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Deconvolution of the Partial Anodic and Cathodic Processes during the Corrosion of Carbon Steel in Concrete Pore Solution under Simulated Anoxic Conditions

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ABSTRACT

A mixed potential model has been developed to deconvolve the negative total current density that is observed at potentials more negative than the open circuit potential, E_{corr}, during potentiostatic polarization of carbon steel in the simulated concrete pore solution under anoxic conditions into its partial anodic and cathodic components as a function of potential across the passive range. Deconvolution was successfully achieved by optimizing a Mixed Potential Model (MPM) comprising the Point Defect Model (PDM) to describe the partial anodic process and the Generalized Butler-Volmer equation to describe the partial cathodic process of hydrogen evolution. In this manner, the corrosion rate can be determined across the entire passive range, including the range of potential ($E < E_{corr}$) within which the net observed current density is negative. It is found that the corrosion rate increases significantly when the potential is lowered below a certain value, possibly due to the change of the oxidation state of iron within the outer-layer of the film.

1. Introduction

The current plans of ONDRAF/NIRAS for the disposal of high level nuclear waste (HLNW) in Belgium calls for encapsulating the processed or un-reprocessed waste in "supercontainers (SCs)" having the general configuration shown in Fig. 1. This container comprises an inner overpack of carbon steel, which contains the waste, and an outer stainless steel envelope, which confines the environment that is in immediate contact with the overpack. The annular space between the overpack and the envelope is filled with a concrete buffer having a composition similar to that of Portland cement. Therefore, the corrosion medium of the overpack is concrete pore water, which is saturated $Ca(OH)_2$ with a pH at 25 °C of 13.5 by the addition of NaOH.

Once the envelope is closed, the oxygen gas trapped inside the annular space will be gradually consumed by corrosion occurring simultaneously at the outer surface of carbon steel overpack and inner surface of stainless steel envelope. The decreasing oxygen partial pressure will drive the corrosion potential of the carbon steel overpack and the stainless steel envelope in the negative direction, and at a certain point the potential will be sufficiently negative to render hydrogen evolution, via the reduction of water, the predominant cathodic reaction. The process of hydrogen evolution in the designated system primarily takes the form of water, rather than proton reduction, which continuously produces hydrogen gas and releases it into the annulus containing the concrete buffer. Superimposed upon this potential change is that due to the fall in temperature due to the decay of the radionuclides resulting in a positive shift in the corrosion potential over the first 300 to 3000 years of storage, depending upon the form of the waste. Eventually, assuming the gas tightness of the stainless steel envelope, such that the hydrogen gas cannot escape, the annulus is predicted to become pressurized, which further lowers the corrosion potential. This continuous decrease in the corrosion potential defines the anoxic stage of the corrosion of the carbon steel overpack. Thus, it is predicted that over the short term (a few decades) the impact of falling temperature dominates over the reduction of the oxygen concentration and that the corrosion potential will at first decrease due to the consumption of oxygen and then increase due to the falling temperature and then begin a long term shift in the negative direction over the remaining life of the repository, due to the gradual build-up of hydrogen in the annulus. Thus, the carbon steel over most of the repository life (>99.99%) will be exposed to

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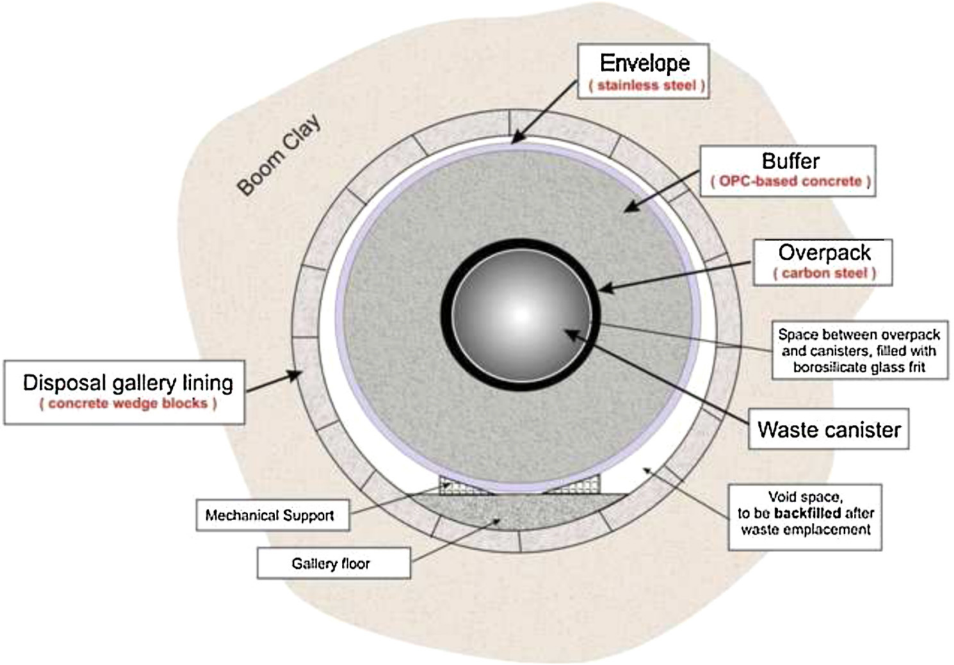

