

Reactive transport modeling of effects of CO₂ injection with variable impurities on deep saline reservoirs

Jolanta Kazmierczak¹, Knud Dideriksen¹

¹Geological Survey of Denmark and Greenland (GEUS)

Introduction and objective

CO₂ streams from the emitters contain impurities that upon injection into deep saline reservoirs may cause physical and chemical changes in the formation properties, and thus influence CO₂ injection and geological storage capacity and dynamics.

Interactions between CO₂ stream with oxidizing mix of impurities and potential host reservoirs were assessed to support the site selection and planning of storage strategies in Denmark.

Methods

2D reactive transport modelling in ECO2N and TOUGHREACT.

Injection of CO₂ stream with SO₂, NO₂ and O₂ (0.00007, 0.0001 and 0.0067 mole fraction, respectively) into saline reservoirs for 0.5 year. Equilibrium between gas and aqueous phase (Table 1). Kinetic interactions between aqueous species (Table 2).

Table 1. Log₁₀K_H for oxidizing impurities.

Reaction	Log ₁₀ K _H							
	0°C	25°C	60°C	100°C	150°C	200°C	250°C	300°C
O ₂ (g) → O ₂ (aq)	-2.66	-2.90	-3.06	-3.11	-3.04	-2.87	-2.65	-2.35
SO ₂ (g) → SO ₂ (aq)	0.65	0.24	-0.26	-0.61	-0.85	-0.97	-1.01	-0.96
NO ₂ (g) → NO ₂ (aq)	-1.59	-1.91	-2.28	-2.62	-2.95	-3.21	-3.42	-3.59

Mineralogy: (1) inert system, (2) quartz reservoir with a small fraction of calcite, K-feldspar, siderite and oligoclase, (3) reservoir with abundance of iron minerals (glauconite, siderite). Kinetics: glauconite, K-feldspar, oligoclase. Remaining minerals modelled at equilibrium.

Table 2. Reaction rates and power terms for interactions between oxidizing mixture of impurities and water.

Reaction	Rate [mol L ⁻¹ s ⁻¹]	Power terms
SO ₂ (aq) + H ₂ O + 0.5 O ₂ (aq) → SO ₄ ²⁻ + 2 H ⁺	2.7 × 10 ⁶	[SO ₂ (aq)] ¹
SO ₂ (aq) + 2 NO ₂ (aq) + H ₂ O → SO ₄ ²⁻ + 2 H ⁺ + 2 NO ₂	1.24 × 10 ⁷	[NO ₂ (aq)] ¹ [SO ₂ (aq)] ¹
2 SO ₂ (aq) + 2 NO ₂ + H ₂ O → 2 SO ₄ ²⁻ + 2 H ⁺ + N ₂ O	142	[H ⁺] ^{0.5} [NO ₂] ¹ [SO ₂ (aq)] ¹
2 NO ₂ (aq) + H ₂ O → NO ₂ ⁻ + NO ₃ ⁻ + 2 H ⁺	8.4 × 10 ⁷	[NO ₂ (aq)] ²

Results – pH and mineralogy

After 0.5 yr of the injection the gas mixture migrated up to 500 m from the injection well into the reservoir (Figure 1).

