

# INVENTORY OF GEOCHEMICAL SENSORS AVAILABLE FOR MONITORING AN UNDERGROUND SITE OF NUCLEAR WASTE REPOSITORY RESEARCH PATHWAYS FOR NEW DEVELOPMENTS

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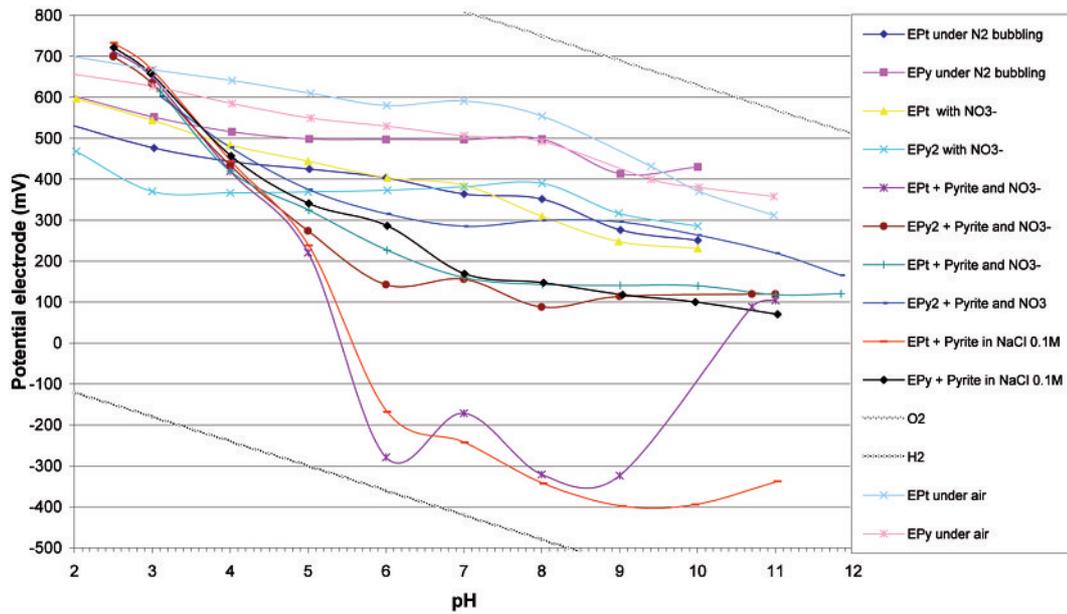
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The principle of the nuclear waste storage is based on the installation of a whole of robust barriers in order to make safe the secular containment of waste. In many industrial countries deep argillaceous formations are considered as potential host media for high level radioactive wastes. This is because clayey geomaterials have the ability to adsorb a large amount of ions and they possess the low permeability required to slow down the percolations of fluids. Containers with radioactive waste will be also protected with barriers made from porous materials such as bentonite. For the safety assessment of long-term radioactive waste disposals, a critical issue is the continuous disposal monitoring of the repository. In this framework, it is desirable to have non-invasive tools in order to determine *in situ* some geochemical, thermal and mechanical parameters for the suitable detection of changes that can take place during the life of the underground repository.

