#CLAY00609

CORROSION DENSITY OF THE CARBON STEEL API 5L X65 IN CONTACT WITH CALLOVO-OXFORDIAN CLAY PORE WATER ASSESSED BY USING VARIOUS ELECTROCHEMICAL METHODS

TOPIC 07: Chemical processes, including microbial effects

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Abstract

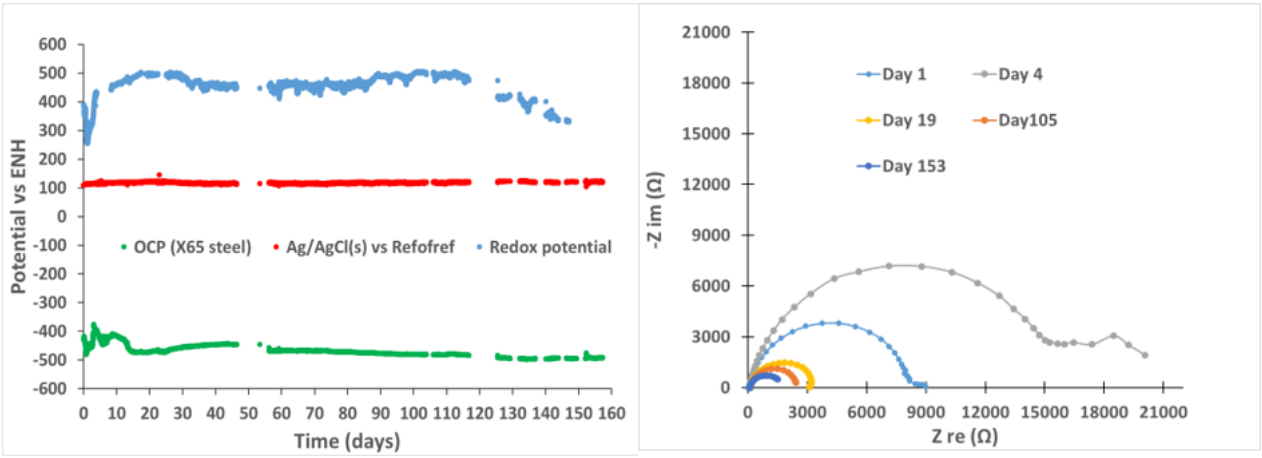
Nuclear Waste Disposal (NWD) programs mainly focus on deep geological storage, as this is the most appropriate strategy for ensuring the long-term safety of people and environment. Cigeo is a future deep NWD facility for high-level and intermediate-level long-lived radioactive waste, to be built in France, at 500 m depth within the clayey Callovo-Oxfordian formation (COx). Anoxic conditions prevail in the COx pore-water, where temperature, pH and pCO_2 are constant and remain key parameters for monitoring its evolution. Deep knowledge of the mechanisms as well as the kinetics of corrosion occurring at the surface of tubings or canisters made of API 5L X65 carbon steel in contact with pore water of COx, is essential for a reversible NWD management of the site. The development of on-site integrated tools, capable of reliable analysis over a long period of time and data transmission, is therefore of paramount importance.

This work aims to determine and compare by various electrochemical techniques, the corrosion kinetics of the carbon steel API-5L X65 in contact with COx pore water flowing continuously through a multi-parameter probe (MPP), an innovative device for long-term monitoring, placed at 490 m depth into a gallery of the Underground Research Laboratory of Andra at Bure. An electrochemical triplet, constituted of an X65 working electrode of an exposed surface of 0.64 cm², a $Ag/AgCl_{(s)}$ solid reference electrode and a Pt counter electrode, is electrochemically monitored. Another X65 electrode remains without external perturbation: only its Open Circuit Potential (OCP) was measured versus another $Ag/AgCl_{(s)}$ (Fig. 1).

The results are shown in figures 1 and 2. All $Ag/AgCl_{(s)}$ and Pt electrodes showed stability and robustness for over 156 days (Fig. 1). Flow rate variation on day 115 (increases to 1.6 g/h) caused a gradual decrease in the OCP of Pt (redox) down to 330 mV/SHE on day 156 and a very slight variation in the OCP of free X65 electrode.

Impedance spectroscopy (EIS) measurements performed at OCP ofX65, from 1MHz to 1 mHz, allowed to identify a rather classic equivalent circuit model in water and showed that the corrosion is limited by the H^+ reduction (Fig 1). The Tafel plot method (± 200 mV around OCP scanning 0.1mV/s) and then the VaOCP (±50 mV at a sweeping rate of 0.1mV/s) were performed and gave a Gary Stern parameter between the start and the end of the experiments of around B 15 mV. B will then be used to determine the X65corrosion densities from both the polarization resistances obtained through the EIS (R_{pw}), and the polarization resistances from the Rp method (± 20 mV at 0.1 mV/s) (Fig. 2). From 5 µA/cm² in the first hours, the corrosion density decreases until day 5 to reach less than 1 µA/cm². The EIS analysis (Nyquist mode) revealed the appearance during this period of an increasing second loop at low frequencies, corresponding to a protective deposit on the steel surface (Fig. 1). The corrosion rate then increases from day 5 to reach 10 µA/cm² (ie. 120 µm/year on day 25). This corrosion density acceleration is confirmed by the disappearance of the low-frequency capacitive loop, which means that the deposit no longer protects the steel from corrosion. The corrosion then stabilizes between day 25 and 156 at 10-15 µA/cm² despite the change in flow rate.

OCP and EIS of X65 and OCP of Pt and AgCls vs time



Corrosion density of X65 working electrode vs time