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FUNDAMENTAL ELEMENTS OF GEOLOGIC CO_2 SEQUESTRATION IN SALINE AQUIFERS

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Introduction

Geologic sequestration represents a promising strategy for isolating CO_2 waste streams from the atmosphere. Successful implementation of this approach hinges on our ability to predict the relative effectiveness of subsurface CO_2 migration and sequestration as a function of key target-formation and cap-rock properties, which will enable us to identify optimal sites and evaluate their long-term isolation performance. Quantifying this functional relationship requires a modeling capability that explicitly couples multiphase flow and kinetically controlled geochemical processes.

We have developed a unique computational package that meets these criteria, and used it to model CO_2 injection at Statoil's North-Sea Sleipner facility, the world's first saline-aquifer storage site. The package integrates a state-of-the-art reactive transport simulator (NUFT[1]) with supporting geochemical software and databases (SUPCRT92[2]). In our Sleipner study[3], we have quantified—for the first time—the influence of intra-aquifer shales and aquifer/cap-rock composition on migration/sequestration balance, sequestration partitioning among hydrodynamic, solubility, and mineral trapping mechanisms, and the isolation performance of shale cap rocks.

Here, we review the fundamental elements of geologic CO_2 sequestration in saline aquifers as revealed from model XSH of our Sleipner study[3]; this model, unlike CSH[3] and DSH[3], does not address the complicating (yet advantageous) presence of intra-aquifer shales.

Reactive Transport Modeling of CO_2 Injection at Sleipner

In the Sleipner field, CO_2-rich natural gas is produced from 3500 m below the seabed. Excess CO_2 is removed from the production stream by amine absorption on the platform, then stripped from the amine and injected—at the rate of one million tons per year since 1996—into a saline aquifer (the Utsira) 2500 m above the hydrocarbon reservoir.[4] The 200-m-thick Utsira is a highly permeable, fluid-saturated sandstone, which is capped by the Nordland Shale. Hydrologic and compositional properties of the Utsira are relatively well constrained, while those of the Nordland Shale are virtually unknown, and must therefore be estimated.[3]

Our reactive transport simulations of CO_2 injection at Sleipner focus on the near-field sequestration environment. The adopted spatial domain extends 600 m horizontally and 250 m vertically; it contains a 200-m-thick saline aquifer (35% porosity, 3-darcy permeability), 25-m-thick shale cap rock (5% porosity, 3-microdarcy permeability), and an overlying 25-m-thick saline aquifer.[3] Pure CO_2 is injected at the rate of 10,000 tons/yr into the basal center of this domain (37°C, 111 bars), which corresponds to a 1-m-thick cross-section though the actual 100-m screen length at Sleipner.[3,4]

Compositionally, the saline aquifers are represented as impure quartz sand (80% quartz, 10% K-feldspar, 5% plag-ab_{80}, 3% muscovite, 2% phlogopite), while the shale cap rock is represented as 60% clay minerals (50% muscovite, 10% Mg-chlorite), 35% quartz, and 5% K-feldspar.[3] Mg end-member components (phlogopite, Mg-chlorite) are used to represent Fe/Mg solid solutions because *in situ* oxidation states are unknown.[3] The saline aquifers and shale are all saturated with an aqueous phase of near-seawater composition.[3,4]

The simulations are carried out for 20 years, with equal-duration prograde (active-injection) and retrograde (post-injection) phases.

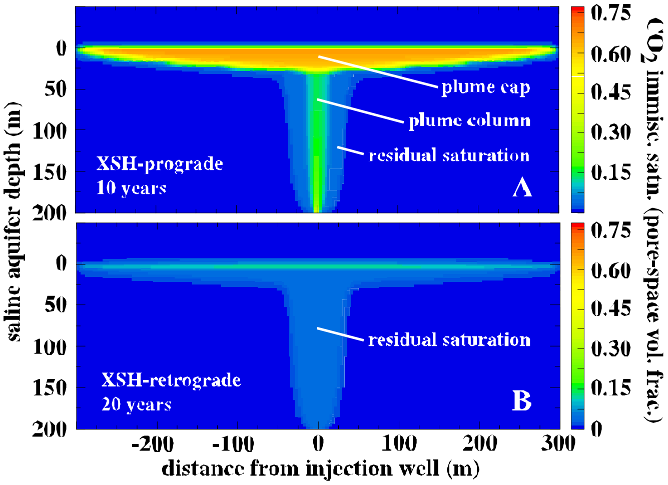

Figure 1. Steady-state configuration of the immiscible CO_2 plume during (A) the prograde phase after 10 years of continuous injection, and (B) the retrograde phase 10 years after injection has ceased.

