to a no-flow condition, representing an upper confining unit above the aquifer. A highly refined

grid of 1m^2 blocks is used to discretize the domain from the left boundary to a distance of 450 m laterally, at which point the grid blocks increase exponentially in area with further distance to yield a quasi-infinite boundary condition on the right side of the domain. The left boundary of the domain is specified as no-flow and may be conceptualized as a fault or sedimentary basin margin. Grid cells in this left boundary are specified with a low injection rate, resulting in a net flux of 1 cm/day from left to right in the aquifer to represent regional groundwater flow. The bottom boundary of the domain constitutes the upper section of the primary CO_2 injection reservoir, and is separated from the overlying aquifer by a thin, horizontal caprock. The initial thermophysical conditions of the system are shown in Table 1. Prior to initialization, a pressure of 17 MPa and a temperature of 55 °C are specified across the domain. These values fall within the range bounded by the hydrostatic and lithostatic gradients and correspond to an approximate depth of 1 – 1.5 km below land surface. To separate the injection reservoir from the overlying aquifer, permeability in the caprock is set to $1 \times 10^{-20} \text{ m}^2$, eliminating any flow through this portion of the domain. Two adjacent grid cells within the caprock unit centered 150 m from the left boundary of the domain are assigned an initial z-permeability less than that of the surrounding caprock to create a 2 m wide ‘defect’ in the otherwise impermeable unit. Two starting values of z-permeability for this defect of 1.0×10^{-15} and $1.0 \times 10^{-17} \text{ m}^2$ were tested in model simulations

At the specified temperature and pressure range of these simulations, two liquid phases are present as saline H_2O and supercritical CO_2 . Relative permeability of the H_2O liquid phase (k_{rl}) is calculated based on H_2O saturation (S_l) using a van Genuchten relation [49] for a specified irreducible water saturation as (all parameters defined in Table 1):

$$k_{rl} = \sqrt{S^*} \{1 - (1 - [S^*]^{1/m})^m\}^2 \quad (1)$$

where $S^* = (S_l - S_{lr}) / (1 - S_{lr})$. Relative permeability of the CO_2 phase (k_{rc}) is calculated using a Corey relation [50] based on H_2O saturation, irreducible water and CO_2 saturation (Table 1) as:

$$k_{rc} = (1 - S')^2 (1 - (S')^2) \quad (2)$$

where $S' = (S_l - S_{lr}) / (S_l - S_{lr} - S_{gr})$. The capillary pressure (p_{cap}) necessary to overcome interfacial tension between H_2O and CO_2 phases in the porous media is also calculated using a van Genuchten relationship [49] as:

$$p_{cap} = -P_0 ([S^*]^{-1/m} - 1)^{1-m} \quad (3)$$

Table 1: Hydrogeologic parameters for the confined aquifer

model parameter		value
k_x	x permeability (m^2)	1.0×10^{-12}
k_z	z permeability (m^2)	1.0×10^{-13}
ϕ	porosity	0.15
τ	tortuosity	0.5
c	compressibility (Pa^{-1})	1×10^{-9}
T	temperature (°C)	55
D	diffusion coefficient (m^2s^{-1})	1×10^{-9}
relative permeability		
m	exponent	0.457
S_{lr}	irreducible water saturation	0.3
S_{gr}	irreducible gas saturation	0.05
capillary pressure		
m	exponent	0.457
S_{lr}	irreducible water saturation	0.0
P_0	strength coefficient (kPa)	19.61

2.2. Geochemical conditions

In the TOUGHREACT code, chemical mass balance is calculated in terms of the total number of linearly independent (basis) species [51], leading to a mixed equilibrium – kinetic (*i.e.* differential – algebraic) equation set [52]. The short timespan of the current simulation relative to the chemical trapping mechanisms supports the use of simplified geochemical conditions, as the extent of primary silicate dissolution expected to occur is extremely limited. The initial reservoir composition was thus simplified to 80% quartz, 20% feldspar. The feldspar composition is a 20% anorthite, 80% albite solid solution ($\text{Ca}_{0.2}\text{Na}_{0.8}\text{Al}_{1.1}\text{Si}_{2.8}\text{O}_{7.8}$) with temperature-dependent equilibrium constants calculated from Arnórsson and Stefánsson [53] to account for non-ideal mixing. The regression coefficients necessary to obtain this temperature dependence were refit from the Arnórsson and Stefánsson [53] values to match the equation used in the TOUGHREACT code.

