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Multi-Parametric Devices with Innovative Solid Electrodes for Long-Term Monitoring of pH and Redox-Potential of the actual pore water of CO_x formation in a future Nuclear Waste Repository

Daoudi Jordan^{1,2}, Betelu Stephanie¹, Tzedakis Theodore³, Lundy Melanie³, Bertrand Johan³, Ignatiadis Ioannis^{1*}

¹ BRGM, French Geological Survey, 45060 Orléans, France;

j.daoudi@brgm.fr ; s.betelu@brgm.fr ; i.ignatiadis@brgm.fr

² Université de Toulouse III Paul Sabatier, 31062 Toulouse, France; tzedakis@chimie.ups-tlse.fr

³ Andra, French National Radioactive Waste Management Agency, 55290 Bure; France;

melanie.lundy@andra.fr; 92298 Chatenay Malabry, France; johan.bertrand@andra.fr ,

Summary

We present innovative electrochemical probes for the monitoring of pH and redox potential in pore water in near-field rocks of a future deep geological radioactive waste repository at 500 m depth within the clayey Callovian-Oxfordian (CO_x) formation. The conceived experimental set-up assembles two multi-parameter probes (MPPs), used together throughout two series of several months duration measurements *in situ* into the underground research laboratory of Andra at Bure, France. The two MPPs, connected in series, were up-flow fed with actual pore water of CO_x formation during several with a very low flowrate. Each MPP is composed of different individual probes containing the following: two monocrystalline antimony electrodes for pH sensing; eight AgCl/Ag-based reference or Cl⁻ selective electrodes; four Ag₂S/Ag-based reference or S²⁻ selective electrodes; eight platinum electrodes; two gold electrodes; two glassy-carbon electrodes; two ruthenium and two inox 316 electrodes, for redox potential measurements. The Open Circuit Potential (OCP) measurements of the developed sensors under different conditions and in quasi-actual conditions were compared to conventional reference electrode and pH electrodes in terms of performance, reliability and robustness and allowed to create calibration curves. Conductivity measurements, carried out along MPPs, will not be presented here. Overall, the conceived bundle of electrodes as designed works reliably during a timescale that is promising for monitoring the CO_x formation during its envisaged use for hosting a nuclear waste repository.

1. Introduction

1.1. Context

Near-neutral pH and low redox potential (Eh) are considered to be favourable conditions for nuclear waste disposal in clay formations, because most radionuclides, including actinides, have a low solubility under such conditions [1]. Radioactive waste-management programmes today mainly focus on deep geological storage, as this is currently the most appropriate strategy for ensuring the long-term safety of people and environment. “Cigeo” is the name of a future deep geological

disposal facility for high-level and intermediate-level long-lived radioactive waste, to be built in France, at 500 m depth within the clayey COx formation. The COx formation is a 130 m thick clay-rich rock, dating back to 160 million years ago and lying at a depth of 400 to 600 m. It is a water-saturated environment with extremely low permeability, porosity and hydraulic conductivity. The temperature, pH and CO₂ partial pressure of the COx pore-water solution are constant at 21-22 °C, 7.2 (±0.2) and 8.10⁻³ atm, respectively. Anoxic conditions prevail in the COx formation. Within the mineralogical assemblage [2], geochemical models predict Eh values ranging from -180 to -200 mV, corresponding to an equilibrium between pyrite and pore-water sulphate [S(+VI)] concentrations, and iron-bearing phases such as Fe-bearing carbonates or nanogoethite [3–5].

1.2. Objectives

pH and redox potential are thus key parameters for monitoring the evolution of pore water in the above COx formation [6]. The objective was to choose the appropriate material for electrodes and to design, create and optimize a robust multi-parameter probe for reliable on-site monitoring of pH (±1 pH unit) and redox potential (±100 mV) in order to ensure the long-term safety of the operation.

