

## **Iron isotopes used to investigate water-rock interactions and well-pipe corrosion as sources of dissolved Fe in brine from CO<sub>2</sub> storage sites**

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### **Abstract**

The concentrations of dissolved Fe in oil-field waters are relatively low, generally in the order of 10-100 mg/L, but may reach values close to 500 mg/L in a few metal-rich brine localities. Much higher concentrations of Fe (up to 1200 mg/L as Fe<sup>++</sup>) were obtained in brines collected from two wells from the Frio I and II Brine Pilot tests carried out during 2004-2008 from a site located within the South Liberty oil field, near Dayton, Texas. More than 200 brine and gas samples were collected from these tests; some before CO<sub>2</sub> injection for baseline geochemistry, the bulk of them were obtained from an observation well located 30 m up dip of the injection well following CO<sub>2</sub> injection into the Frio "C" Formation and the Frio Blue Sandstone at a depth of 1500 m and 1530 m, respectively. The samples were subjected to detailed organic and inorganic chemical and isotope analyses of brine, associated gases, and added tracers. Published results show major changes in chemical and isotopic compositions of formation water, including a dramatic drop in calculated brine pH, (initially from 6.3 to 3.0) and major increases in alkalinity (from 100 to 3000 mg/L as HCO<sub>3</sub>); results also show mobilization of metals, including Fe (from 30 to 1200 mg/L), Mn and Pb, and organic compounds (DOC from 5 to 700 mg/L), including BTEX, PAHs, and phenols following CO<sub>2</sub> injection (Kharaka et al. 2009).

To investigate the source of high Fe concentrations, the  $\delta^{56}\text{Fe}$  values for 13 selected brine samples from Frio II test were determined and compared with three values obtained from complete dissolution of pieces of carbon steel tubing used in the wells at this site. The steel pipes had  $\delta^{56}\text{Fe}$  values of  $0 \pm 0.5\%$ , whereas brine samples before CO<sub>2</sub> injection had  $\delta^{56}\text{Fe}$  values of  $-2.0 \pm 0.5\%$ . Brine samples following CO<sub>2</sub> injection have  $\delta^{56}\text{Fe}$  values that fall between those of the steel pipe and brine before CO<sub>2</sub> injection. The isotope results show that up to 100% of the dissolved Fe measured in these samples originated from the corrosion of well pipe. Geochemical modeling and other chemical data support results of Fe isotopes that both the corrosion of well pipe and dissolution of Fe-oxyhydroxides contribute to the very high Fe concentrations obtained following CO<sub>2</sub> injection. Iron isotopes could prove useful not only in investigating the geochemistry of Fe but also in the study of well-pipe corrosion in oil and gas fields, a topic of high economic importance to the petroleum industry.

### **Introduction**

The concentrations of dissolved Fe in oil-field waters are relatively low, generally in the order of 10-100 mg/L, but may reach values close to 500 mg/L as reported by Kharaka et al. (1987) in metal-rich brines from the central Mississippi Salt Dome Basin, USA. Even higher concentrations of Fe (up to 1200 mg/L as Fe<sup>++</sup>) were obtained in brines collected from the Frio I and II Brine Pilot tests, where CO<sub>2</sub> injection was carried out during 2004-2008. The Frio Brine site was located within the South Liberty oil field, near Dayton, Texas. Wells in this field were drilled in the 1950s, with production from the Eocene Yegua Formation at depths of ~2900 m. The Oligocene Frio Formation is shallower and has a dip of ~16° to the south; it comprises several reworked fluvial sandstone and siltstone beds that are separated by transgressive marine shale. The sandstones are generally subarkosic to arkosic, fine-grained, moderately sorted quartz and feldspar sandstone, with minor amounts of illite/smectite, calcite, pyrite and iron oxyhydroxides (Hovorka

et al., 2006). The sandstones have high mean porosity that exceeds 30% and very high permeability of 2–3 Darcies.

The Frio Brine pilot was a multi-laboratory field study, funded by US DOE, to investigate the potential for geologic storage of CO<sub>2</sub> in saline aquifers and to develop geological, geochemical and geophysical tools, and multi-phase simulation programs to track the injected CO<sub>2</sub> and predict its interactions with reservoir brine and minerals (Benson et al., 2005; Hovorka et al., 2006; Xu et al., 2010; Daley et al., 2011). For Frio-I, approximately 1600 tons of CO<sub>2</sub> were injected during October 2004 into a 24-m thick “C” sandstone of the Oligocene Frio Formation (Hovorka et al., 2006). Using a variety of tools, fluid samples were obtained before CO<sub>2</sub> injection for baseline geochemical characterization, during the CO<sub>2</sub> injection to track its breakthrough into the observation well, and after injection to investigate changes in fluid composition and leakage into the overlying “B” sandstone. New geophysical (Daley et al., 2011) and geochemical tools were deployed and additional detailed tests were carried out during the Frio-II Brine test (September, 2006 to October 2008), where ~300 tons of CO<sub>2</sub> were injected into a 17-m thick Frio “Blue” Sandstone, located ~30 m below the Frio “C”. Geochemical tools and methods deployed for Frio-II, included online pH, electrical conductance (EC) and temperature probes, field determinations of Fe<sup>2+</sup> and Fe<sup>3+</sup> and sample collection and analyses for a large number of metals using ICP-MS, as well as organic compounds using IC and other methods discussed in Kharaka et al., 2009.

