INFLUENCE OF STEEL-CONCRETE INTERFACE AND PRE-EXISTING OXIDES LAYER ON PASSIVE REINFORCING STEEL CORROSION

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ABSTRACT

This paper deals with the influence of the steel-concrete interface quality and preexisting oxides layer on reinforcement corrosion in passive state. In passive state, steel corrosion rate in concrete is considered null for conventional civil engineering structures due to the relatively short design service life time. On the contrary, for the nuclear waste facilities, due to a very long design life time, this low corrosion rate can become a risk. Previous studies, dealing with chloride induced steel corrosion propagation. The purpose of this work is to study the influence of steel-concrete interface defaults and preexisting oxides layer on steel passivity and the consequences on the corrosion rate. Electrochemical methods and destructive surface analysis techniques were used to assess the corrosion rate of the embedded steel bars. Results confirm that the quality of the steel-concrete interface and the preexisting oxides layer affect the steel corrosion rate in passive state.

Keywords: nuclear waste facilities, corrosion rate, passive state, steel-concrete interface, preexisting oxides layer.

1. INTRODUCTION

Steel is considered an important raw material in various applications. Its wide use in several industries, because of its low cost, excellent mechanical properties and availability for the manufacture of various materials [1].

In recent years, the phenomenon of corrosion has a negative impact on the industry [2]. Reinforced concrete structures are widely used in the nuclear industry for nuclear waste storage facilities. For these specific applications, it is necessary to know and envisage the physical and chemical evolutions in the time of this material in order to prevent any deterioration related to the degradation of reinforced concrete structures.

The deterioration of reinforced concrete structures due to corrosion is a major problem all over the world. In general, the cement hydration provides a high pH non-aggressive environment to the embedded reinforcements by forming an insoluble oxide film on the surface [3]. This passive layer limits the corrosion of reinforcement steel to very low values (the steel corrosion in passive state). In the passive state, steel corrosion rate in concrete is considered null for conventional civil engineering structures due to the relatively short design service life time. On the contrary, for the long life (> 1000 years) nuclear waste storage facilities, due to a very long design life time, this low corrosion rate can become a risk. Indeed, the corrosion products layer growth induces mechanical stresses in concrete which leads to concrete cracking [4] and thus may contribute to reduce the

capacity of the reinforced concrete structure to confine the nuclear wastes.

Researches carried out in the LMDC on corroded beams, submitted to 25 years chloride aggression and sustained loading, showed that corrosion firstly occurred on the reinforcements with a bad steel-concrete interface quality due to the "top-bar effect" or due to mechanical damages [5] [6] [7] [8]. A good adhesion between steel and concrete provides better protection against steel corrosion. This result is in accordance with other works conclusions [9], [10]. Regarding the importance of the steel-concrete interface quality on chloride induced corrosion, this work aims to assess the influence of such interface defects on steel corrosion in passive state. Results should help to improve the life time prediction of nuclear waste storage facilities.

In this study, the influence of steel-concrete interface quality on reinforcement corrosion in passive state is investigated. Several concrete specimens including steel bars with different steel-concrete interface conditions were cast and stored indifferent ageing environments in aerated or non-aerated media with different hygrometric or temperature conditions. These different ageing conditions are supposed to reproduce the different phases of the real life time conditions of the waste storage structures according to ANDRA estimations.

The concrete specimens ageing analysis is planed over a period of three years. In this paper, only the first results obtained on samples stored in aerated media with two hygrometric conditions (RH = 80 %, 95 %) and at temperature 20°C are presented.



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2. EXPERIMENTAL PROGRAM

a. Concrete Mixtures and Casting Conditions

Using the concrete composition presented in Figure-1, high size concrete members were cast including horizontal the PVC-conventional ribbed reinforcing bars located at different levels in order to create the defaults at the steel-concrete interface. The steel-concrete interface defaults generated, using this method, are due to the wellknown "top-bar effect" [11], [12], leading to voids formation under the horizontal top bars regarding to the concrete casting direction. These steel bars were distributed with 105 mm spacing over the 1100 mm height of the concrete elements (Figure-1). The concrete compressive strength and elastic modulus measured after 28 days were 50 MPa and 37000 MPa respectively.



Figure-1. High size concrete elements, concrete composition, location of the steel bars and concrete casting direction.