2. Materials and methods

To achieve our objective, various types of electrodes made of different sensitive solid materials were studied and the electrochemical measurements (mainly OCP) of the developed sensors under quasi-actual conditions were examined in terms of performance, reliability and robustness. Each MPP is composed of different individual probes containing the following: two monocrystalline antimony electrodes for pH sensing; eight AgCl/Ag-based reference or Cl⁻ selective electrodes; four Ag₂S/Ag-based reference or S²⁻ selective electrodes; eight platinum electrodes; two gold electrodes; two glassy-carbon electrodes; two ruthenium and two inox 316 electrodes, for redox potential measurements. Several among these electrodes will be used for conductivity measurements, carried out along MPPs, but the results will not be presented here. We built up an innovative multi-parameter probe device, carrying up to 20 electrodes for such long-term monitoring, directly placed at 490 m depth into a gallery the Meuse/Haute Marne Underground Research Laboratory (URL) of Andra at Bure, France. The conceived experimental set-up assembles two multi- MPPs, connected in series, which receive the seepage water extracted from the borehole EPT1201. Preserved from air contact, the water feeds up the two MPPs during several months, with a low flowrate of 1-2 mL/h. The MPPs were down fed to avoid bubble formation and thus two-phase flow. Two series of measurements were carried out, which both lasted several months. The difference between the two series resides in the progressive appearance or not, of highly sulphate-reductive conditions in the water passed through the MPPs. In the case of progressive arrival of highly sulphate-reductive conditions, the reason for sulphide production is the organic content of conventional pH electrodes used for comparison with the monocrystalline antimony Sb₂O₃/Sb electrode. These two series were rich in results, and they allow the comparative electrochemical behaviour of all the electrodes (the OCP of solid electrodes versus reference electrodes) for pH and redox potential, during several months of immersion, as well as in the absence and the presence of hydrogen sulphide (H₂S, HS⁻, S²⁻).

3. Results and discussion

In the absence of sulphide, all the electrodes behave (left part of Fig. 1A) as predicted by the calibration lines obtained in glovebox (GB) conditions in laboratory [6]. The calibration lines for Sb₂O₃/Sb electrode allowed the conversion and monitoring of pH as presented in Fig. 1B, where the

pH measurements are coherent with those obtained by a pH conventional electrode over 8 months duration. **The calibration lines in the presence of sulphide**, obtained also in glovebox conditions in laboratory [6] from OCP measurements of all the electrodes (see Fig. 1C for Sb_2O_3/Sb electrode), enable us to deduce the pH under these *in situ* conditions.

