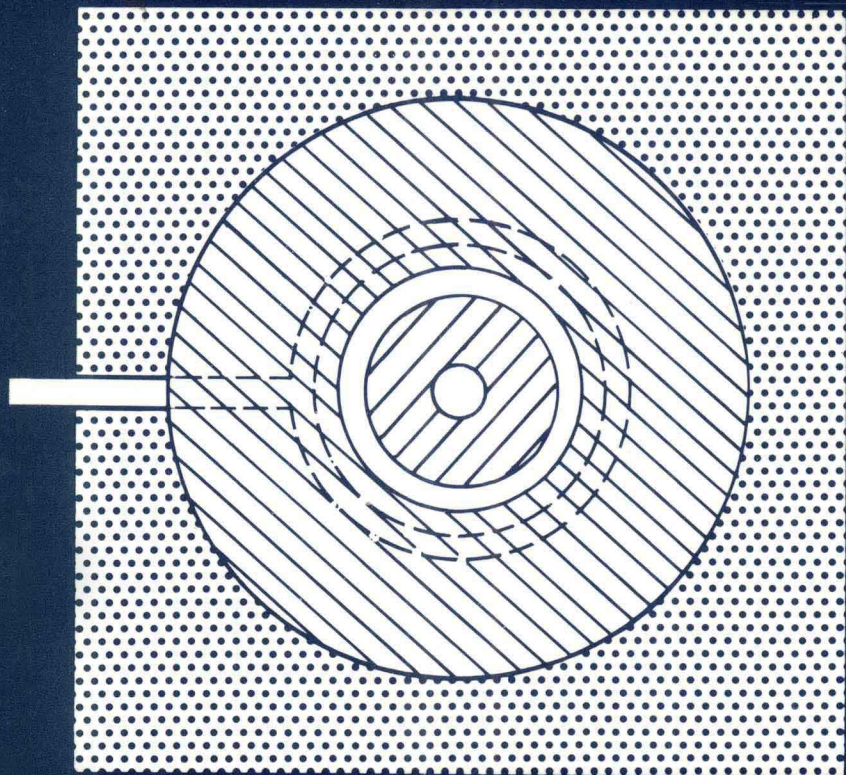


# Corrosion Rates of STEEL in CONCRETE



erke/Chaker/Whiting, editors



STP 1065

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# *Corrosion Rates of Steel in Concrete*

*Neal F. Berke, Victor Chaker, and David Whiting, editors*



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## Foreword

The symposium on Corrosion Rates of Steel in Concrete was held in Baltimore, Maryland, on 29 June 1988. The symposium was sponsored by ASTM Committee G01 on Corrosion of Metals and ASTM Committee C09 on Concrete and Concrete Aggregates and its Subcommittees C09.03.08 on Admixtures and C09.03.15 on Concrete's Resistance to Its Environment. Neal S. Berke, W. R. Grace and Company, Victor Chaker, Port Authority of New York and New Jersey, and David Whiting, Construction Technology Laboratories, Presided as symposium cochairmen and are editors of this publication.

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# Overview

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Steel reinforced concrete is a widely used and durable structural material. The concrete environment protects the steel from direct atmospheric corrosion. However, this protective environment can be compromised due to the ingress or addition of chloride ions, or by carbonation, or both. Indeed, the widespread use of steel reinforced concrete in bridge and parking decks subjected to chloride deicing salts, and the use of reinforced concrete in marine environments has resulted in early need of repair due to reinforcement corrosion. Other failures have occurred in reinforced pipes and other structures where carbonation has reached the reinforcement level. Often the corrosion damage cannot be determined until visible signs of cracking and spalling are evident.

ASTM Committee G01 on Corrosion of Metals is actively involved in the writing and evaluation of test methods related to corrosion of metals. Subcommittee G01.14 on Corrosion of Reinforcing Steel is the committee addressing rebar corrosion. An active goal of Subcommittee G01.14 is to develop test methods that can be used to determine and predict the corrosion rates of steel in concrete. Nondestructive techniques would be quite useful in assessing the condition of reinforced concrete in laboratory and more importantly field conditions. The results could be used to develop maintenance and repair schedules, and to evaluate new corrosion protection methods. The symposium thus provides a useful starting point in the evaluation of test methods to be developed by ASTM.

Realizing that corrosion of steel in concrete is also of interest to ASTM Committee C09 on Concrete and Concrete Aggregates, G01.14 is cooperating closely with subcommittees in C09. This Special Technical Publication (STP) is the result of a joint symposium cosponsored by Subcommittees G01.14, C09.03.08.04 (Corrosion Inhibitors), and C09.03.15 on Methods of Testing the Resistance of Concrete to Its Environment.

