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Chapter 05

Figure 5.1 *Morris et al.* [2016] investigated the interactions between natural fractures and stress barriers. This side view of hydraulic fracture development at (a) 300 and (b) 720 s (colors reflect the time at which that portion of the fracture was opened) suggest that height growth may be encouraged if the hydraulic fracture passes near the tip of a natural fracture (NF2). If the hydraulic fracture passes through the midpoint of the natural fracture, the height growth may even be delayed.

Figure 5.2 *White et al.* [2014] explored a range of fracture/fault reactivation and hydraulic fracture extension scenarios (a) motivated by seismic data, stress data, and surface deformation observations (b). They concluded that the double-lobe surface deformation above the KB-502 well (b) is consistent with a dilation of vertical hydrofractures within the lower portion of the caprock (a).

Figure 5.3 Fracture dissolution simulations carried out over a broad range of Da and Pe . Flow of an undersaturated fluid from bottom to top in each

simulation led to change in fracture aperture, Δb , caused by dissolution of the fracture surfaces. Values of k and $\langle q \rangle$ were varied, but all other parameters including the initial aperture field were identical for each simulation. Each simulation ran until $\langle b \rangle = 2\langle b \rangle_0$. These results show the broad range of plausible dissolution-induced fracture alteration scenarios, which range from very uniform dissolution when reaction kinetics are slow and/or flow rates are high (i.e., large Pe and small $Da \cdot Pe$) to very compact dissolution channels when reaction kinetics are fast and flow rates are low such that local dissolution rates are limited by mass transport rather than local reaction kinetics (i.e., small Pe and large $Da \cdot Pe$). Uniform dissolution may result in fracture closure in fractures subjected to significant normal stress, whereas the formation of dissolution channels is more likely to generate a persistent leakage pathway.

Figure 5.4 A demonstration of the influence of fracture length scale, L , on the formation of dissolution-induced preferential flow paths. Preferential flow paths in the $4 \text{ m} \times 4 \text{ m}$ fracture with $k = 0.8 \cdot 10^{-10} \text{ m/s}$ differ from those in a $1 \text{ m} \times 1 \text{ m}$ portion of the same fracture at the same value of $\langle q \rangle$ and k , but are very similar to those in the $1 \text{ m} \times 1 \text{ m}$ fracture with $k = 3.2 \cdot 10^{-10} \text{ m/s}$. Due to the direct dependence of Da on both k and L , concurrently decreasing L and increasing k leads to no change in Da and very similar dissolution pathways. The scaling behavior of the fracture dissolution process has significant implications when using laboratory-scale observations to infer field-scale fracture alteration.

Figure 6.1 Schematic of multi-scale fracture system in the shale gas reservoir after hydraulic fracturing operations. Natural fracture, microfracture, and hydraulic fractures coexist.

Figure 6.2 2D matrix-fracture system with increasing fracture density. The fracture is represented by lines embedded in the matrix. The fracture density is 0.001, 0.01, 0.1, 0.2, 0.4, and 0.6 from top left to bottom right.

Figure 6.3 Velocity magnitude $|\mathbf{u}| =$

$$\sqrt{u_x^2 + u_y^2}$$

in a matrix-fracture system with fracture density as 0.1 and $k_f/k_m = 10^6$.

Figure 6.4 Relationship between fracture density and effective permeability under different k_f/k_m .

Figure 6.5 3D matrix-fracture systems generated using the DFN.

Figure 6.6 Relationship between fracture density and effective permeability with $k_f/k_m = 10^8$.

Figure 6.7 Fracture propagation process. (a) Model setup for the numerical simulations, (b) experimental results [Carey *et al.*, 2015], and (c) FDEM results for case 1.

Figure 6.8 (a-e) Evolution of the fracture patterns obtained from the FDEM simulation and (f) relationship between fracture density and effective permeability with $k_f/k_m = 10^6$.

Chapter 07

Figure 7.1 Mineral content (wt%) from bulk XRD of core between 1101 and 1225.5 m depth from the Chinchilla 4 well, Surat Basin. According to the

original stratigraphy, cores from 1190 to 1225.5 m are classified as the Precipice Sandstone, and 1179 m and above are classified as the Evergreen Formation. Created based on data from the supplementary material of *Horner et al.* [2014].

Figure 7.2 SEM images of core from the Chinchilla 4 well, Surat Basin. Note the variability in grain size and packing between sections of the Precipice Sandstone reservoir, the Evergreen Formation caprock, and the overlying Hutton Sandstone.

Figure 7.3 Mineralogy of core from the Chinchilla 4 well, Surat Basin, created from data in *Farquhar et al.* [2015]. Minerals labeled D dissolved during experimental scCO₂-water reaction. Dissolution of 1% calcite content in the 1138 m core was also observed (not shown), along with dissolution of trace amounts of fine-grained siderite and ankerite from all cores. Minerals labeled D dissolved and C additionally corroded during experimental scCO₂-SO₂-water reaction based on data from *Pearce et al.* [2015b].

