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Mechanistic and kinetic study of pyrite (FeS₂)-hydrogen (H₂) interaction at 25°C using electrochemical techniques

S. Betelu¹, C. Lerouge¹, G. Berger², E. Giffaut³ and I. Ignatiadis¹*

¹BRGM, Environment and Processes Division, 3 Avenue Claude Guillemin, BP 36009, 45060 Orléans Cedex, France (*corresponding author: i.ignatiadis@brgm.fr)
²IRAP, Observatoire Midi-Pyrénées 14 av. E. Belin, 31400 Toulouse, France
³ANDRA, Scientific Division, Environmental Survey and Disposal Monitoring Department (DS/OS), 1-7, rue Jean-Monnet, 92298 Châtenay-Malabry, France

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 (FeS₁₋ₓ), according to: FeS₂ + (1-x) H₂ = FeS₁₋ₓ + (1-x) H₂S (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.](image)

Pyrite linear sweep polarization (LSP) (figure 2) clearly shows the metastable behaviour of its surfacic S°. When pyrite is at the corrosion potential (EₚPy) surfacic S° simultaneously oxidizes to thiosulfates and reduces to sulphide. Potentiometric measurements demonstrated that both Eₚ and EₚPy decrease in the presence of H₂ to reach a stable redox potential.
Experiments are in progress in order to determine the kinetics of FeS\textsubscript{2} dissolution by H\textsubscript{2} 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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