This STP contains eleven papers dealing directly with methods of determining corrosion rates of steel in concrete. Several of these papers and the other two papers also address other issues of interest such as chloride ingress, the effects of pozzolans, concrete properties, corrosion inhibitors, different metals and repair techniques, and mechanisms of corrosion. Not all of the methods or mechanisms discussed are universally used or accepted, but they do show the active interest in this area of study, and the diversity of views.

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# The Threshold Concentration of Chloride in Concrete for the Initiation of Reinforcement Corrosion

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**REFERENCE:** Hansson, C. M. and Sørensen, B., "The Threshold Concentration of Chloride in Concrete for the Initiation of Reinforcement Corrosion," *Corrosion Rates of Steel in Concrete*, ASTM STP 1065, N. S. Berke, V. Chaker, and D. Whiting, Eds., American Society for Testing and Materials, Philadelphia, 1990, pp. 3–16.

**ABSTRACT:** The mechanism by which chlorides initiate corrosion is by locally breaking down the passive film which forms on steel in the highly alkaline concrete pore solution. However, the breakdown of passivity requires a certain concentration of chlorides. The aim of the project described in the paper has been to determine the influence of a number of factors on the critical concentration of  $\text{Cl}^-$  necessary for initiation of corrosion of steel embedded in concrete. The variables investigated include hardening conditions, water/cement ratio, cement type, reinforcing steel surface condition, and salt type.

Mortar samples containing a steel rod have been cast, hardened, and subsequently exposed to a sodium chloride or calcium chloride solution. The corrosion current of the embedded steel has been monitored electrochemically and initially was of the order of  $10^{-4}$  A/m<sup>2</sup>, corresponding to a corrosion rate of approximately 0.1  $\mu\text{m}/\text{year}$  from the steel surface. After a period of time, the corrosion current increased by several orders of magnitude indicating that the chloride had penetrated to the steel surface and had initiated corrosion. The rate of this penetration, the chloride concentration in the mortar adjacent to the steel at the onset of corrosion, and the subsequent corrosion rate have all been measured to determine the influence of the preceding variables.

**KEY WORDS:** critical chloride concentration, chloride diffusion, cement type, water/cement ratio, corrosion rates, corrosion, steels, concrete

In good quality portland cement concrete, steel develops a protective passive layer because of the high alkalinity of the pore solution. In the passive state, the steel corrodes at an insignificantly slow rate, typically of the order of 0.1  $\mu\text{m}/\text{year}$  [1,2]. Unfortunately, however, chloride ions can break down this passivity and allow the steel to actively corrode at rates several orders of magnitude higher than the passive rate.

The critical amount of chloride necessary for the breakdown of the passive film and the onset of active corrosion has been the subject of controversy among scientific investigators for many years. Moreover, its corollary—the amount of chloride which can be tolerated without risk of corrosion—is of major interest to the practicing engineer who would like to use accelerators or other chloride-containing additives in concrete or to those who must build constructions in areas where the mixing water or aggregate are contaminated by chlorides (for example in the Middle East). A knowledge of the chloride threshold value for reinforcement corrosion is also of utmost importance to those involved in inspection,

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repair, and maintenance of constructions which are exposed to chlorides from seawater or from de-icing salts.

The reason for the scientific controversy and practical confusion is basically a question of "which concrete and when?" because the amount of chloride which can be tolerated is highly dependent on a large number of factors including: (1) whether the chloride is present in the original concrete mix or penetrates the concrete from the atmosphere, (2) the composition and history of the concrete, and (3) the atmospheric conditions.

The majority of laboratory investigations have either been carried out in synthetic cement pore solution to which chlorides have been added [3–6] or cement paste or mortar mixes containing chlorides [5–12]. On the other hand, the majority of practical investigations of critical values of chloride have involved constructions into which chloride ions have penetrated from the environment [13–18].

The present project is aimed at bridging the gap between these two types of investigations by making laboratory investigations of the actual amount of chloride necessary to initiate active reinforcement corrosion in mortar samples when the salt penetrates from the environment.

From the viewpoint of reinforcement corrosion, it is the amount of "free" chloride present in the cement paste pore solution rather than the total chloride concentration which is critical. The difference between these two, the amount or proportion of "bound" chloride is primarily dependent on the composition of the cement used in the concrete, particularly the cement's aluminium phase content [19], its pH [20,21] and, probably, its specific surface area [22]. Thus, the advent of new cement types containing, for example, fly ash, slag, or microsilica, can have a strong influence on the amount of "free" chlorides present in the pore solution.

