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Threshold chloride concentration for stainless steels activation in concrete pore solutions

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ABSTRACT

The threshold chloride concentration for stainless steels activation in concrete environments depends not only on chemical composition of the steel and on pH level of concrete pore solution but is also considerably affected by the superficial state of the steel. The presence of scales leads to significant decrease of corrosion resistance. This study evaluates the corrosion resistance of various stainless steels exposed to pore solutions of fresh concrete by means of electrochemical methods. All tested materials with bare surface, except for martensitic chromium steel FeCr12, proved to be completely resistant to fresh concrete pore solution containing chlorides. If the surface is scaled, the identically high resistance cannot be expected even for the most alloyed stainless steels.

1. Introduction

The economic and effective way of eliminating corrosion of reinforcement bars is replacing the normally used carbon steel with any type of stainless steel. Cramer et al. present [1] that stainless steel bars add a 10% premium to the total project costs compared to black iron bars but are expected to reduce cumulative costs by 50% over 120 years of coastal bridge life. In the case of structures with such a long planned service-life, the probability of reaching the reinforcement level by carbonation front within this period is increased. The carbonation process leads to activation of carbon steel. Another usual agent that depassivates steel is chloride ions, which may ingress into the concrete from the outside environment. The corrosion rate after activation is affected by the accessibility of water and oxygen onto the corroding metal. Stainless steel is used to make sure that the corrosion resistance of stainless steel bars does not limit the service life of the reinforced concrete structure. Ideally, the reinforcement should be resistant against corrosion activation under all conditions that may occur in the structure. In usual atmospheric conditions, the most aggressive environment possible is represented by carbonated concrete pore solution with high concentration of chloride where the content of oxygen is in equilibrium with atmosphere.

All types of stainless steels are simultaneously passivable in starting conditions (fresh concrete). The advantage of stainless steel reinforcement should be in the stability of a passive layer even after carbonation of the concrete layer, provided that the concrete is not contaminated with chlorides. The effect of chloride ions results in the breakdown of the passive layer when their concentration exceeds certain threshold value. The susceptibility to chloride-induced corrosion would be usually assessed according to the PRE coefficient (wt.% Cr + 3.3 * wt.% Mo), which enables the resistance of various types of steels to be compared based on their composition [2]. Nitrogen is an important alloying element that is added into duplex steels in the amount from 0.1 to 0.3% [3]. The passive layer resistance against breakdown depends highly on the superficial state of the given alloy. When exposed to air during heat treatment, a layer of chromium-depleted material forms under chromium-enriched scales. Even in the case of high-alloyed steels, the chromium concentration may drop under 12% [3]. A roughly machined surface, geometric defects and tension [4] are also among the factors contributing to pitting corrosion.

Numerous publications have been written on the corrosion behaviour of stainless steels in concrete environment. A large group of steels was dealt with in the publication [5]. The results imply an apparent effect of the pore solution pH and the material composition on the value of the threshold chloride concentration for activation, the study, however, does not reflect the superficial state. When describing the corrosion behaviour, most of the publications focus merely on two basic types of austenitic steels, i.e. AISI 304 and 316 [6–10]. Also cheaper types of stainless steels might meet the requirements specified by ASTM A955M standard, however, only if the sufficient corrosion resistance is sustained under given conditions.

In recent years, several articles have been published in Cement and Concrete Research dealing with the corrosion behaviour of stainless steels in concrete environment. Actually, only few of the studies concentrated directly on the stainless steel resistance. One of the works [11] rather evaluates the impedance spectroscopy method. It was discovered that a non-representative stainless steel Nitronic33 has remarkably higher resistance even in concrete containing 4.5%

