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COMPARING THE STEEL-CONCRETE INTERFACE STATE AND ITS ELECTROCHEMICAL IMPEDANCE

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ABSTRACT

The object of this investigation is to validate a model of electrical impedance of steel-concrete interface, which has been previously published. In this model, a part of the impedance is related with the products formed directly on steel. Another part of the impedance corresponds to the transition zone between steel and concrete. The third part corresponds to the inhomogeneity of the products formed at the interface.

The validation of this model was obtained by testing reinforced concrete specimens made of three cements and aged in solutions containing chloride or sulphate. The results obtained with measuring electrochemical impedance were compared with the actual condition of steel.

RÉSUMÉ

L'objet de cette étude est de valider un modèle électrique publié antérieurement, sur l'impédance de l'interface acier - béton. Dans ce modèle, une partie de l'impédance est liée aux produits directement formés sur l'acier. Une autre partie de l'impédance correspond à la zone de transition entre l'acier et le béton. La troisième partie correspond à l'hétérogénéité des produits formés à l'interface.

La validation de ce modèle a été obtenue en essayant des éprouvette de béton armé armé, faites avec trois ciments et placées dans des solutions contenant des chlorures ou des sulfates. Les résultats de mesure d'impédance électrochimique ont été comparés à l'état réel de l'acier.

Introduction

The electrochemical impedance of the interface between concrete and embedded steel has recently been described with a model applicable which takes into account the products formed by reactions between cement paste and metal (1).

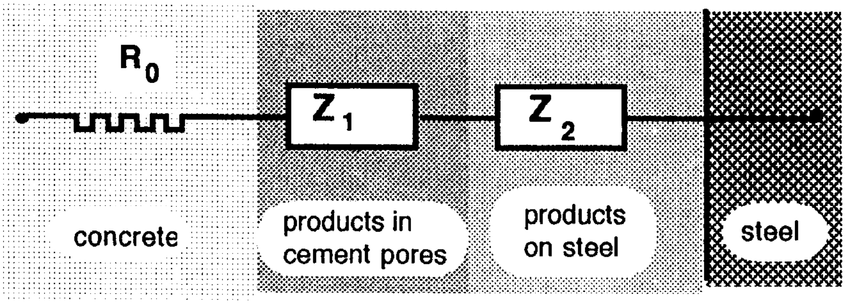

FIG. 1.
Electric model of the steel-concrete interface.

The object of this paper is to compare this electrochemical model with the physical properties of steel-concrete interface.

It is to be noted that the electrochemical impedance is measured at high and low frequencies, as well. So, it corresponds not only to the chemical and microstructural change in concrete (2), but also to the interface between steel and concrete (3).

Modelling the Electrochemical Impedance of Steel-Concrete Interface

Electrochemical Impedance Model. The model of electrochemical impedance which has previously been proposed (1) for steel-concrete interface, includes the following items (Figure 1):

- a part of the impedance is related with the iron products formed directly on steel surface, and which are more or less thick, depending on the metal passivation state,

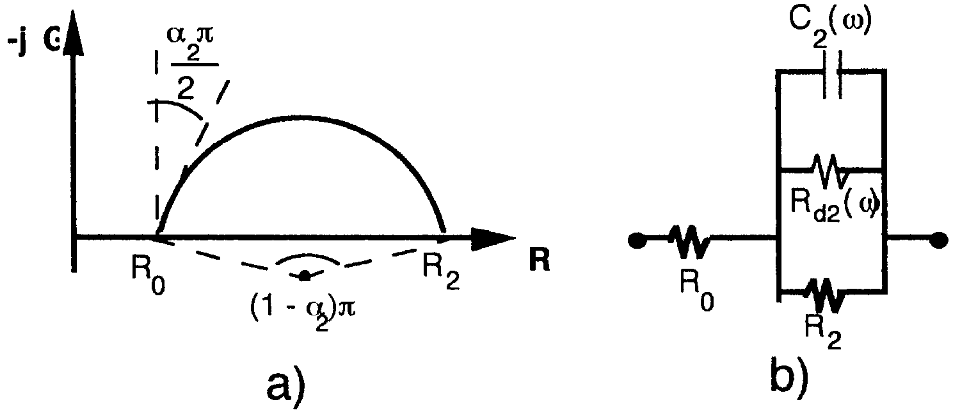

FIG. 2.
Low frequency part of the impedance: a) loop in the Nyquist plot and b) equivalent circuit.

