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Stéphanie Betelu, Catherine Lerouge, Gilles Berger, Eric Giffaut, Ioannis Ignatiadis. Mechanistic and kinetic study of pyrite (FeS<sub>2</sub>)-hydrogen (H<sub>2</sub>) interaction at 25°C using electrochemical techniques. International meeting "Clays in Natural and Engineered Barriers for Radioactive Waste Confinement", Oct 2012, Montpellier, France. hal-00703578

**HAL Id: hal-00703578**

**<https://brgm.hal.science/hal-00703578>**

Submitted on 3 Jun 2012

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# Mechanistic and kinetic study of pyrite (FeS<sub>2</sub>)-hydrogen (H<sub>2</sub>) interaction at 25°C using electrochemical techniques

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After the closure of the underground nuclear waste repository, aqueous corrosion of the steel canister and, to a lesser extent, radiolysis of water would produce significant amounts of H<sub>2</sub>. This H<sub>2</sub> can interact with materials from the repository and with the surrounding clay host formation. The COx formation contains pyrite (FeS<sub>2</sub>), which has been demonstrated to react with Hydrogen gas (H<sub>2</sub>) (Truche *et al.* 2010) at temperature ranging from 90°C to 180°C.

This work aims at understanding these interactions at 25°C. With regards to E-pH equilibrium diagrams at 25°C for the two systems S-H<sub>2</sub>O and Fe-S-H<sub>2</sub>O with a total dissolved S concentration of 0.1 mole S per liter (about pH<sub>2</sub>S=1bar), FeS<sub>2</sub> must be an oxidant for H<sub>2</sub> at pH higher than 9, and FeS<sub>2</sub> should transform into Pyrrhotite (FeS<sub>1-x</sub>), according to:  $\text{FeS}_2 + (1-x) \text{H}_2 = \text{FeS}_{1+x} + (1-x) \text{H}_2\text{S}$  (with  $0 < x < 0.125$ ) and at pH higher than 12.5 FeS<sub>2</sub> should transform into Mackinawite. Investigations were thus conducted at pH higher than 9, in agreement with the alkaline perturbation in the clay-rock pore-water.

After pyrite electrodes had been assembled (figure 1A), various electrochemical disturbances were applied to this material (and to platinum for comparison) while it was submerged in a partially reconstituted solution of COx pore water (pH 9.5), enclosed in a **Low Pressure Thermo-Reactor (LPTR)**, figure 1B), in the absence and in the presence of pyrite grains (particle size between 40 and 63 µm) and H<sub>2</sub> (PH<sub>2</sub> = 0 or 1 bar) (Ignatiadis *et al.*, 2012). The H<sub>2</sub> present in the LPTR was produced *in situ* by water electrolysis by using an external generator and two platinated titane electrodes (anode & cathode) (figure 1B). In addition to the electrochemical behaviour of the platinum and the pyrite, the pH, temperature and pressure of the liquid medium were monitored.