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of chlorides by weight of cement than carbon steel. Rather than emphasizing stainless steel corrosion, another article concentrated on studying the properties of Calcium Aluminate Cement [12]. The subject of another paper published in C&CR, elaborated by Gu et al. [13] was a study of behaviour of carbon steel reinforcement coated with AISI 316 steel by means of linear polarisation and impedance spectroscopy. Corrosion resistance may be substantially reduced by the defects occurring in the stainless steel layer in a form of pores and oxides. Later on, Bautista et al. focused on the comparison of corrosion behaviour of traditional FeCrNi and FeCrNiMo stainless steels with low-Ni austenitic stainless steel, showing the way of decreasing initial costs by selection of low-cost but still high-corrosion resistant materials [14]. Two studies of García-Alonso dealt with low-Ni stainless steels as well [15,16]. Authors of all the publications [14–16] are aware of the risk of limited corrosion resistance of scaled and temper-coloured stainless steels. Higher corrosion rates were identified for welded materials [16].

The goal of this paper is to provide C&CR readers with the summary of corrosion resistance of basic types of stainless steels under conditions that may occur in non-carbonated concrete, i.e. the dependence of particular types of stainless steel in fresh concrete pore solution on the concentration of chloride ions.

2. Experimental

Five grades of stainless steels were used for laboratory tests. Each grade, in terms of the structure, was represented in the testing set. Chemical and structural composition of the materials is given in Table 1. One of the aims of this paper was to determine the effect of the presence of scales forming in the atmosphere at high temperatures (welding, heat treatment). In order to obtain two different superficial states, the specimens were pre-treated — bare (wet grinding (P 280)) and scaled (wet grinding (P280) — followed by 15-minute heating at 1080 °C). Heat treatment under specific conditions ensured homogeneity and compactness of the oxide layer.

Laboratory tests were performed in model solutions which, taking alkalinity into consideration, simulated pore solutions of fresh concrete. Two different levels of pH were selected. Saturated $Ca(OH)_2$ should not be split into two lines solution (pH 12.5) represents pore solution of fresh concrete with cement which contrary to reality contains no Na_2O or K_2O. Saturated solution $Ca(OH)_2$ with addition of KOH up to pH 13.5 represents pore solution of fresh concrete with cement which contains extremely great amount of oxides of alkali metals. The model solutions with addition of NaCl up to 150 g Cl^-/l were used to determine the activation threshold chloride level, while the concentrations of 15 and 80 g Cl^-/l were found to be close to 0.4 and 3 wt.% Cl^-/cem, respectively, when concrete moisture is in equilibrium with RH 90% air. No exposure to chloride-free environment preceded the corrosion tests in order to avoid any short-time delay of corrosion attack by preceding passivation in case that the delay would be longer than the duration of the test. The fundamental idea of the tests is that the material will be permanently resistant in chloride containing concrete if the material is resistant under the corresponding chloride concentration in the model pore solution.

As a criterion for evaluation of corrosion behaviour, free corrosion potential and polarisation resistance were used. The values were recorded for at least three days of exposure. The figures present data which were obtained for three parallel specimens. The symbols in graphs represent the mean value and the error bars minimum and maximum value recorded at the last day of exposure. The method of linear polarisation, which was used to determine polarisation resistance, proceeded within the interval −10 to +10 mV vs. free corrosion potential at the rate of 0.5 mV/s. Polypropylene cells used for testing were equipped with an integrated graphite counter electrode and a reference electrode made of activated titanium. At the end of exposure, the potential of each activated titanium electrode was measured by a silver–silver chloride reference electrode. The results are therefore presented in milivolts vs. ACLE (silver–silver chloride electrode), the potential of which is approximately +200 mV vs. SHE. The steel specimens served as a bottom of the cell (Fig. 1). The electrolyte formed a 30-mm layer above the tested material.