- a part of the impedance corresponds to the products resulting from reactions between corrosion products and cement paste, such as iron products,
- a part of the impedance corresponds to the bulk concrete cover.

It is similar to a model proposed for steel under coatings (4).

In this model of impedance, a resistance R_0 corresponds to the concrete cover which is an electrolyte.

The part of the impedance (Z_1) corresponding to the products formed in the transition zone, is composed of a resistance R_1, in parallel with a dispersion impedance Z_{d1}. This impedance Z_{d1} is assumed to have two components, in parallel: a dispersion capacitance $C_1(\omega)$ and a dispersion resistance $R_{d1}(\omega)$, which depend on the signal frequency (ω). The dispersion takes into account the inhomogeneity of the concrete surrounding steel.

The part of the impedance (Z_2) which corresponds to the direct interface between steel and concrete is composed of a resistance R_2 (of the interface) in parallel with an impedance Z_{d2} which has two components in parallel: a dispersion capacitance $C_2(\omega)$ and a dispersion resistance $R_{d2}(\omega)$, which depend on the frequency (ω) (Figure 2). The dispersion elements give an indication of the homogeneity of the products present on the metal surface.

So, the model proposed applies for the various types of Nyquist diagrammes including two loops or only one, and with or without a straight segment. But the present study has been more focussed on Nyquist diagrammes which include no straight segment.

Theoretical Relationships Between Electrochemical Impedance and Physical Properties of Steel-Concrete Interface. According to their definition, the various components of the electrochemical impedance of the steel-concrete interface have physical meanings.

When no steel corrosion occurs, no product is formed in the cement pore. Then the Nyquist diagram shows only one loop. It means that in impedance Z_1 vanishes (i.e. $Z_{d1} = 0$) . So, the model with only the dispersion elements, $C_2(\omega)$ and $R_{d2}(\omega)$, applies. The impedance Z (Fig. 3) is then given by

$$\frac{1}{Z - R_0} = \frac{1}{R_2} + \frac{1}{R_{d2}} + j C_2 \omega \tag{1}$$

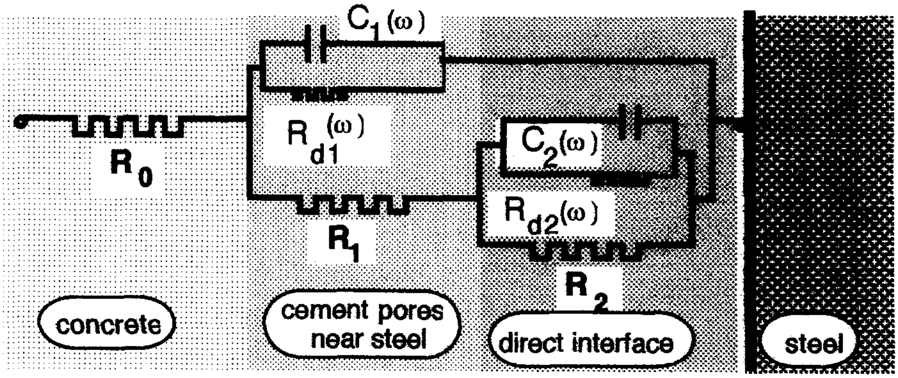

FIG. 3.
Model for an electrochemical impedance including two loops in the Nyquist plot.

where
*R_0 is the resistance of the electrolyte (in ohm),
*R_2 is the extent of the arc (in ohm), equivalent to a polarization resistance (or to a charge transfer resistance),
*$\omega = 2\pi f$ is the pulsation (in rad/s), where f is the frequency,

The dispersion parameter α_2 (Figure 2a) which is ranging between 0 and 1, is defined by the following relationship:

$$Z = R_0 + \frac{R_2}{1 + (j\omega\,\tau_2)^{1-\alpha_2}} \tag{2}$$

where $j = \sqrt{-1}$, and τ_2 is a time constant (in second) So,

$$\frac{1}{Z - R_0} = \frac{1}{R_2} + \frac{(\omega\,\tau_2)^{1-\alpha_2}\sin\left(\frac{\pi\,\alpha_2}{2}\right)}{R_2} + j\,\frac{(\omega\,\tau_2)^{1-\alpha_2}\cos\left(\frac{\pi\,\alpha_2}{2}\right)}{R_2} \tag{3}$$