Each wall had ten reinforcing bars. Special methodology was developed to ensure that steel bars are fully embedded in the concrete. The embedded reinforcing bar was composed of two 12 mm diameter conventional ribbed steel bars, which were glued together by PVC tube as shown in Figure-2. As shown in the Figure-2, the steel bars were machined in order to ensure a sufficient strength at the connection with the PVC tubes during the concrete

casting. The steel bars were stored in the laboratory environment before to be cast in the concrete elements, then, they are affected by an initial atmospheric uniform corrosion. An electrical wire was connected with one of the ribbed steel bars to perform electrochemical measurement every three months, the second bar is used to perform destructive mass loss measurement after 1, 2 and 3 years.



Figure-2. PVC-steel rebar cast in the high concrete members.

After 28 days of curing in the water (T = 20° C), the high concrete members were sawn to obtain, for each element, samples including only one steel bar. Ten horizontal sawing were performed always under the rebars in regard to concrete casting direction. One vertical sawing over the height of the high concrete elements was performed in the middle, thus through the PVC tubes. The small specimens obtained are 12,5x10x8 cm³ including only one reinforcing bar with 20 mm of concrete cover in the bottom interface side so on the side of the interfacial voids (Figure-3). The two end lateral surfaces were then coated by using a specific epoxy resin in order to prevent water and carbon dioxide penetration from these surfaces. This method ensures that the steel bars are totally embedded in the concrete and exposed to steel corrosion process in passive state.

Several high size concrete members were cast for this study. In total, about 100 small size specimens were obtained after the sawing process. Part of these specimens were stored in aerated media with four hygrometric



conditions (RH = 80%, 90%, 95%, and saturated media) and at different temperature (T = 20 °C or 50°C). The relative humidity is controlled by using specific saturated salt solutions. The other part of the specimens was stored in non aerated media at the CEA with the same relative

humidity or temperature conditions as for the aerated media. In order to perform a comparative analysis, for each ageing condition, both small specimens with or without steel-concrete interface defects are considered.



Figure-3. Specimen after sawing and interface defect location regarding to the lower concrete cover.

b. Experimental Methods

Steel-concrete interface observation

Steel-concrete interface was analysed by using a video-microscope with an enlargement of 25 times. The interface quality can be characterised in terms of two parameters: the maximum width of void and the unbonding length (Figure-3(b)).

Linear Polarisation resistance measure

The polarisation resistance (R_p) method is a very popular and effective non-destructive technique for the evaluation of corrosion in reinforced concrete structures. In this paper, polarization resistance (R_p) of specimen was measured by a Potentiostat G300 conducting a linear polarization scan in the range of \pm 20 mV of the corrosion potential. The scan rate is 0.125 mV/s. Polarization resistance (R_p) can be correlated to the corrosion current (I_{corr}) by using the Stern-Geary equation [13], [14], [15] (Eq. (1)):

$$I_{corr} = \frac{\beta_a \times \beta_c}{2.3 \times R_p \times (\beta_a + \beta_c)} = \frac{B}{R_p}$$
(1)

Where, β_a and β_c are anodic and cathodic Tafel constants respectively. To simplify the calculation, a constant value B was adopted by some researchers [16], [17]. The value of B is assumed to be 25 mV for the active corrosion state and 50 mV for the passive state. The corrosion of steel bar in concrete is assumed uniform over

the area of reinforcement polarized. The corrosion current density (i_{corr}) , which is always used to represent the corrosion rate, can be calculated by using Eq. (2).

$$i_{corr} = I_{corr} / A \tag{2}$$

Where, A is the surface area of the steel polarized.

Corrosion products analysis

Destructive tests were performed on four samples in order to analyze the type of rust present at the steelconcrete interface after a maximum period of one year. Specimen's cross-sections analysis was performed. Raman micro-spectroscopy technique and SEM-EDS were used to identify the nature of the rust present at the steel interface of two specimens (with or without interface default). Two other specimens (also with or without interface default) were broken in order to observe the surface condition of the ribbed reinforcing bars (simple visual observation).

3. EXPERIMENTAL RESULTS

In this paper, only the first results obtained on 4 samples stored in aerated media with two hygrometric conditions (RH = 80 %, 95 %) and at temperature 20 °C are presented.