Modeling Results and Discussion

CO_2 migration/sequestration balance is most conveniently evaluated in terms of contributions from three interdependent yet conceptually distinct processes: CO_2 migration as an immiscible fluid phase, direct interaction of the immiscible plume with formation waters, and indirect plume interaction with formation minerals through the aqueous wetting phase. The first process is directly linked to hydrodynamic trapping, the second to solubility trapping and pH evolution, and the third to mineral trapping.

CO_2 immiscible migration and hydrodynamic trapping. Steady-state configuration of the immiscible CO_2 plume during the prograde phase is realized within one year. In the narrow, sharply delineated plume cap zone, CO_2 immiscible saturation increases from 0.55 at this time to 0.65 at 10 years (Figure 1A). The plume column represents the main conduit of immiscible CO_2 migration, while the residual saturation zone (where immiscible CO_2 is no longer a contiguous migrating phase) marks the wake of initial plume ascent.

In the near-field environment, roughly 85% of injected CO_2 remains and migrates as an immiscible fluid phase ultimately subject to hydrodynamic trapping beneath the cap rock—a very effective seal in this model (Figure 1). The immiscible plume establishes and defines the spatial framework of prograde solubility and mineral trapping. During the retrograde phase, residual CO_2 immiscible saturation (Figure 1B) effectively maintains the prograde extent of solubility trapping and continually enhances that of mineral trapping.

Solubility trapping and pH evolution. As the immiscible plume interacts and equilibrates with saline formation waters, intra-plume aqueous CO_2 concentration (primarily as $CO_2(aq)$ and HCO3-) rapidly achieves the solubility limit, while pH decreases:

$$CO_2(f) + H_2O \leftrightarrow CO_2(aq) + H_2O \leftrightarrow HCO_3^- + H^+ .$$

For the present chemical system and P-T conditions, equilibrium aqueous CO_2 solubility is 1.1-1.2 molal (Figure 2A), accounting for about 15% of injected CO_2. Owing to residual saturation of immiscible CO_2 (Figure 1B), this degree of solubility trapping is virtually constant throughout the prograde and retrograde phases.

The initial pH drop caused by prograde solubility trapping—from 7.1 to 4.5—catalyzes silicate dissolution, which after 20 years has increased pH from 4.5 to 5.3 (Figure 2B). This dissolution hydrolyzes potential carbonate-forming cations (here, primarily Na,

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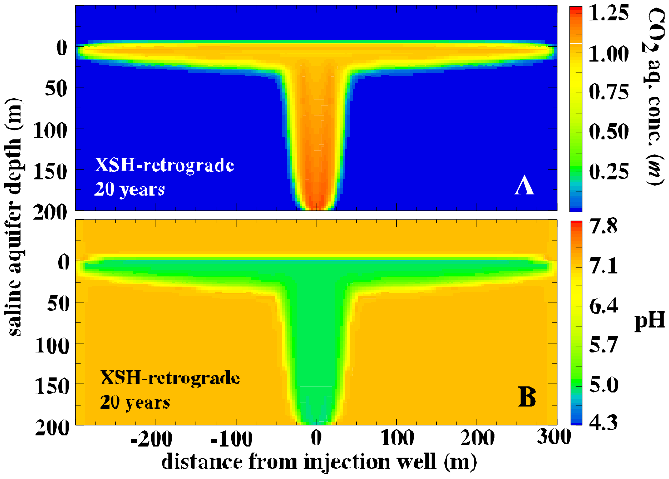

Figure 2. (A) Solubility trapping and (B) pH after 20 years.

Al, and Mg) within the immiscible-plume source region, and thus represents the critical forerunner of all mineral trapping mechanisms.

Mineral trapping. There are four distinct mechanisms whereby CO_2 precipitates as carbonate minerals.

Intra-plume dawsonite cementation (Figure 3A) is catalyzed by high ambient Na^+ concentration, plume-induced CO_2 aqueous solubility, and acid-induced K-feldspar dissolution:

$$\underset{\text{K-feldspar}}{\underline{KAlSi_3O_8}} + Na^+ + CO_2(aq) + H_2O \leftrightarrow \underset{\text{dawsonite}}{\underline{NaAlCO_3(OH)_2}} + 3\,\underset{\text{qtz+chal+crist}}{\underline{SiO_2}} + K^+$$

This kinetic reaction proceeds to the right with an increase in solid-phase volume of 17%; hence, it leads to a slight (0.02%) decrease in intra-plume aquifer porosity over 20 years.[3] Pervasive dawsonite cementation will likely be characteristic of saline aquifer storage in any feldspathic sandstone. In fact, there is a natural analog for this process: widespread dawsonite cement in the Bowen-Gunnedah-Sydney basin of Eastern Australia, which has been interpreted to reflect magmatic CO_2 seepage on a continental scale.[5]