More than 200 brine and gas samples were collected from these tests; some before CO<sub>2</sub> injection for baseline geochemistry, the bulk of them were obtained from an observation well located 30 m up dip of the injection well following CO<sub>2</sub> injection into the Frio “C” Formation and the Frio Blue Sandstone at a depth of 1500 m and 1530 m, respectively. The samples were subjected to detailed organic and inorganic chemical and isotope analyses of brine, associated gases, and added tracers. Results show major changes in chemical and isotopic compositions of formation water, including a dramatic drop in calculated brine pH, (initially from 6.3 to 3.0) and major increases in alkalinity (from 100 to 3000 mg/L as HCO<sub>3</sub>); results also show mobilization of metals, including Fe (from 30 to 1200 mg/L), Mn and Pb, and organic compounds (DOC from 5 to 700 mg/L), including BTEX, PAHs, and phenols following CO<sub>2</sub> injection (Kharaka et al. 2009).

To investigate the source of high Fe concentrations obtained, the δ<sup>56</sup>Fe values for 13 selected brine samples from Frio II test were determined by methods described in Bullen and Eisenhauer (2009). The δ<sup>56</sup>Fe values for three pieces of carbon steel tubing used in the wells at this site were also determined following complete dissolution of the pieces in Aqua Regia and separation of Fe using ion exchange resins. Results of Fe isotopes show that both the corrosion of well pipe and dissolution of natural Fe-oxyhydroxides contributed to the very high Fe concentrations obtained following CO<sub>2</sub> injection.

## Results and discussion

Results of chemical analyses of samples collected prior to CO<sub>2</sub> injection show that the Frio brine is a Na-Ca-Cl type water, with a salinity of ~93,000 mg/L TDS, with relatively high concentrations of Mg and Ba, but low values for SO<sub>4</sub>, HCO<sub>3</sub>, DOC and organic acid anions. The high salinity and the low Br/Cl ratio (0.0013) relative to sea water indicate dissolution of halite from the nearby salt dome (e.g., Kharaka and Hanor, 2014). The brine has 40–45 mM dissolved CH<sub>4</sub>, which is close to saturation at reservoir conditions (60 °C and 150 bar), and CH<sub>4</sub> comprises ~95% of total gas, but the CO<sub>2</sub> content is low at ~0.3% (Kharaka et al., 2006; 2009).

On-site measurements of EC on samples obtained after CO<sub>2</sub> reached the observation well, exhibited only a small increase from a pre-injection value of ~120 mS/cm at ~22°C. However, there were major changes in some chemical parameters, including a sharp drop in pH, from 6.5 to 5.7 (measured at surface conditions), and large increases in alkalinity, from 100 to 3000 mg/L as HCO<sub>3</sub><sup>-</sup> (Kharaka et al., 2006). Additionally, laboratory determinations showed major increases in

dissolved Fe (from 30 to 1200 mg/L) and Mn, and significant increases in the concentration of Ca. On-site analysis of gas samples obtained from the U-tube system (Freifeld et al., 2005) also showed CO<sub>2</sub> concentrations increasing from 0.3% to 3.6% and then quickly to 97% of total gas.

Results of geochemical modeling, using updated SOLMINEQ (Kharaka et al., 1988) indicate that the Frio brine in contact with the supercritical CO<sub>2</sub> would have a pH of ~3 at subsurface conditions, and this low pH causes the brine to become highly undersaturated with respect to carbonate, aluminosilicate and most other minerals present in the Frio Formation. Because mineral dissolution rates are generally higher by orders of magnitude at such low pH values, the observed increases in concentrations of HCO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup> likely result from the rapid dissolution of calcite via the reaction:

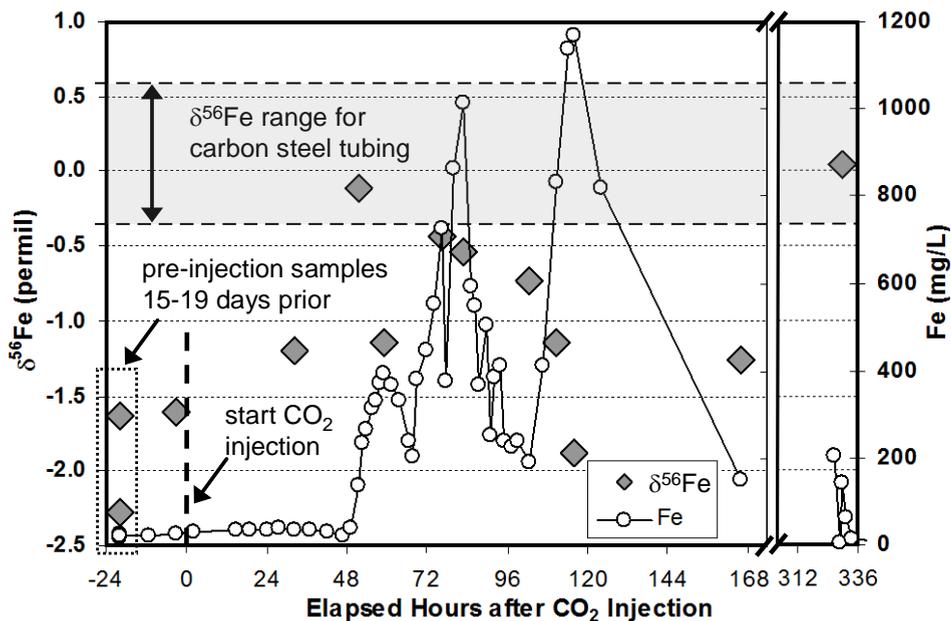
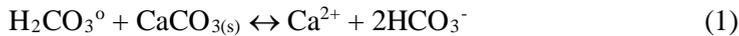
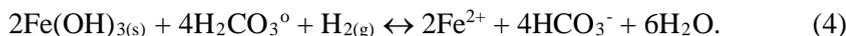
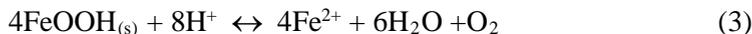
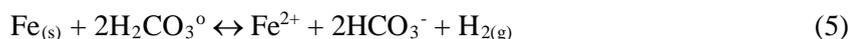


Fig. 1- The concentrations of Fe (o) and  $\delta^{56}\text{Fe}$  values (♦) for selected brine samples from Frio II. Samples with high Fe values following CO<sub>2</sub> injection have  $\delta^{56}\text{Fe}$  values that fall between those of the carbon steel tubing and preinjection brine, indicating a mixed origin for dissolved Fe.

The large increases observed in the concentrations of dissolved Fe could result from dissolution of one or more of the Fe-bearing minerals present in the Frio sandstone depicted in equations 2-4. No siderite was observed in the retrieved core, but Fe increases could result from dissolution of the observed iron oxyhydroxides depicted in equations (3-4) (Hovorka et al., 2006).



However, some of the increase in dissolved Fe and equivalent bicarbonate could also result from corrosion of pipe and well casing that contact the produced low pH brine (Kharaka et al., 2009; Hitchon, 2000), as indicated by the redox-sensitive reaction:



Corrosion is a natural potential hazard associated with oil and gas production and transportation. The inherent corrosivity of the aqueous phase is strongly dependent on CO<sub>2</sub> partial pressure that controls the water pH; it is also dependent on temperature, H<sub>2</sub>S concentration and total salt content (Hitchon, 2000).

Recent advances in instrumentation and technique in both thermal ionization mass spectrometry (TIMS) and multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) have greatly improved our ability to use stable isotopes of Fe and other metals as tracers of metal sources and processes involving metals in laboratory and field-based studies (Dauphas and Rauxel, 2006; Bullen and Eisenhauer, 2009).

The concentrations of Fe measured in all the samples obtained from the Frio II test, together with the  $\delta^{56}\text{Fe}$  values for 13 selected brine samples from that test using TIMS are shown in Figure 1. The three steel-pipe pieces had  $\delta^{56}\text{Fe}$  values of  $0 \pm 0.5\%$ , whereas brine samples before CO<sub>2</sub> injection had  $\delta^{56}\text{Fe}$  values of  $2.0 \pm 0.5\%$ . Brine samples following CO<sub>2</sub> injection have  $\delta^{56}\text{Fe}$  values that fall between those of the steel pipe and brine before CO<sub>2</sub> injection. The isotope results, using first order mixing, show that 0-100% of the dissolved Fe measured in these samples originated from the corrosion of well pipe. Geochemical modeling and other chemical data support results of Fe isotopes that both the corrosion of well pipe and dissolution of Fe-oxyhydroxides contribute to the very high Fe concentrations obtained following CO<sub>2</sub> injection. More data are required from field and laboratory experiments, but Fe isotopes could prove useful not only in investigating the geochemistry of Fe but also in the study of well-pipe corrosion in oil and gas fields, a topic of great economic importance to the petroleum industry.

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