Steel-concrete interface default observation

Figure-4 shows two examples of steel-concrete surface default observation by using a video-microscope. The bars located above 30 cm height in the high concrete elements show default width superior to $200 \,\mu$ m due to the



Top-bar effect and are labelled default-max samples. On the contrary, the two lower bars present no default and are labelled default-min samples. These observations show the

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efficiency of the experimental method to generate both samples with or without steel-concrete interface defects.



Interface default (Default-max)



Perfect interface (Default-min)

Figure-4. Surface default observation by using a video-microscope (x 25).

Linear Polarisation resistance measure

environment at controlled relative humidity (RH(%): 80% and 95%) for up to two years.

Figures 5 and 6 show the corrosion current densities evaluated on specimens stored in a ventilated



Figure-5. Corrosion current evolution – RH(%) 80.



Figure-6. Corrosion current evolution – RH(%) 95.

The evolution of corrosion current densities evaluated during these first two years of conservation remains low, of the order of 0.023 ± 0.009 to $0.047 \pm 0.020 \,\mu$ A/cm. The values of the corrosion current densities correspond to corrosion of the steel in the passive state.

For these maturities and given the dispersions observed in the results, it is not possible to show an influence of the quality of the steel-concrete interface on corrosion in the passive state. Corrosion current densities of flawless samples appear to increase very slightly at 95% relative humidity. Indeed, after 2 years of storage the corrosion current density varies from 0.034 ± 0.010 to $0.047 \pm 0.017 \,\mu$ A/cm² between HR(%) 80 and HR(%) 95 for samples without interface defects. In the case of samples with interface defects the corrosion current density varies from 0.034 ± 0.009

 μ A/cm² between HR(%) 80 and HR(%) 95.These values remain very insignificant given the dispersions observed.

Corrosion products analysis

The frameworks used in our work are covered by an initial oxide layer, so a characterization of the initial state of the frameworks was necessary, to characterize the initial state we used SEM to determine the thickness of the initial oxide layer and its chemical composition. The results of this characterization show that the thicknesses of the initial layer are very variable from one zone to another, these thicknesses vary globally from about 2 to 20 μ m. (Figure-7).

		Steel
Measurement areas	150	
Average Thickness(µm)	6,4 ± 0,5	
Maximum thickness (µm)	20,1 ± 0,5	Resin
Minimum thickness (µm	2,0 ± 0,5	15kV X500 50мm

Figure-7. Thickness of the initial oxides layer.

EDS analyses show that this initial layer is composed mainly of iron and oxygen, with an Fe/O ratio close to 3. (Figure-8).



Figure-8. EDS analysis of the pre-existing oxide layer before casting.

After one year's storage in an aerated environment with controlled relative humidity, the SEM-EDS observations on the samples stored under these storage conditions were carried out. For each storage condition, one specimen with a "max defect" (D1) and one specimen with a "min defect" (N1) were analysed. Figures 9 and 10 show examples of analysis areas on samples stored for one year in a ventilated environment at controlled relative humidity (HR(%) 80 and HR(%) 95).



Figure-9. EDS analysis areas after 1 year - aerated environment at RH(%) 80.



Figure-10. EDS analysis areas after 1 year - aerated environment at RH(%) 95.

Table-1 show the mass percentages of the main elements present in the areas analysed (Fe, O and Ca) on

the samples kept in an aerated environment with controlled relative humidity.

		Mass percentage of element (%)		
Sample	Analysis zone	% (Fe)	% (Ca)	% (O)
	1	54,75	6,52	33,70
AE-RH80-D1 (Aerated media, RH(%) 80 « default-max »)	2	55,49	9,60	32,36
	3	35,60	16,89	35,88
	4	76,72	0,39	22,82
	5	74,90	0,25	24,79
	1	68,28	10,99	19,24
AE-RH80-N1	2	63,49	8,75	26,01
(Aerated media RH(%) 80	3	65,59	9,81	23,50
« default-min »)	4	62,75	9,58	26,91
	5	79,95	0,36	19,51
AE-RH95-D1 (Aerated media, RH(%) 95 « default-max »)	1	50,44	15,72	32,89
	2	58,61	8,99	31,38
	3	50,57	10,96	37,21
	4	69,40	0,66	29,72
AE-RH95-N1	1	68,82	8,27	21,96
	2	64,92	5,87	28,79
(Aerated media, RH(%) 95	3	70,89	4,66	23,83
« default-min »)	4	83,22	0,52	16,06

Table-1. Mass % of existing elements on SEM analysis areas after 1 year in aerated environment at controlled RH(%).