The reciprocal R_p [17,18] is directly proportional to the corrosion rate of metal that is subject to uniform corrosion. Factor B, the constant of proportionality, is given by the combination of Tafel slopes of anodic and cathodic polarisation curves presented in semi-logarithmic coordinates. Considering stainless steels, which are passive at the pH level of pore solutions of both fresh and carbonated chloride-free concrete, it may be anticipated that any prospective corrosion attack induced by increasing concentration of chlorides would be of a localised nature. Then the corrosion rate calculated from the polarisation resistance would not be relevant even if the value of B were known precisely. R_p is determined as a slope of a summary polarisation curve, which is presented in linear coordinates, in the vicinity of the free corrosion potential (±5 mV), i.e. in the area where the curve is approximately linear. Nevertheless, the curve linearity generally declines as the difference between the Tafel slopes of both reactions increases, and the interpretable area thus shrinks [19]. Therefore, the linear polarisation method should be preferentially used in systems where the rate of both partial reactions is controlled by a charge–transfer rate. Another oxidation–reduction reaction present in the system and high electrolyte resistance affect and imprecise the value of polarisation resistance [17,20–22]. An electrochemical reaction, e.g. magnetite transformation to rust on the metal surface, that is faster than the corrosion reaction, may decrease the polarisation resistance. On the other hand, significant electrolyte resistance may increase it, because the value measured by means of the linear polarisation technique is in fact a sum of real polarisation resistance and ohmic resistance of the electrolyte. The polarisation rate must be effectively low enough to secure steady state conditions [19].

The value of 30 $\Omega\,m^2$ has been adopted by us in recent studies [23,24] as the threshold polarisation resistance distinguishing between corrosion in active or passive state, emphasizing the irrelevance of calculation of corrosion current densities from polarisation resistance by using questionable B value.

3. Results and discussion

3.1. Fresh concrete pore solution — bare surface

With respect to high alkalinity of both of the fresh concrete pore solutions used (pHs 12.5 and 13.5), high-corrosion resistance of

Table 1
Chemical and structural composition of stainless steel specimens (M — martensitic, F — ferritic, A — austenitic, D — duplex).

Material	Content of elements [%]									
	C	Mn	Si	P	S	Cr	Ni	Mo	Cu	Others
FeCr12 (M)	0.15	0.48	0.37	0.028	0.017	12.17	0.13	0.08	0.068	
FeCr16 (F)	0.07	0.30	0.38	0.026	0.009	16.2	0.17	0.10	0.10	
FeCr18Ni10 (A)	0.08	1.40	0.64	0.023	0.020	18.06	10.20	0.16	0.12	Ti = 0.41
FeCr18Ni10Mo2 (A)	0.07	0.98	0.25	0.025	0.014	17.84	9.86	2.06	0.12	
FeCr22Ni6Mo3 (D)	0.02	1.59	0.29	0.022	0.006	21.80	5.92	3.09	0.05	$N = 0.116$

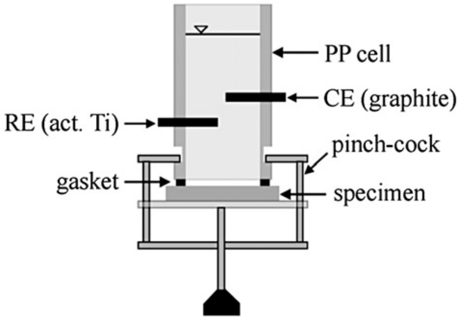

Fig. 1. Design of the testing cell.

stainless steel may be expected even in the case of contamination with chloride ions. This assumption was validated by electrochemical measurements performed on bare-surface specimens. The dependence of free corrosion potential on chloride concentration is earmarked for both levels in Figs. 2 and 3. The decrease of potential was observed only for the martensitic steel FeCr12. At pH 12.5 and for at least one of the parallel specimens, the potential decreased already at 15 g Cl$^-$/l, while at pH 13.5, the potential decreased, in the case of one specimen, only at the highest concentration. Identical dependence was detected also for the polarisation resistance (Figs. 4 and 5).

