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Water Rock Interaction [WRI 14]**Kinetic rate of iron release during artificial CO₂ injection in a shallow aquifer: preliminary results**J. Rillard ^{a,b*}, P. Gombert ^b, P. Toulhoat ^b, P. Zuddas ^{a,c}^a Earth Sciences Department UMR CNRS 5276 University of Lyon 1, Villeurbanne, FRANCE^b INERIS French National Institut of Environmental and Industrial Risk Survey, Underground Risk Division, Verneuil en Hallate, FRANCE^c University Pierre and Marie Curie Paris-Sorbonne, ISTEP, Paris, FRANCE**Abstract**

We performed an injection of CO₂-saturated water in a shallow aquifer following a "push-pull" test protocol. A specific protocol was designed to measure *in situ* fluid pH and redox potential with careful sampling. We found increases of dissolved calcium, magnesium, alkalinity, iron and manganese, and other trace elements. Concentrations of Fe resulting from reactivity were estimated using measured concentrations of Fe corrected by a calculated fluid dynamics coefficient. Thermodynamic equilibrium calculations suggested that ferrihydrite Fe(OH)₃ dissolution is the main source of iron release. The kinetic rate of Fe(OH)₃ dissolution estimated by a surface protonation model indicates that the reaction order is two. Since laboratory experimental results show a reaction order of zero, we propose that the mechanism of ferrihydrite dissolution proceeds by a more complex mechanism under natural conditions.

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Keywords: CO₂-water-rock interaction, dissolved metals, field experiment, kinetic rate of dissolution.**1. Introduction**

Metals remobilization in high CO₂-water systems is of primary importance in several environmental issues such as Carbon Capture and Storage and storage of waste in underground conditions. Previous investigations indicated that injection of CO₂ into aquifers induces an increasing of dissolved heavy metals and organic compounds with perturbation of the groundwater composition [1-3].

We performed a field experiment in carbonate sandstone aquifer naturally rich in metal oxides, situated in the south of France. This experiment was performed specifically for studying the behavior of major

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cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) anions (SO_4^{2-} , Cl^- , F^-), alkalinity, divalent metal species (Fe^{2+} , Mn^{2+}), trace metals and the pH and redox evolution. A strong effort was made to collect representative results and data of field condition.

2. Material and methods

The experiment consisted on injection of CO_2 -saturated water and extraction of the solution/groundwater mixture following a push pull test protocol. A volume of 3 m^3 of water saturated in CO_2 was injected into an isolated fractured zone at 56 m depth. A time laps of 80 h was waited before re-pumping the mixture of injected solution/aquifer water. The extracting phase consisted of 72 h of continuous pumping. A specific packer system was used to isolate the injection zone from the surrounding water venues. An original protocol allowed *in situ* measurement of pH, Redox potential and temperature of fluid during the experiment. Injection, extraction and sampling line was equipped with inert stainless and plastic materials to minimize the risk of sampling contamination. Measurements at the well head were carried out under a closed glove box filled up by inert nitrogen gas. Total reduced iron and alkalinity were measured on the field by spectrophotometer and Gran titration method, respectively. Samples were analyzed in laboratory for major cation, anion species and trace element concentration.