This relationship gives

$$\frac{1}{R_{d2}} = \frac{(\omega\,\tau_2)^{1-\alpha_2}\sin\left(\frac{\pi\,\alpha_2}{2}\right)}{R_2} \tag{4}$$

and

$$C_2\,\omega = \frac{(\omega\,\tau_2)^{1-\alpha_2}}{R_2}\cos\left(\frac{\pi\,\alpha_2}{2}\right) \tag{5}$$

When steel corrodes in concrete, its corrosion products can react with cement. So, the Nyquist plot has two loops. Then, the value of impedance Z is given by the model with the four dispersion parameters $C_1(\omega)$, $R_{d1}(\omega)$, $C_2(\omega)$ and $R_{d2}(\omega)$:

$$\frac{1}{Z - R_0} = \frac{1}{R_{d1}} + \frac{1}{R_1 + \cfrac{1}{\cfrac{1}{R_2} + \cfrac{1}{R_{d2}} + j\,C_2\,\omega}} \tag{6}$$

With

$$\frac{1}{Rd_1} = \frac{(\omega\tau_1)^{1-\alpha_1}\sin\frac{\pi\alpha_1}{2}}{R_1} \tag{7}$$

and

$$C_1 \omega = \frac{(\omega \tau_1)^{1-\alpha_1}}{R_1} \cos \frac{\pi \alpha_1}{2} \tag{8}$$

It is to be noted that when the Nyquist diagram includes one loop, this relationship gives the dispersion resistances and capacitances corresponding to this loop.

Table 1 gives the meanings of the various parameters included in the above relationships and particularly the dispersion parameters. These parameters α give indications on the homogeneity of the products. So, parameter α_1 corresponds to the inhomogeneity of products formed in cement pores and α_2 corresponds to the quality of iron products on steel.

When steel corrodes and corrosion products remain at its contact, in a thick layer, a diffusion process can occur in it. In this case, the Nyquist plot has one loop (high frequency) and a straight line (low frequency) (5). Then, the low frequency part of the impedance Z includes a diffusion (Warburg) parameter. It means that a diffusion process occurs between steel and the solution introduced in the pores of corrosion products.

Experimental Validation of the Model

Products Formed During the Cement Hydration. Before presenting the experimental work for validating the model, the following data are to be reminded.

The structure of the transition zone in a concrete contacting steel is different from that of the bulk material. For example, it has been observed that the concrete porosity is higher in this zone, which also has a higher calcium hydroxide content and a lower anhydrous cement content than elsewhere in the material (6).

The steel storage before use has also an influence. When a polished steel specimen is placed in sound concrete, a "passivating film" is formed at its surface. It deals with a mixture of iron products and possibly calcium hydroxide. The iron products are either FeOOH, or $Fe(OH)_2$, or $Fe(OH)_3$. This "passivating film" which is formed on bare steel in sound concrete, is homogeneous and continuous (7).

When a reinforcement is stored outdoor before embedment, the formed rust layer contains mainly lepidocrocite, goethite or magnetite. This layer is usually between 0.01 and 0.5 mm thick and it is highly porous (pore volume content up to 90%) (8).

When fresh concrete surrounds a rusted steel, mixing water flows into the rust pores. Then it pushes the air out of these pores , thus possibly forming bubbles in the cement paste. So, the water composition near a rust layer is different from that of the bulk cement paste: in the rust pores, cement hardens slowerly and its components react with the iron products. These reactions result in the formation of hexagonal hydrated calcium ferrite, $4CaO.Fe_2O_3.13H_2O$. After

TABLE 1

Parameters Derived from Experimental Nyquist Impedance Plots with Two Loops

Meaning of the parameters	High frequency loop	Low frequency loop
Extent of the arc on the real axis, equivalent to a resistance (in ohm)	R_1 resistance of products in cement pores	R_2 interface resistance
Time constant (in s)	τ_1	τ_2
Dispersion constant (see Fig. 2a)	α_1	α_2

several months, this compound changes into cubic hydrated calcium ferrite, $3CaO.Fe_2O_3.6H_2O$. In the case when the steel-concrete interface is carbonated, this compound changes into hexagonal hydrated calcium carboferrite $3CaO.Fe_2O_3.CaCO_3.12H_2O$ (8, 9).

