Intercomparison of Ta and Ti solid-electrodes for pH measurements under oxic and anoxic conditions in reconstituted waters of a future nuclear waste disposal

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Oral or poster presentation; Topic 10: Monitoring (from initial state to post-closure)

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In France, the deep geological disposal has been chosen to manage long-lived high and middle activity nuclear waste. This project is supervised by "the *Agence National pour la Gestion des Déchets Radioactif*" (ANDRA - French national radioactive waste management agency). An underground research laboratory (URL), dedicated to host-rock properties characterization was built at approximately -490m depth in the Callovo-Oxfordian geological formation (COx), which is a potential candidate for nuclear waste disposal. Based on this overall strategy, Andra has analysed the technical requirements that must be met by adapted monitoring equipment. First, these must be able to provide information on key THMCR (Thermal-Hydraulic-Mechanical-Chemical and Radiological) processes, to provide a three-dimensional image of its behaviour and thus to understand the underground installation functioning, in particular the cell interactions with the near-field.

This study aims to develop innovative all-solid-state electrodes made of iridium (Ir), ruthenium (Ru), tantalum (Ta), titanium (Ti), tungsten (W), niobium (Nb) and a tin-lead alloy (Sn/Pb), for pH measurement. Moreover, the potentiometric response of these electrodes is mainly based on Metal Oxide (M_xO_y)/Metal (M) equilibriums, which make them react to changes of oxygen partial pressures. For now, the antimony electrode (Sb) showed excellent results regarding the measure of pH under oxic and anoxic conditions. Nevertheless, it is necessary to multiply the electrode materials considered for pH measurements, for preventing a dysfunction of electrodes which could occur over time. By multiplying the electrode materials for pH measurement, we indirectly increase, firstly, the measurement reliability by giving the possibility to inter-compare the potentiometric responses of the set of the electrodes dedicated to pH, and secondly, the monitoring duration, in the case of electrode surface alterations, which could be caused by variations of the physical and chemical parameters within the nuclear waste repository. In other words, this would provide alternatives electrode materials for pH measurements, in prevention to possible electrode surface alterations.

Thus, the influence of pH from 5 to 13, on the potentiometric responses of the several electrodes was investigated by means of pH buffers solutions or by continuous and regulated addition of H_2SO_4 or NaOH, under both oxic (exposed at air) and anoxic conditions (in glove box: 99% N_2, 1% CO_2 and $[O_2] < 2$ ppm, 25°C).

Titanium (Ti) and tantalum (Ta) electrodes showed a potentiometric linear response to pH variations, as shown on figures 1 and 2. In absence of oxygen, the Ti electrode showed a linear response to pH (from 5.8 to 11), close to the theory. After pH 11, a drop of potential is observed. In presence of oxygen, the response to pH is linear but further to the theory. In the same way, the potentiometric behaviour of the Ta electrode to pH variations is linear, but much more sensitive under anoxic conditions. The fact that the Ta electrode is very sensitive

under anoxic condition is an advantage since it results in a more accurate pH measurement. If the oxygen concentration is unknown, it can become difficult to determine with accuracy the pH of the solution since, as this is the case for the titanium electrode, open circuit potential values in presence and in absence of oxygen are close. The inter-comparison of the electrodes responses could be in this case very helpful and could at the same time gives some information regarding the oxygen abundance of the medium.