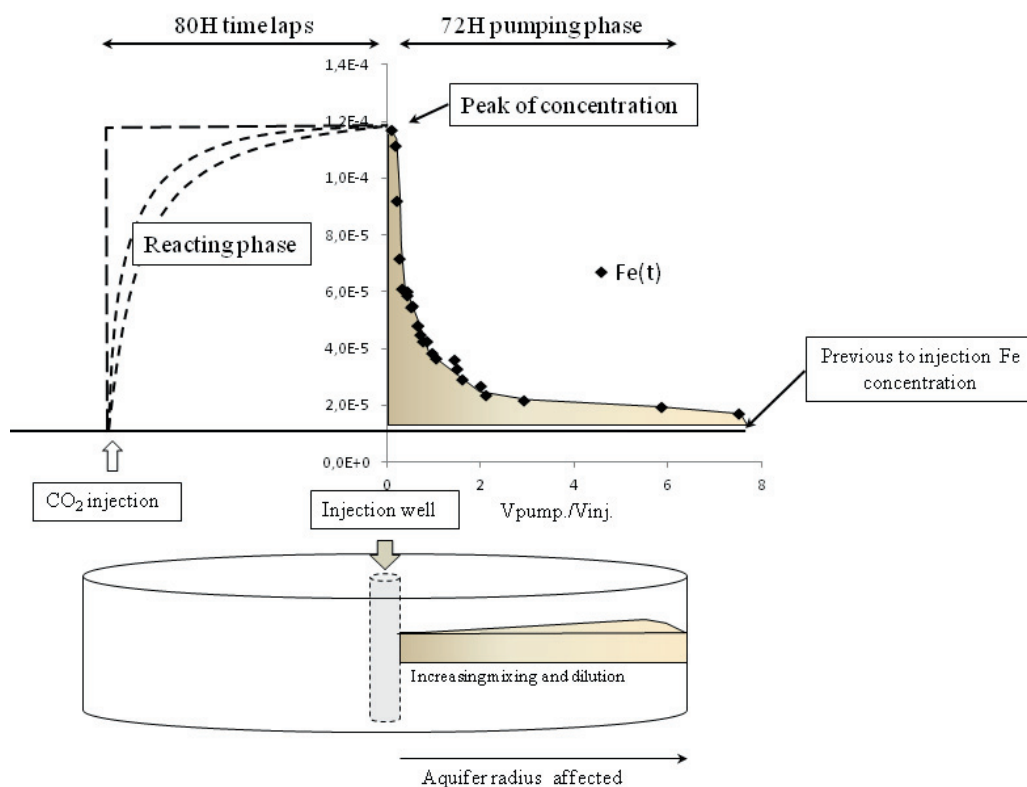


Fig.1. Breakthrough curve resulted from push-pull test. Chemical concentration of Fe is plotted as function of pumped volume. The time since injection stopped is also mentioned. The proportion of aquifer close to the injection/extraction well with increasing dilution and mixing effect away from the well is represented.

3. Results and discussion

Results of our experiment showed significant modification of groundwater chemical composition following the CO₂-water injection. A decrease in pH from 7.3 to 5.7 was observed. An increase of about 30% is also observed in concentration of major cations Ca²⁺ and Mg²⁺, while other major cations stay constant (Na⁺ and K⁺). An increase in alkalinity by a factor 2 was observed, correlated to dissolved calcium and magnesium, compared to their pre-injection concentration. Total Dissolved Fe and Mn were enriched by one order of magnitude.

For all of reactive elements, the peak of concentration was observed in the early stage of pumped fluids (see Fig.1), after 80 h from the CO₂ injection. The evolution of Cl⁻ and SO₄ as a function of the pumped fluid proportion suggests that both elements were not affected by the reaction processes. Furthermore, SO₄ and Cl concentrations in the injected solution have a different signature compared to the aquifer, thus can be used as inert tracers only affected by fluid dynamic (i.e. dispersion, advection, diffusion, mixing). On the other hand, Fe evolution as a function of the pumped fluids is controlled by both mineral-fluid reactivity and fluid dynamics. We estimated a fluid dynamic correction factor by the difference between injected and extracted amount of Cl and SO₄. The amount of iron resulting from the chemical reactivity, Fe_{react}, has been estimated by the total measured iron, corrected by a fluid dynamics factor.

The aquifer volume influenced by the push/pull process is estimated assuming (1) a radially symmetrical flow field around the injection well (cylindrical model), (2) an effective porosity of 2%, (3) a homogeneous confined aquifer of 3 meters thickness (i.e. the inter-packer distance).

We may estimate, at every stage, the total volume of aquifer affected. The total surface rock S in contact with reacting fluids was calculated assuming an aquifer composed by 2 mm spherical grains with a 2% connected porosity. Average bulk rock dissolution rates, or chemical elements release rate was calculated using the following rate equation:

$$R(\text{Fe}) = \frac{F_{\text{react}}(t) \cdot V_{\text{pumped}}}{t_r \cdot S} \quad (1)$$

where R is the in-situ rate of dissolution, defined in mol per square meter of rock in contact with the interacting fluid per hour (mol/m²/h). S gives the surface rock in contact with the reactive fluid into the aquifer and Fe_{react} corresponds to concentration added by reaction. V_{pumped} is the pumped volume and t_r is the time since CO₂ injection stopped.