The composition of the concrete and its history (that is, age, temperature, and humidity history) determine the degree of porosity and amount of free water (pore solution) in the cement paste phase. These factors, in turn, determine the rate at which chlorides can penetrate into the reinforcement and, thus, the initiation time for corrosion. They also determine the concentration of  $\text{Cl}^-$  in the pore solution which effects the total chloride threshold value for corrosion. Finally, they determine the access of oxygen from the environment and the electrical resistivity of the concrete which, together, control the corrosion rate after initiation.

In the present investigation, the time to initiate corrosion, the total chloride concentration in the mortar adjacent to the steel at the time of initiation, and the subsequent corrosion rate have been determined with the following parameters as variables: (1) cement type, (2) water/cement ratio, (3) curing conditions, (4) state of the reinforcement, and (5) salt type. In addition, the proportion of "bound" chloride has been determined for a single sample of each cement type.

It should be noted that the exact value of threshold concentration cannot be used in practice because each part of each construction is likely to have its own unique value. However, the aim of the project has been to determine the relative influence of the different factors so that the risk of corrosion due to penetrating chlorides can be minimized in future constructions.

## **Experimental Procedure**

### *Sample Preparation*

The samples investigated were mortar prisms (40 by 40 by 160 mm<sup>3</sup>) with a cement:sand ratio of 1:3 and with the cement type and water/cement (w/c) ratios given in Table 1 and

TABLE 1—Summary of samples tested. Six samples of each type were cast and tested.

Mortar Type	Sample Designation	w/c	No. of Days at 100% RH	Salt
EFFECT OF CEMENT TYPE				
Danish ordinary portland cement	DK-OPC	0.50	14	NaCl
Danish low alkali sulphate resistance portland cement	DK-SRPC	0.50	14	NaCl
Danish rapid hardening portland cement	DK-RHPC	0.50	14	NaCl
Danish standard flyash cement	DK-STD	0.50	14	NaCl
Austrian ordinary portland cement	A-OPC	0.50	14	NaCl
Swedish ordinary portland cement	S-OPC	0.50	14	NaCl
90% Swedish ordinary portland cement + 10% microsilica	S-SiO <sub>2</sub>	0.50	14	NaCl
EFFECT OF WATER/CEMENT RATIO				
Danish ordinary portland cement	DK-OPC/40	0.40	14	NaCl
Danish ordinary portland cement	DK-OPC/45	0.45	14	NaCl
Danish ordinary portland cement	DK-OPC/50	0.50	14	NaCl
Danish ordinary portland cement	DK-OPC/60	0.60	14	NaCl
EFFECT OF HARDENING CONDITIONS				
Danish OPC	DK-OPC-03	0.50	3	NaCl
Danish OPC	DK-OPC-07	0.50	7	NaCl
Danish OPC	DK-OPC-14	0.50	14	NaCl
Danish OPC	DK-OPC-31	0.50	31	NaCl
EFFECT OF SALT TYPE				
Danish OPC	DK-OPC-Ca	0.50	14	CaCl <sub>2</sub>
Danish standard flyash cement	DK-STD-Ca	0.50	14	CaCl <sub>2</sub>
EFFECT OF STEEL SURFACE CONDITION				
Danish OPC with cleaned reinforcing steel	DK-OPC-cr	0.50	14	NaCl
Danish OPC with as-received reinforcing steel	DK-OPC-ar	0.50	14	NaCl
Danish OPC with rusted reinforcing steel	DK-OPC-rr	0.50	14	NaCl

containing a centrally placed, smooth, plain carbon steel rod, as illustrated in Fig. 1. The compositions of the cements investigated are given in Table 2. After casting, the samples were kept for 24 h in 100% relative humidity (RH) before demolding. Except where indicated in Table 1, the prisms were then stored in 100% RH (that is, over water in a closed container) for an additional 13 days and, thereafter, in the laboratory atmosphere at approximately 50% RH for 16 days. Six samples of each composition or hardening condition or both were prepared and tested.

As indicated in the Results section of this paper, the threshold value of chloride concentration measured for these samples was judged to be unrealistically high. Therefore, three additional sets of samples were prepared using profiled reinforcing steel instead of the smooth steel rod. In one set, the reinforcement was used in the slightly rusted "as-received" condition; in the second set, it was cleaned by sand-blasting; and in the third set, it was further rusted by outdoor exposure for two weeks.