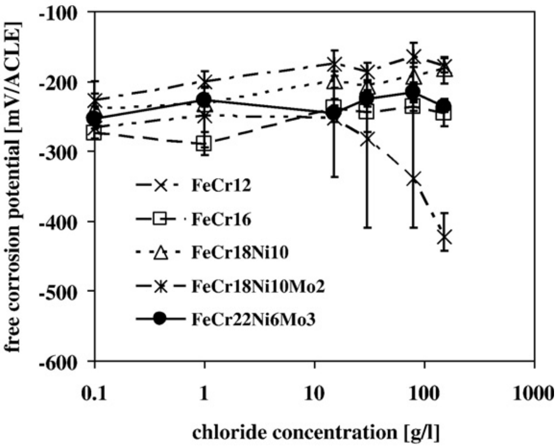

Fig. 2. Free corrosion potentials of bare-surface materials depending on chloride content in the pore solution with pH 12.5 in the last day of exposure.

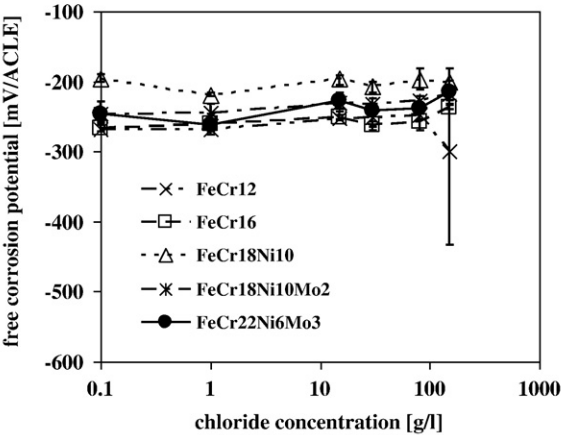

Fig. 3. Free corrosion potentials of bare-surface materials depending on chloride content in the pore solution with pH 13.5 in the last day of exposure.

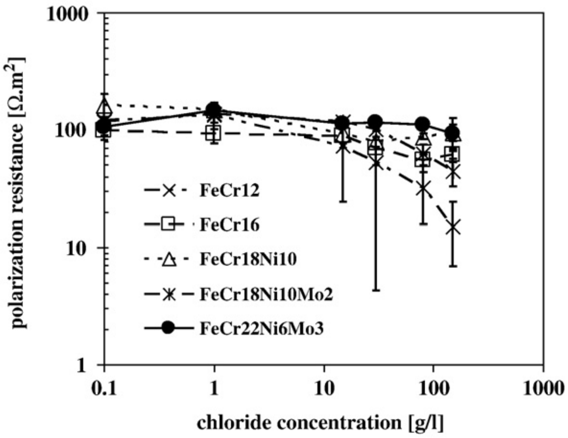

Fig. 4. Polarisation resistances of bare-surface materials depending on chloride content in the model pore solution with pH 12.5 in the last day of exposure.

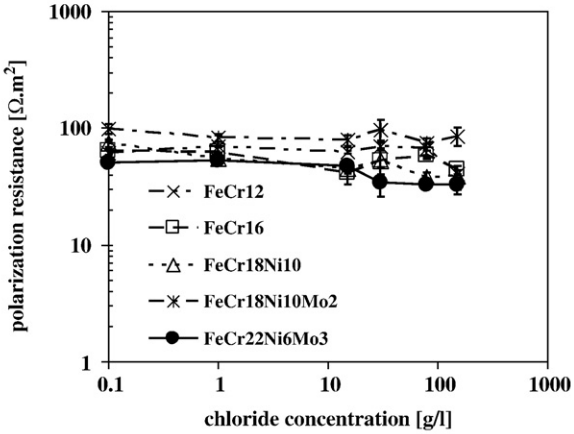

Fig. 5. Polarisation resistances of bare-surface materials depending on chloride content in the model pore solution with pH 13.5 in the last day of exposure.