Thus, the main physical feature of the true interface between concrete and reinforcement is the presence of a transition zone which depends on the initial rusting of steel and on the weathering of the concrete cover, as well.

Steel Corrosion After Depassivation. If the concrete surrounding steel contains chloride ions, the products formed on steel surface are no more passivating. A depassivation process occurs at small areas, as for usual pitting. This reaction process includes the formation of "green rust" which changes either to lepidocrocite (γ-FeOOH), or to goethite (α-FeOOH), or to magnetite (Fe_3O_4), or even to akaganeite (β-FeOOH). These products can contain more or less chlorine, depending on the chloride and oxygen contents in concrete (10, 11).

When a depassivation process starts, the corrosion product layer is inhomogeneous, i.e. only some parts of the steel surface are covered with "passivating film". As the corrosion process increases, the depassivated areas grow, so that the steel surface is finally entirely covered with a thick layer of rust. This iron product is porous and the embedded (corroded) steel is contact with an electrolyte whose composition is unknown, because corrosion occurs then in occluded cells (12).

Materials Tested and Ageing of Specimens. An experimentation was run for checking the validity of the model proposed (1). The test pieces were specimens, 40x40x160 mm in dimensions. They were made of concrete designed as follows:

- cement : 250 kg/m^3,
- sand (dia < 5mm) : 650 kg/m^3, -gravel (dia < 12 mm): 1420 kg/m^3,
- water-cement ratio: 0.6.

A steel rebar, (6.5mm in diameter, 130 mm long) was placed along the longitudinal axis of the specimen. The composition of this steel was (in weight percent):

C = 0.22%, Mn = O.089%, Si = 0.24%, S = 0.016% and P = 0.046%.

Rebars were polished, rinced in distilled water and dried in warm air before being placed in concrete.

Three types of cements were used: two normal portland cements OPC (P1 and P2) and a blended portland cement with calcareous fillers (P3). Their compositions are given on table 2.

These specimens were placed in five aggressive solutions (A through E), whose compositions are given in Table 3. Some reference specimens were only stored in air.

TABLE 2

Cements Compositions (in weight percent)

Cement	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Free CaO	Loss on ignition	Insoluble
P1	21.73	5.39	3.36	61.99	1.19	2.04	0.49	1.9	0.70
P2	21.75	3.85	4.68	64.14	1.44	1.74	0.30	1.0	0.32
P3	18.5	3.80	3.80	62.30	1.50	1.20	0.35	4.5	1.6

TABLE 3

Compositions of the Aggressive Solutions

Solution label	pH	Distilled water	NaCl (g/l)	$MgSO_4$,7 H_2O
A	6.4	x		
B	7.8	x	30	
C	6.7	x	90	
D	6.8	x		18.5 g/l
E	6.7	x	90	18.5 g/l

The ageing procedures of the specimens are given in table 4. Some specimens were continuously immersed (IC test) during about 72 or 144 weeks. The other specimens were under alternate immersion-drying cycles (ISA test): they were immersed in the aggressive solution for 48 hours, and dried in a chamber, at 40°C. The number of applied ISA cycles were either 33 or 120.

After its ageing, every specimen was taken out of the aggressive solution, the electrochemical impedance of the embedded steel was measured. For such a measurement, the counter-electrode was a stainless steel (Cr: 18%, Ni: 10%) sheet was placed on the specimen surface. The reference electrode was also placed on this surface. It dealt with a saturated calomel electrode.

The electronic arrangement included Solartron Schlumberger equipments (transfer function analyzer S.S. 1250, interface S.S. ECP 1186), a Tektronix 2 channel oscilloscope (Re. 5103N). The data were proceesed with an Apple IIe microcomputer. The applied voltage was about 8 mV, with a frequency ranging between 10 mHz and 50 kHz.

After this measurement, this specimen was split and the steel surface was visually examined.

Results of the Exprimentation

Electrochemical Impedance. For assessing the validity of the model, the various parameters of the electric circuit Z (Fig. 3), were determined in the following way, by using Nyquist plots:

- the values of resistances R_0, R_1 and R_2 were determined on the real axis of the plot,
- the dispersion parameters α_1 and α_2 were determined according to the scheme of figure 2a,
- the values of R_{d2} and C_2 were calculated according to equations (4) and (5). The values of R_{d1} and C_1 were calculated in a simlar way using equations (7) and (8).