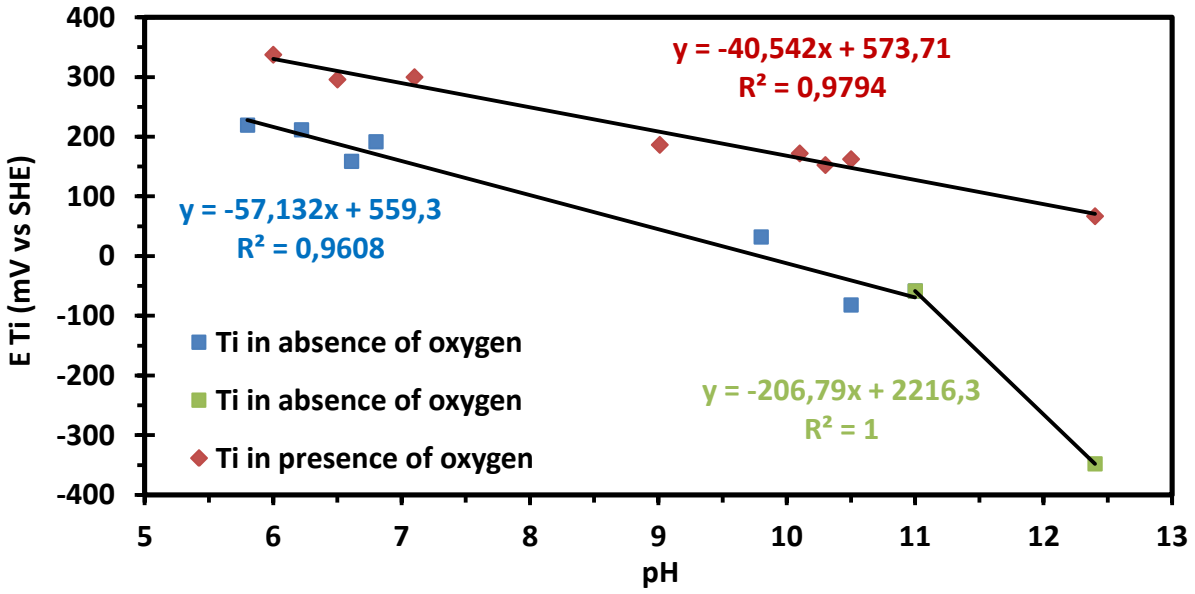

Figure 1 – Open circuit potential of the Ti electrode as a function of pH under oxic and anoxic conditions.

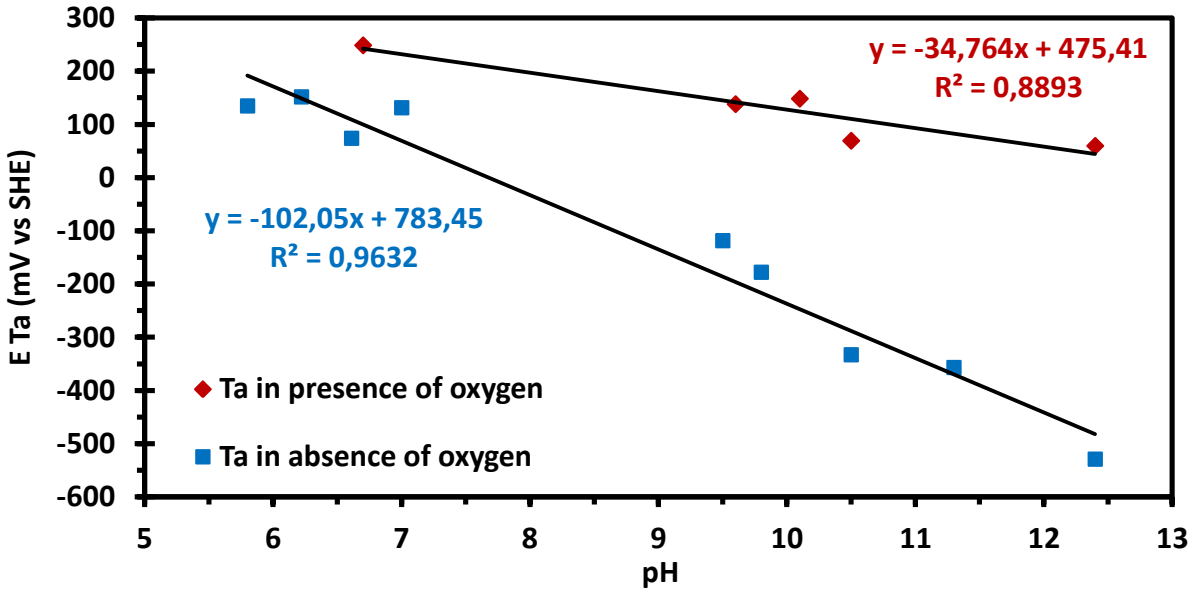

Figure 2 – Open circuit potential of the Ta electrode as a function of pH under oxic and anoxic conditions.

The electrode responses to pH changes are based on electrochemical reactions, for Ti: Ti_2O_5 + $10H^+ \leftrightarrow$ 2Ti + $5H_2O$ and for Ta: Ta_2O_5 + $10H^+ \leftrightarrow$ 2Ta + $5H_2O$. In contact with either oxygen contained in air or dissolved oxygen in water, these oxides are spontaneously and slowly produced. Clean and homogenous oxide films on the electrode surface, realized in a control way should clearly enhance the electrode response to pH changes. Thereby, further

experiments are currently under progress and aim at first, optimizing the anodic deposition at electrode surface and then comparing the electrode response to pH variations before and after the anodization process.