Investigation of dental amalgam electrode behaviour for the long term monitoring of nuclear waste disposals

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Poster presentation; Topic 10: Monitoring (from initial state to post-closure)

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Nuclear waste disposals are being installed in deep excavated rock formations in some places in Europe to isolate and store radioactive waste. Near-neutral pH and low redox potentials (E_h) are considered favourable conditions for immobilization of most of radionuclides in deep disposal systems in clay geological formations. These are the reason why deep excavated rock formations such as Callovian-Oxfordian formation (COx) in France, or Opalinus Clay in Switzerland (OPA) are 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.

The main difficulty lies on the fact that no maintenance of the devices will be feasible once installed on site.

Dental amalgam (DA) has been used by dentists for more than a century and is the most thoroughly researched and tested restorative material among all those in use (Castaño *et al.*, 2008; Colon, 2003; Brett *et al.* 2002; Acciari *et al.*, 2001; Toumelin-Chemla *et al.*, 1998; Marek, 1993). It is made by combining elemental mercury (approximately 50%), silver, tin, copper and possibly other metallic elements. During the trituration process, the surface layer of a silver-tin alloy dissolves in the liquid mercury and the reaction causes new phases to be formed. For low-copper amalgams, these new solid phases cause solidification such as:

$$\underset{\Upsilon\text{-}phase}{Ag_3Sn} + AgCu + Hg \rightarrow \underset{\Upsilon_1\text{-}phase}{Ag_2Hg_3} + \underset{\Upsilon_2\text{-}phase}{Sn_{7-8}Hg} + \underset{\Upsilon\text{-}phase}{(Ag_3Sn + AgCu)_{residual}}$$

All the works described in the bibliography show that the dental amalgam corrosion depends essentially on the constitutive phases of the material. Briefly, Υ_1*-phase* is the most noble (Acciari et al., 2001), Υ*-phase* is weakly altered due to its electrochemical stability in the buccal environment (Toumelin-Chemla et al., 1998) and Υ_2*-phase* is described as the most reactive (Acciari et al. (2001)), probably by the formation of a Sn(IV) oxide. Dental amalgam is nevertheless described as stable alloy, i.e. highly resistant to wear. Dental amalgam is

therefore of great interest to be tested in conditions close to those which can be encountered in the context of geological storage.

Performances, reliability and robustness of a homemade dental electrodes, containing respectively 8, 15, 34 and 43% of Cu, Sn, Ag and Hg, were examined by potentiometric measurements at 25°C. Data were compared to those obtained by three individual electrodes: coper, silver and tin electrode. Investigations were limited in pH, ranging from 5.5 to 12, close to those encountered in the environment of the nuclear waste disposals. Experiments were conducted into two buffer solutions based on $NaH_2PO_4/NaHPO_4$, NaCl (0.1 $mol.L^{-1}$) or $NaHCO_3/Na_2CO_3$, NaCl (0.1 $mol.L^{-1}$). 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 P_{O2} about 0.2 atm) while the influence of the O_2/H_2O redox couple was being studied, several measurements were also done in a glove box in an oxygen-free atmosphere (100 % nitrogen).

Under the investigated conditions, the open circuit potential taken by the homemade dental amalgam electrode (E_{OCDA}) is more analogous to those taken by silver or copper electrodes.

Under atmospheric conditions and for pH values closed to neutral pH (5.5-~9), the E_{OCDA} appeared to be fixed by Cu-Ag/AgCl NaCl 0.1M at ~222 mV/ENH. This result is explained by a double phenomenon. The presence of chloride ions in an oxygenated solution promotes the oxidation of Ag (Ag + Cl- $\rightarrow$AgCl↓+ e-) in the form of an AgCl coating on the surface of the Ag electrode. This phenomenon results in a decrease of the oxidizing power of Ag. Over the investigated pH range, this phenomenon gives rise to an anodic protection of copper by silver. That is why the expression of E_{OCDA} is influenced by Ag/AgCl 0.1M NaCl. Between pH values 9 and 11, in carbonate medium, the E_{OCDA} is rather be fixed by a mixed Ag-Cu(II)/Cu(I) such as E_{OCDA} (mV/ENH)=-24pH+422. For higher pH values, the E_{OCDA} tends to decrease strongly such as the dental amalgam electrode is fixed by a mixed potential, including Sn, Cu and Ag redox couples.

Under anaerobic conditions, the dental amalgam is rather fixed by a Ag-Cu_2O/Cu redox potential such as E_{OCDA}(mV/ENH) = -62 pH + 514.

Under the investigated conditions, the home made dental amalgam electrode showed different behaviours. The E_{OCDA} values tend to demonstrate the influence of the residual Ag-Cu phase. Under the atmospheric conditions, the home made dental amalgam electrode can be used as a reference electrode in the range 5.5-9. For higher pH values, work is in progress to precisely calibrate the electrode. Under anoxic conditions, the dental amalgam was established to exhibit a near-Nernstian behaviour in the pH domain ranging from 5.5 to 12 at 25°C. Electrode response was slightly affected by the direction of the pH change. Electrode reliability was clearly demonstrated for pH monitoring. The investigation of the electrode robustness is in progress in a synthetic solution whose composition in major elements and pH was representative of COx pore water.

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