Knowing the values of all these parameters, impedance Z was computed at any frequency ω. So, the calculated Nyquist plot could be compared with the experimental one. Tables 5 and 6

TABLE 4

Procedures for Ageing the Reinforced Mortar Specimens in Aggressive Solutions

Ageing	Continuous immersion (IC)		Immersion-drying cycles (ISA)	
Duration	72 weeks	144 weeks	33 cycles	120 cycles
Aggressive solutions	A B C D E	A B D	A B C D E	A D

TABLE 5

Calculated Values of Dispersion Parameter α_1, for Nyquist Plots Including Two Loops

Ageing procedure	Ageing duration	Aggressive solution	Parameter α_1 for cement		
			P1	P2	P3
Continuous immersion (IC test)	72 weeks	A	0.1	0.2	0.3
		B	0.6	0.5	0.4
		C	0.5	0.5	0.5
		D	0.8	0.6	0.5
		E	0.48	0.5	0.5
	144 weeks	A	0.4	0.4	0.5
		B	0.6	0.5	0.5
		D	0.75	0.55	0.6
Immersion-drying cycles (ISA test)	33 cycles	A	0.6	0.6	0.5
		B	0.4	0.6	0.5
		C	0.7	0.6	0.6
		D	0.6	0.6	0.6
		E	0.5	0.7	0.5
	120 cycles	A	0.6	0.5	0.4
		D	0.8	0.6	0.6

give the calculated values of α_1 and α_2. These values were determined by plotting $\mathrm{Ln}(R_{d1})$ and $\mathrm{Ln}(R_{d2})$ against $\mathrm{Ln}(\omega)$ and using a lineair regression method.

Comparison of the Nyquist Diagramme and the Condition of Steel Surface.

Nyquist plots with one loop. For steel embedded in sound concrete, which was 40 day old and stored during 12 days in laboratory atmosphere, the Nyquist plot has only one loop. This is a

TABLE 6

Calculated Values of Dispersion Parameter α_2, for Nyquist Plots Including Two Loops

Ageing procedure	Ageing duration	Aggressive solution	Parameter α_2 for cement		
			P1	P2	P3
Continuous immersion (IC test)	72 weeks	A	0.1	0.1	0.2
		B	0.4	0.4	0.4
		C	0.5	0.6	0.5
		D	0.3	0.1	0.1
		E	0.4	0.4	0.4
	144 weeks	A	0.2	0.1	0.2
		B	0.4	0.3	0.6
		D	0.35	0.06	0.2
Immersion-drying cycles (ISA test)	33 cycles	A	0.002	0.16	0.2
		B	0.4	0.4	0.4
		C	0.4	0.5	0.5
		D	0.14	0.1	0.11
		E	0.6	0.6	0.4
	120 cycles	A	0.45	0.4	0.6
		D	0.75	0.6	0.6

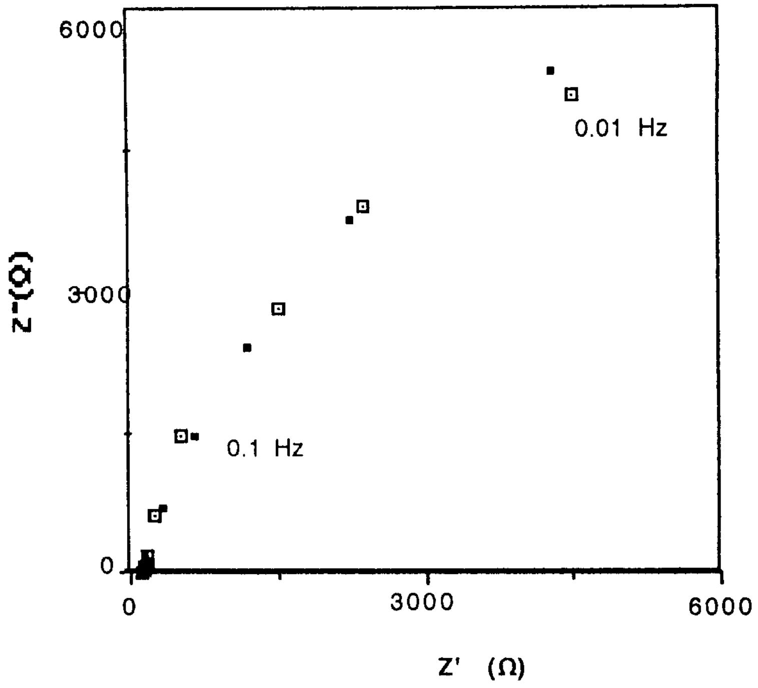

FIG. 4.
Nyquist diagram of steel in sound concrete (Steel area: 24.5 cm^2) dots: experimental values; open squares: calculated values.