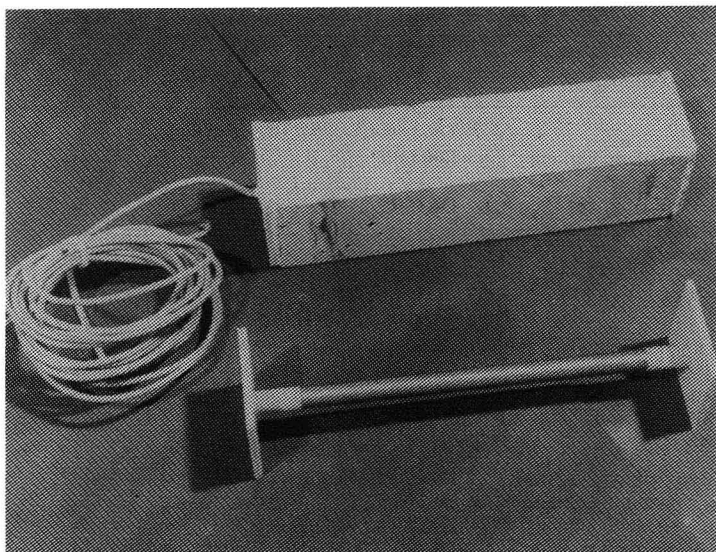


FIG. 1—Mortar sample containing a centrally placed steel rod.

### *Exposure Procedure*

Thirty days after casting, the samples were immersed in a 1 *N* sodium chloride ( $\text{NaCl}$ ) or calcium chloride ( $\text{CaCl}_2$ ) solution containing calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and coupled to potentiostat. They were held at a constant applied potential of 0.00 mV saturated calomel electrode (SCE) and the current flowing between each embedded steel rod and an external stainless steel counter electrode was monitored daily. The initial current densities monitored were of the order of  $10^{-4}$  A/m<sup>2</sup> (approximately 0.1  $\mu\text{m}/\text{year}$ ) and continued unchanged until the chloride penetrated the cover and initiated corrosion at which time the current increased by over three orders of magnitude in the course of a few days.

At this time, three samples of each set were removed and broken to expose the mortar surface adjacent to the steel. Small samples, of the order of 1 g, were removed in approximately 2 to 3 mm from this surface, dissolved in hot nitric acid ( $\text{HNO}_3$ ), cooled and analyzed for  $\text{Cl}^-$  by potentiometric titration against silver nitrate ( $\text{AgNO}_3$ ).

In addition, very small samples, of the order of 5 mg, were scraped from the surface adjacent to both the noncorroding part of the steel and to the corroded part. These were analyzed for  $\text{Cl}^-$  by energy dispersive X-ray fluorescence spectrometry (XRF). In this technique, the ratio of the intensities of the characteristic X-rays for chlorine and calcium were determined for a number of samples containing known amounts of sodium chloride and the results plotted as a calibration curve. The chloride content of the samples was then determined by comparing their  $\text{Cl}/\text{Ca}$  intensity ratios with those on the calibration curve.

The remaining three samples were disconnected from the potentiostat and positioned vertically with the lower 2 to 3 cm in the chloride solution. Their free potentials were monitored over a period of several weeks and their corrosion rates were determined by polarization resistance measurements. The reason for their being partially exposed to the atmosphere is that earlier experiments showed that the initial corrosion rate is so high that the oxygen dissolved in the pore solution of totally submersed samples is rapidly depleted and the corrosion reaction is stifled despite the high chloride content of the mortar.

TABLE 2—Analyses of the different cement types investigated. Compositions are given in percent by weight.

Cement Type	D-OPC	A-OPC	S-OPC	D-SRPC	D-RHPC	D-STD
Loss on ignition (1000°C)	2.4	2.3	2.3	0.9	0.2	0.2
Insoluble residue	0.6	0.6	0.4			
SiO <sub>2</sub>	19.6	19.9	19.6	24.4	22.4	22.4
Al <sub>2</sub> O <sub>3</sub>	6.0	5.5	4.8	2.6	4.9	4.9
Fe <sub>2</sub> O <sub>3</sub>	3.0	2.8	2.1	3.1	2.8	2.8
CaO	62.9	61.7	62.8	65.1	66.2	66.2
MgO	0.9	2.4	3.0	0.6	1.0	1.0
SO <sub>3</sub>	2.7	2.7	2.8	2.0	0.6	0.6
Alkalis	1.9	2.1	2.2	0.4	0.9	0.9
"Bogue composition"						
C <sub>3</sub> S	54.7	51.2	63.4	49.0	58.0	58.0
C <sub>2</sub> S	15.0	18.5	8.5	33.0	21.0	21.0135
C <sub>3</sub> A	10.8	9.8	9.2	2.0	8.0	8.0
C <sub>4</sub> AF	9.1	8.5	6.4	9.0	8.0	8.0
Flyash additions	...	...	...	...	3.0	22.0
Specific surface area, m <sup>2</sup> /kg	300	355	390	300	400	440

At the end of this exposure period, the bound chloride content was determined for a single sample of each cement type by the following procedure. The lower half of the sample (that is, that which had been partially submersed in the NaCl solution) was removed and crushed. One part was weighed, dried for 48 h at 110°C, and reweighed to determine the free water content. The total chloride content of these samples was determined by dissolving the dried mortar in 0.01 *N* HNO<sub>3</sub> and analyzing the solution for Cl<sup>-</sup> by potentiometric titration against AgNO<sub>3</sub>. The pore solution was expressed from the remaining part of the samples and analyzed for both OH<sup>-</sup> and Cl<sup>-</sup> by chemical and potentiometric titration, respectively.