The overall evaluations are summarised in Table 2. Concerning the concentrations critical for activation, it may be stated that:

- Bare martensitic stainless steel FeCr12 is completely resistant to fresh concrete whose pore solution contains a maximum of 1 g Cl$^-$/l. Local activation is likely to occur at higher concentrations of chloride ions. Higher alkalinity of a pore solution positively affects the resistance against pitting and crevice corrosion.
- All other types of stainless steel (FeCr22Ni6Mo3, FeCr18Ni10Mo2 and FeCr18Ni10) are completely resistant to both model fresh concrete pore solutions, independently of the content of chloride ions.

Table 2
Summary evaluation of corrosion resistance of stainless steel specimens with bare surface in fresh concrete pore solution (+ … all parallel specimens remain passive, 0 … at least one of the parallel specimens is active/passive, − … all three parallel specimens activate).

	pH 12.5						pH 13.5					
Cl$^-$ (g/l)	0.1	1	15	30	80	150	0.1	1	15	30	80	150
FeCr12	+	+	0	0	0	−	+	+	+	+	+	0
FeCr16	+	+	+	+	+	+	+	+	+	+	+	+
FeCr18Ni10	+	+	+	+	+	+	+	+	+	+	+	+
FeCr18Ni10Mo2	+	+	+	+	+	+	+	+	+	+	+	+
FeCr22Ni6Mo3	+	+	+	+	+	+	+	+	+	+	+	+

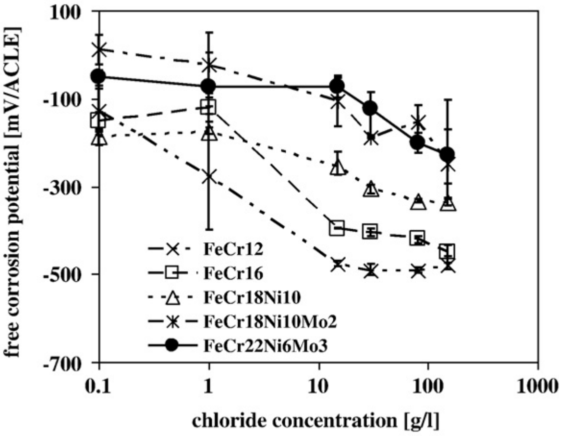

Fig. 6. Free corrosion potentials of scaled materials depending on chloride content in the pore solution with pH 12.5 in the last day of exposure.

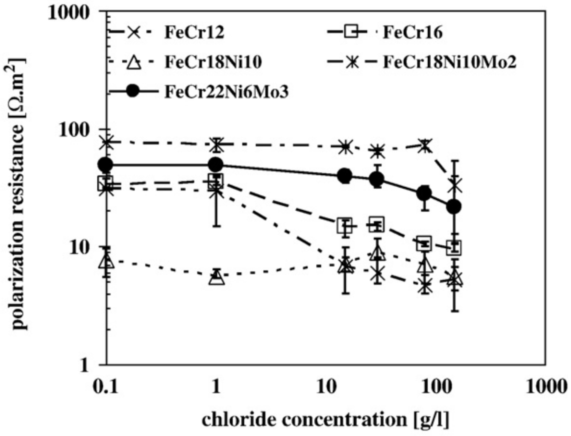

Fig. 8. Polarisation resistances of scaled materials depending on chloride content in the pore solution with pH 12.5 in the last day of exposure.

3.2. Fresh concrete pore solution — scaled surface

Considering fresh concrete pore solution, determination of polarisation resistance became complicated because of non-symmetrical curves of linear polarisation. While the free corrosion potential of FeCr18Ni10 steel specimens does not substantially differ from other high-alloyed materials (Figs. 6 and 7), the obtained polarisation resistances are lower by an order of magnitude (see Figs. 8 and 9) when following regular evaluation process of linear polarisation curves — interpolation of the measured curve in the close vicinity of the free corrosion potential corresponding to zero current density (Fig. 10). The result complies with the values acquired for activated specimens of chromium steels although there is no reason for active corrosion of FeCr18Ni10 in alkaline solution containing almost no chlorides. The difficulties with evaluation of the non-linear polarisation curves are reported elsewhere [25]. The shape of polarisation curves was considered in the overall evaluation of corrosion behaviour of stainless steels. Thus, the specimens with low polarisation resistance value were considered to be corrosion resistant if its polarisation was highly deviated from linear shape.

