

C. Corrosion of reinforcement in concrete due to calcium chloride

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Summary

An investigation was made into the binding of chloride by hydrated cement in mortar or concrete and into the velocity of penetration of chloride into a cement sand mortar (1:3, wcr = 0.50).

Of great influence appeared to be the degree of hydration of the cement, the maximum capacity of binding chloride of the relevant cement, the volume porosity of mortar or concrete, the pH and the circumstances of hydration (dry or wet conditions).

1 Introduction

Chloride is regarded as extremely dangerous in causing the corrosion of prestressing steel in concrete, and in most countries the addition of chloride to concrete which is to be prestressed by pretensioning or posttensioning is prohibited for this reason. In the case of pretensioned steel a similarity with ordinary (untensioned) reinforcement in concrete could be thought to exist, but for the fact that the corrosion of prestressing steel may proceed in a different manner in consequence of the phenomenon of stress corrosion which is now more and more attributed to hydrogen embrittlement. In reinforced concrete, too, considerable caution is, however, exercised in the use of, for example, calcium chloride as an admixture (accelerator) added to the mix. In this context it must also be borne in mind that the mixing water itself may contain chlorides.

The environment in which the reinforced concrete or prestressed concrete is used may also contain chloride, however: for example, sea-water or salt-laden atmosphere. Chloride from de-icing salts may penetrate into concrete road surfacings. Concrete which comes into contact with gases containing hydrochloric acid, e.g., formed as a result of the combustion of PVC plastics, is likewise exposed to chloride action. It is therefore of importance to investigate more closely the transport of chlorides in concrete and their behaviour.

The problem splits up into three parts:

- a. The binding of chloride in concrete to which chloride has been added. It is known from cement chemistry that chloride can be chemically bound (combined) during the hardening of concrete. The question is how much chloride can thus be combined, whether such chloride remains combined under all circumstances, and how much so-called free chloride is still able to make its way to the reinforcement.

- b. The rate of penetration of chloride from the surrounding environment into concrete which has already hardened.
- c. The effect of chloride in mortar and concrete upon the corrosion behaviour of reinforcement in this concrete.

In all three cases the composition of the concrete – type of cement, water/cement ratio, aggregate/cement ratio, pore system, conditions of hardening (wet, dry, carbonation), and age – and furthermore the depth of concrete cover to the steel are important. The variables involved are so numerous that a limited choice had to be made for the purpose of the research, namely, those variables which could be expected to provide an insight into the factors likely to affect the behaviour of chloride.

The starting point in these considerations was the binding of chloride by cement. Since chemical binding can take place only as a result of reaction with hydrated calcium aluminate derived from C_3A , which does occur in portland cement but is not or hardly present in portland blast furnace slag cement, these two types of cement were included in the research (ENCI class A and CEMIJ class A respectively).

As for the composition of the concrete, it was decided to keep this constant and to give the mortar the same composition as that of the standard mix used in cement testing (micro-concrete in accordance with Netherlands Standard NEN 3072: 1 part of cement, 1 part of fine sand 0.075–0.50 mm, 1 part of medium sand 0.50–1.2 mm, 1 part of coarse sand 1.2–2.4 mm, parts by weight, water/cement ratio = 0.50), in which the type of cement was varied. Difference in binding was obtained by varying the degree of hydration, i.e., by varying the length of the hardening time under water and then, after these various hardening times, investigating the effect of further hardening under drying conditions (in air). As an extreme limiting case a completely carbonated mortar was investigated. It was expected in this way to ascertain the limits of binding (maximum for long hardening time under water, minimum for carbonated mortar) and therefore also the limits of the free chlorine ion concentrations. In each case mortar with and without chloride ($CaCl_2 \cdot 2H_2O$) was tested; the mortar containing “no” added Cl (however, cement itself contains some chloride: portland cement approx. 0.02%) was, after hardening in the manner indicated above, immersed in an aqueous solution containing 2% $CaCl_2 \cdot 2H_2O$ with a view to investigating the rate of penetration of the chloride as a function of this immersion time and to ascertaining the form in which this chloride was then present (combined and/or free). This research was based on cement suspensions which were obtained by allowing cement to undergo hydration (with continuous agitation) with an excess of water (water/cement ratio = 1, 1.5, 2 or 2.25), with the addition of $CaCl_2 \cdot 2H_2O$ if desired, so that hydration but no hardening could occur and the free chloride concentration in the aqueous phase could easily be determined.

2 Assessment of the binding of chloride

There is no known direct method of determining the quantity of combined chloride.

This quantity can be calculated indirectly from the difference between the total chloride and the free chloride. The latter was measured by placing a selective chloride electrode in the solution, suspension or mortar and measuring the potential difference with respect to a saturated calomel electrode (sce) with the aid of a digital voltmeter. The free chloride concentration was calculated by making use of calibration curves.

