Multi-parametric device with innovative all-solid-state electrodes for long term monitoring of pH, redox and conductivity in reconstituted anaerobic water of a future nuclear waste disposal

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Nuclear waste disposal 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 favorable conditions for immobilization of most of radionuclides in deep geological disposal facility in clay geological formations. Callovian-Oxfordian formation (COx) in France or Opalinus Clay (OPA) in Switzerland are potential candidates for nuclear waste geological disposal. To ensure long term safety and to provide reliable data for future decision-making process (reversibility) regarding critical parameters of the disposal, it is necessary to implement monitoring tools for long term measurement. Thereby, robust, sustainable and reliable sensors have to be developed to measure the most important physical and chemical parameters. The main difficulty lies on the fact that no maintenance of the devices will be feasible once installed on site, which considerably restricts the choice of the electrodes to be incorporated in the system.

In addition to medium temperature, among the chemical and the physical parameters, the most significant are pH, redox potential and conductivity.This study aims at developing and optimizing a multi-parametric device (cf. fig.1) composed of all-solid-state electrodes for the long term monitoring of pH, oxidation-reduction potential (ORP) and conductivity. The multi-parametric device consists of a limited number of inert or/and weakly alterable electrodes, allowing auto-controlled and redundant measurements. To be able to tolerate temperature variations ranging from 25°C to 90°C, the device and the electrode bodies are respectively made of PVDF (Polyvinylidene fluoride, also called Kynar, made by Arkema in France) and PEEK (PolyEtherEtherKetone).

Based upon the reversible interfacial redox processes involving H^+, Sb_2O_3-Sb system has been regarded among the most promising technologies to be devoted to the monitoring of pH into the underground components of nuclear repositories due to its physical and chemical stability, with regards to temperature, pressure and aggressive environments [1]. For redox potential measurements, platinum wires (Pt-Ir alloy; 90-10%) were selected among the "inert" conductive material presenting physical and chemical stability properties.

Solid-state AgCl/Ag$_{coated}$-Ag was selected for the development of non-conventional reference electrodes since (i) its potential only depends on Cl^- concentration and since (ii) the prediction of physical and chemical parameters evolution highlighted the fact that the on-site Cl-concentration should remain relatively stable on the long term [2]. The Ag coating

electrodeposition procedure as well as the AgCl electrolytic assisted coating process were performed and optimized at the BRGM laboratories.

The monitoring of pH and redox potential is based on measurements of open circuit potential differences inter-electrodes in semi-continuous way. Performance and reliability were examined by potentiometric measurements at 25°C, under atmospheric conditions as well as in a thermo-regulated (25°C ± 1°C) "oxygen free" glove box (99% N_2, 1% CO_2 and $[O_2]$<2ppm). Investigations were limited in pH, ranging from 5.5 to 13.5, close to those encountered in the environment of the nuclear repositories. Robustness was then investigated over six months in a synthetic solution whose composition in major elements and pH was representative of COx pore water.
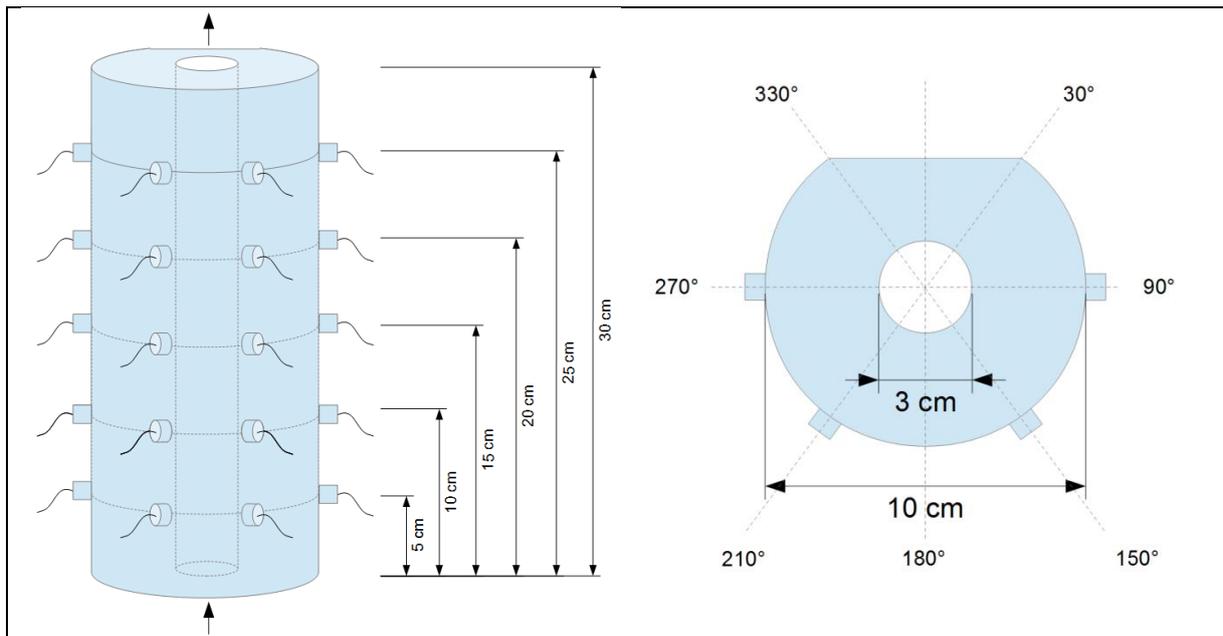

Figure 1 - Schematic representation of the multi-parametric device with its all-solid-state electrodes, from a front view (to the left) and from overhead (to the right).

For conductivity measurements, both platinum wires (Pt-Ir alloy; 90-10%) as well as Ag_{coated}-Ag/AgCl were used. The methodology has consisted in applying (by means of a potentiostat-galvanostat) a known alternating current (AC) between the two most distant electrodes and to measure the induced potential between all the possible couples of electrodes located between the two current injecting electrodes. The calibration procedure was consisted in measuring the resistance of different solutions whose resistivity values were well known. From these measures, the ohm law gave the resistance of the solution (R in Ω), which can then be converted in term of resistivity ρ (in Ω. m) with the following equation: $\rho = k.R$, where k (in m) is the geometric factor. This k factor depends on the distance between the two measurement electrodes and is determined for each couple. For redundant measurements, the k factor was determined all along the multi-parametric device.

Tests were then conducted into the representative of COx pore water. The antimony electrode, whose potential is based on the Sb_2O_3/Sb solid couple, proved to be reliable for pH measurements. In the absence of any redox couple, excepted O_2/H_2O (under atmospheric conditions or into the glove box under O_2 saturation), the platinum electrode showed a potentiometric linear response to pH variations. The all-solid-state AgCl/Agcoated-Ag electrode showed a stable potentiometric response similar to the one we could have obtain

with a commercial AgCl/Ag electrode filled with support electrolyte, even when subjected to pH variations.

The long-term monitoring of the pH and the redox via the multi-parametric device is feasible. Further investigations are in progress regarding the influence of redox species such as S(VI)/S(-II) or Fe(III)/Fe(II).

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