

Potential environmental issues of CO₂ storage in saline aquifers: Geochemical results from the Frio Brine pilot tests, Texas, USA

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Deep saline aquifers in sedimentary basins provide advantageous locations close to major anthropogenic sources of CO₂ and large potential capacity for the storage of huge volumes of this greenhouse gas. To investigate the potential for the long-term storage of CO₂ in such aquifers, 1600 t and 300 t of CO₂ were injected, respectively, into the "C" and "Blue" sandstone sections of the Frio Formation, a regional reservoir in the U.S. Gulf Coast. Fluid samples obtained before CO₂ injection from the injection well and an observation well 30 m updip showed a Na-Ca-Cl-type brine with ~100,000 mg/L TDS at saturation with CH₄ at reservoir conditions, but CO₂ was low at 0.3% of total gas. Following CO₂ breakthrough, ~50 h after injection, samples showed sharp drops in pH (from 6.5 to as low as 3.7 with in-line probe), major increases in alkalinity (from 100 to up to 3200 mg/L as HCO₃) and Fe⁺⁺ (from 30 to 1200 mg/L) and significant shifts in the isotopic compositions of H₂O, Sr, DIC, and CH₄. Geochemical modeling of these data indicates rapid dissolution of minerals, especially calcite and Fe-oxyhydroxides caused by low pH values (~3.0 initially) of the brine in contact with the injected supercritical CO₂.

These geochemical parameters, together with perfluorocarbons (PFTs) and other tracer gases, proved powerful tools for tracking the migration of the injected CO₂ in the injection sandstones and into the overlying Frio "B", composed of a 4-m-thick sandstone bed and separated from the "C" by ~15 m of shale and siltstone beds. Data on brine and gas compositions of samples obtained from the Frio "B" 6 mo after injection show significant CO₂ (2.9 % compared with 0.3% CO₂ in gas) migration into the overlying "B" sandstone. Except for two PFT tracer gases, which could be explained by desorption, results of samples collected 15 months after injection show no additional CO₂ migration into the "B" sandstone. The presence of injected CO₂ in Frio "B" has important environmental implications as it shows initial leakage through the remedial cement behind the well casing or migration through the shale and siltstone beds. Environmental impacts could be major if large volumes of buoyant and reactive CO₂ and/or brine with mobilized metals and organics migrated into overlying potable groundwater resources. Sampling and geochemical analyses of fluids in deep monitoring zones together with geophysical imaging, if properly carried out, are potential early detection methodologies that could trigger remediation action should leakage of CO₂ and/or brine take place.

Hydrochemical and isotopical tracers in groundwaters from coastal zone of the Primorye, Far East of Russia

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The deep saline and brackish waters in coastal zone of the Primorye region have been studied in this investigation. Razdol'noe manifestation of deep brackish waters is located in coastal zone of the Primorye region (Far East of Russia) and it was discovered with drilling during geothermal exploration in 1992. Wells are situated in the mouth of Razdol'naya River, about 25 km from seashore. Wells disclose two different types of cold (13°C) waters: Ca-Na-Cl and Na-HCO₃.

Aquifer with Ca-Na-Cl type water occurs in Miocene sedimentary rocks at 30-130 m depth and has TDS 4.5–13.7 g/l. Ratio of major ions Ca/Mg (1.3); Ca/SO₄ (2.1) and Na/Cl (0.4), Cl/SO₄ (0.98) are close to seawater ratios. Aquifer with Na-HCO₃ type water occurs in Mesozoic sedimentary rocks at 130-500 m depth, has lower TDS - 2.5–6.0 g/l, and is being used by local spa and bottled as well. Numerous tectonic fractures are spread across the study area and located under the cap of the Miocene – Quaternary sediments in southeast and east trends. The width of the fault zone is not less than 100-150 m.

Na-HCO₃ water has prominent hydraulic continuity with upper saline water aquifer, and is enriched by B (9.37 mg/l), F (6.00 mg/l), Li (up to 1.50 mg/l), Sr (up to 0.7 mg/l), Br (0.25 mg/l) and has low contents of I (0.002). Ratio of Ca/Mg is 1.1; Ca/SO₄ –57.5; Na/Cl –10.1 and Cl/Br is 364.2 (much higher than in seawater). Positive correlations between Sr and Ca, Na, Mg, Cl, Fe and B (r=1.00); Ca-Mg (r=0.99), SiO₂-Al (r=1.00), K-Cl (r=0.81) and negative correlation between SiO₂ and major cations (Ca, Na, K) and F (r=1.0) are observed for both types of water. δ¹⁸O and δ²H isotopic ratios show that brackish water has a meteoric origin. The main recharge zone of this aquifer occurs in the north where the sediment complex outcrops.

Received data indicate that saline waters are result of mixing of ancient seawater with infiltrate waters and brackish water has a meteoric origin and mineralization is forming as a result of water-rock interaction. Mass balance calculation and bedrock investigations proves that the albite dissolution, with or without deep-seated mantle origin of CO₂, is a dominant factor controlling the chemical composition of groundwater.