In addition to the quartz and feldspar initially present in the domain, the secondary minerals kaolinite and calcite are allowed to form. As noted previously, the small time interval of this simulation negates appreciable accumulation of these secondary clays and carbonates, but they are included for completeness. All thermodynamic data other than those specified for the albite-anorthite solid solution were taken from Wolery [54]. Initialized fluid concentrations, mineral volume fractions and kinetic rate parameters for the current simulations are provided in Table 2.

Table 2: initial fluid and solid compositions and rate constants

primary species	concentration (M)	
pH	7.0	
HCO_3^-	4.55E-02	
AlO_2^-	7.03E-08	
Cl^-	1.0	
Br^-	1.0E-13	
Na^+	9.92E-01	
Ca^{2+}	6.49E-05	
$\text{SiO}_{2(\text{aq})}$	8.45E-04	
mineral	volume fraction (m^3 min./ m^3 porous med.)	rate constant ($\text{mol}/\text{m}^2/\text{s}$)
quartz	0.8	1.0E-14
albite-anorthite s.s.	0.2	2.7E-13 6.9E-11 (H^+) 2.5E-16 (OH^-)
kaolinite	0.0	6.9E-14 4.9E-12 (H^+) 8.9E-18 (OH^-)
hypothetical sealant	0.0	7.3E-08
calcite	0.0	equilibrium

2.3. CO_2 leak and sealant

The primary injection well for CO_2 into the lower reservoir is located outside of the current high-resolution model domain. As a result, the presence of a CO_2 source is simulated by fixing the grid cell in the lower left boundary of the domain to a constant CO_2 saturation of 75% and an elevated pressure. Two fixed pressure values of 18 MPa and 20 MPa (approximately 1 MPa and 3 MPa higher than the ambient pressure in the upper aquifer, respectively) were tested. For each combination of caprock defect permeability and initial CO_2 reservoir pressure (Table 3), a 1 year simulation was run prior to implementing any sealant or hydrodynamic mitigation in order to establish the presence of a CO_2 leak in the upper aquifer.

Table 3: simulated parameter scenarios

Scenario	Caprock defect permeability (m ²)	Fixed CO ₂ reservoir pressure (MPa)
A	1.0x10 ⁻¹⁵	20
B	1.0x10 ⁻¹⁷	20
C	1.0x10 ⁻¹⁵	18
D	1.0x10 ⁻¹⁷	18

A pH-dependent silica-based sealant (“hypothetical sealant”) was simulated using the thermodynamic and kinetic properties of amorphous silica. Due to the lack of published data on Si polymers, we use the properties of SiO_{2(aq)} and SiO_{2(am)}, and increase the molar volume of SiO_{2(am)} to 500 cm³/mol to represent a hypothetical gel or polymer that undergoes a large volume increase during gelation. Dissolved silica is introduced to the system through a pumping well along the left boundary of the upper aquifer at a uniform fluid injection rate of 0.001 kg/m²/s for a total fluid injection across the boundary of 0.047 kg/s. This injection raises the pressure near the left boundary of the aquifer to approximately 18.2 MPa. The injectate solution is comprised of the same initial concentrations as aquifer formation water (Table 2) but equilibrated with Na₂SiO₃ such that pH is increased to 10, SiO_{2(aq)} is increased to 0.1 M. Bromine, to serve as an inert tracer, is increased to 0.01 M. The concentration of sodium in this alkaline flood is also slightly increased.

The accumulation of the hypothetical sealant at the interface between the alkaline flood and acidic CO₂ plume is intended to reduce the porosity and thus the permeability of the aquifer in the region of reactivity. This porosity-permeability relationship is difficult to constrain and is often dependent upon site-specific geometry and reactivity of a given porous media. The present simulations utilize a modified Hagen-Poiseuille [55]:

$$k = C_k \frac{NP \times \pi \times d^4}{128} \quad (4)$$

where C_k is the number of pore throats connecting to an individual pore, NP is the number of pores in a given area of porous media and d is the average diameter of a pore throat (which will decrease with secondary mineral precipitation). This relationship is suggested as an accurate description of the porosity-permeability relationship in conglomerates and sandstones [55]. Typical values for C_k and NP of 2 throats/pore and 1000 pores/m² were used, respectively [56,57].

Primary injection of CO₂ into the lower reservoir and the associated pressure build-up due to this injection continue uninterrupted regardless of the development of a leak or any remediation efforts tested in the upper aquifer. As will be shown in the subsequent sections, this continued CO₂ injection pressure is required in order to establish a reactive mixing zone sufficient to precipitate substantial quantities of sealant.