Thermodynamic equilibrium calculations using PhreeqC [4] and redox calculation using Fe^{II}/Fe^{III} couple [5] suggested that main source of iron affected by CO₂ perturbation in our experiment is controlled by ferrihydrite Fe(OH)₃ dissolution.

The rate of iron oxide-hydroxide dissolution has been generally described by protonation of active site onto metal oxides surface [6], and active site density is directly proportional to H⁺ concentration, according to:

$$R(\text{Fe}) = k[\text{H}^+]^n \quad (2)$$

Where R(Fe) is the rate of oxide dissolution (mol/m²/h), k is the coefficient rate of reaction (mol/m²/h), [H⁺] the proton concentration, and n is an empirical coefficient, usually comprised between 0 and 0.5, meaning that dissolution by H⁺ protonation of iron hydroxide surface is following a zero order or pseudo zero order reaction.

We found that kinetic rate of the reaction R(Fe) calculated by Eqn 1 plotted as a function of pH fit the following relationship:

$$R(\text{Fe})=4.89[\text{H}^+]^{1.94} \quad (3)$$

This suggest that kinetic rate of hydroxide iron ferrihydrite $\text{Fe}(\text{OH})_3$ dissolution follows a complex order of reaction, close to two, indicating that the dissolution mechanism is more complex compared to the laboratory experimental results.

It is important to note however that R(Fe) term was calculated using total surface rock in contact with reactive fluids, composed by a mix of different minerals. Thus iron hydroxide is not pure ferrihydrite, but a mixture of different iron hydroxides. On the other hand, kinetic rate law is determined in laboratory using pure mineral phase, with difference in reactive surface area comparing to the field. However, this would affect the absolute value for k in equation (2) but not the order of reaction n .

4. Conclusion and perspectives

Results of this experiment show that CO_2 perturbation induces rapid and significant change in the concentration of inorganic elements. Despite the low perturbation in some major species, an enrichment of one order of magnitude is observed in metal species (Fe, Mn) due to oxy-hydroxide dissolution. This dissolution is due essentially to acidification of water by CO_2 .

The observed results for iron, manganese and alkalinity in this field experiment are comparable with previous experiments at larger scale in sedimentary basin in Frio [1,2] and comparative scale in shallow aquifer [3]. These results highlight the role of iron hydroxide dissolution in the release of metals induced by artificial CO_2 injection in aquifer. A kinetic reaction rate of ferrihydrite dissolution was estimated using surface protonation model and indicates that mechanism of ferrihydrite dissolution is ruled by a complex order of reaction, close to two.

References

- [1] Kharaka YK, Thordsen JJ., Hovorka SD., Nance HS., Cole DR., Phelps T.J., Knauss K.G., Potential environmental issues of CO_2 storage in deep saline aquifers: Geochemical results from the Frio-I Brine Pilot test, Texas, USA, *Applied Geochemistry* 2009, **24**: 1106-1112.
- [2] Kharaka YK, Cole DR, Geochemistry of Geologic sequestration of carbon dioxide. *Frontiers in Geochemistry: Contribution of Geochemistry to the Study of the Earth*. Russell S. Harmon, Andrew Parker, editors. Blackwell Publishing Ltd, 2011.
- [3] Kharaka YK, Thordsen JJ, Kakouros E, Ambats G, Herkelrath WN, Beers, SR, Birkholzer JT, Apps JA, Spycher NF., Zheng L, Trautz RC, Rauch WR, Gullickson KS. Changes in the chemistry of shallow groundwater related to the 2008 injection of CO_2 at the ZERT field site, Bozeman, Montana. *Environ Earth Sci* 2010; **60**: 273-284
- [4] Parkhurst D L, Appelo CAJ. User's Guide to Phreeqc (version 2) – A Computer Program for Speciation. Batch-Reaction. One-Dimensional Transport and Inverse Geochemical Calculations. U.S. Department of the Interior/ U.S. Geological Survey. Denver, Colorado, 1999.
- [5] Criaud A., Fouillac C., Etude des eaux thermomérales carbogazeuses du massif central Français: Potentiel d'oxydo-réduction et comportement du Fer, *Geochimica et Cosmochimica Acta* 1986, **50**: 525-533
- [6] Stumm W., Wollast R., Coordination chemistry of weathering: kinetics of the Surface-Controlled dissolution of Oxide Minerals, *Review of Geophysics* 1990, **28**: 53-69