Table 3 contains the overall evaluation of corrosion behaviour of scaled stainless steels which, in addition to polarisation resistances and free corrosion potentials, also considers the shape of linear polarisation curves.

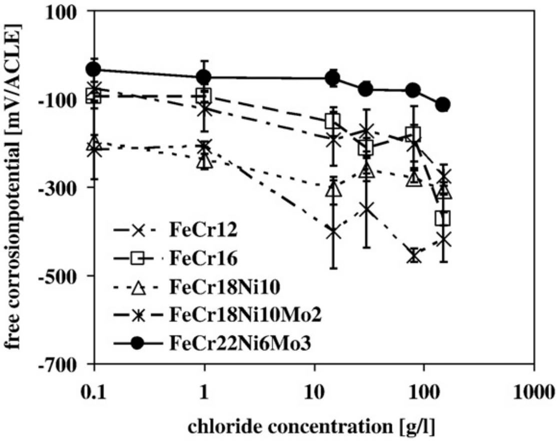

Fig. 7. Free corrosion potentials of scaled materials depending on chloride content in the pore solution with pH 13.5 in the last day of exposure.

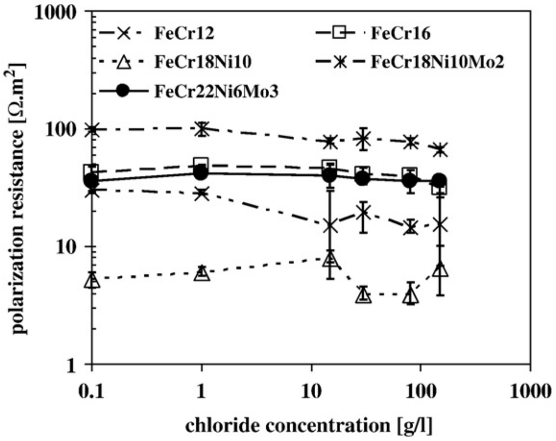

Fig. 9. Polarisation resistances of scaled materials depending on chloride content in the pore solution with pH 13.5 in the last day of exposure.

The results imply that:

- Scaled martensitic stainless steel FeCr12 is completely resistant to fresh concrete, the pore solution of which contains not more than

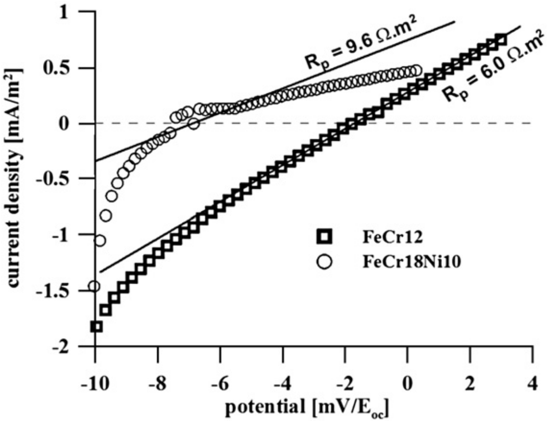

Fig. 10. Polarisation curves obtained by potentiodynamic polarisation in the vicinity of free corrosion potential (E_{oc}) for scaled FeCr12 and FeCr18Ni10 after three days of exposure in fresh concrete pore solution (pH 12.5) with chlorides (15 g Cl^-/l).