A further important question is to know at what free chloride concentration corrosion of the reinforcement will occur. This was ascertained by measuring polarization curves [1] and determining when the concentration of free chloride has such a value that it has no appreciable effect on the shape and position of the polarization curves (as compared with a chloride-free solution, suspension or mortar).

The chloride penetration depth was measured by means of a difference in colour produced on fresh cleavage surfaces by the application of a 1% AgNO_3 solution to them. As a result, the cleavage surface preserves approximately its normal colour in those parts where chloride has penetrated (formation of white AgCl), while a darkening of the colour (due to AgOH and Ag_2O) occurs at greater depths, at any rate if the mortar has not become carbonated there.

The current density measured for steel (in mortar) at a potential of +200 mV/(sce) was also found to be a serviceable – though somewhat awkward to determine – criterion for the presence of chloride penetrated into the mortar. Other methods, such as the use of penetrating radioactive chloride, X-ray fluorescence, and different diffusion tests on hardened cement paste with the same anions (Cl^-) or the same cations (Na^+), did not lead to distinct quantitative conclusions, but did yield qualitative information on the mechanism involved.

3 Corrosion activity of concrete to which calcium chloride has been added

3.1 Good curing

The effect of lime-water with increasing chloride concentration on polarization curves has already been discussed [1]. It was found that from a concentration of 0.024 gram ion of Cl^- per litre upwards* there is a risk that the passive film on reinforcing steel is locally disrupted. In cement suspensions the free chloride concentration at which corrosion activity became perceptible was found to be somewhat higher: the limit value of the concentration between passivation and pitting was 0.038 gram ion per litre. This does indeed appear quite logical, since other inhibitors besides lime, e.g., alkali hydroxides and silicates are present in cement. Now when chloride is added to mortar (of standard composition as applied in cement testing), it is found, after the elapse of some hydration time (under water) and depending on the chloride content, that measurements nevertheless often indicate passivation: in other words, the chloride is combined and there remains a concentration of free chloride not exceeding 0.038 gram ion per litre, which is the limit below which passivation is achieved.

* A minimum value of 0.017 was repeatedly found for a total of 159 measurements.

Fig. C1 indicates that (for hydration under water) there is a distinct difference between portland cement (pc) and portland blast-furnace slag cement (hc) as the cementing agent in mortar with regard to the binding of chloride (1d or 3d means 1 day or 3 days of hydration under water). This is more particularly manifest in the 24 hour values and when 4% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is present. After 24 hours' hardening, no

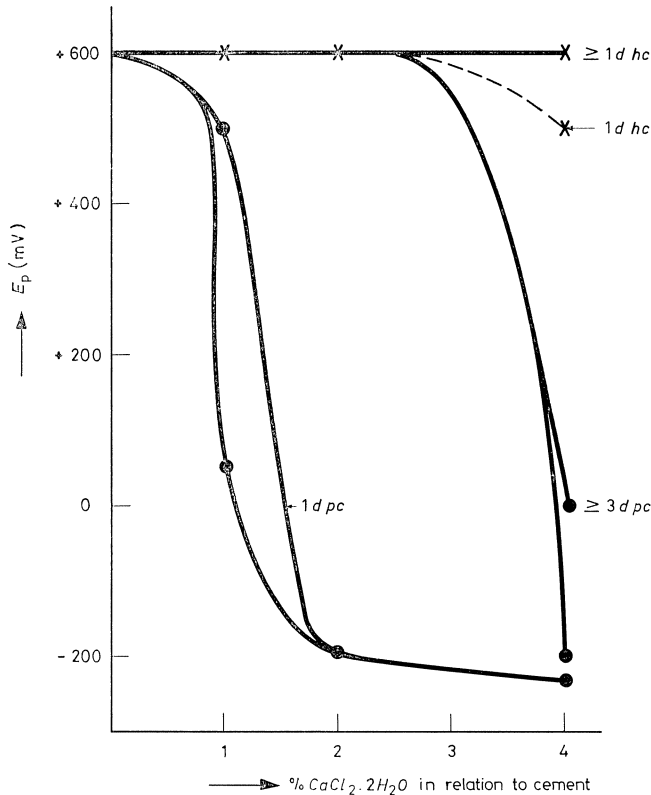


Fig. C1. Pitting potentials of portland cement and blastfurnace cement mortar electrodes for various amounts of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

passivation had occurred ($E_p < +600$ mV) in portland cement mortar with 1% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, whereas it was found to have occurred in portland blastfurnace slag cement mortar with this same content of chloride. With 4% $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ added, no passivation occurred in portland cement mortar even after 12 weeks, but in blast-furnace cement mortar it occurred already within 7 days. This means therefore that CEMIJ blastfurnace cement binds more chloride and does this more rapidly than ENCI portland cement does under moist conditions, despite the fact that portland cement can combine chemically with chloride.

Besides the pitting potential it is possible also to determine from the polarization

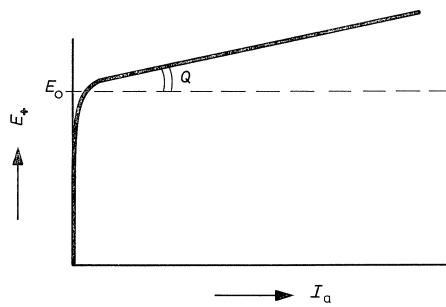


Fig. C2.

