

## PROBING Fe (III)/Fe (II) REDOX POTENTIAL IN A CLAYEY MATERIAL

**Christophe Tournassat<sup>1</sup>, Fabien Chainet<sup>1</sup>, Jean-Marc Greneche<sup>2</sup>, Stéphanie Betelu<sup>1</sup>,  
Jebril Hadi<sup>1</sup>, Eric C. Gaucher<sup>1</sup>, Laurent Charlet<sup>3</sup>, and Ioannis Ignatiadis<sup>1</sup>**

1. BRGM, 45060, BP6009 Orleans Cedex, France (c.tournassat@brgm.fr)

2. LPEC UMR CNRS 6087, Université du Maine, 72085 Le Mans, France

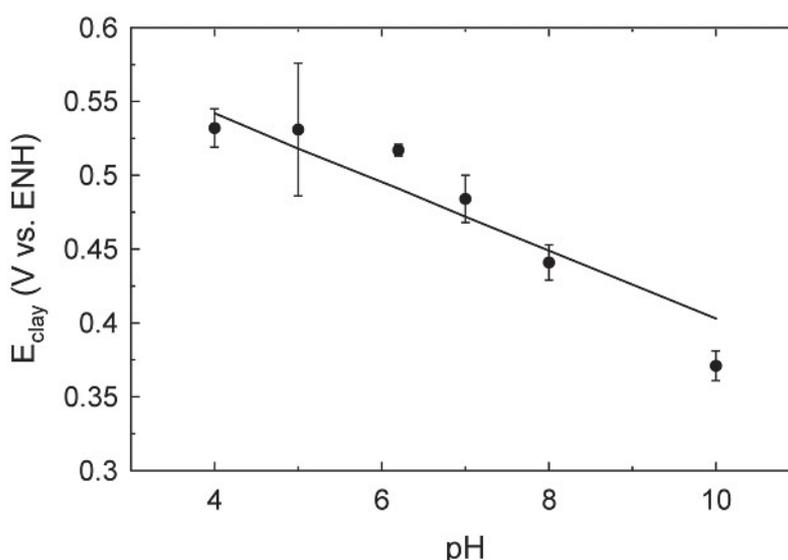
3. LGIT, BP53, 38041, Cedex 9, Grenoble, France.

Redox is one of the main factors affecting the migration of redox-sensitive radionuclides. As a consequence reducing conditions are considered of strategic importance for the confinement properties of a clayey formation towards nuclear waste. A representative redox potential of clay formation such as Callovian-Oxfordian (COx) can be derived from thermodynamic calculations considering equilibrium between observed redox phases such as pyrite and siderite. However, there is little information on the reactivity of the different reservoirs of redox constituents in this type of complex material. The present study aims at investigating the reactivity of the Fe(III)/Fe(II) redox couple in the structure of clay minerals using different investigation methods: electrochemistry and O<sub>2</sub> reduction kinetic experiments.

Clay modified electrodes were specifically designed to probe Fe(III)/Fe(II) redox potential in the structure of clay minerals. The clay fraction of a Callovian-Oxfordian argillite sample originating from the same level than ANDRA underground research laboratory was used after pre-treatment to remove organic matter and accessory minerals such as pyrite that could influence redox potential measurements. These electrodes were used to verify the validity of the model of Favre *et al.* (2006) that links the redox potential ( $E_{\text{clay}}$ ) to the Fe(II)/Fe<sub>tot</sub> ratio in the structure ( $m_{\text{rel}}$ ), the pH and the sodium concentration in solution:

$$E_{\text{clay}} = E^{\circ} + \frac{0.059}{1 + K_0 m_{\text{rel}}} \log[\text{Na}^+] - \frac{0.059 K_0 m_{\text{rel}}}{1 + K_0 m_{\text{rel}}} \text{pH} \quad \text{Equation 1}$$

The good agreement between direct potential measurements and model prediction provides a strong evidence of the relevance of this model in our experimental conditions (Figure 1) although the clay composition and its too low Fe content do not *a priori* fulfil the conditions set by Drits and Manceau (2000) for the calculation of  $K_0$  parameter.



**Figure 1:** Comparison between redox potential measured at a clay modified electrode (symbols) with predicted redox potential according to equation 1 ( $E_0$  taken at 0.67 V).

Following the verification of the model, we tried to apply it to the specific case of a Callovian-Oxfordian sample that had been very well preserved from oxidation using transportation under liquid N<sub>2</sub> from drilling site to laboratory glove-box. The  $m_{rel}$  parameters for clay minerals in this sample were measured by combining acid digestion method and Mössbauer spectrometry. Sodium concentration (~0.06 mol/L) and pH (~7.2) of the solution contacting the clay are known from thermodynamic modelling (Gaucher *et al.*, 2009) and direct measurement in instrumented boreholes on site (Vinsot *et al.*, 2008). As a consequence, application of Equation 1 should lead to a correct estimate of the redox potential in the clay rock. Calculated  $E_{clay}$  is equal to + 0.32 V. This value is clearly not realistic. Expected value is in the range [-0.2 V; -0.16 V] according to the presence of sulphate and pyrite in the system. This disagreement points out (i) either an absence of true equilibrium between the redox state as probed by the Fe(III)/Fe(II) couple in the clay structure and the redox state of solution species or (ii) the non-applicability of Equation 1 for very reduced clay with low iron content. Additional O<sub>2</sub> kinetics experiments and use of the empirical relationship relating O<sub>2</sub> consumption kinetics to the redox potential of Fe(III)/Fe(II) redox couple defined by Wehrli (1990) seems to support the second hypothesis together with preliminary cyclic voltametric measurements on our clay modified electrodes.

### References:

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