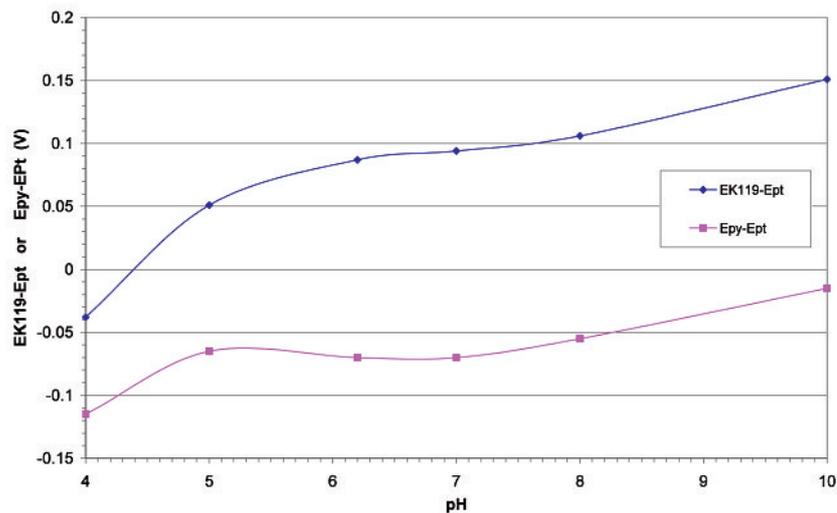
The major objective of this work is to carry out a detailed inventory of robust geochemical sensor concepts being able to be devoted (after adaptation or development and/or implementation) to the observation and monitoring of the underground components of a nuclear waste storage. These sensors must answer precise specifications related to the requirements and constraints of observation and monitoring of the storage components (architecture, geological environment and associated phenomenology). In addition to the technical aspects, the major constraint seems to be the operation life, which will have to be based on the robustness and the perseverance (durability) of the principle of the sensors. Among the geochemical parameters to be followed, the most significant are: temperature, pH, conductivity, redox potential, the speciation of certain elements, and measurement of H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>S. The inventory and the assessment of the currently available methodologies and tools for these parameters indicate that today there are not suitable geochemical sensors for monitoring nuclear waste storing systems. On the basis of this report, we are led to propose some realistic pathways of research and development to be initiated or continue to mitigate the lack of geochemical sensors dedicated to the underground storage of nuclear waste.

For that purpose, R&D pathways will be (i) the development of geophysical-electrochemical sensors and (ii) the development and manufacture of geochemical sensors made of robust and unalterable material (gold, platinum, glassy carbon). They must possess active principles everlasting, or protected or restored easily. Moreover, solid-state sensors fabricated with a few component of the argillaceous formations (pyrite, raw or purified argillite K119, ) or silicon semiconductor technology (such as ion sensitive field effect transistors, ISFETs) for measuring pH and interdigitated structures (IDS) for measuring conductivity and redox potential can be designed for use. Response characteristics of these sensors must be tested in aqueous samples with compositions similar to those present inside an underground repository and results were compared with those obtained with commercial electrodes obtaining a good agreement between commercial and the sensors.

Electrochemical methods will be in the base of the sensors assessments. These approaches will be consisted in the continuous or semi-continuous analysis of large surface electrodes (pyrite, argillite, ) immersed in solutions with or without oxidant (nitrate, selenate and selenite) or reducer (sulfide, Fe<sup>2+</sup>). The



**Figure 1:** Measurement of electrode potential of Pyrite and Platinum electrodes immersed in different media (different pH, and presence or absence of nitrate and or pyrite in grains).



**Figure 2:** Measurement of the difference of potential between two couples of electrode (purified COx or Pyrite versus Platinum) as a function of pH.

electrochemical behavior of these electrodes was compared to those of known inert and unattackable electrodes (Pt, Au, glassy carbon) positioned in the same operating conditions. Measurements realized by voltammetry (at open circuit potential and cyclic voltammetry), by Tafel polarization analysis and by electrochemical impedance spectroscopy (EIS) were used to identify, monitor and compare the electrochemical reactions and kinetics occurring during immersion, both in solution and on the surface of electrodes. The combination of chemical and electrochemical approaches appears to be an appropriate method to investigate the redox reactivity of COx components versus predicted redox perturbations. As example, Figure 1 presents the measurements of electrode potentials (versus Saturated Calomel Electrode) for Pyrite and Platinum electrodes immersed in different media (in pH and in composition). With answers in potential of this type, it is obvious that it will be possible to manufacture systems of solid and robust electrodes where the reference electrode is unnecessary. It will be also possible, provided that the potential difference is known, to deduce the pH of the solution, as it is demonstrated in figure 2.