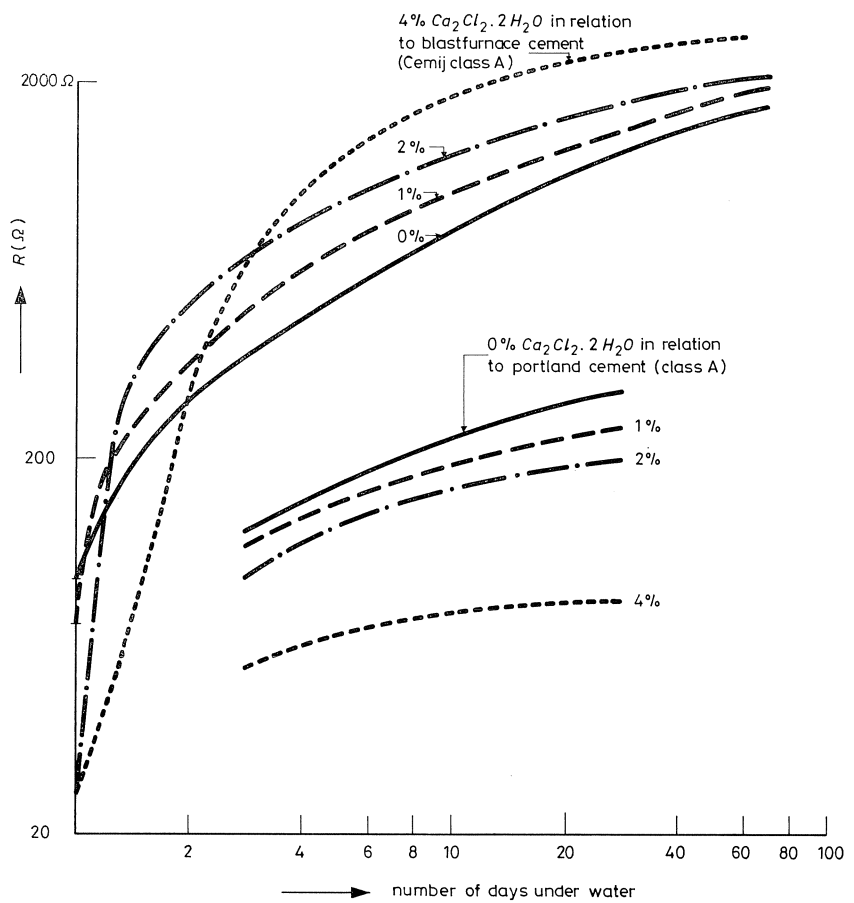


Fig. C3. Resistance of mortar electrodes as a function of hydration time for blast furnace cement and portland cement mortar.

cues the electrolytic mortar electrode resistance R at potentials above the oxygen potential when no pitting occurs:

$$E = E_o + R \cdot I_a \text{ where } R = \text{electrolytic mortar resistance} = \tan Q \text{ (Fig. C2)}$$

R has been plotted as a function of the hydration time in Fig. C3, revealing the difference between blastfurnace cement mortar and portland cement mortar. For example, after 28 days' moist hardening the value of R was 1200 ohms for blastfurnace and 300 ohms for portland cement mortar. This resistance is a measure of the mobility of the free ions in the mortar, the number of free ions and the pore width in the mortar. Practically complete hydration is found to have occurred at the end of three or four weeks.

Furthermore, a higher resistance associated with a given potential difference indicates lower intensity of the current through the mortar. The protection provided by CEMIJ blastfurnace cement mortar is therefore greater than that provided by portland cement mortar. In such cases the presence of increasingly large quantities of chloride raises the already higher resistance of the former and lowers the already relatively low resistance of the latter (for hydration under moist conditions).

3.2 Pore system

That there is a difference in pore system between portland cement and blastfurnace cement is also evident from [2]. Fig. C4 has been reproduced from that publication: hardened blastfurnace cement paste therefore has a higher degree of gel porosity and a lower degree of capillary porosity than hardened portland cement paste, for equal overall porosity.

The effect of CaCl_2 on the pore system is, for example, indicated in [3] for hardened

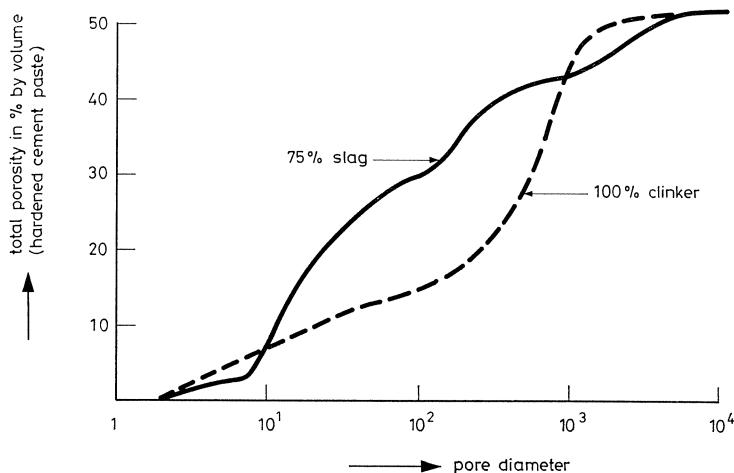


Fig. C4. Relation between porosity and pore diameter [Å].

