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Mechanistic and kinetic study of pyrite-hydrogen interaction at low temperature using electrochemical techniques

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Within the context of the investigation of the impact of the geochemical evolutions of the nuclear waste storages on the surrounding material, the objective of the work presented here was the characterization of pyrite interaction with hydrogen at low temperature (25-90°C). The emphasis was put on the understanding in depth of both phenomenology and kinetics.

For this purpose, the use of electrochemical techniques in combination with pyrite mineral electrodes has constituted a novel experimental and complementary approach in comparison with the geochemical research realized by Truche et al. (2010) under hyper-thermal temperatures, from 90 to 180°C and under H₂ partial pressures p_{H₂} ranging from 8 to 18 bars.

Experiments were conducted in a wide range of conditions (pH, temperature, ionic composition, gaseous environment) close to the expected evolution of the repository groundwater chemistry. More specifically, after pyrite electrodes had been designed and assembled (figure 1A), various electrochemical disturbances were applied to FeS₂ electrode (and to platinum electrode (Pt) for comparison) while it was submerged in a partially reconstituted CO₂ pore water solution, enclosed in a **High Pressure Thermo-Reactor (HPTR)** at 90°C (figure 1A) or in a **Low Pressure Thermo-Reactor (LPTR)** (figure 1B) at 25°C, in the absence and in the presence of (i) pyrite grains (particle size ranging from 40 to 63 µm) and (ii) H₂ (p_{H₂} ranging from 0 or 1 bar).

Experiments that were performed in carbonaceous buffers (HCO₃⁻/CO₃²⁻ buffer, pH 8.6 and 10.0) in the **HPTR** (at 90°C, which is the maximal temperature expected in the repository) with or without hydrogen led us to determine mechanism and estimate pyrite corrosion rates.

Experiments that were performed in anoxic environment (N₂ and/or H₂) in carbonaceous buffer in the **LPTR** (at 25°C) in which hydrogen was produced *in situ* by electrolysis led to complex phenomenology at higher pH, from 9.3 to 11.2. Indeed polarization provided H₂ and OH⁻ formation in the solution, and thus its progressive alkalization.

Mechanism was established by using potentiometric measurements, linear sweep polarization (**LSP**) and Electrochemical Impedance Spectrometry (**EIS**).

Both electrochemical (Tafel plots and Polarisation Resistance (R_p)) and gravimetric (mass loss) approaches were used as complementary methodologies to estimate pyrite corrosion rates.

In addition to the electrochemical behaviour of platinum and pyrite electrodes, pH, temperature and pressure of the liquid medium were monitored. FeS₂ morphological and chemical characterizations were realized by *Scanning Electron Microscopy (SEM)* and Energy-dispersive X-ray spectroscopy (**EDS**).

A) Electrochemical measurements into HPTR

- FeS₂ working electrode



- Pt electrode: redox measurements
- Hastelloy: counter electrode
- Reference electrode (Ag-AgCl/3MKCl)
- pH electrode



B) Electrochemical measurements into LPTR

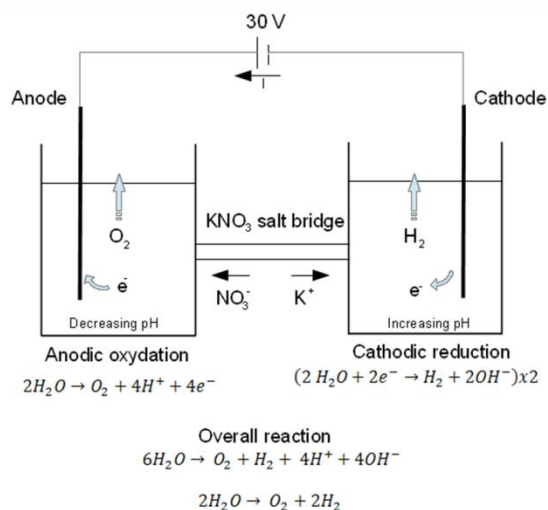


Figure 1: A) FeS₂ electrode made with "pure" Peruvian pyrite for experiments realized in a Hastelloy High Pressure Thermo-Reactor (HPTR)

B) Electrolysis scheme experiment of the Low Pressure Thermo-Reactor (LPTR).

The elucidation of the mechanism governing the reduction of the sulphur S⁰ of the FeS₂ was the first challenge we answered. Indeed, the S⁰ is reduced to sulphide (HS⁻/S²⁻), which is freed in solution, whereas the pyrite turns superficially into pyrrhotite (FeS_{1+x} with 0 < x < 0.125), forming a layer that slows down the reduction process. Experiments conducted into HPTR and LPTR lead to approach phenomenology (which will be discussed) versus pH.

Investigations conducted by electrochemistry (at 90°C in high pressure thermo-reactor) allowed us to provide Pyrite corrosion rates in the absence and in the presence of hydrogen. It is worth noting that they are of the same order of magnitude 10⁻³ mm.year⁻¹ whatever the pH (in the range 0.5 mm.year⁻¹ - 3.6 10⁻³ mm.year⁻¹). In parallel, experiments conducted by gravimetric measurements were of prime importance. Both electrochemical and gravimetric measurements allow us to identify and distinguish the following phenomena on pyrite: (i) corrosion and corrosion-scaling measurable by electrochemistry, (ii) corrosion and chemical dissolution measurable by gravimetric measurements.

Results provided by electrochemical and gravimetric measurements will be discussed and compared to the calculated corrosion rates using the rate law determined by Truche *et al.* (2010).

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