part of a circle whose center is slightly below the real axis (Figure 4). For the cements tested, the dispersion parameter α_2 was equal to 0.1 for cements P1 and P3 and equal to 0.01 for cement P2.

A visual examination of the steel wire showed that steel was not corroded but covered with a whitish product (photo 1).

So, for these cases, the proposed model for the electrochemical impedance is in accordance with the physical condition of steel embedded in sound concrete.

Nyquist plots with two loops. Most of the Nyquist plots of steel in aged concrete include two loops (Figure 5). According to the proposed model, it means that products were formed in the cement pores.

The visual examinations showed that a two loop Nyquist plot corresponds to steel which was hardly or partially rusted (photos 2, 3, 4).

To check the validity of the model, only the two dispersion parameters, α_1 and α_2, are discussed. It is to be recalled that, according to the model, the value of dispersion a parameter α_1 is higher when the products formed are inhomogeneous.

The experimental results for α_1 show that, for continuous immersion test (IC),

the lowest α_1 values (about 0.2) correspond to specimens which had been immersed in solution A (distilled water),

- the highest α_1 values (about 0.8) correspond to specimens which had been placed in solutions D and E. These solutions contain sulphate ions which result in formation of swelling ettringite in concrete.

For ISA test (immersion-drying cycles), α_1 values are ranging between 0.4 and 0.7 for all solutions. On specimens giving $\alpha_1 > 0.4$, the visual examinations showed that products formed in the cement pores (close to steel) are highly inhomogeneous (photos 3, 4, 5). It means that the inhomogeneity of the products formed in the cement pores is related to the dispersion parameter α_1.

The results concerning dispersion parameter α_2 (which corresponds to the steel surface) can be related to the condition of steel surface, as observed visually:

- the lowest values of α_2 correspond to steel where small rust was observed (solution A, for example, photo 2),
- when the values of α_2 are ranging between 0.4 and 0.8, steel surface is covered with dots of rust (solutions C and E, for example, photos 3 and 4).

So, the dispersion parameter α_2 is indeed related with the homogeneity of products formed directly on steel in concrete. It means that if α_2 value is high, steel is highly corroded and α_2 indicates the degree of metal corrosion.

Nyquist plots with a linear segment. When a Nyquist plot includes a high frequency loop and a low frequency straight segment, the steel wire appeared to be covered with a thick layer of corrosion products (photo 5). This type of diagram (Figure 6) was obtained with specimens

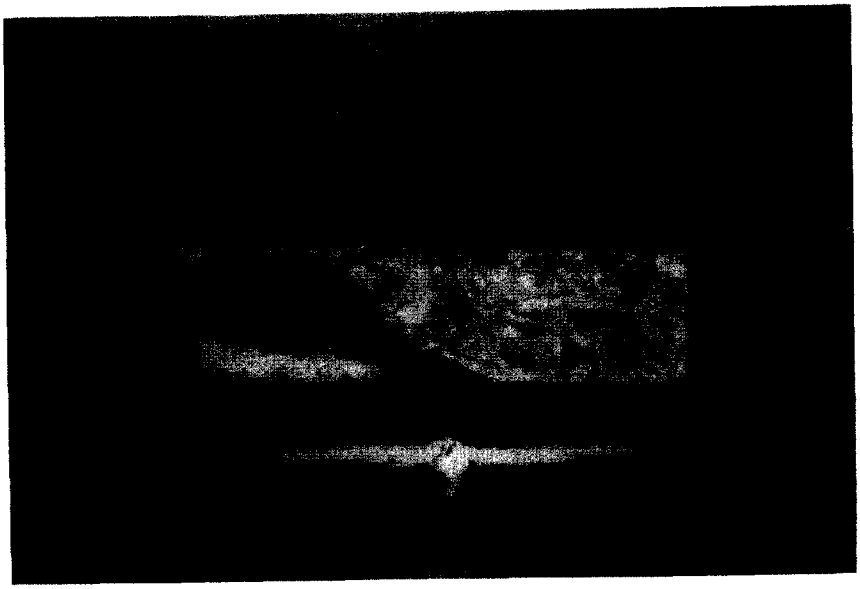

PHOTO 1.
Steel covered with whitish products. Concrete specimen not carbonated.