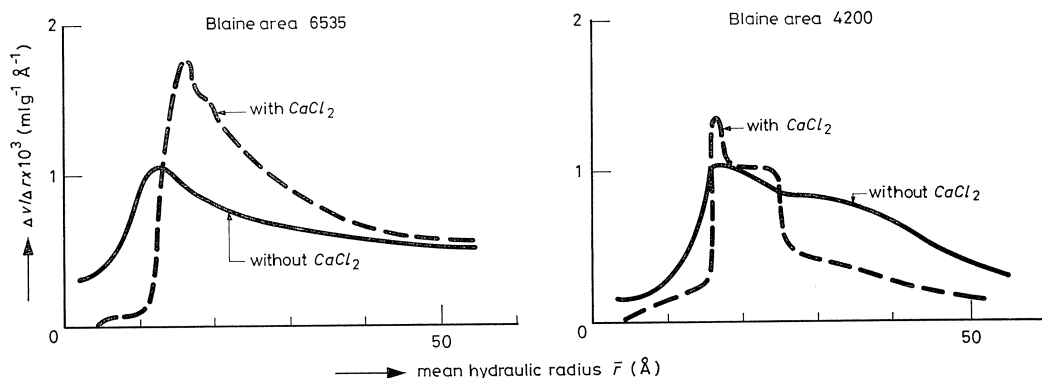


Fig. C5. Pore volume distribution curves for slag cement paste with and without 2% CaCl_2 .

blastfurnace cement paste with a water/cement ratio of 0.25, for specific surface areas of $4200 \text{ cm}^2/\text{g}$ and $6535 \text{ cm}^2/\text{g}$, respectively: see Fig. C5.

From this diagram it appears first of all that without addition of CaCl_2 the specific surface area of blastfurnace cement is important: a low specific surface area is associated with higher overall porosity and distinctly increased pore radius (17 \AA as compared with 13 \AA).

Addition of CaCl_2 results in a further increase in the overall porosity and pore radius ($17\text{--}24 \text{ \AA}$). For blastfurnace cement with a high specific surface area there is an even greater increase in overall porosity and pore radius ($16\text{--}19 \text{ \AA}$) as a result of the addition of CaCl_2 , so that the corrosion behaviour is affected because a more open structure is brought about. This is more particularly apparent from the great increase in the mean hydraulic radius. Especially the wider pores are affected and it is these which – because of better diffusion possibilities they offer the Cl^- ion – play a more important part than the narrower pores in the corrosion process.*

With the above-mentioned value of the water/cement ratio it was found in the research reported in [3] that the maximum permissible amounts of CaCl_2 at which passivation still occurred for blastfurnace cement with specific surface areas of 3600 , 4200 and $6535 \text{ cm}^2/\text{g}$ were 1.50, 1.75 and 1.90% respectively.

An idea of the difference in structure of concrete made with portland cement and with blastfurnace cement, and allowed to harden under moist and under dry conditions, is provided by Fig. C6, which comprises four scanning electron micrographs.

These micrographs with a magnification of $5500\times$ were obtained at a fresh fracture surface of hardened cement paste (water/cement ratio 0.40). For hardening under “dry” conditions the concrete was stored in an enclosed space for 3 days after casting and then in the open air for 25 days; for “wet” conditions of hardening it was stored under water for 28 days.

It is evident from the micrographs that “dry” or “wet” hardening has a considerable effect on the micro-structure of hardened portland cement paste. Drying greatly

* The specific surface area of the Cemij cement investigated was $3700 \text{ cm}^2/\text{g}$.



Photo 1. Hardened portland cement paste, hardened "dry".

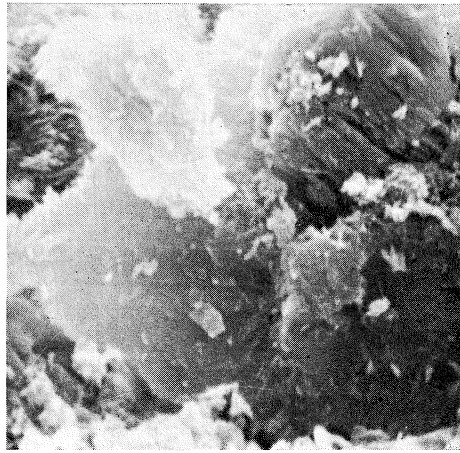


Photo 2. Hardened portland cement paste, hardened "wet".