3. Results and discussion

Each leak was allowed to develop for 365 days of simulation prior to introducing any hydrodynamic or chemical mitigation measures. These parameters resulted in a variety of initial scenarios ranging from substantial influx and pooling of CO₂ against the upper no-flow boundary of the domain (scenario A), to moderate infiltration that may be barely possible to detect by seismic methods (scenarios B and C), to virtually undetectable presence of CO₂ within the caprock (scenario D). The flux rate of CO₂ out of the top of the caprock defect at 365 days of uninterrupted flow for scenario A is 3.60 g/s. This is the largest flux rate considered in these simulations. Scenario C corresponds to a CO₂ flux rate of 0.56 g/s. The flux rate for scenario B is 0.05 g/s and that for scenario D is 0.02 g/s, both virtually undetectable after 365 days of CO₂ injection. Each of these scenarios will be used as the initial conditions for introduction of an alkaline flood containing a hypothetical sealant from the left boundary.

For the conditions generating the largest CO₂ leak rate (scenario A), amendment of the alkaline flood continues for three consecutive years. Interaction of the alkaline flood with the acidic CO₂ plume results in some enhanced mixing at the pH boundary [58], though this reactive front stabilizes after approximately two years of continuous flooding and forms a fairly stable reactive front thereafter (Fig. 1). At the specified sealant injection rate of 0.047 kg/s, the introduction of this flood pressurizes the overlying aquifer such that CO₂ flux through the top of the caprock defect is reduced from 3.60 to 3.03 g/s (i.e. by 16%). However, the pressure from the underlying CO₂

injection reservoir is still great enough that the shape of this stabilized profile is influenced by the balance between injection of alkaline flood at the left boundary, infiltration of CO₂ from the bottom of the domain at x = 150 m and a quasi-infinite right boundary.