The results of SEM observations of the surface of the reinforcement in cross-section after one year of storage, in an aerated milieu at controlled RH (%). show the formation of a new oxide layer on both sides of the metal-oxide layer interface. The elemental initial characterization (EDS) shows that iron and oxygen, present in the initial oxide layer before casting, and calcium with a mass percentage ranging from 5 to 17% are present. This layer of oxides new-formed after one year of conservation was observed on all the samples analysed (stored in a aired milieu at controlled HR(%)).In the majority of cases, In most cases, this layer contains less iron, more oxygen compared to the initial oxide layer characterized before casting (Figures 5 and 6) and especially much more calcium. In the images issued from the SEM observations, these new formed oxide layers, which systematically contain calcium, differs from the initial oxide layer by its dark grey tint (presence of an element which is lighter than iron calcium.

Surface condition after splitting

Since the micro-Raman and SEM-EDS in torque analyses cover only a very small part of the surface (a few zones per sample), the specimens recovered after the cuts, realized for surface analysis (SEM-EDS and micro-Raman), were broken by splitting in order to visually observe surface condition of the armatures. Figures 11 and 12 shows some views of the frames recovered after splitting. For each armature, the lower and higher surfaces were observed. Immediately after splitting, in order to compare the surface condition of the cohesion side (superior face) with that of the decohesion side (inferior face) in the case of a specimen with «defect max », this as compared with specimens without interface defects.

	Bottom half-bar	Top half-bar
Interface with default "default-max" AE-RH80-D1		
Interface without default "default-min" AE-RH80-N1		

Figure-11. View of the lower surface according to concrete casting direction of a default-min and a default-max specimen (on the side of the void) -1 year in aerated media, RH(%) 80.

	Bottom half-bar	Top half-bar
Interface with default "default-max" AE-RH95-D1		
Interface without default "default-min" AE-RH95-N1		

Figure-12. View of the lower surface according to concrete casting direction of a default-min and a default-max specimen (on the side of the void) - 1 year in aerated media, RH(%) 95.

After splitting samples stored in aerated storage at controlled RH(%), stains of corrosion products have been observed, immediately after concrete removal, on the surfaces of the armatures on the side of the steel-concrete decohesions (undersides face) in the case of samples with « max defect ». These products observed on some micro-Raman analysis areas may correspond to a poorly crystallised iron oxyhydroxide in the case of samples stocked in an aerated environment at HR(%) 95 or at the calcium-rich layer observed at the SEM-EDS on most of the samples analysed and in priority in the presence of defects.

For each sample, a single cross-section is made and analysed using micro-Raman. Furthermore, only highly dispersed corrosion product stains were observed on the surfaces of the frameworks with "max defect" on the decohesion side. These observations may explain the absence of Raman spectra corresponding to the corrosion product stains observed.

At the end of one year, there is a difference between the «min default » case and the «max default » case. Corrosion product stains observed on the lower part of the test specimen reinforcements with «max defect» (decohesion side) are not observed on the upper part of these same reinforcements. They are also not raised on the surface of the reinforcement of the test specimens with «min defect » (Figures 11 and 12).

4. CONCLUSIONS

Experimental method was developed in order to manufacture concrete specimens including steel-concrete interface default resulting from the top-bar effect. Moreover, PVC-steel bar was also developed in order to ensure that the whole steel part is inside the concrete specimens ensuring a passive state.

Section surface analysis results (micro-Raman and SEM-EDS) on all samples, stored in an aerated environment at controlled RH(%), show the presence of oxides produced by hot steel corrosion then a new layer of oxides formed after pouring could be observed on all the samples whatever the conservation medium. This newly formed oxide layer is mainly characterized by a high calcium mass percentage of up to 33%.

The mass percentages of Iron, Calcium and Oxygen obtained in the SEM-EDS analyses seem to confirm the presence of this hydrated calcium ferrite as a new oxide layer formed after pouring on our samples. The presence of interface defects seems to increase the kinetics of formation of the calcium-rich neoformed layer, by transformation of pre-existing oxides such as magnetite. In effect, the maximum rate of areas on the perimeter of the steel-concrete interface where the presence of this neoformed layer was observed was only 8,2 % at most for a sample with a defect in the interface.