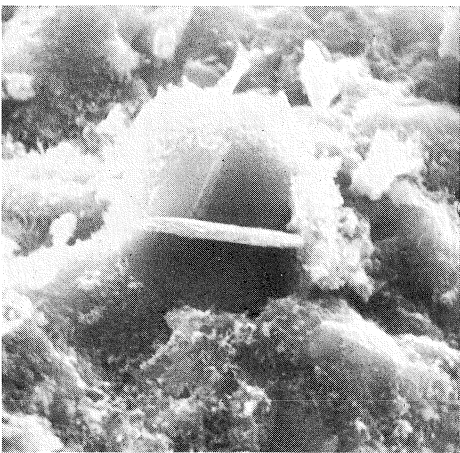


Photo 3. Hardened blast furnace cement paste (Cemij), hardened "dry".

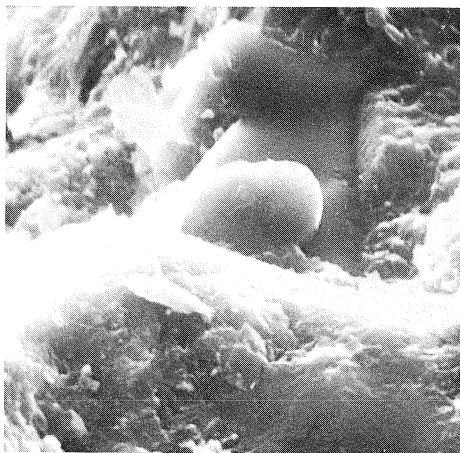


Photo 4. Hardened blast furnace cement paste hardened "wet".

Fig. C6.

impedes the hydration of the paste: there is an open and acicular structure, i.e., with needle-shaped features (clusters of needles). Under wet conditions of hardening the space between the needles is filled up, so that there is little evidence of an acicular structure. In hardened blastfurnace cement paste there is little detectable difference between "wet" and "dry" conditions of hardening. The structure is dense in both cases. The rougher character of the crystal mass as compared with hardened portland cement paste is a notable feature.

3.3 No curing

Having regard to these differences in structure between portland cement and blast-

furnace cement mortar and the effect of CaCl_2 on it, the lack of curing can likewise be expected to be of major importance. The polarization curves and electrical resistance measurements show this indeed to be so. For blastfurnace cement mortar there was found to be hardly any difference between the polarization curves for the mortar electrodes with 0, 1, 2 and 4% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ which, after 24 hours' hydration, were allowed to harden in air for 28 days. The pitting potential nowhere dropped below +600 mV (passivation); with 4% CaCl_2 added to the mortar this potential even rose to above +600 mV.

The electrical resistance (Fig. C7), which at first rose both with increasing age and with increasing chloride content, reached a maximum at a point of time depending on the chloride percentage.

Early drying therefore does not adversely affect the passivation of steel in blast-furnace cement mortar – not even if 4% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ has been added. For portland cement mortar, however, the opposite is true (Fig. C8).

From these measurements it is clearly apparent that the pitting potential goes down

