

# ABIOTIC PYRITE REACTIVITY VERSUS NITRATE, SELENATE AND SELENITE USING CHEMICAL AND ELECTROCHEMICAL METHODS

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This work is part of ReCosy European project ([www.recosy.eu](http://www.recosy.eu)), whose main objectives are the sound understanding of redox phenomena controlling the long-term release/retention of radionuclides in nuclear waste disposal and providing tools to apply the results to performance assessment/safety case.

Redox is one of the main factor affecting speciation and mobility of redox-sensitive radionuclides. Thus, it is of a great importance to investigate the redox reactivity of the host radioactive waste formations, particularly when exposed to redox perturbations. Callovo-Oxfordian formation (COx), a clay rock known as an anoxic and reducing system (Gaucher *et al.*, 2004), was selected in France as the most suitable location to store nuclear waste. Iron (II) sulfide, mostly constituted of pyrite (FeS<sub>2</sub>), iron (II) carbonate, iron(II) bearing clays and organic matter are considered to account almost entirely for the total reducing capacity of the rock.

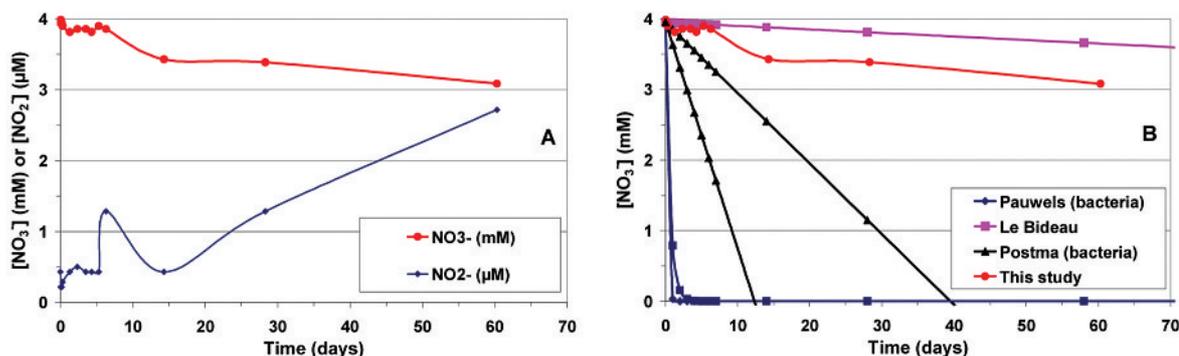
We report here the redox reactivity of pyrite upon exposure to nitrate (N(V)), selenate (Se(VI)) and selenite (Se(IV)) that possibly occur in the nuclear storage. Both, chemical and electrochemical kinetic approaches were simultaneously conducted such as to (i) determine the kinetics parameters of the reactions and (ii) understand the kinetic mechanisms.

In order to reach similar conditions that are encountered in the storage system, all experiments were realised in NaCl 0.1 M, near neutral pH solutions, and an abiotic glove box (O<sub>2</sub> less than 10<sup>-8</sup> M).

Chemical approach has consisted to set in contact pyrite in grains with solutions containing respectively nitrate, selenate and selenite. Reactants and products chemical analyses, conducted at different contact times, allowed us to assess the kinetics of oxidant reduction.

Electrochemical approach has consisted in the continuous or semi-continuous analysis of large surface pyrite electrodes immersed in solutions with or without oxidant (nitrate, selenate and selenite). The electrochemical behavior of these electrodes was compared to those of known inert and unattackable electrodes (Pt, Au, glassy carbon) positioned in the same operating conditions. Measurements realized by voltammetry (at open circuit potential and cyclic voltammetry), by Tafel polarization analysis and by electrochemical impedance spectroscopy (EIS) were used to identify, monitor and compare the electrochemical reactions and kinetics occurring during immersion, both in solution and on the surface of pyrite electrodes.

Figure 1A presents nitrate and nitrite evolutions during pyrite-nitrate chemical interaction versus time. With a rate equation of the type  $-d[\text{NO}_3^-]/dt = k [\text{NO}_3^-]^n$ , our results give an order  $n$  equal to zero and a kinetic constant  $k$  equal to 0.015 mM/day, demonstrating the slow denitrification kinetics in anaerobic conditions. As shown in Figure 1B, which presents the comparison between our kinetics and those of the literature (for Le Bideau (1996)  $n=0$ ,  $k=0.005$  mM/day; for Postma *et al.* (1991)  $n=0$ ,  $k=0.1$  to  $0.32$  mM/day; for Pauwels *et al.* (1998)  $n=1$ ,  $k=1.61$  to  $4.83$  mM/day), our  $k$  value is 3 times greater than the one obtained by Le Bideau (1996), probably due to our greater pyrite grains specific surface. It is worth noting that our kinetic experiment will be continued during one year.



**Figure 1:** Nitrate and nitrite evolution versus time (A) and comparison between our kinetics and those of the literature in the presence of pyrite as reducer (B).

Tafel polarization analysis and EIS were used to determine the corrosion rates and charge-transfer resistances associated with  $\text{NO}_3^-$  removal by  $\text{FeS}_2$ . Although  $\text{NO}_3^-$  is an oxidant,  $\text{FeS}_2$  oxidation rates were not proportional to the aqueous  $\text{NO}_3^-$  concentrations due to anodic control of  $\text{FeS}_2$  oxidation. Results obtained confirm the slow kinetics of denitrification by  $\text{FeS}_2$  and show that the zero order removal kinetics can be explained by anodic control of  $\text{FeS}_2$  oxidation and the concomitant anodic control of  $\text{NO}_3^-$  reduction.

Contrary to the results obtained with nitrate and in agreement with those reported in literature (Myreni *et al.*, 1997), both selenate and selenite reductions by  $\text{FeS}_2$  grains (pH 4.5-5.0) prove to be fast reactions. With a rate equation of the type  $-\text{d}[\text{Se(IV)}]/\text{dt} = k [\text{Se(IV)}]^n$ , our preliminary results gave an order  $n$  equal to 1 and a kinetic constant  $k$  equal to  $2.0 \cdot 10^{-5} \text{ s}^{-1}$ . Similar order and kinetic constant were obtained for  $\text{Se(VI)}$  reduction. However, it is worth noting that, Naveau *et al.*, 2007 have established the pH dependence of  $\text{Se(IV)}$ - and  $\text{Se(VI)}$ -adsorption on pyrite surfaces. Electrochemical measurements are thus in progress to appreciate the different redox and adsorption-desorption processes for  $\text{Se(IV)}$  and  $\text{Se(VI)}$  and to establish these mechanisms at the pyrite surface.

The combination of chemical and electrochemical approaches appears to be an appropriate method to investigate the redox reactivity of COx components versus predicted redox perturbations.

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