## Results and Discussion

The values of time to initiate corrosion,  $t_o$ , the critical chloride concentration,  $C_o$ , the steady-state corrosion rate,  $i_o$ , the proportion of free chloride given as a percentage of the total chloride content, the pH value of the pore solutions expressed from the samples together with the pH values of the same cements without chloride additions, are given in Table 3. The effects of the different parameters investigated are presented in graphical form in association with the following discussions.

The pH values (calculated from hydroxyl ion contents) of the pore solutions after long-term exposure to sodium chloride solution vary very little from cement to cement and are all lower than might be expected. This may be explained, however, by the previous observation [20] that an ion-exchange takes place at the surface of concrete exposed to salt solutions, the hydroxyl ions being leached out while the chloride ions diffuse in. Thus, the low, fairly constant values of pH reflect the result of this exchange.

It can be seen from Table 3 that the threshold value of chloride concentration at the onset of corrosion is not as pronounced as might be expected and appears, unexpectedly, to be independent of the proportion of the total chloride remaining in the pore solution.

The actual value of the threshold concentration determined by potentiometric titration—

TABLE 3—The average values ( $\bar{x}$ ) and standard deviations (s) of the values of the time to initiate corrosion ( $t_0$ ), the critical chloride concentration ( $C_0$ ), the subsequent corrosion current density ( $i_{cs}$ ), the electrical resistance, and free  $Cl^-$  content given as % of the total average chloride content of the sample.

Sample Designation	$t_0$ , days		$C_0$ (titr), % mortar		$C_0$ (XRF), % mortar		$i_{cs}$ , mA/m <sup>2</sup>		Electrical Resistance		Free $Cl^-$ , % total Cl	pH of Sample	pH of Paste (Ref. 25)
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s			
DK-OPC-03	27	17	0.139	0.004	0.050	0.026	0.78	0.61	88				
DK-OPC-07	49	19	0.231	0.024	0.102	0.049	0.57	0.31	86	10			
DK-OPC-14	48	19	0.212	0.031	0.085	0.035	0.96	0.91	115	16			
DK-OPC-31	88	14	0.284	0.069	0.173	0.075	1.20	0.70	115	4			
DK-OPC/40	199	39	0.287	0.032	0.170	0.040	2.80	0.10	419	249			
DK-OPC/45	99	8	0.258	0.023	0.137	0.015	0.94	0.39	219	34			
DK-OPC/50	48	19	0.212	0.031	0.085	0.035	0.96	0.91	115	16			
DK-OPC/60	38	11	0.257	0.012	0.080	0.045	7.10	1.10	128	11			
DK-SRPC	78	5	0.212	0.028	0.094	0.030	1.60	1.90	129	15	71	12.75	13.28
DK-RHPC	236	58	0.237	0.120	0.102	0.062	1.60	0.70	372	7	30	12.38	...
DK-STD <sup>a</sup>	389	18	0.140	0.017	0.123	0.022	0.83		1087	40	28	12.62	13.42
DK-OPC	48	19	0.212	0.031	0.085	0.035	0.96	0.91	115	16	40	12.38	13.58
A-OPC	110	26	0.263	0.059	0.150	0.037	3.20	2.00	172	25	35	12.60	13.63
S-OPC	80	13	0.252	0.043	0.159	0.054	2.50	0.80	160	2	86	12.56	13.79
S-SiO <sub>2</sub>	190	96	0.099	0.015	0.051	0.036	4.90	2.90	359	79	33	12.56	12.93
DK-OPC-Ca	58	14	0.343	0.066	0.167	0.018	3.80	3.20	152	4			
DK-STD-Ca	96	5	0.215	0.083	0.125	0.019	1.60	0.90	397	22			
DK-OPC-cr	67	2	0.303	0.115	0.220	0.020	0.60	0.20	103	6			
DK-OPC-ar <sup>b</sup>	59	12	0.260	0.123	0.180	0.033	8.10	8.40	133	14			
DK-OPC-rr <sup>c</sup>	94	13	0.391	0.048	...	...	...	...	104	7			

<sup>a</sup> Three samples have not yet begun to corrode after 600 days' exposure. None of a second series of samples has yet begun to corrode after 120 days' exposure.

<sup>b</sup> One sample has not yet begun to corrode after 120 days' exposure.