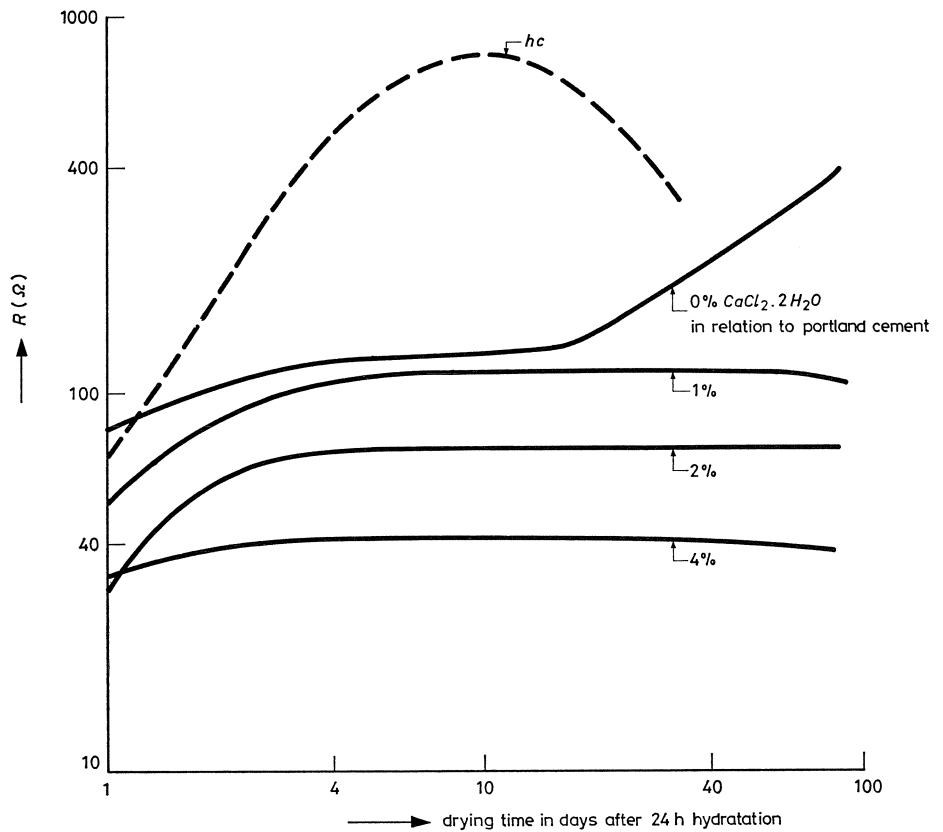


Fig. C7. Resistance of mortar electrodes as a function of drying time for blast furnace cement and portland cement mortar.

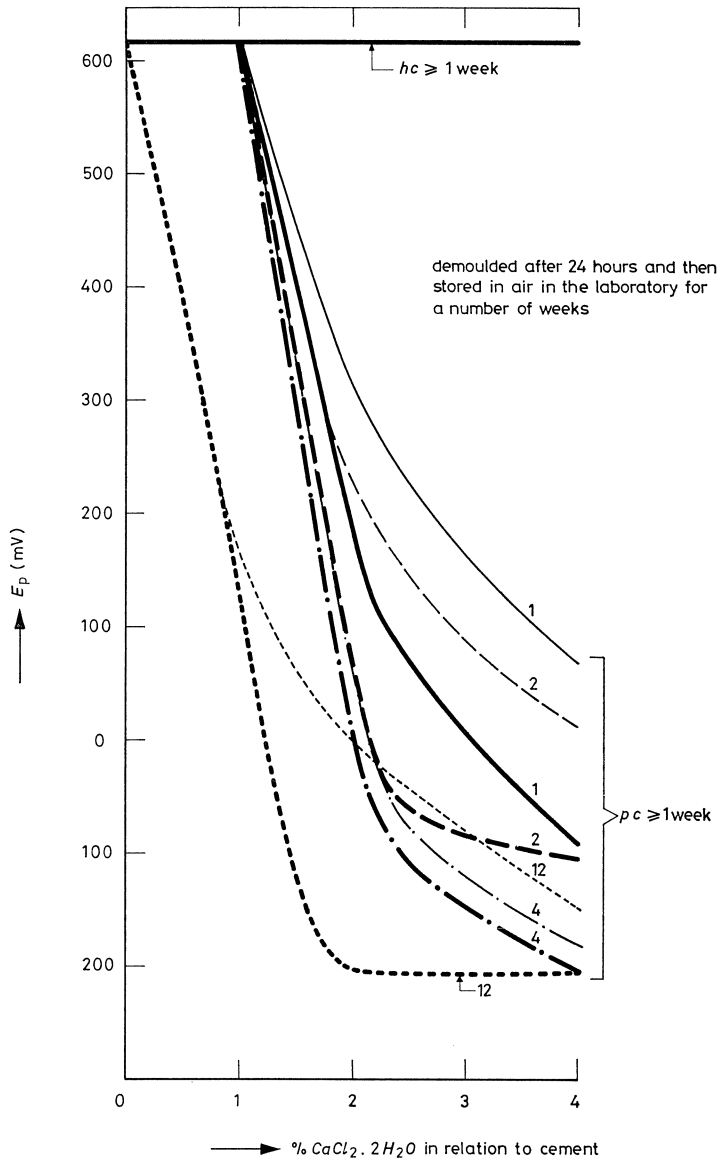


Fig. C8. Pitting potential E_p as a function of drying time for blast furnace cement and portland cement mortar.

with the increase in drying, so that in this case even with a 1% addition of CaCl_2 there is no passivation, although the mortar around the steel is alkaline. Whereas with wet hardening the borderline between “active” and “passive” was approximately at 2% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, after 1–2 weeks’ drying this borderline lay between 1 and 2% and after 1–3 months’ drying it lay between 0 and 1% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Hence non-

active chloride becomes active again when the mortar dries, this being true even of the 1% addition of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

It is apparent from Fig. C7 and Fig. C3 that the electrical resistances for specimens which are allowed to dry are distinctly lower than the resistances attained when hydration occurs under moist conditions – a clear indication of increased current intensity.

3.4 Carbonation

The effect of carbonation was then investigated for portland cement mortar, both for normal exposure to air and for hardening of the specimens in a CO_2 atmosphere. Theoretically the chemical combination between cement and chloride can be dissociated into CaCO_3 and CaCl_2 as a result of carbonation.

