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Pyrite-electrode potential measurements in reference solutions versus measured and computed redox potential: at the roots of an innovative generic pH electrode for nuclear waste repositories

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Within the framework of the geochemical observation and monitoring into the underground components of nuclear repositories, the purpose of the study was to investigate, in a semi-continuous mode of monitoring, the redox potential of reference and natural solutions via a bunch of electrodes.

Because, each electrode response depends upon its material nature as well as its surface properties, gold (Au) and glassy carbon (GC) electrodes were investigated as inert indicator electrodes (IIE) in addition to platinum (Pt). Indeed, platinum differs from gold as it has the higher exchange current density (10 mA/cm² for Pt, against 0.3 mA/cm² for Au). However, gold is known as a more inert material: Pt is susceptible to catalyze reactions, form oxides and adsorb H₂; in contrast, gold does not. Gold has moreover a greater potential range (-0.8 to 1.8 V/NHE) towards the positive potentials (≈ 400 mV) than Pt. In comparison, glassy carbon possesses a larger potential range (-1.0 to 1.0 V/NHE) towards the negative potentials (≈ -200 mV) than Au and Pt. In addition to inert indicator electrodes pure pyrite (FeS₂) was selected as alterable or alternative electrode. Its interest for potentiometric measurements in bio-leaching has already been demonstrated by Cabral and Ignatiadis (2001). It was even more interesting because pyrite occurs naturally in the Callovo-Oxfordian (COx) formation. It was thus of a great interest to integrate it to the bunch of electrodes and to identify the relevance of different redox reactions at the vicinity of the pyrite electrode surface.

The test offered an advantage of great importance, because it provided information on the simultaneous behaviour of different electrodes under identical conditions. Electrode performances and robustness were examined versus time “long term measurements”. This work also aimed to:

- identify the redox reactions controlling the measured potential, both into solution and at the electrode/solution interface
- compare the obtained results with speciation measurements and geochemical modelling.

Because Fe³⁺/Fe²⁺ couple has thus a decisive influence on the behaviour of pyrite electrode, the robustness of the complementary approaches to obtain the voltage measurement it-self and its interpretation was investigated in low organic matter content samples where iron redox-active species dominated redox reactions. [Fe³⁺]/[Fe²⁺] ratios were analysed in different supporting electrolytes (NaCl, CaCl₂ and MgCl₂) at different pH (ranging from 1 to 12) and/or ionic strengths (supporting electrolytes concentration ranged from 0.1 to 5 mol.L⁻¹). Investigations were also conducted in not balanced systems: i) Fe⁰ powder immersed in pH-buffered and unbuffered solutions, ii) mackinawite suspension. PHREEQC® geochemical code was used to determine Eh and aqueous speciation by thermodynamic methods with the appropriate associated thermodynamic database (THERMOCALC® thermodynamic database generated by BRGM).

Potentiometric measurements demonstrated that the potential acquired by all the immersed **IIE** generally converges to a value of the same order of magnitude, independently of the sample. Acquired potentials were in good agreement with **modelling**. This fact demonstrates that, under the same experimental conditions, the redox couples fix identically the potential of inert electrodes (i.e. outcome of the same equilibrium state whatever the inert electrode). In the case when acquired potential did not converge, interface phenomena occurred (adsorption, oxidation, reduction, precipitation, accumulation of ions...).

Concerning FeS_2 electrode, different behaviours have been observed as a function of pH:

- Pyrite behaviour in acidic media ($\text{pH} \leq 2$): pyrite electrode acquired a potential which was increasingly lower than that of the platinum, which measures the redox potential of the solution. The lower value of pyrite at this pH can be explained by the interfacial pyrite oxidation, leading to the increase in Fe^{2+} at the vicinity of pyrite electrode. As the pyrite electrode has Nernstian behaviour (Cabral et Ignatiadis, 2001), the equilibrium value is decreased because the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio at the electrode interface is lower than that of the solution.
- Pyrite behaviour at circum-neutral pH ($4.7 \leq \text{pH} \leq 7.0$): it is important to note that, at low ionic strength, the potential of both pyrite and platinum electrodes were practically identical. The similar voltage measured by the two electrodes implies that the processes at the vicinity of the electrodes were the same. This result is in agreement with those already obtained by Cabral et Ignatiadis (2001), demonstrating that, in particular conditions, pyrite can act as redox electrode. These conditions can, for example, be encountered in the initial COx formation. In comparison with acidic media, at low ionic strength, pyrite oxidation/dissolution is lowered. The increase in pH diminishes the oxidizing capacity of Fe^{3+} . The redox potential is thus fixed, for the two electrodes (Pt and Py), via the $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ couple, which is dependent of $\text{Fe}(\text{OH})_3$ solubility as a function of pH. High ionic strength, leads to an increase in the oxidizing capacity of Fe^{3+} versus pyrite. It thus leads to an accumulation of Fe^{2+} at the vicinity of pyrite electrode, consequently generating progressive decrease in the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ ratio at the pyrite/solution interface and thus in the electrode potential.
- Pyrite behaviour under alkaline conditions ($\text{pH} \approx 9$ or higher): a higher potential value of pyrite at these pH in comparison with the potential acquired by platinum can be explained by an anoblissement process on the pyrite surface. Indeed, at higher pH than 7 iron hydroxide coagulates and stabilizes chemically to form an iron hydroxide coating at the pyrite electrode surface. The combination of equation 1 and 5 leads to Fe^{3+} depletion in solution and in the pyrite/solution interface. $\text{Fe}(\text{OH})_3$ coating onto the pyrite electrode responsible for the lowering of pyrite oxidation/dissolution. According to the following reaction $\text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_3 + 3\text{H}^+$, pyrite resulting anoblissement lead to the decrease in pH at the electrode. When the solution redox potential (Pt) is fixed by $\text{Fe}(\text{OH})_{3(s)}/\text{FeOH}^+$ couple (with $E_{\text{eq}} = -1.14 - 0.06 \log[\text{FeOH}^+] - 0.03 \log[\text{OH}^-]$), the pyrite electrode potential is fixed by $\text{Fe}(\text{OH})_{3(s)}/\text{Fe}^{2+}$ couple (with $E_{\text{eq}} = -1.46 - 0.06 \log[\text{Fe}^{2+}] - 0.01 \log[\text{OH}^-]$).

These results confirmed, with absolute clarity, that the behaviour of pyrite is a function of the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ ratio at the interface. These results are even more interesting because they lead to highlight the double interest of pyrite electrode as both redox and pH indicator when integrated in the bunch of electrodes. In fact, in natural conditions, i.e. those of initial COx formation, pyrite can operate as redox electrode (its potential is similar to that of an IIE). An increase of its potential versus the potential of an IIE can be correlated to an alkaline environment: pyrite electrode can thus behave as a pH indicator. This can be applied in the case of COx formation during its envisaged evolution as nuclear waste repository.

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