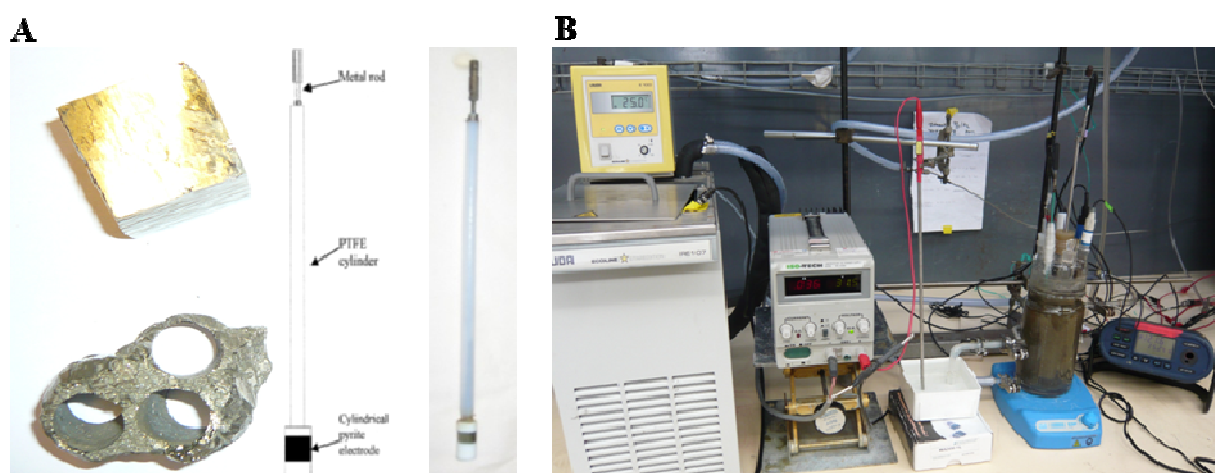
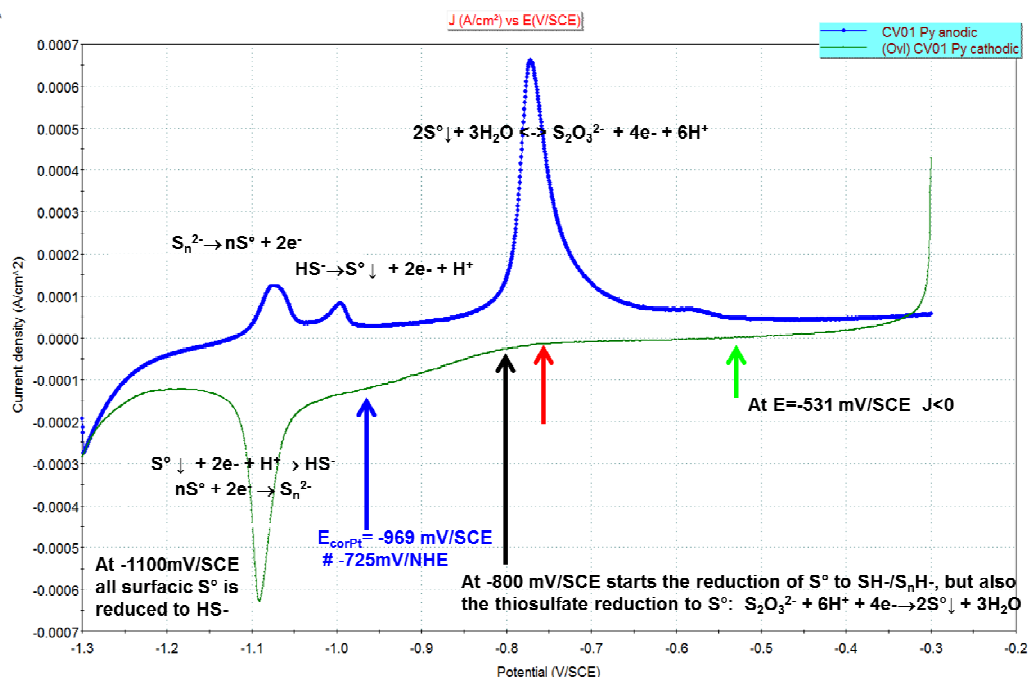


Figure 1: A) Pyrite electrodes B) The Low Pressure Thermo-Reactor and control unit.

Pyrite **linear sweep polarization (LSP)** (figure 2) clearly shows the metastable behaviour of its surfacic S°. When pyrite is at the corrosion potential (E<sub>py</sub>), surfacic S° simultaneously oxidizes to thiosulfates and reduces to sulphide. **Potentiometric measurements** demonstrated that both E<sub>pt</sub> and E<sub>py</sub> decrease in the presence of H<sub>2</sub> to reach a stable redox potential.



**Figure 2: Significant FeS<sub>2</sub> electrode reactions during LSP. pH 11.8 at 25°C in the LPTR with P(H<sub>2</sub>)=1bar.**

In comparison,  $E_{py}$  remains higher ( $E_{py} = -750 \text{ mV/SCE}$ ) during the entire period; corresponding to the alkaline dissolution/reduction of pyrite by H<sub>2</sub>, but without the pyrite's being entirely covered by pyrrhotite (results provided by MEB/EDS). That is the reason why  $E_{py}$  remains at  $-750 \text{ mV/SCE}$ , in agreement with results provided by LSP. Pyrite electrode potential is fixed by the  $\text{S}_2\text{O}_4^{2-}/\text{S}^0$  redox couple which equilibrium at 25°C is written as follows:  $E(\text{S}_2\text{O}_4^{2-}/\text{S}^0) = 0.007 - 0.0443 \times \text{pH} - 0.0074 \times \log[c]$ ;  $c$  represents the total concentration of sulphur. **Electrochemical Impedance Spectrometry** demonstrated that the corrosion currents are strong on pyrite in the presence of H<sub>2</sub> and increase with the imposed cathodic potentials. The initial reduction-reaction rate is rapid due to the high reactivity of pyrite surface, hence the rapid increase in the HS<sup>-</sup> content in the bulk solution, which seems to hinder the progress of the reaction up to a rapidly reached HS<sup>-</sup> concentration plateau. Pyrite dissolution and pyrrhotite precipitation are coupled reactions. The fluid composition remains fairly steady when pyrite dissolution balances pyrrhotite precipitation, the iron content remaining very low in the solution.

Experiments are in progress in order to determine the kinetics of FeS<sub>2</sub> reduction by H<sub>2</sub> at 25°C. The prospects for this work are, therefore, the exploitation of these data and their extrapolation to storage conditions.

### Acknowledgement

Research has received funding from i) the European Union's European Atomic Energy Community's FP7/2007-2011 under grant agreement n° 212287 (RECOSY project) and ii) the ANDRA under the BRGM-ANDRA partnership (TRANSFERT project).

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