Fig. 1. The illustration of the cross-section and longitudinal-section of the high level nuclear waste super-container.

a "super anoxic" environment with the corrosion potential being as negative as -1.0 V_{she} corresponding to a hydrogen pressure of several hundred atmospheres. Because it is not feasible to simulate these conditions under open circuit conditions in the laboratory by imposing the requisite hydrogen atmosphere, it is necessary to simulate the conditions potentiostatically, by controlling the potential at the predicted corrosion potential. However, in doing so, the potential is much more negative than the equilibrium potential of the cathodic partial reaction of hydrogen evolution, with the result that the observed current is negative and hence cannot be used to estimate the corrosion rate. Accordingly, the research presented in this paper is focused on deconvolving the observed steady-state current density as a function of voltage into its partial anodic and cathodic components and the subsequent calculation of the corrosion rate using Faraday's law. Deconvolution is achieved by optimizing a Mixed Potential Model (MPM) comprising the Point Defect Model (PDM) to describe the partial anodic process and the Generalized Butler-Volmer Equation (GBVE) to describe the partial cathodic process of hydrogen evolution by using a genetic algorithm. Electrochemical Impedance Spectroscopy (EIS) is a powerful, *in situ* technique for studying the nature of the processes that occur at metal/solution interfaces in contact with aqueous environments, primarily because it is a small signal technique, thereby lending itself to mechanistic analysis, because the data can be validated independently via Kramers-Kronig transformation, and because relaxations ranging over at least six orders in magnitude of relaxation time are accessible in a single experiment.

2. Experimental

Carbon steel specimens were investigated in a typical three-electrode double-wall cell with a capacity of 300 ml. The simulated concrete pore solution (SCPS) was composed of saturated $Ca(OH)_2$ solution with the pH adjusted to 13.5 at 25°C by adding NaOH. All chemicals employed were of analytical reagent grade.

A Hg/HgO (2 M NaOH) reference electrode was selected in this work, due to its good stability in highly alkaline solutions. The reference electrode was connected to the electrolyte by a straight Luggin tube with a ceramic frit at the tip to minimize solution contamination. The inside of the tube was filled with the same working solution as in the glass cell. The equilibrium potential of the Hg/HgO (2 M NaOH) reference electrode versus the standard hydrogen electrode (SHE) was calculated thermodynamically by accepting the activity coefficient of OH^- as 0.766 and the activity of H_2O as 0.950 [1]. The obtained reference potential equals +0.0861 V_{SHE}. All potential values reported in this report are expressed on the SHE scale.

The working electrode was a machined carbon steel cylinder with a diameter of 15 mm and a length of 10 mm, which is coupled to a 20 cm insulated copper wire by a threaded joint at the center of top face. Miccrostop, a "stop-off" lacquer, was applied on the side of the cylinder to prevent crevice corrosion before the specimen was cast in epoxy resin. The bottom is exposed as the test surface with an area of 1.77 cm^2. The specimen was then wet-grounded to a 1200 grit surface finish by SiC paper and rinsed with ethanol, after which the electrode was immediately placed into the cell. A 5cm × 5 cm nickel mesh was placed surrounding the side surface of the working electrode cylinder as the counter electrode.

After assembly of the experimental apparatus, the cell contents were vigorously purged with ultra-high purity argon gas (99.999%) to expel any oxygen. Deaeration was then continued throughout the whole experiment by injecting argon gas with lower flow rate into the solution to avoid contamination by oxygen. A potentiodynamic scan was performed from -1000 mV to +800 mV at a rate of 0.1667 mV/s to determine the approximate passive range of the carbon steel. Several potentials were then selected within the passive region, but close to the cathodic end as the film formation potentials (from -600 mV to 0 mV with an interval of 100 mV, as reported in later section), in order to simulate the "super-anoxic" conditions that exist in the repository. Prior to commencing the potentiostatic experiments, a negative voltage (-1000 mV) was applied for 10 minutes on the specimen to reduce any air-formed oxide film, so that a more reproducible initial test surface could be created. Potentiostatic polarization at film formation potentials were then immediately conducted after the cathodic treatment. At each film formation potential, potentiostatic polarization was kept for 48 hours to ensure an "operational" steady state of the system, followed by the EIS measurement at this potential. A side experiment