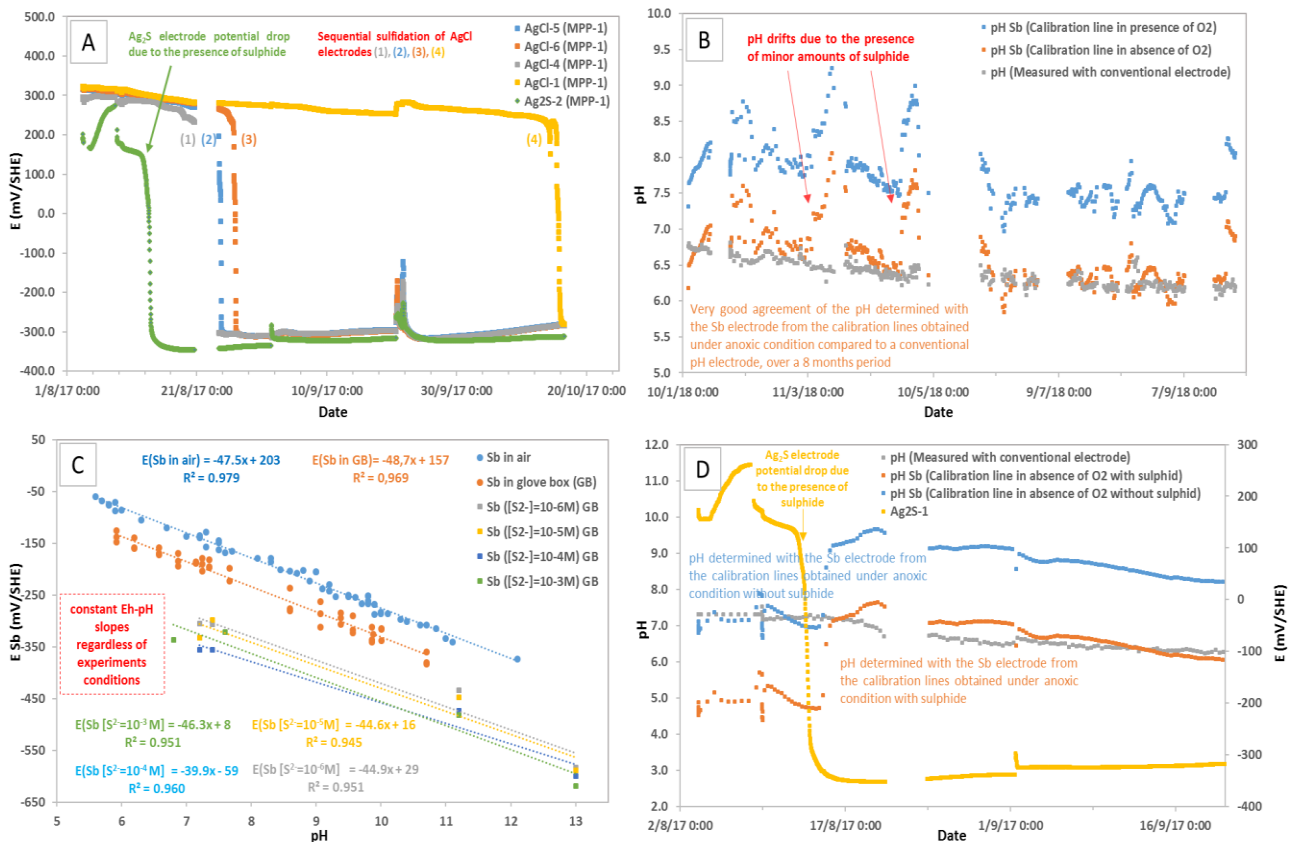


Figure 1: A: OCP of four AgCl/Ag and one Ag₂S/Ag electrodes versus time during exposition *in situ*, with progressive sulphidisation of water. B: pH versus time from conventional pH electrode and from Sb₂O₃/Sb electrode using calibration curves obtained in glovebox (GB) conditions (absence and presence of O₂). C: Calibration curves (OCP of Sb₂O₃/Sb electrode versus pH from conventional pH electrode) obtained in glovebox (GB) conditions using various sulphide concentrations. D: pH versus time from conventional pH electrode and from Sb₂O₃/Sb electrode using calibration curves obtained in glovebox conditions (absence of O₂ and presence of sulphide); and simultaneous OCP monitoring of Ag₂S/Ag electrode versus time.

The OCP of Ag₂S/Ag electrode, initially close to those of AgCl/Ag, detects the progressive appearance of sulphide in the pore water passed through the MPPs, as its potential progressively decrease and stabilise approximatively at the value of -350 mV versus AgCl/Ag conventional reference electrode (Fig 1A). In addition, all the four AgCl/Ag electrodes (Fig 1A), progressively behave as Ag₂S/Ag electrodes as their surface was covered by a thin layer of Ag₂S. The progressive replacement of the Cl⁻ in the surface of AgCl/Ag electrodes by S²⁻, according to the reaction $AgCl \downarrow + S^{2-} \rightarrow Cl^- + Ag_2S \downarrow$, is one of the reasons why the AgCl/Ag electrodes, progressively became Ag₂S/Ag electrodes. The speed of this conversion is governed by the preparation conditions of solid AgCl/Ag electrodes (see Fig. 1A right, the last converted AgCl/Ag electrode in yellow).

Figure 1D presents the pH measured by Sb₂O₃/Sb electrode by using calibration curves obtained in GB conditions without sulphide. These measurements are coherent with the pH measured by the

conventional electrode, as long as there is no sulphide. Once the presence of sulphide underlined with the $\text{Ag}_2\text{S}/\text{Ag}$ electrode (Fig. 1D yellow curve), one sees that the pH isn't coherent anymore with the pH measured by the conventional pH electrode. This is the reason why further calibration lines were established at the laboratory (see Fig. 1C) to characterize the behavior of $\text{Sb}_2\text{O}_3/\text{Sb}$ electrode according to the pH, in the presence of various sulphide concentrations. Figure 1C illustrates that the sensitivity of $\text{Sb}_2\text{O}_3/\text{Sb}$ electrode is constant and does not depend on the conditions of the medium such as the presence/absence of O_2 or the presence of sulphide. On the other hand, these parameters have an influence on the standard potential. Thus, by using the calibration lines in the presence of sulphide presented in Figure 1C, the pH measured by the $\text{Sb}_2\text{O}_3/\text{Sb}$ electrode is coherent with the one measured by the conventional pH electrode (Figure 1D).

4. Conclusion

Innovative electrochemical probes for the monitoring of pH and Eh have been implemented on site and allowed two series of measurements to be made on the seepage water extracted from a borehole in the COx clay-rich rock. Overall, the conceived bundle of electrodes, as designed, worked reliably during a timescale that is promising for monitoring the evolution of the pore water composition in the COx formation during its envisaged use for hosting a nuclear waste repository. Further work is ongoing to develop calibration lines for a more accurate calibration of some new probes. Experiments, for estimating corrosion rates of the new electrode materials in reconstituted COx solution are planned. After these developments, it could be possible to envisage their use during the operational period of Cigeo, on the decade timescale.

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