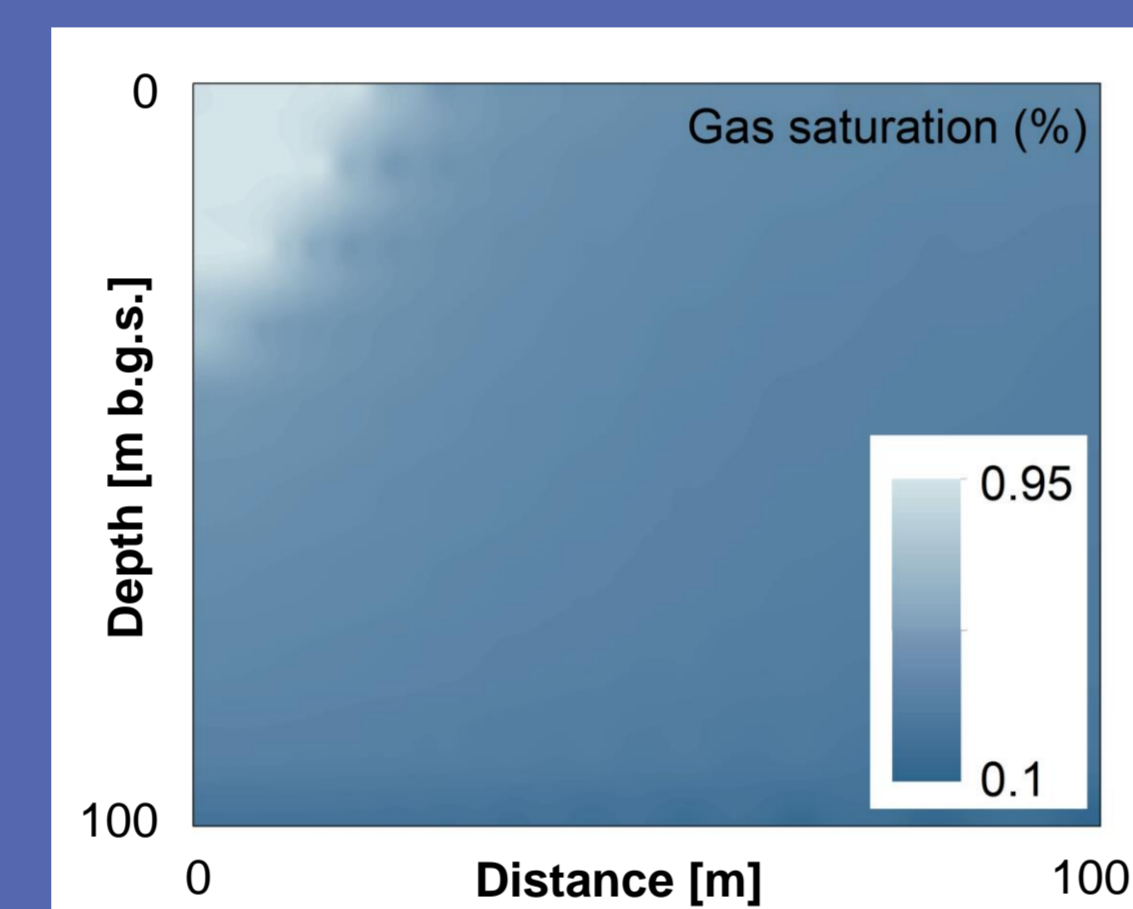


Figure 1. Gas saturation in the reservoir after 0.5 yr of CO₂ injection with variable impurities.

The most severe acidification of the brine was modelled in the inert system. Dissolution of the minerals effectively buffers pH (Figure 2).