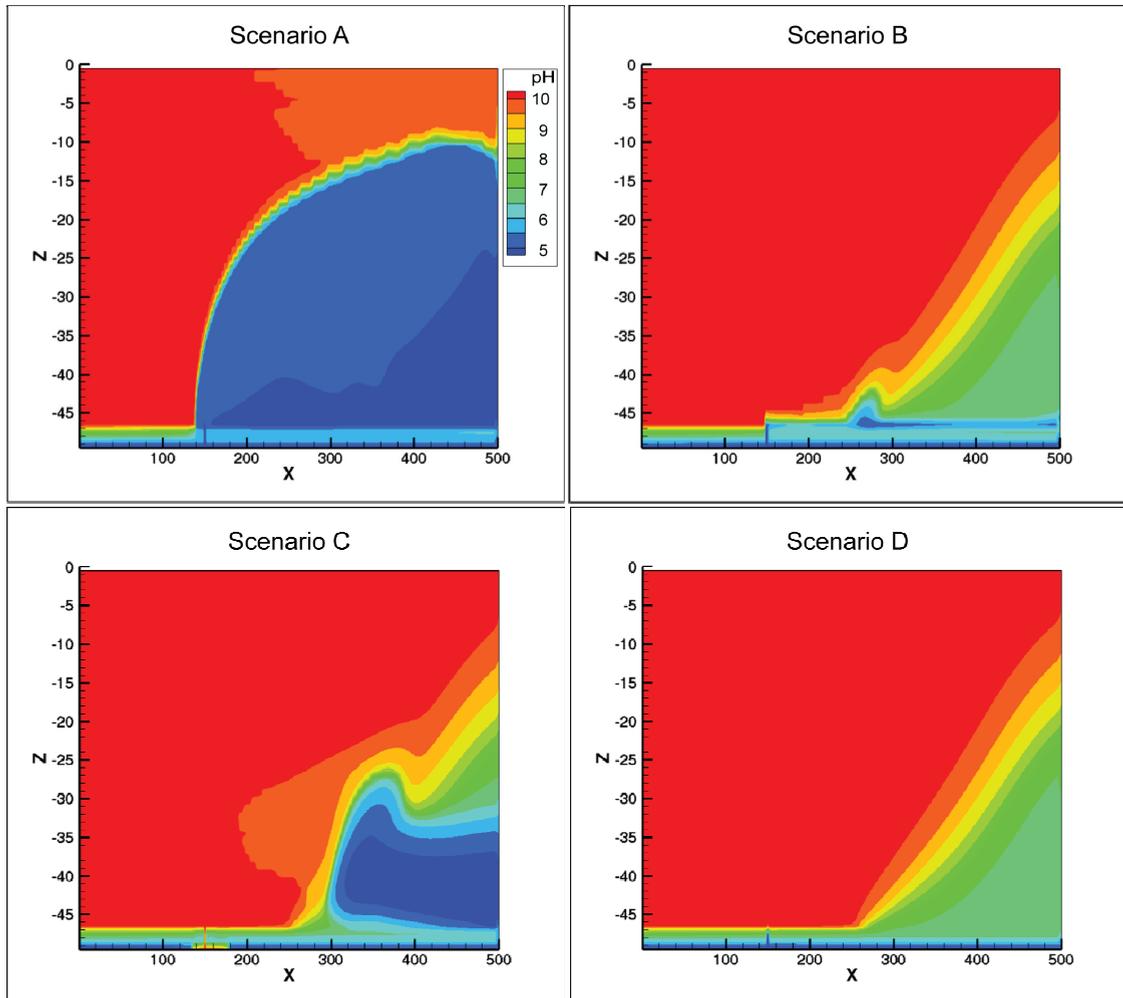


Figure 1: pH of fluid after 3 years of constant sealant amendment from the left boundary. Sealant is formed in the mixing zone between the alkaline flood (pH 10, red) and acidic CO₂ plume (pH 5, blue). All distances reported in meters.

In the case of a high (3 MPa; scenarios A&B) pressure differential between the lower CO₂ reservoir and upper aquifer, a reactive mixing front develops between the alkaline Si-flood and acidic CO₂ plume resulting in the precipitation of large volumes of silicate polymer (ca. 2% of the total volume of solid.) This porosity decrease is associated with a substantial reduction in permeability, as high as 16 orders of magnitude assuming the modified Hagen – Poiseuille porosity – permeability relationship (eq. 4). However, the high injection reservoir pressure supports rapid infiltration of CO₂ into the upper aquifer even during sealant delivery, thus precluding the formation of a coherent barrier. After three consecutive years of flooding, the sealant injection well was shut off and the simulation continued, demonstrating no observable decrease in CO₂ flux rate into the upper aquifer despite substantial accumulation of sealant in the area adjacent to the leak. Thus, for a high pressure differential between the injection reservoir and upper aquifer the accumulation of precipitated sealant may influence the location and flow velocity of CO₂, but will not decrease the loss of CO₂ from the injection reservoir while primary CO₂ delivery is still active.

In contrast, simulations at a lower pressure differential (1 MPa; scenarios C and D) result in a less distinct

mixing zone as a result of the high pressure in the upper aquifer that forces the alkaline, sealant-bearing fluid into the primary CO₂ reservoir. Sealant introduced to this portion of the domain is rapidly precipitated as a result of mixing with the acidic, CO₂-rich plume (eq. 2) and interaction with residual CO₂ trapped within the low-permeability caprock (eq. 3). In contrast to the previous cases, this rapid consumption of dissolved sealant is not easily replenished by incoming alkaline flood, as the flow rate of the alkaline fluid into the primary CO₂ reservoir is very low. Since reactant is not easily supplied to this mixing zone, the total accumulation of solid phase sealant is quite small compared to scenarios A and B. For both scenarios C and D, the minimum permeability in the lower reservoir after 730 days of flooding is only decreased to 85% of the original value. However, this minor decrease occurs in the area immediately adjacent to and within the caprock defect itself, leading to formation of a coherent seal that limits CO₂ migration. After sealant delivery is stopped, the newly emplaced seal reduces the net flux of CO₂ through the defect by 21% of the original value in scenario C and 90% in scenario D. This outcome represents a substantial reduction in the leakage rate of CO₂ while the primary injection reservoir remains active, provided that the pressure differential between the lower CO₂ reservoir and upper aquifer remains small.

4. Summary and conclusions

Emplacing a seal where CO₂ leakage has already occurred is challenging because of multiphase flow dynamics. These results demonstrate that effective delivery of a pH-dependent sealant to a leaking damage zone during active CO₂ injection requires that the pressure buildup during seal emplacement to be comparable to the pressure buildup in the underlying CO₂ reservoir. However, if a sealant with a higher viscosity is able to penetrate the CO₂ plume, this constraint may be relaxed. For a pH-dependent sealant, generating an effective seal requires establishing a mixing zone between the alkaline flood and the acidic CO₂-rich water. Development of the mixing zone is enhanced by providing a constant supply of both fluids to the reaction front, which requires a continued flux of CO₂ during the emplacement process. Shutting off injection prior to sealant emplacement can limit the creation of a mixing zone and hence, limit the establishment of an effective barrier.

These results are predicated on the assumption of a porosity-permeability relationship that achieves large permeability reduction for fairly small changes in mineral volume fraction. If a relationship such as the Kozeny-Carman or cubic law provides a better description of the behaviour observed in a given reservoir, then generation of an effective seal through precipitation of a solid phase at the CO₂-flood boundary will be much harder to achieve. Therefore a fundamental result of this study is the recognition that sealant properties must be developed in conjunction with an accurate understanding of the porosity-permeability relationship of the target system.

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