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Corrosion monitoring in mixture cement paste – bentonite

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Abstract – *Electrochemical Impedance Spectroscopy (EIS) has been used to monitor at the same time the curing process of cement – bentonite mixture and the iron corrosion rate in this mixture. It has been shown that the curing process has extended over a period of at least 100 days at room temperature. During this period, the iron corrosion rate was always low i.e. about 2 nm/year in aerated condition and about 1 nm/year in anaerobic condition. These values have confirmed that such cement – bentonite mixture would be an efficient environment to avoid iron corrosion damages even in aerated condition.*

I. INTRODUCTION

In the underground radioactive waste repository it studies, Andra plans to inject cement-bentonite mixture between the liner and the wall of the vitrified waste cell drilled in the Callovo-Oxfordian layer. This mixture has two main functions: the first one is to neutralize the acidity due to oxidation of the sulfurs in the claystone after drilling operation; the second one is to limit oxygen diffusion into the claystone during the exploitation phase. The formulation of the mixture may adapt these specifications, with for example an initial pH > 10. The pH in the genuine claystone at room temperature is about 7. This shift towards basic pH would decrease the corrosion rate of the liner steel. At longer time, the pH would decrease and the corrosion rate should increase only slightly because of steel passivation at basic pH at shorter time. The purpose of this paper is to present the first corrosion results obtained in the framework of the Andra program.

II. EXPERIMENTAL SETUP

The combination of impedance measurements on iron and linear scanning voltammetry on gold electrode allow tracking the evolution of (i) iron corrosion rate in cement - bentonite mixture but also (ii) the curing process of the mixture. In the methodological model studied here, the mixture contained 16% CEM III/C Rombas and 4% Bentonite with 80% Evian mineral water. Experiment has been performed at 21°C in initial aerated condition in autoclave to ensure sealing condition. So corrosion of iron and cure of cement – bentonite mixture ran both in fully closed condition. Iron samples were made of ArmoTM iron and gold electrode consisted in a nickel covered with 0.3 µm gold layer deposited by sputtering.

Electrochemical Impedance Spectroscopy (EIS) has given 2 experimental results. In high frequency range (100-

1 kHz), ionic conductance of the mixture was available. In low frequency range (1-0.1 mHz) corrosion rate could be evaluated thank to the Stern-Gary method¹.

III. EXPERIMENTAL RESULTS

III.A. Monitoring of the cement-bentonite mixture curing

At initial time, the cement-bentonite mixture was pasty i.e. solid particles embedded in mineral water. With time this mixture has solidified. This process corresponds to the built-in of a solid phase containing pores filled with ionic solution. As a consequence, the seeming ionic conductance of the mixture has decreased with time. As shown on figure 1, the ionic conductance Y_e has decreased continuously with time from about 1 S to tend toward a quasi-steady-state value of about 30 mS. From this time evolution, it can be concluded that the cure time of the mixture is about 100 days at 21°C. It must be emphasized that in the range 80-100 days some slow decrease for Y_e could be still observed. But this decrease was lower and lower with increasing time.

III.B. Corrosion monitoring of iron in the cement-bentonite mixture

The evaluation of the iron corrosion rate has been performed thank to the Stern-Gary method. This method assumes that the corrosion process consists in the sum of an anodic process describing the oxidation of metal and a cathodic process describing the reduction of oxidant contained in the environment. Both anodic and cathodic processes are assumed to be described by Butler-Volmer laws². This gives a relation between the transfer resistance R_t get from IES and corrosion current density j_{corr} :

$$j_{\text{corr}} = \frac{1}{\alpha_a n_a + \alpha_c n_c} \frac{RT}{F} \frac{1}{R_t} \quad (1)$$

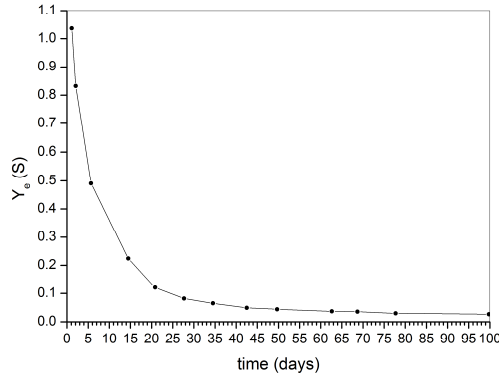


Fig. 1. Time evolution of the ionic conductance Y_e of the cement-bentonite mixture at 21°C.

where α_a and α_c are respectively the Butler-Volmer coefficients of the anodic and cathodic processes. n_a and n_c are the numbers of electron involving in the anodic and cathodic processes respectively. R is the ideal gas constant, F the Faraday and T the temperature in K. Previous studies performed in the framework of the nuclear waste repository have shown that the term $\alpha_a n_a + \alpha_c n_c$ was about 2. This value was obtained by calibrating such a corrosion monitoring with either final weight loss³ or cross section observations⁴ of corroded samples in clay environments. Finally, the corrosion rate was calculated using the Faraday's law:

$$v_{corr.} = \frac{j_{corr.}}{n_a F} \frac{P_M^{Fe}}{\rho_{Fe}} \times 3155.76 \quad (2)$$

where P_M^{Fe} is the molar mass of iron and ρ_{Fe} its density. The factor 3155.76 allows expressing the corrosion rate in $\mu\text{m}/\text{year}$. The observed corrosion rate evolution during the experiment is shown in figure 2.