<sup>c</sup> Two samples have not yet begun to corrode after 120 days' exposure.

approximately 0.15 to 0.35% by weight of the mortar, giving a value of 0.6 to 1.4% by weight of the cement—is significantly higher than expected from practical measurements of chloride concentrations in constructions in which the reinforcement is actively corroding. There are two possible explanations for this.

First, only a small amount (approximately 1 g) of mortar is removed from the sample adjacent to the steel and it is likely that the cement:sand ratio in this sample is higher than in the bulk of the sample. Therefore, to convert the total amount of chloride present to weight percentage of the cement, the multiplication factor should be lower than the theoretical value of  $\times 4$ .

Second, the steel used was smooth and clean whereas normal reinforcing steel is both profiled and more or less covered by a rust layer at the time the concrete is cast. The profiling gives a larger specific surface area and, together with the rust, can also give rise to corrosion at lower chloride contents by the phenomenon known as crevice corrosion.

The values of critical concentration determined by X-ray fluorescence are consistently lower than those determined by titration. One reason for this is that they are determined on very small amounts (approximately 5 mg) of material scraped from the layer immediately adjacent to the steel whereas those for titration are obtained from samples drilled from the mortar adjacent to the steel to a depth of approximately 2 mm. Assuming a linear concentration gradient exists from the surface of the sample to the steel, the difference in XRF and titration values can partly be accounted for by the difference in  $\text{Cl}^-$  concentration over these 2 mm.

A second effect is that the XRF determinations were made by comparison of the intensities of the Cl and Ca characteristic X-ray emissions with those of standard samples prepared in the same manner. By this technique, the uncertainties in the content of sand in the sample are eliminated. It is felt, therefore, that XRF results are the more realistic values.

A very good correlation is observed between the time to initiate corrosion,  $t_0$ , and the electrical resistance of all the hardened samples, as illustrated in Fig. 2. This suggests that electrical resistance of fully saturated concrete or mortar could be used as a simple and inexpensively determined parameter to rank their resistance to penetration of salts.

### *Effect of Curing Time*

The transfer of samples from 100% RH to the laboratory atmosphere of approximately 50% RH results in a drying out of the mortar and effectively stops hydration. Thus, samples which were cured at 100% RH for only three days and allowed to dry out for 27 days can be expected to contain significant amounts of unhydrated cement and to be extremely porous. When the sample is subsequently immersed in NaCl solution, the chloride ions will penetrate the mortar very rapidly together with the water as it is drawn in by capillary suction. The unhydrated cement can then begin to react and will be affected by the presence of the  $\text{Cl}^-$  ions which will have a greater chance of being chemically bound than if they penetrated fully hardened cement paste and may also have an accelerating effect on the hydration.

The longer the period of moist curing, the slower will be the penetration of chlorides but the degree of chemical binding can also be expected to be lower. The first hypothesis is confirmed by the results shown in Fig. 3: the initiation time for corrosion increases approximately linearly with an increasing period of moist curing. On the other hand, any increase in chemical binding is not reflected in a higher critical chloride concentration for corrosion and, in fact, the tendency is the opposite. One possible cause could be that a moist curing period of only three days was not sufficient to allow a fully protective passive film to be formed before the chlorides penetrated the mortar cover.

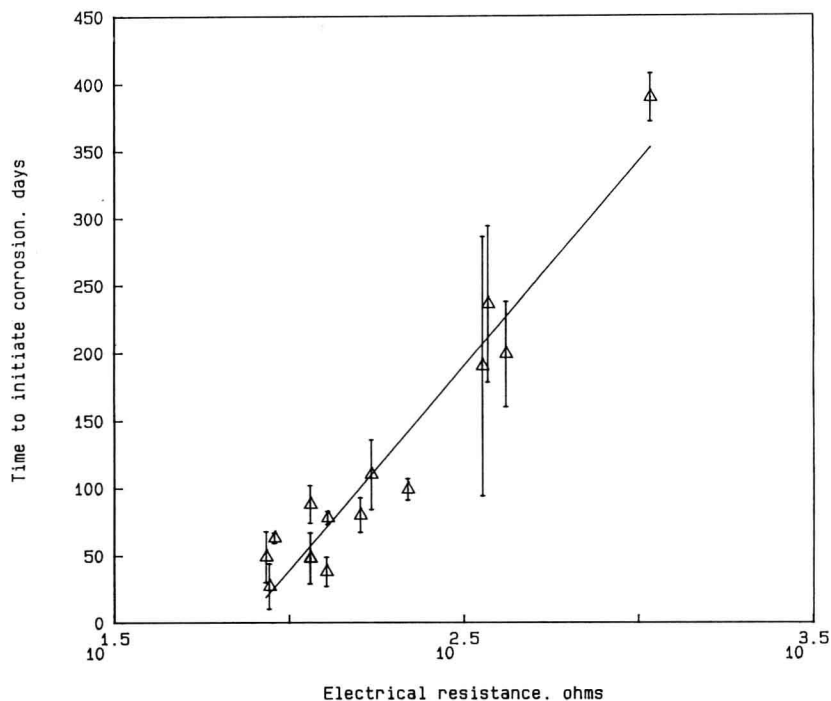


FIG. 2—The time to initiate corrosion as a function of the electrical resistance of the hardened samples.

