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Calibration of antimony-based electrode for pH monitoring into underground components of nuclear repositories

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Nuclear waste repositories are being installed in deep excavated rock formations in some places in Europe to isolate and store radioactive waste. In France, Callovo-Oxfordian formation (COx) is potential candidate for nuclear waste repository. It is thus necessary to measure in situ the state of a structure's health during its entire life. The monitoring of the near-field rock and the knowledge of the geochemical transformations can be carried out by a set of sensors for a sustainable management of long-term safety, reversibility and retrievability. Among the chemical parameters, the most significant are pH, conductivity and redox potential.

Based upon the reversible interfacial redox processes involving H⁺, metal-metal oxides electrodes should be regarded among the promising technologies to be devoted to the observation and monitoring of pH into the underground components of nuclear repositories due to their physical and chemical stability, with regards to temperatures, pressures and aggressive environments (Pourbaix, 1963). Metal-metal oxides electrodes present furthermore the advantage of being easily miniaturised.

Among the metal-metal oxide group, antimony-antimony oxide system, for which improved properties were obtained using mono-crystalline antimony, has been the first and then the most investigated and disputed for pH sensing; the fact remains that it has been the most frequently used in practical pH measurements. Nevertheless, numerous conflicting data exist concerning the disturbances of their potential by various physical and chemical parameters, which require calibrating the electrode under conditions similar to those in which it is to be applied (Caflisch et al. 1978; Głab et al. 1981).

This work aimed to calibrate mono-crystalline Sb electrode (99.999 %, m = 500 mg, d = 6.7) for pH measurements into the underground components of nuclear repositories. The electrode presented the advantage of being strong in the conception: it presented an important reserve of material. Mono-crystalline Sb was used without any (pre)treatment over the experiments (16 month). The high binding energy led to a low corrosion rate and therefore the surface was only slowly changed and occluding oxide was almost completely avoided. The uniform binding energy promoted a uniform (or generalized) corrosion on the surface.

Performances, reliability and robustness were examined by potentiometric measurements at 25°C. Investigation has been limited in pH, ranging from 5.5 to 13.5, close to those encountered in the environment of the nuclear repositories. The feasibility of measuring pH with Sb-based electrodes was first tested in NH₄Cl/NH₃ buffer solutions, leading to electrode calibration over the widest range of pH, from around neutral to basic pH. The influence of the presence P(V), Cl(-I), N(V), on the analytical signal was studied from solutions plug NaH₂PO₄/NaHPO₄ (Ionic Strength (IS): 0.1), NaCl (0.1 mol.L⁻¹), NaNO₃ (1 to 6 10⁻³ mol.L⁻¹). Experiments were also conducted in NaHCO₃/Na₂CO₃ buffer samples, similar to conditions prevailing in the COx formation. Ionic strength was investigated from 0.05 to 0.2. When necessary, NaOH was used to extend the curve to the region of high pH value. In addition to measurements done under atmospheric oxygen saturation (with PO₂ about 0.2 atm) while the influence of the O₂/H₂O redox couple was being studied, several measurements were also done in a glove box (GB or BAG) in an oxygen-free atmosphere (100 % nitrogen). These were done to the anticipated decrease in the redox potential in the COx pore water caused by the decrease in the O₂ concentration. The same measurements were also done using a 10-mm disk platinum electrode with a surface of 78.54 mm². Figure 1 only presents the results obtained for the linear range part. The general convergence of the stabilization potential revealed the occurrence of an equilibrium state under the experimental conditions. Sb-based electrodes rapidly responded to changes in pH (≤ 30 s) with regard to the relative standard deviation (RSD) based on repeatability (RSD≤3%).
The equilibrium state remains unchanged with regard to pH variations, considering the RSD based on reproducibility (RSD ≤ 10%). Whatever the ligand, no complex has competed with both the antimony hydrolysis and the oxygen depletion. The Sb electrode potential (E_{Sb}) varied linearly as a function of pH. Electrodes exhibit almost ideal Nernstian response (sensitivity -(48 ± 1)mV/pH). There was sufficient oxidation at the metal surface to ensure the equilibration conditions. Moreover, E_{Sb} was somewhat affected by hysteresis. The potential of the platinum electrode (E_{Pt}) under atmospheric oxygen saturation is fixed by the O_2/H_2O redox couple. Under these conditions, E_{Pt} is governed by the PtO/Pt couple via PtO + 2H^+ + 2e^- ⇌ Pt + H_2O with E_{PtO/Pt} (mV/NHE) = 60.5 pH + 902. At the same pH and under aerobic conditions, a difference of about 700 mV (pH 0) is observed between E_{Pt} and E_{Sb}. This difference is reduced to about 330 mV under anoxic conditions where O_2/H_2O is the predominant redox couple with a very low quantity of oxygen. Moreover, the slope of the E_{Sb}-pH line remains the same regardless of the medium, which is very important, while the intercept giving the potential at pH = 0 differs by about 50 mV. This shows the dependence, although weak, of the Sb-based electrodes on the O_2/H_2O redox couple in the solution. This work provides information concerning the simultaneous but different behavior of two different electrodes under identical conditions and the same reference electrode. Knowledge of their electrochemical curves will allow us to draw potential-pH diagrams when observing and monitoring pH in the underground components of radioactive waste repositories where reference electrodes will not be used. Mono-crystalline Sb electrode appears to be appropriate for accurate measurements of pH in these conditions. Work is in progress to demonstrate the robustness of the Sb-electrode into COx over a long period.

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References