An initial decrease was observed in the first 5 days followed by an increase extending up to about 60 days. Suddenly, the corrosion rate fell down. Then the corrosion rate seemed to tend toward a quasi-steady-state value around 1 nm/year. This result was in contrast to those obtained for the monotonic time evolution of the ionic conductance shown in figure 1. The decrease observed in the first 5 days could be related to the built-in of the cement-bentonite mixture because a decrease of available aerated water for iron corrosion could be assumed. But the following increase and the sudden decrease cannot be explained because the cure process of the mixture would continuously decrease the amount of free water available for iron corrosion. This seeming contradiction suggests that the corrosion rate doesn't depend on the amount of free

water only. Two chemical features could be considered. One was the evolution of the pH of the free porewater. The second was the amount of dissolved oxygen available for iron corrosion. In order to follow qualitatively such chemical features, a gold-nickel electrode has been introduced in the autoclave.

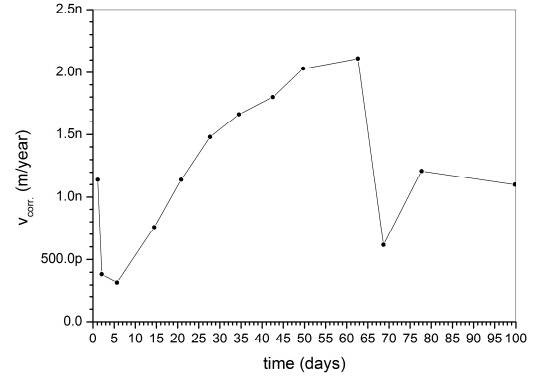
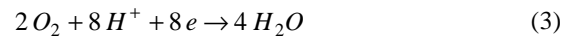


Fig. 2. Time evolution of the iron corrosion rate in the cement-bentonite mixture at 21°C.

III.C. Scanning Voltamperometry study of the cement-bentonite mixture

The purpose of this experimental part was to get some additional information about the evolution of the cement-bentonite mixture during the experiment in order to explain the iron corrosion rate presented in the previous section. The Scanning Voltamperometry (SV) method consists in the measurement of the cathodic current on gold-nickel electrode as its electrochemical potential is decreased linearly with time. It must be emphasized that this electrochemical method involve chemical perturbations especially in porous environment. The cathodic process in aerated water is actually the sum of 2 elementary reactions. The first one is the reduction of dissolved oxygen:



The second one is the reduction of water into dissolved hydrogen:



From thermo-electrochemical considerations, the former reduction occurs at higher potential than the later. From these two electrochemical equations it is obvious that the run of these electrochemical reactions leads to the consumption of available dissolved oxygen and also to an increase of the pH. In bulk solution, the consumption of O_2 and H^+ or production of OH^- in the vicinity of the electrode will be encompassed by a supply from the bulk solution. But in porous environment this supply will be restricted by diffusion in solution. This was confirmed by the important shift of the free potential of the gold-nickel electrode

observed after the SV method was performed. As a consequence, the SV method could not be used as frequently as the EIS method because it was needed to wait for a long time before to perform another SV. Only 3 SV experiments have been performed during the experiment. But it was enough to qualitatively describe the cathodic process evolution during the experiment. The 3 current voltage curves obtained are depicted on the figure 3 in Tafel representation. It must be outlined that there has been no reference electrode in the autoclave because such an electrode needs to be controlled and/or re-conditioned over a 100 days experiment. This is a technical limitation due to the fact that it was impossible to extract a reference electrode from the autoclave without perturbing the evolution of the iron corrosion process. So a second iron electrode has been introduced in place and has been used as pseudo-reference electrode. As a consequence, the potential is referred to the free corrosion potential of iron. It was not a drawback because the purpose of the SV method was to compare step by step the current-voltage variations.