### Effect of Water/Cement Ratio

A major effect of increasing the w/c ratio is an increase in the porosity. This has a threefold negative effect from the point of view of reinforcement corrosion: a more rapid diffusion of chloride ions in to the steel surface; easier ingress of oxygen and lower electrical resistivity. Increasing the w/c ratio has two additional effects: first, it results in a lower pH of the pore solution [20] which, in turn, influences both the degree of chloride binding [20,21] and the critical concentration of chlorides required to break down the passive film [23]. Second, a higher w/c ratio gives a greater total amount of free water and, therefore, a more dilute chloride concentration in the pore solution [20].

The net effect of these factors is negative, however, as illustrated in Fig. 4, with a rapidly decreasing initiation time for corrosion and a similar decrease in the critical chloride concentration for corrosion (as determined by XRF). It should be noted that the effect of w/c ratio on the initiation time is considerably greater than that of curing shown in Fig. 3.

### The Effect of Cement Type

The critical chloride concentrations and the initiation times for corrosion for mortars prepared with all seven types of cement are given in the bar diagram in Fig. 5. In Fig. 6, the values of  $t_0$  for samples prepared with the three Danish cements, sulphate resistant portland cement (SRPC), rapid-hardening portland cement (RHPC) and standard cement,



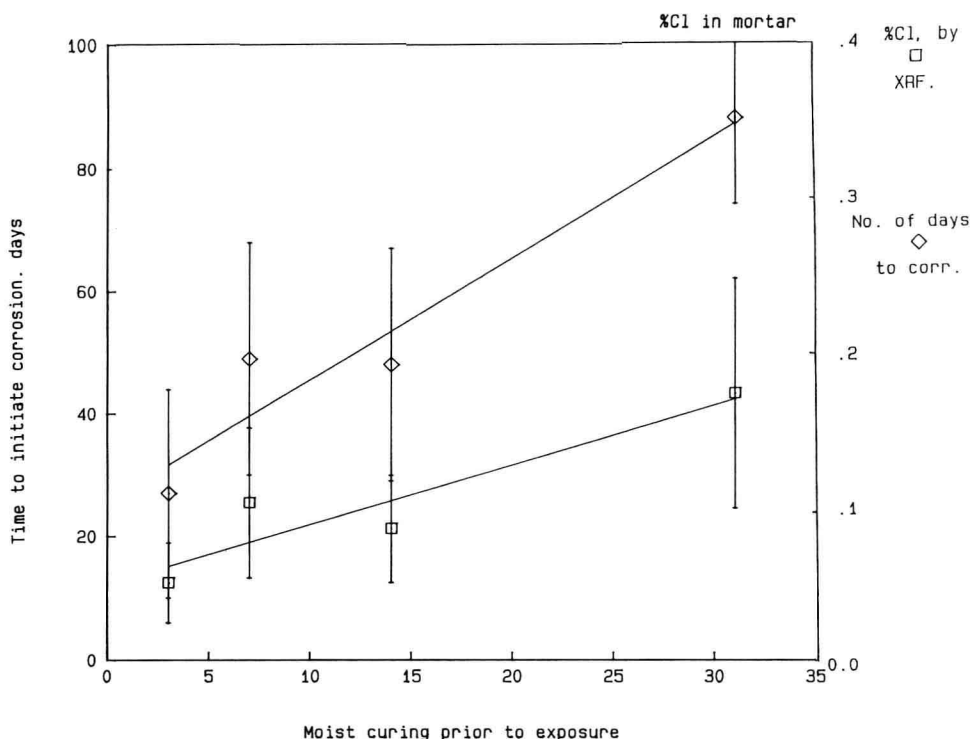


FIG. 3—The corrosion initiation time and critical chloride concentration (determined by XRF) for Danish OPC mortar samples as a function of the period of moist curing.

are plotted versus the steady-state diffusion coefficients determined for 28 day old paste samples of the same cements also with  $w/c = 0.50$  published previously [24]. The correlation is excellent and confirms that steady-state diffusion measurements on paste samples can be used as an indication of resistance of mortar and concrete to penetration of chlorides.