The fundamental changes in the polarization curves are shown in Fig. C9. With carbonation, both with and without the addition of chloride, distinctly different polarization curves are obtained, without a vertical portion with $I_a = 0$. The equilibrium potential E_o goes down to -700 mV. Instead of pitting, there is now more general and uniform rusting. The anodic curves may rise steeply and are similar to

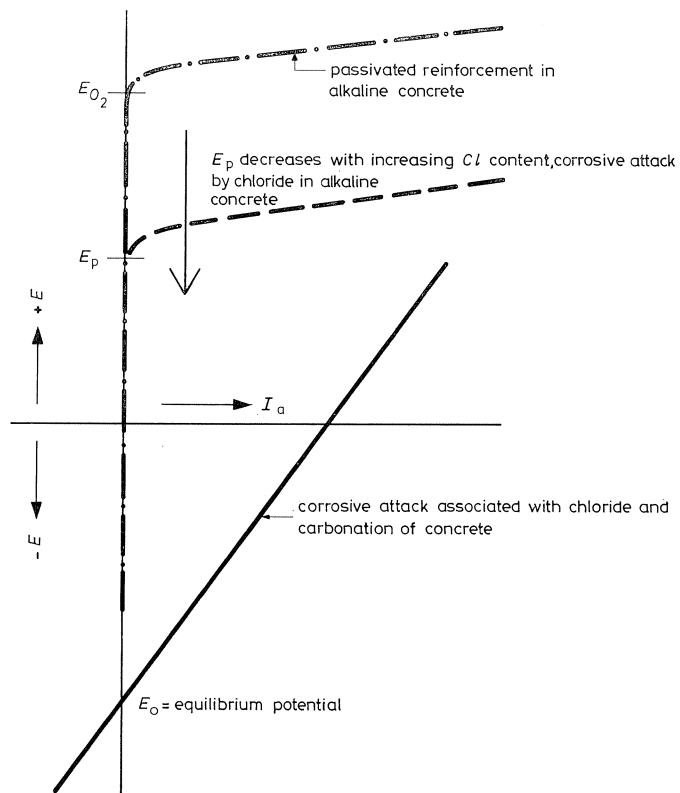


Fig. C9. Change in polarisation curves due to chloride and due to carbonation.

those found in electrolyte solutions (NaCl, H₂SO₄) in earlier research [1]. Later measurements showed that chloride, initially present in combined form, was reactivated by the action of CO₂.

The most favourable conditions with regard to chloride are therefore provided by permanently moist environment, while the content of chloride is limited to a certain permitted amount (see 3.1). A drying environment was found to have an unfavourable effect in circumstances where air (and therefore also CO₂) was able to penetrate into the young mortar and reactivate the chloride.

The most unfavourable conditions exist when reinforcement is situated in the carbonated zone of mortar or concrete containing chloride. Surface corrosion occurs as a result of lowering of the pH and the effect of chloride, while the liberated chloride moreover ensures good conduction of current. In the case of carbonation in the absence of chloride, complete carbonation of the concrete cover to the steel will not necessarily result in heavy corrosion – at any rate, not if the mortar or concrete is of high density. In that case a skin or coating of carbonate is formed which seals off the steel and prevents corrosion. If this skin is ruptured, however (in consequence of mechanical or thermal influences), corrosion will occur.

3.5 *Effect of elevated temperature*

Concrete structures are often exposed to thermal radiation (sun), so that the surface temperature of the concrete may rise to something like 50°C. Polarization curves were therefore measured for mortar electrodes (of standard mortar as used for cement testing) with 0, 1, 2 and 4% CaCl₂·2H₂O added, which were demoulded after 24 hours and were then either dried at 50° for 24 hours and measured or were first allowed to harden in air in the laboratory for 6 days and then dried at 50°C for 7 days before being measured. In relation to the measurements performed at 20°C (see 3.3 and 3.1) the temperature was found to be of minor influence in comparison with the effect of moisture.

4 **Penetration of chloride into concrete**

The mechanism of chloride penetration may vary. If the surface of the concrete is dry at the time of coming into contact with a chloride solution, there first occurs capillary absorption of liquid, attended by expulsion of air. In that case the rate of chloride penetration is determined by *capillary movement of liquid* in the concrete and by the concentration of chloride in the solution.

When the concrete has become saturated, further penetration of chloride occurs by diffusion in the aqueous phase in concrete under the influence of the concentration gradient. Transfer of chloride by *diffusion* also takes place if the concrete was already wet at the time of coming into contact with chloride. Diffusion of chloride into moist concrete is not “pure” diffusion conforming to Fick’s law; it is influenced by the following factors:

1. the pore structure of the cement gel;
2. the combining of chloride by hydrated cement products.

and it will accordingly be a longer time before practically significant quantities of chloride penetrate further by diffusion.

In blastfurnace cement mortar (Cemij class A) the depth of chloride penetration was, under comparable conditions, found to be always less, by a factor ranging from 2 to 5, than in portland cement mortar. Fig. C11 shows the difference between the two kinds of mortar for specimens exactly 1 day old which had been immersed in a 2% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ for varying lengths of time.

In the case of concrete made with blastfurnace cement the resistance to chloride penetration is relatively more sharply lowered when proper curing of the concrete is omitted than in the case of portland cement concrete. This is probably due to a more rapid enlargement of the specific surface area, a denser structure (greater wall effect) and a higher maximum capacity combining with chloride in blastfurnace cement mortar as compared with portland cement mortar.

