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Redox potential measurements in a claystone

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Near-neutral pH and low redox potentials (E_H) are considered favorable conditions for immobilization of most of radionuclides in deep repository systems in clay geological formations. The range of pH values in claystones pore waters has been well constrained by collection and analysis of *in situ* seepage water or water samples squeezed from core samples [1-3] and by geochemical modeling [4-7], especially for foreseen host-rocks, such as Callovian-Oxfordian formation (COx) in France, or Opalinus Clay in Switzerland (OPA). These rocks are considered to host reducing conditions because of the presence of pyrite in their mineralogical assemblages. The exact redox potential conditions prevailing in the pore waters of these “reduced claystones” are however not well known. Geochemical models that take into account redox sensitive species and minerals predict E_H values close to -200 mV/NHE, which correspond to equilibrium between pyrite, *in situ* sulfate concentrations and iron bearing phases identified in reduced claystones [8]. Measurements in borehole seepage water, which were well preserved from atmospheric O₂ perturbations, also yielded E_H values close to -200 mV/NHE. This apparent agreement between these two E_H evaluation methods must however not occlude the question of the feasibility of an equilibrium of pyrite with sulfate in the absence of microbiological mediation, nor the fact that, regardless of the type of experiment, the development of microorganisms in instrumented boreholes systems could never be avoided completely [7]. Obtaining a thorough understanding of redox processes involving reactions with minerals has proven to be extremely challenging [9-11]. In laboratory, on condition that the preservation of the samples from the atmospheric O₂ are met, voltage measurement problems essentially arise because the electron transfer to and from minerals can involve concurrent processes that complicate interpretation [9]. In order to overcome this major problem, electrochemical mediated approaches appear as the most promising methods for the determination of the mineral redox properties by potentiometric or amperometric measurements [9]. In these experimental approaches, an electroactive redox mediator improves the rate of electron transfer from the redox active solid to the electrode such as to facilitate redox equilibration between the working electrode and the mineral. The present study aimed to measure the redox potential at equilibrium with claystones samples well preserved from oxidation by coupling successively amperometric and potentiometric measurements.

All measurements were carried out on COx core samples in a thermo-regulated glove box (GB) in an oxygen-free atmosphere (N₂/CO₂ (99/1%)) at 25.0± 0.5 °C, in presence of a synthetic solution whose composition in major elements and pH were representative of COx pore water.

After several tests, CyanoMethyl Viologen (CMV) with $E^\circ = -0.14$ V/NHE) was selected as one of the most appropriate redox mediator candidate for the experiments.

Chronoamperometry was used to impose the desired redox potential to the bulk solution. Potentiometric measurements were then recorded under free potential value, in the absence and in the presence of COx.

The good agreement between the redox experiments conducted onto the COx oxidizing and reduced electroactive sites (i) clearly validates the obtainment of a measurable steady state (Figure 1) and (ii) highlights the robustness of the developed methodology. The measured redox potential of the investigated COx samples reached -210 mV/NHE at pH = 7.35, in agreement with the range of values previously reported and that were obtained by geochemical modeling and/or measurements in borehole seepage waters [4,12-15].

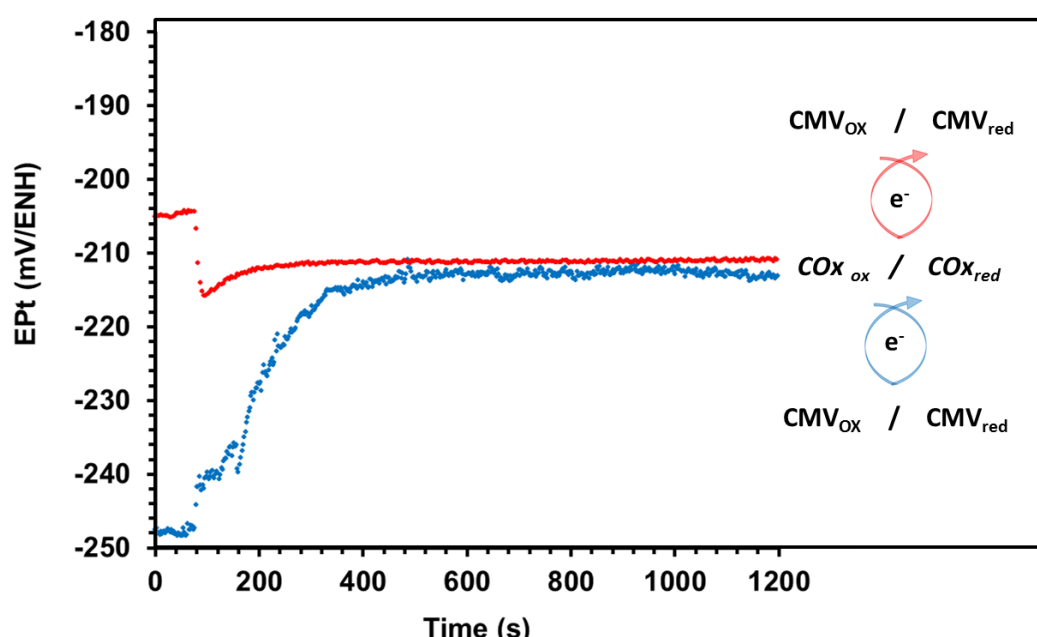


Figure 1: Potentiometric measurements during the interaction between Callovian-Oxfordian formation claystone (COx) and CyanoMethyl Viologen (CMV) redox mediator.

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