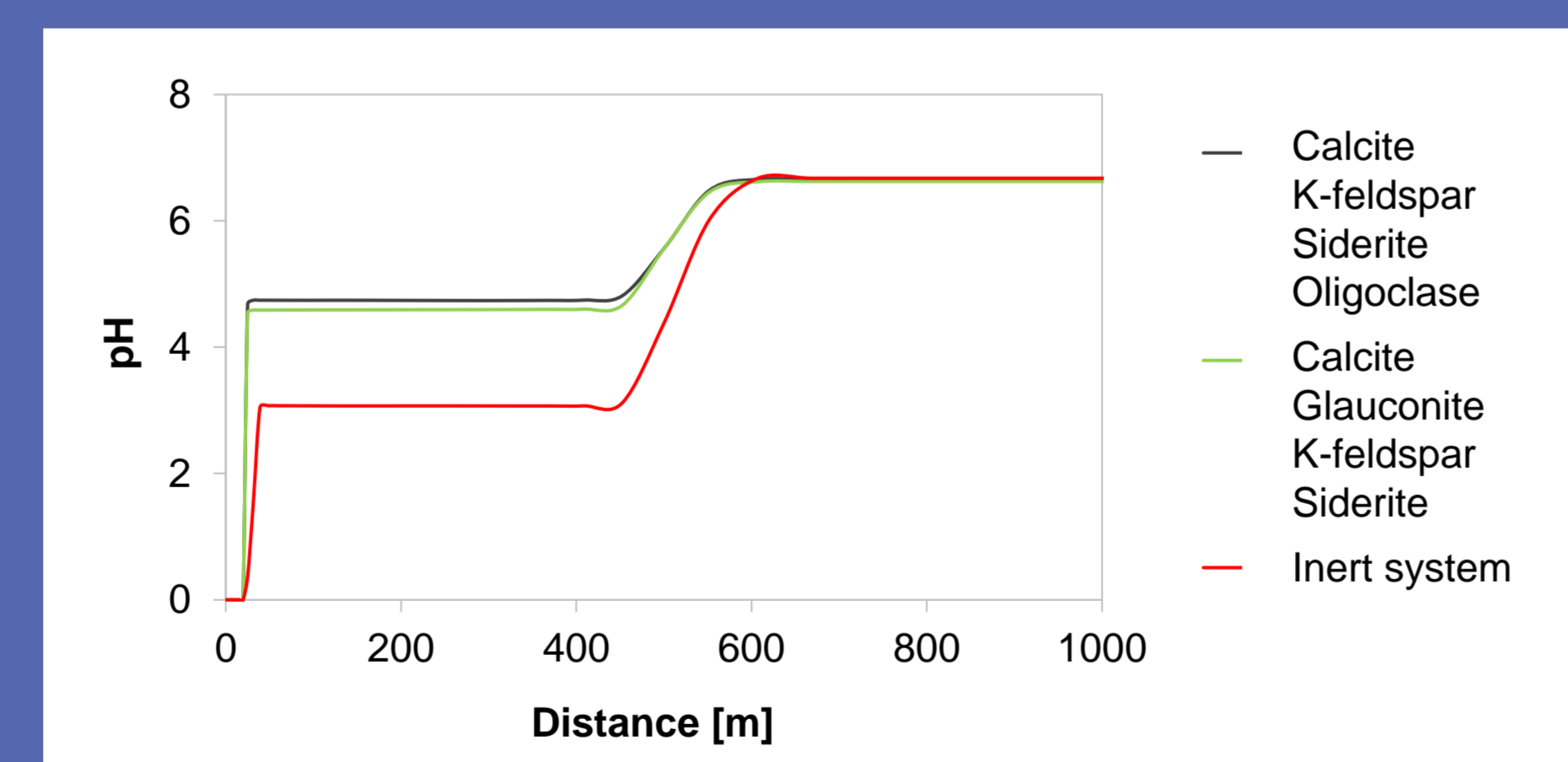


Figure 2. Modelled distribution of pH for the first 1000 m from the injection well after 0.5 yr of CO₂ injection with variable impurities.

Dissolved minerals: calcite, glauconite, K-feldspar, siderite, oligoclase.

Precipitated minerals: anhydrite (upon presence of calcite dissolution), hematite.