*The Ordinary Portland Cements (OPCs)*—Despite the fact that the composition of all three OPCs lie within the general specification for ordinary portland cement, their response to exposure to chlorides is quite different. The present results confirm a previous observation [25] that the Swedish OPC has a much lower binding capacity for chlorides than do the Danish or Austrian OPCs. The reason for this is not clear but is probably a combination of the effects of the lower total aluminium content (that is, tricalcium aluminate ( $C_3A$ ) + tetracalcium aluminate ferrite ( $C_4AF$ )), the higher pH of the pore solution (which has been shown to decrease the chloride binding [20,21]) and, possibly, the additions of ferrous sulphate to this cement.

Although the concentration of chlorides remaining in solution in the Swedish OPC is much greater than that if the other OPCs, the critical total chloride concentration necessary to initiate corrosion is the highest of the three OPC cements. It must be concluded, therefore, that the high dissolved chloride content which can be tolerated is a result of the very high pH of this cement.

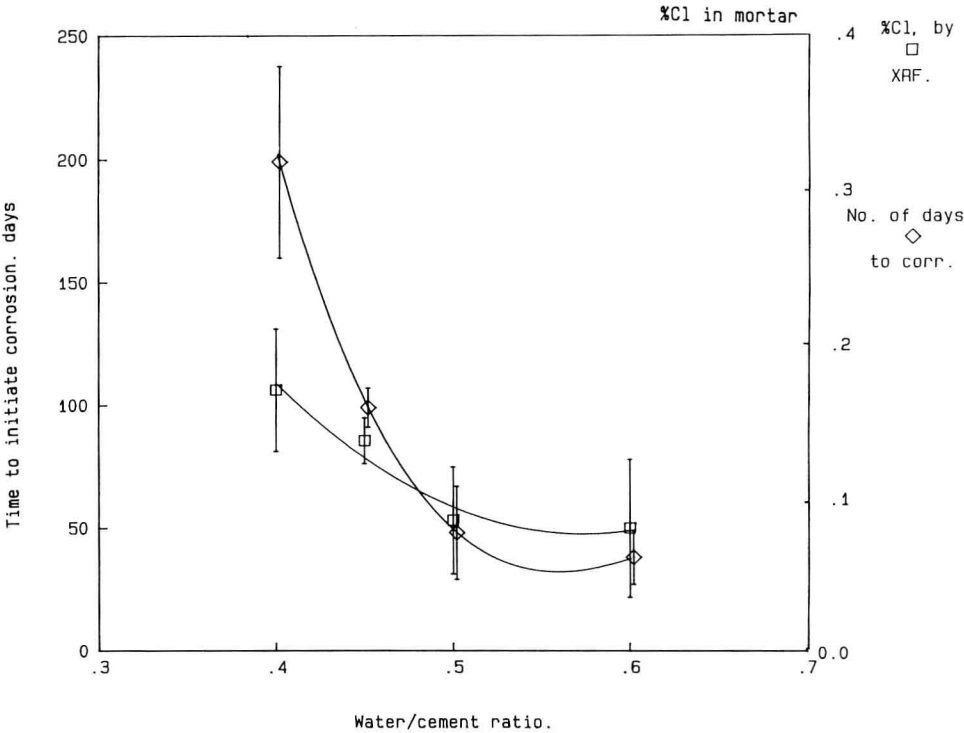


FIG. 4—The effect of water/cement ratio of Danish OPC mortar samples on the time to initiate corrosion and the critical chloride concentration (determined by XRF).

There is no relationship between the values of  $t_0$  for samples made with these three cements and, for example, the specific surface area of the cement which must play a role in the pore size distribution of the hardened paste. That the Danish OPC had the lowest value of all seven cements is probably due to its coarse particle size but the Swedish OPC has the highest specific surface area of the three but a lower value of  $t_0$  than the Austrian OPC samples. The additions of ferrous sulphate to the Swedish OPC which have a mild accelerating effect may, however, result a more open pore structure and, thereby, allow more rapid penetration of the chloride solution. Ferrous sulphate is also normally added to Danish cements, but the OPC used in this project was one prepared for experimental purposes and did not contain this additive.

*Sulphate Resistant Portland Cement*—Apart from the Swedish OPC which was just discussed, samples prepared with SRPC exhibited the lowest degree of chloride binding, as expected from its low  $C_3A$  content.

It should be noted, however, that despite previous reports [26] that SRPC has a lower resistance to chloride diffusion than OPC, the present results show very little difference in the behavior of SRPC samples relative to those prepared with the three OPCs.

*Cements with Microsilica or Fly Ash*—The previous observation [25] of a significant increase in the binding of chlorides by additions of silicon dioxide ( $SiO_2$ ) to the Swedish OPC