With regard to the presence of steel-concrete interface defects, even if an acceleration of the transformation kinetics is observed, this doesn't seem to represent a risk for the lifetime of the storage facilities for the reason mentioned before.

The measured passive corrosion rates remain equivalent with or without interface defects and less than 0.6μ m/an (0, 05μ A/cm²).

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REFERENCES

- [1] Merimi I., Benkaddour R., Lgaz H., Rezki N., Messali M, Jeffali F, Oudda H and Hammouti B. 2019. Insight into corrosion inhibition behavior of a triazole derivative for mild steel in hydrochloric acid solution, journal of Materilas Today: Proceeding. 13: 1008-1022.
- [2] Merimi I., E. L. Ouadi Y., Benkaddour R., Lgaz H., Messali M., Jeffali F. and Hammouti B. 2019. Materials Today: Proceedings, Improving corrosion inhibition potentials using two triazole derivatives for mild steel in acidic medium: Experimental and theoretical studies. 13: 920-930.
- [3] Tuutti K. 1982. Corrosion of steel in concrete. CBI Research Report n°4.82, Swedish Cement and Concrete, Research Institute, Stockholm, Sweden.
- [4] Millard A., L.'Hostis V., Beddiar K., Berthaud Y., Caré S. 2004. Modelling the cracking of a reinforced concrete structure submitted to corrosion of steels first validation of a damage model based on

experimental tests. CSNI/RILEM Workshop on use and performance of concrete in NPP fuel cycle facilities, Madrid, Espagne, 15-16 mars 2004.

- [5] Castel A., Vidal T., François R., Arliguie G. 2003. Influence of steel-concreteinterface quality on reinforcement corrosion induced by chlorides. Magazine of Concrete Research. 55(2): 151-159.
- [6] Vidal T., Castel A., François R. 2007. Corrosion process and structural performance of a 17 year old reinforced concrete beam stored in chloride environment. Cement and Concrete Research. 37: 1551-1561.
- [7] Söylev T. A., François R. 2003. Quality of steelconcrete interface and corrosion of reinforcing steel, Cement and Concrete Research. 33(9): 1407-1415.
- [8] Söylev T. A., François R. 2005. Corrosion of reinforcement in relation to presence of defects at the interface between steel and concrete. Journal of materials in civil engineering © ASCE/July/August 2005.
- [9] Otsuki N., Miyazato S., Diola N., Suzuki H. 2000. Influences of bending crackand water-cement ratio on chloride-induced corrosion of main reinforcing bars and stirrups. ACI Materials Journal. 97(4): 54-464.
- [10] Mohammed T. U., Otsuki N., Hisada M. 1999. Corrosion of steel bars with respect to orientation in concrete. ACI Materials Journal. 96(2): 154-159.
- [11] Jeanty P. R, Mitchell D., Mirza M. S. 1988. Investigation of Top Bar Effects in Beams. ACI Structural Journal. 85(3): 251-257.
- [12] Castel A., Vidal T., Viriyametanont K., François R. 2006. Effect of reinforcing bar orientation and location on bond with self-consolidating concrete, ACI Structural Journal. 03(04): 559-567.
- [13] Mangat P. S, Molloy B. T. 1991. Influence of PFA, slag and microsilica onchloride induced corrosion of reinforcement in concrete, Cem. Concr.Res. 21(5): 819-834.
- [14] Macias A., Andrade C. 1987. Accuracy of different electrochemical laboratory techniques for evaluating corrosion rates of galvanized reinforcement, Proceedings of the 4th International Conference on Durability of Building Materials and Components, Singapore. 516-522.





- [15] Khatri R. P., Sirivivatnanon V., Heeley P. 2004. Critical polarization resistance in service life determination, Cement and Concrete Research. 34(5): 829-837.
- [16] Andrade C., Alonso C. 1996. Corrosion rate monitoring in the laboratory and on-site, Constr. Build. Mater. 10(5): 315-328.
- [17] Millard S. G., Law D., Bungey J. H., Cairns J. 2001. Environmental influences on linear polarization corrosion rate in reinforced concrete, *NDT & E Int.* 34, 409-417.