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**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. To ensure long term safety and to provide reliable data for future decision making process, it is necessary to implement long-term monitoring sensors. Thereby, robust, sustainable, reliable and autonomous sensors (no-maintenance required) have to be developed to measure the most important physical and chemical parameters.

This study aims at developing and optimizing a multi-parametric device composed of all-solid-state electrodes for the long term monitoring of pH, redox potential (ORP) and ionic conductivity. The multi-parametric device consists of a limited number of inert or/and weakly alterable electrodes, allowing auto-controlled and redundant open circuit potential differences measurements in semi-continuous way.

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 disposal due to its physical and chemical stability, with regards to temperature, pressure and aggressive environments<sup>1</sup>. For redox potential measurements, platinum wires (Pt-Ir alloy; 90-10%) were selected among the "inert" conductive material presenting physical and chemical stability properties. All-Solid-state  $AgCl/Ag_{coated}/Ag$  was selected for the development of non-conventional reference electrodes since its potential only depends on  $Cl^-$  concentration and because the on-site  $Cl^-$  concentration should remain relatively stable on the long term<sup>2</sup>.

Performance and reliability were examined by potentiometric measurements in various pH buffer solutions at 25°C, under atmospheric conditions as well as in an "oxygen free" gloves 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 the Callovo-Oxfordian (COx) pore water. For conductivity measurements, both platinum wires as well as  $AgCl/Ag_{coated}-Ag$  electrodes were used. The Galvanostatic Electrochemical Impedance Spectroscopy (GEIS) was used, which consisted in applying a known alternating current (AC) between the two most distant electrodes and to measure the induced potential between two other electrodes. The Sb-electrode proved to be reliable for pH measurements. In the absence of any redox couple, except  $O_2/H_2O$ , the platinum electrode showed a linear potentiometric response to pH variations. The all-solid-state  $AgCl/Ag_{coated}-Ag$  electrode showed a stable potentiometric response over several months even when subjected to pH variations. According to our results, the long-term monitoring of pH and ORP via the multi-parametric device is feasible. Further investigations are in progress regarding: (i) the influence of redox species such as  $S(VI)/S(II)$  or  $Fe(III)/Fe(II)$  and (ii) corrosion rates of each electrode materials in order to estimate electrodes lifetime and therefore of the device.

## Références

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