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Mechanistic and kinetic study of pyrite (FeS₂)-hydrogen (H₂) 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 H₂. This H₂ can interact with materials from the repository and with the surrounding clay host formation. The COx formation contains pyrite (FeS₂), which has been demonstrated to react with Hydrogen gas (H₂) (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-H₂O and Fe-S-H₂O with a total dissolved S concentration of 0.1 mole S per liter (about pH₂S=1bar), FeS₂ must be an oxidant for H₂ at pH higher than 9, and FeS₂ should transform into Pyrrhotite (FeS_{1-x}), 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 FeS₂ 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 H₂ (PH₂ = 0 or 1 bar) (Ignatiadis *et al.*, 2012). The H₂ 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.

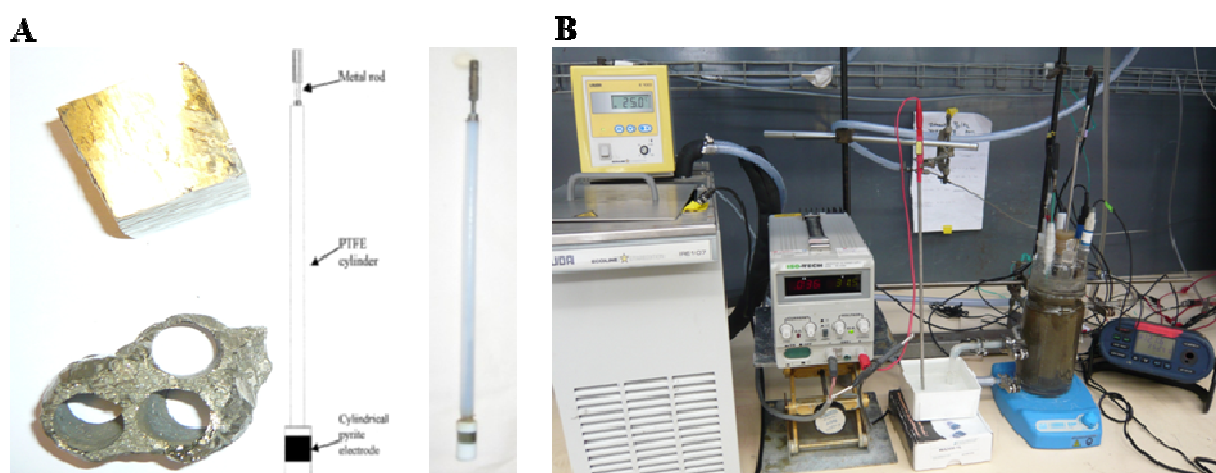


Figure 1: A) Pyrite electrodes B) The Low Pressure Thermo-Reactor and control unit.

Pyrite linear sweep polarization (LSP) (figure 2) clearly shows the metastable behaviour of its surfacic S°. When pyrite is at the corrosion potential (E_{py}), surfacic S° simultaneously oxidizes to thiosulfates and reduces to sulphide. **Potentiometric measurements** demonstrated that both E_{pt} and E_{py} decrease in the presence of H₂ to reach a stable redox potential.

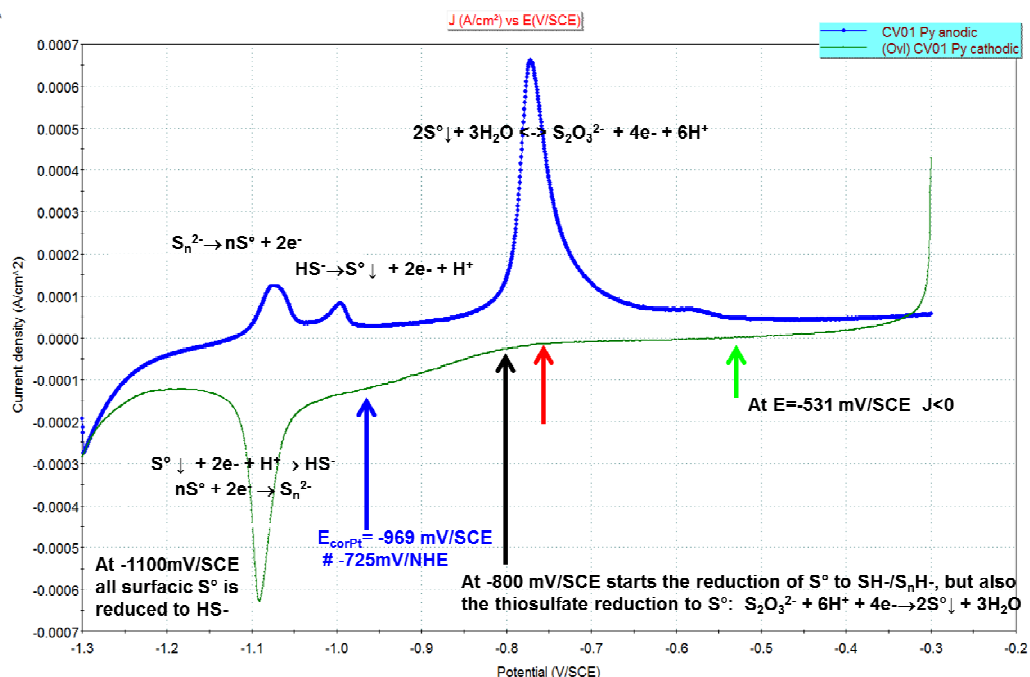


Figure 2: Significant FeS₂ electrode reactions during LSP. pH 11.8 at 25°C in the LPTR with P(H₂)=1bar.

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 H₂, but without the pyrite's being entirely covered by pyrrhotite (results provided by MEB/EDS). That is the reason why E_{py} remains at -750mV/SCE , in agreement with results provided by LSP. Pyrite electrode potential is fixed by the $\text{S}_2\text{O}_4^{2-}/\text{S}^2$ redox couple which equilibrium at 25°C is written as follows: $E(\text{S}_2\text{O}_4^{2-}/\text{S}^2) = 0.007 - 0.0443 \times \text{pH} - 0.0074 \times \text{Log}[c]$; c represents the total concentration of sulphur. **Electrochemical Impedance Spectrometry** demonstrated that the corrosion currents are strong on pyrite in the presence of H₂ 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⁻ content in the bulk solution, which seems to hinder the progress of the reaction up to a rapidly reached HS⁻ 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 FeS₂ reduction by H₂ at 25°C. The prospects for this work are, therefore, the exploitation of these data and their extrapolation to storage conditions.

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