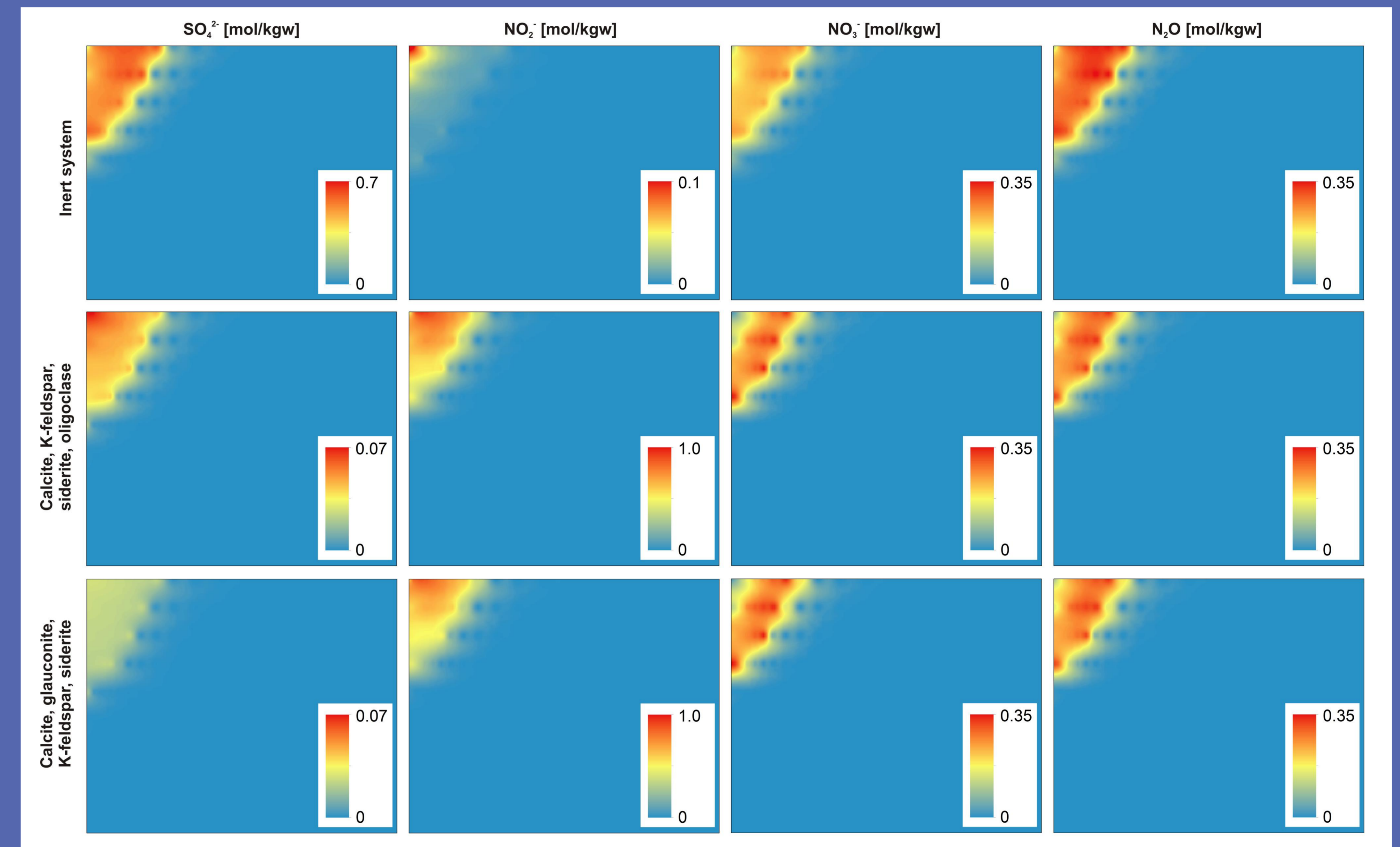
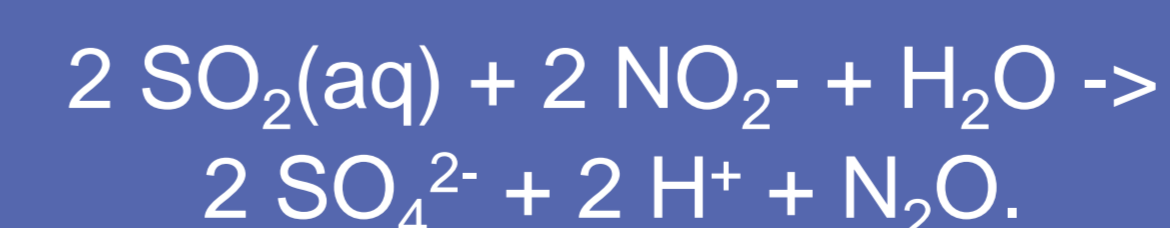


Figure 3. Modelled spatial distribution of SO₄²⁻, NO₂⁻, NO₃⁻ and N₂O in the reservoir after 0.5 yr of CO₂ injection with oxidizing mixture of impurities. For horizontal and vertical scale see Figure 1.

Results – products of the kinetic reactions

Brine chemistry was altered, especially in the inert system. SO₄²⁻ and NO₃⁻ accumulated at the boundary between very high gas saturation and mixed saturation, in the vicinity of the injection well (Figure 3).

When minerals were present, concentration of NO₂⁻ increased at the expense of SO₄²⁻ due to the pH dependence of the reaction:



Some of the SO₄²⁻ precipitated as anhydrite.

Conclusion and perspectives

The acidification from impurities upon calcite presence will not pose a critical problem for the durability of infrastructure or induce reactions that cause deterioration of the formation strength.

The impact of impurities on the reservoir properties could scale with the amount of impurities injected, or different injection strategies.

Future work, uncertainties and room for the improvement: the impurities reaction kinetics in the diffusive regime, reduction of N species by Fe²⁺, application of Pitzer model for activity calculations.