Table 3
Summary evaluation of corrosion resistance of stainless steel specimens with scaled surface in fresh concrete pore solution.

	pH 12.5						pH 13.5					
Cl^- (g/l)	0.1	1	15	30	80	150	0.1	1	15	30	80	150
FeCr12	+	0	−	−	−	−	+	+	0	0	−	−
FeCr16	+	+	−	−	−	−	+	+	+	+	+	0
FeCr18Ni10	+	+	0	0	0	0	+	+	0	0	0	0
FeCr18Ni10Mo2	+	+	+	+	+	0	+	+	+	+	+	0
FeCr22Ni6Mo3	+	+	+	+	+	0	+	+	+	+	+	+

0.1 g Cl^-/l. Higher concentrations take a risk of localised corrosion. Scaled FeCr12 steel gets spontaneously activated at concentrations higher than 1 g Cl^-/l. Higher alkalinity has a positive impact on pitting and crevice corrosion resistance.

- Substantial influence of pore solution alkalinity was also observed for ferritic stainless steel FeCr16 which shows similarly low corrosion resistance to saturated $Ca(OH)_2$ solution as FeCr12 to pH 13.5 solution. The growth of OH^- concentration by an order of magnitude, however, increases the threshold concentration for activation to more than 80 g Cl^-/l.
- The same threshold concentration for activation in pH 12.5 solution was detected for scaled FeCr18Ni10 as well. Unlike FeCr16, higher concentration does not lead to spontaneous activation, however there is some uncertainty due to low values of polarisation obtained from the non-linear curves. Nevertheless, increase in pH will not enhance the resistance.
- Corrosion resistance of scaled austenitic steel alloyed with molybdenum is also independent of pH, and its critical concentration is not lower than 80 g/l.
- In case of scaled steel FeCr22Ni6Mo3, corrosion resistance is ensured throughout the entire interval of chloride concentration at pH 13.5.

It is likely that the drop of corrosion resistance of scaled materials is induced by depleting chromium (transferring to scales) from the metallic top layer. It is evidenced by a profile analysis of the specimens' scaled surface (glow discharge spectroscopy). High concentration of chromium in scales is compensated for all steels by the drop of chromium concentration in the metal to the depth of 20 µm (Fig. 11). In the case of FeCr12 steel, the content of chromium at the scale–metal interface drops to 5%, whereby the steel loses the properties of stainless steel. The threshold chromium content of 12%, where steel can still be considered stainless, was reached also by FeCr16, FeCr18Ni10, FeCr18Ni10Mo2. In such case, the drop of corrosion resistance in the presence of chlorides is not surprising at all.

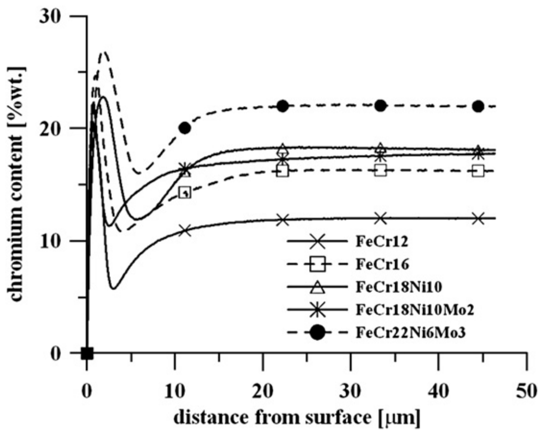

Fig. 11. Chromium concentration vs. distance from scaled specimens.

4. Conclusions

This study focused on the comparison of chloride concentrations critical for activation of usual types of stainless steels widely ranging in chemical composition and structure. The results implied that an important factor affecting the corrosion resistance is the superficial state in terms of the presence of scales. All tested materials with bare surface, except for martensitic chromium steel FeCr12, proved to be completely resistant to fresh concrete pore solution. And vice versa, if the surface is scaled, the identically high resistance cannot be expected even for the most alloyed stainless steels. Therefore, it is obvious that cheaper, low-alloyed steels with bare surface can be more resistant than expensive high-alloyed scaled steels. Increasing pH by a single unit (from 12.5 to 13.5) has less positive effect on corrosion resistance than removal of scales; the pore solution alkalinity, which is given by cement composition, is thus not so important.

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