

Redox potential measurements in a claystone

Stéphanie Betelu^{*1}, Ioannis Ignatiadis¹,
Christophe Tournassat²

¹BRGM, Water, Environment and Eco-technology Division,
F-45060 Orléans Cedex 02, France (*correspondance:
s.betelu@bgrm.fr)

²UMR 7327 Institut des Sciences de la Terre d'Orléans
(ISTO), Université d'Orléans–CNRS/INSU–BRGM,
45071 Orléans, France

The knowledge of the redox potential in the far-field of underground radioactive waste storage is of paramount importance for the prediction of radionuclide solubility and mobility. However, the understanding and quantification of redox processes involving reactions with minerals has proven to be extremely challenging [1]. Innovative techniques are thus needed to estimate E_h values that are truly representative of *in situ* conditions.

In this study we determined the E_h value in claystone samples by coupling successively amperometric and potentiometric measurements, in which an electroactive redox mediator improved the rate of electron transfer from the redox active solid phases to the electrode. Callovian Oxfordian Claystone samples (COx) originated from the main gallery of Andra's underground research laboratory in Bure. Measurements were carried out at 25°C in a thermo-regulated glove box under N₂/CO₂ (99/1%) atmosphere, in presence of a synthetic solution whose composition in major elements and pH were representative of COx pore water. CyanoMethyl Viologen ($E^\circ = -0.14$ V/SHE) was selected as one of the most appropriate redox mediator candidate for the experiments. The good agreement between the redox experiments conducted onto the COx oxidizing and reduced electroactive sites clearly validates the obtainment of a measurable steady state, and highlights the robustness of the developed methodology. The measured redox potential of the investigated samples reached ~ 200 mV/NHE at pH = 7.3, in agreement with the range of values previously reported and that were obtained by geochemical modeling [2].

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[1] Sander, Hofstetter & Gorski. (2015). *Environmental Science & Technology*. 49, 5862-5878. [2] Tournassat, Vinsot, Gaucher & Altmann. In *Natural and Engineered Clay Barriers*; Tournassat, Steefel, Bourg & Bergaya Eds. Developments in Clay Science; Elsevier (2015) Vol. 6, pp. 71-100.

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