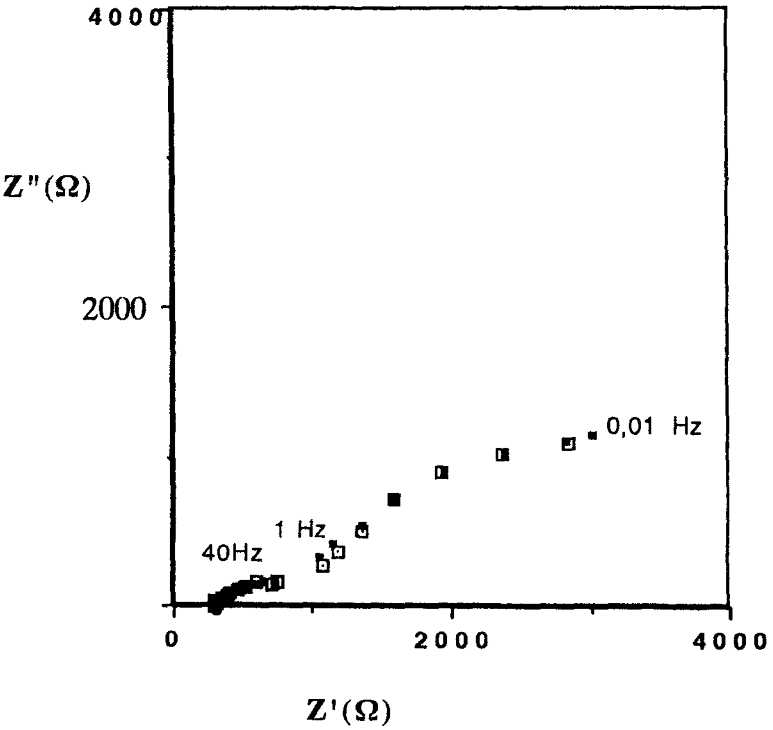

FIG. 5.
A Nyquist diagram with two arcs: specimen immersed in solution B, for 72 weeks (Steel area: 24.5 cm^2) dots: experimental values; open squares: calculated values.

tested in solutions C and E (containing chlorides) for a long time, i.e. 144 weeks for IC test and 120 weeks for ISA test. Then, the impedance of the direct interface is to be modelled with a special element, such as the Warburg diffusion parameter.

So, in these cases again, the model of electrochemical impedance agrees with the steel surface condition.

Conclusions

A model was previouly proposed for the electrochemical impedance of steel in concrete. This impedance includes two parts, depending on the applied potential frequency : the low frequency part corresponds to products directly in contact with steel. The high frequency part is related with products formed in cement pores, in the vicinity of steel. Moreover, in this model, the distribution of these products are not strictly homogeneous. It means that some dispersion parameters (α) were introduced in this model.

The object of the present study was to assess the validity of the model concerning the electrochemical impedance of steel-concrete interface. The results obtained show a fair agreement between the experimental data and the calculated Nyquist diagram.

PHOTO 2.
Small rust dots on steel. Concrete specimen not carbonated.