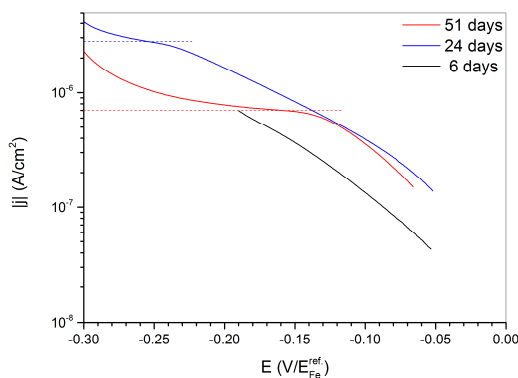


Fig. 3. Current – voltage curves measured on gold – nickel electrode for 3 durations in the cement-bentonite mixture at 21°C.

The comparison of current-voltage curves obtained after 6 and 24 days has shown clearly that the kinetics of the reduction process on the gold-nickel electrode has increased. Two parallel curves were obtained with nearly similar Tafel slopes. Extrapolation to the free voltage gave exchange current which has increased over this period from 14 to 110 nA/cm². The nearly linear variation in Tafel representation has shown that at free voltage, the cathodic process on gold-nickel electrode was under kinetics control. So from (3), the exchange current depended on the O₂ concentration and on the pH. Such an increase for exchange current could be explained by a decrease of pH of the pore solution because the O₂ concentration could not increase. The potential range for the SV method performed after 6 days has been restricted to minimize perturbation of the free potential induced by the SV method.

The comparison of current-voltage curves obtained after 24 and 51 days has shown that the exchange current has decreased from 110 to 40 nA/cm². Moreover at high cathodic over voltage a plateau was observed. This plateau was due to diffusion control of the O₂ reduction. In this voltage range, the intensity of the plateau was only monitored by the concentration of dissolved oxygen. The comparison of the intensities of plateau has shown that the concentration of dissolved oxygen has decreased from 2.7 to 0.7 μA/cm². In other words between 24 and 51 days, the O₂ concentration has been divided by 3.85.

IV. DISCUSSION

The results obtained on the gold-nickel electrode have shown that during a period of time ranging from 6 to 51 days, the pH of the pore solution has decreased. At the same time, the iron corrosion rate has increased (cf. figure 2). The pH decrease was probably due to some geochemical transformations of the cement-bentonite mixture. Electrochemistry cannot describe such transformations but only detects their consequence i.e. the decrease in pH. An indirect consequence of the pH shift to more acid value was that the kinetics of oxygen reduction was also enhanced on all metal surfaces: gold, iron but also the wall of the stainless steel autoclave. As a consequence, the concentration of dissolved oxygen has decreased because the experimental device (autoclave) was fully closed. Likely, the fall down of the iron corrosion rate observed on figure 2 after 60 days was due to the full disappearance of oxygen in the autoclave. It must be emphasized that the time needed for the transition from aerated to anaerobic condition was specific of the experimental design because this time depended on the ratio between all reactive surfaces for O₂ reduction and the total amount of dissolved oxygen initially introduced in the autoclave.

The transition from aerated to anaerobic condition was indirectly confirmed by the following experimental fact. After the fall down of the iron corrosion rate, it was impossible to perform any SV method because the potentiostat fell in overload condition. Such an overload is observed when the current cannot flow between the working electrode (gold-nickel electrode) and counter electrode (wall of the autoclave). This experimental trouble could be explained as follows: in anaerobic condition the cathodic reaction is the reduction of water into hydrogen (4). When the over-voltage was increased the kinetics of hydrogen production was also increased. This led to the formation of hydrogen bubbles. In bulk solution these bubbles could be eliminated from the surface of the working electrode. But in porous environment, these bubbles have been trapped on the surface of the gold-nickel electrode and prevent the current to flow from this electrode. So the potentiostat fell in an overload state. This

implies that SV method cannot be used in anaerobic condition in such porous environment.

During the early aerated condition, SV method has shown that the exchange current on the gold-nickel electrode was enhanced by 7.85. It must be outlined that the iron corrosion rate was enhanced only by 4. The ratio between corrosion rate and acidification gave an order of reaction for the proton roughly equal to 0.5. This implies qualitatively that the iron corrosion process in this cement-bentonite mixture was likely monitored by both anodic and cathodic processes.

V. CONCLUSION

The results presented above have shown that corrosion monitoring of iron or steel was possible in cement – bentonite mixture. This first experiment has been performed at room temperature (21°C). As expected, the iron corrosion rate was low (≈ 2 nm/year) even in aerated condition. In anaerobic condition the corrosion rate has decreased to about 1 nm/year. It was also shown that Scanning Voltamperometry method on gold could be used in aerated condition to monitor the evolution of the reduction of dissolved oxygen. In contrast, this method cannot be used in anaerobic condition because hydrogen bubbles formed are trapped on the gold surface and prevent to measure the electrochemical kinetics of the reduction of water in hydrogen.

The next step will be to increase the temperature of the experiment to simulate the introduction of nuclear waste canisters. Andra has planned an increase of temperature up to 80°C. This experiment is in progress.

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