Figure 7.4 SEM images of Evergreen Formation 897.9 m (Chinchilla 4 well) caprock. (a and b) Horizontally extruded mixed ankerite and Fe-Mg chlorite (1), 2 = organic matter/coal, 3 = albite, and 4 = K-feldspar. (c) Ankerite and chlorite in the core before and (d) after CO₂-water reaction. (e) Before and (f) after CO₂-SO₂-water reaction.

Figure 7.5 SEM images of (a-c) Evergreen Formation 1138 m (Chinchilla 4 well) core: Fe-Mg-Ti mica (1), K-feldspar (2), Ca-Fe-phosphate containing Ce and La (3), Fe-Mg chlorite (4), kaolin (5), and Ti oxide on chlorite (6). (d) After CO₂-SO₂-water reaction with core disaggregated and Fe leached from chlorite,

bright Ti oxide is still present. (e) Hutton Sandstone 799 m pre and (f) post CO₂-SO₂-water reaction with calcite cement (7) dissolved revealing clays (8) and gypsum precipitated on K-feldspar surface (9); inset magnified view of gypsum with image width 150 μm.

Figure 7.6 Micro-CT images of sub-plugs of caprock core (Chinchilla 4 well) at 2.2 μm resolution: Evergreen Formation 897.9 m (a) before reaction, (b) after CO₂-water reaction, (c) difference image where dark areas indicate loss of material or X-ray density. Evergreen Formation 1138 m (d) before reaction, (e) after CO₂-water reaction (stabilized with KCl), and (f) difference image.

Figure 7.7 Water chemistry during CO₂-water or SO₂-CO₂-water reaction of Chinchilla 4 well Evergreen Formation cores (E = Evergreen) from two depths with concentrations normalized to 1 g of reacted core for comparison. (a) solution pH during reaction, (b) Fe concentration, (c) Ca concentration, and (d) Al concentration. Time zero represents a N₂-water-rock soak prior to CO₂ injection.

Figure 7.8 Mineralogy of sandstone (628 m) and siltstone (626 m top and bottom section) cores from the Stuttgart Formation, North German Basin, Germany. Where chlorite = both chlorite and biotite with an Fe (Mg) composition, plagioclase is albite and albite-anorthite, and illite is illite-muscovite. Minerals labeled D were directly observed to dissolve during experimental CO₂-brine reaction. Mineralogy of caprock cores from the Gryfice Beds, Chabowo anticline, Poland, are also shown.

Figure 7.9 Mineralogy of caprock cores from the Chinle Formation outcrop, Utah, USA; the Tournasin

units, Krechba Field site (In Salah), Algeria; the Adventdalen Group; and the Jannusfillet Subgroup, Central Tertiary Basin, Norway. Minerals labeled D were directly observed to dissolve during experimental CO₂-brine reaction. P indicates minerals which also precipitated. Note that smectite precipitation was additionally reported after reaction of the Adventdalen Group.

Figure 7.10 (a) Mineralogy of marl caprock from the Camino Formation outcrop, Hontomin, Spain, where chlorite is clinocllore and the plagioclase is albite. Minerals labeled D were observed to dissolve during experimental CO₂-sulfate brine reaction via SEM and water chemistry. P indicates gypsum also precipitated in reactions with sulfate-rich brine. (b and c) Water chemistry during brine and CO₂-brine reaction of Three Fingers evaporite core; 0 days denotes when CO₂ was added.

Chapter 08

Figure 8.1 CO₂ transport mechanisms with increasing transport rate to the right and schematic illustration of fluid-rock interaction mechanism and their implications for transport of CO₂ through low-permeable clay-rich units.

Figure 8.2 Field example of fluid-rock interaction showing fracture parallel bleaching in permeable siltstone unit within the Entrada Formation, Utah. The bleached zone is found as a 1-10 cm thick zone along the fracture.

Figure 8.3 Solubility of H₂O in CO₂ as a function of temperature (0-100°C) and pressure. (a) Pressure

range of 0–300 bar. (b) Details for pressure range of 0–10 bar, relevant during upward migration.

Figure 8.4 Simulated 1D diffusion of CO₂ over 50 million years varying the effective diffusion coefficient (see Eq. 8.2). The diffusion coefficient of CO₂ penetrating into the Kimmeridge Clay (12 m over 70–80 million years) can be approximated to be 10^{–14} m²/s based on this model.

Figure 8.5 Difference between diffuse (a) and sharp (b) reaction fronts.

Figure 8.6 Pore-scale visualization of salt precipitation in the preferential pathway (fracture) of the heterogeneous microchip. A thick film of brine remains after CO₂ invasion at 5 s after injection. After 50 min, this film evaporates and the drying front shapes a meniscus at the interface between matrix and fracture. After 75 min, aggregation growth starts and occupies the fractures.

Chapter 09

Figure 9.1 (a) Map showing the location of the Gibson Dam site in Montana (top) and a satellite view of the outcrop (bottom). In (b) the actual sample of Duperow dolomite and a selection of micro-cores both whole and split in halves are displayed.

Figure 9.2 Schematics of the HP plumbing system used during the in situ SXR-micro-CT experiment.

Figure 9.3 Curves from ICP-MS plotting the concentrations of the main cation species in the effluent.

Figure 9.4 Panel (a) shows the volume cut images of the dissolution sequence (reaction times at the top of the figures). The sample is vertically cut