Magnesite rind forms along lateral and upper plume boundaries; genetically distinct, these two processes can be described by:

$$\underline{MgCO_3}\ \text{(magnesite)} + 2\,H^+ \leftrightarrow Mg^{+2} + CO_2(aq) + H_2O\,.$$

As intra-plume formation waters, progressively enriched in Mg^{+2} from phlogopite dissolution, migrate outward across lateral plume boundaries, they traverse steep gradients in $CO_2(aq)$ and pH; the net effect strongly promotes magnesite precipitation (Figure 3B). In the plume cap zone, $CO_2(aq)$ concentration and pH are nearly constant, but aqueous Mg^{+2} concentration increases most rapidly here because formation-water saturation is minimized; this leads to magnesite cementation from the cap-rock interface downward (Figure 3B).

However, magnesite precipitation is most extensive from this interface *upwards* (cf. Figures 3B-C), owing to the relatively high concentration of Mg in clay-rich shales. The coupled reaction is:

$$\underset{\text{K-feldspar}}{\underline{KAlSi_3O_8}} + 2.5\,\underset{\text{Mg-chlorite}}{\underline{Mg_5Al_2Si_3O_{10}(OH)_8}} + 12.5\,CO_2(aq)$$
$$\leftrightarrow$$
$$\underset{\text{muscovite}}{\underline{KAl_3Si_3O_{10}(OH)_2}} + 1.5\,\underset{\text{kaolinite}}{\underline{Al_2Si_2O_5(OH)_4}} + 12.5\,\underset{\text{magnesite}}{\underline{MgCO_3}} + 4.5\,\underset{\text{qtz+chal}}{\underline{SiO_2}} + 6\,H_2O.$$

This kinetic reaction proceeds to the right with an increase in solid-phase volume of 18.5% (magnesite accounting for 47 vol.% of the product assemblage), which after 20 years has reduced porosity and permeability of the 5-m-thick cap-rock base by 8% and 22%.[3]

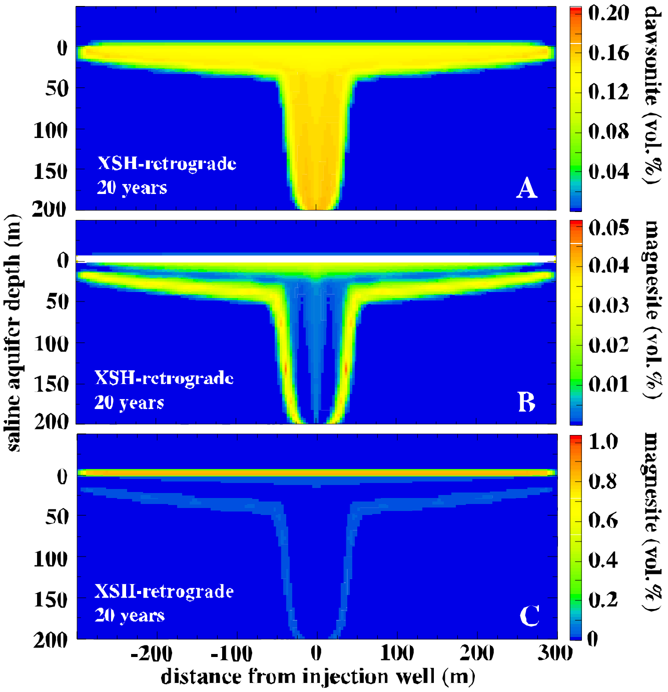

Figure 3. Mineral trapping mechanisms: (A) intra-plume dawsonite cementation, (B) magnesite precipitation—lateral and upper plume boundaries, and (C) magnesite precipitation—shale cap rock.

Conclusions

Geologic CO_2 sequestration in saline aquifers can be subdivided into three fundamental elements: prograde migration of the immiscible plume, direct interaction of the plume with formation waters, and its indirect interaction with formation/cap-rock minerals through the aqueous wetting phase. In the near-field environment of Sleipner-like settings, relative effectiveness of the associated trapping mechanisms on a mass basis is hydrodynamic (85%) >> solubility (15%) >> mineral (<1%).[3]

Although seemingly negligible, mineral trapping has enormous strategic significance: it improves cap-rock integrity and thereby improves containment of the voluminous immiscible plume. Moreover, the prograde extent of mineral trapping is continuously enhanced during the retrograde phase—which spans geologic time scales—by the presence of residual CO_2 immiscible saturation in the aquifer and hydrodynamically-trapped CO_2 beneath the cap rock.[3]

Intra-aquifer shales, solid solutions, and other refinements do not modify the set of fundamental elements reviewed above; they do impose key variations on the style and interaction of these elements.[3]

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