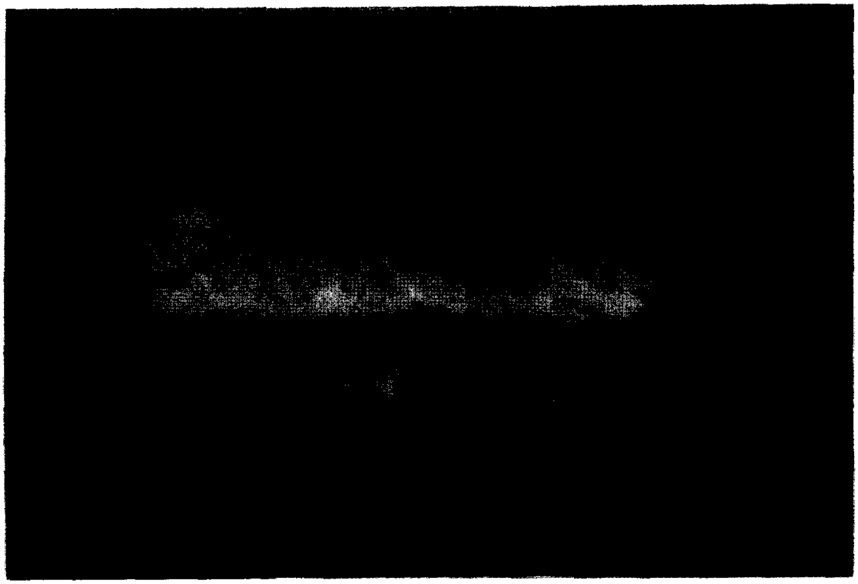

PHOTO 3.
Steel partially rusted. Concrete: average carbonation depth: 20 mm.

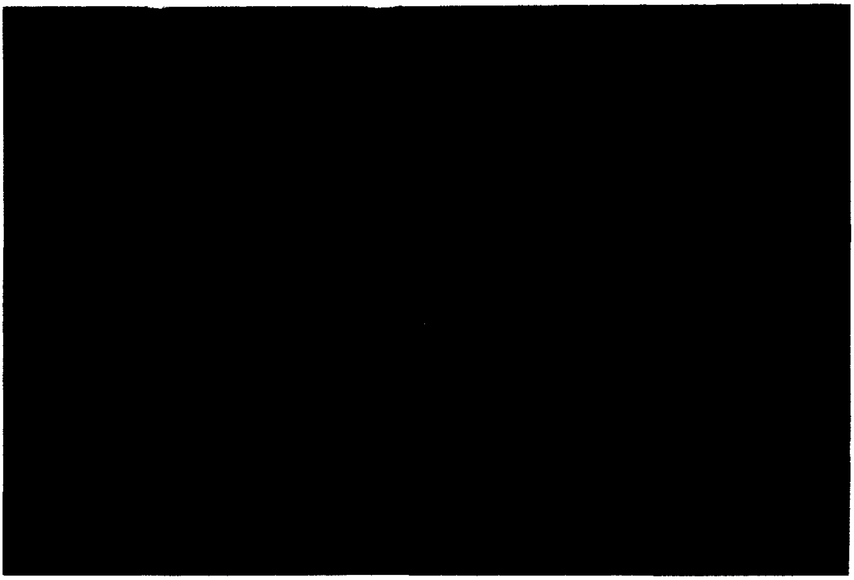

PHOTO 4.
Steel partially rusted. Concrete: average carbonation depth: 10 mm.

PHOTO 5.
Steel totally rusted. Concrete with visible rust in its pores.

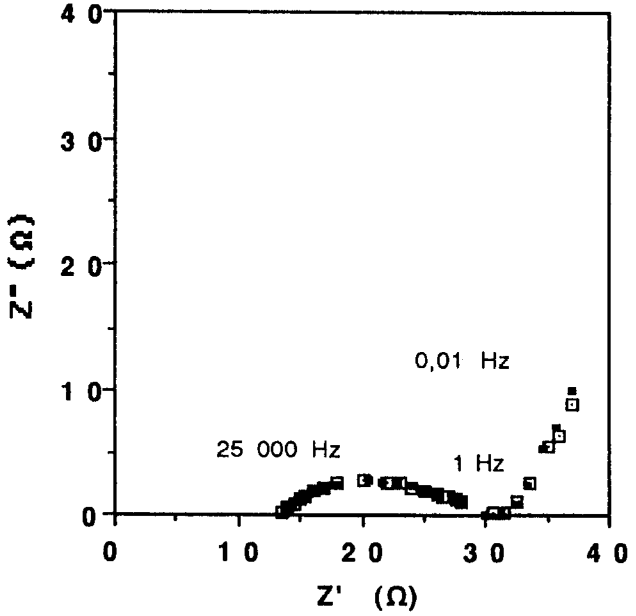

FIG. 6.
A Nyquist diagram with one high frequency arc and a straight line: specimen immersed in solution C, for 144 weeks (Steel area: 24.5 cm^2): dots: experimental values; open squares: calculated values.

Then, the validity of the model was also checked by comparing the results of electrochemical impedance measurements with the steel surface condition. In all cases, it appeared that the model of electrochemical impedance agrees with the condition of steel in concrete.

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