In actual practice the effects of deficient curing will primarily involve the outer layer of concrete, i.e., that part where early drying occurs. The concrete in the core will remain moist for a longer time and will meanwhile have acquired a denser structure by the time the chloride has access to the concrete. In view of this it is therefore important to have a substantial depth of concrete cover to the steel.

5 The binding of chloride

The rate of chloride penetration and the corrosiveness with regard to reinforcement are affected by the combining of chloride with cement. Calcium aluminate hydrate can combine chemically with chloride to form the compound called Friedel's salt, which is comparable to the monosulphate (in which sulphate has been replaced by chloride). Portland cement contains calcium aluminate as a constituent which is present from the outset. In blastfurnace cement, where aluminium is present in the form of aluminosilicates, calcium aluminate hydrate is formed only during the hydration process. Here the chloride competes with sulphate to enter into a compound with the aluminate. In Enci portland cement there is not enough aluminate to combine both with sulphate and with chloride: it is just sufficient to combine with all the sulphate as monosulphate.

In addition to being held in chemical combination as Friedel's salt, chloride is probably also bound mainly by adsorptive action, i.e., incorporated into the electric double layer which has been formed on the surface of the cement. Thus, if ground and 100% hydrated cement is brought into contact with a calcium chloride solution, the chloride is absorbed by the cement gel within ten minutes, a *distribution equilibrium* being established between the amount of chloride that combines with the cement and the free chloride concentration in the solution.

If fresh cement is kept in continuous suspension (water/cement ratio 2) in a calcium chloride solution, the cement will take up chloride from the solution during hydration and will do so until equilibrium is reached after a time. This occurs both with Enci portland cement and with Cemij blastfurnace cement.

With portland cement it takes longer for the state of equilibrium to be reached (5 weeks in a case where the amount of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ is 2% of the amount of cement) than with blastfurnace cement (within 1 week).

The equilibrium can be expressed by the following equation:

$$\log G = -0.40 + 0.79 \log N_e$$

where:

G = the quantity of combined chloride, expressed in gram ions per 100 grams of cement

N_e = the number of gram ions of free Cl' per litre of solution after equilibrium has been established.

This equation corresponds to the adsorption isotherm according to Freundlich. Besides, the measured points correspond to the adsorption isotherm according to Langmuir, from which the *saturation limit* can also be calculated. For Cemij blastfurnace cement the chloride saturation limit was found to be about 5 times higher than for Enci portland cement (proportion of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in relation to cement: 9.2% for blastfurnace as against nearly 2% for portland cement).

In the suspensions the chemical binding of chloride as Friedel's salt is practically negligible in comparison with the amount of chloride that is bound by adsorptive action. There is no fixed relation between chemical and adsorptive binding: it depends on the overall content of chloride and on the water/cement ratio. The chemical effect is relatively most pronounced at low values of the chloride content.

It is presumed that in concrete, too, chloride is bound by adsorptive action besides entering into chemical combination.

6 Conclusions

– Corrosive attack of reinforcement in concrete by chloride occurs only if a certain free Cl' concentration is locally present which exceeds 0.038 gram ion per litre (0.2% CaCl_2 by weight). In that case the passive layer which protects the steel from corrosion is ruptured and corrosion or possibly stress corrosion is then liable to occur. In the laboratory the potential difference between a chloride electrode (in the concrete) and a reference electrode can be measured, and the free Cl concentration can be calculated from these measurements with the aid of calibration curves. A proportion of the total chloride is present as combined chloride. How large this proportion is will depend on the conditions of the concrete (curing) and be subject always to the existence of an equilibrium between the free and the combined chloride quantities. This binding of chloride may be chemical (formation of a compound called Friedel's salt) or adsorptive; there is no definitely fixed relation between the two: it depends on the overall chloride content and on the water/cement ratio. Chemical binding is relatively most pronounced at low values of the chloride content. Depending on circumstances, the chloride may then pass from the combined to the free state, and vice versa.

- With good curing (moist conditions), chloride combines more rapidly and in greater quantity with Cemij blastfurnace cement than with Enci portland cement. Under these circumstances the specific resistance of blastfurnace cement mortar is, for a given potential difference, about 10 times as high as that of portland cement mortar (i.e., the current intensity is correspondingly lower in the former), while in blastfurnace cement mortar an increase in the chloride content causes this specific resistance to increase further, whereas in portland cement mortar the opposite happens, i.e., there is a lowering of resistance in consequence of pore width distribution.
- If no curing is applied, this has practically no adverse effect on Cemij blastfurnace cement mortar, but it does adversely affect portland cement mortar. Non-active (combined) chloride is reactivated in the latter type of mortar, even with relatively small amounts of chloride (1% CaCl_2).
- The most unfavourable conditions exist when reinforcement is in a carbonated zone of concrete containing chloride. General rusting occurs in consequence of a lowering of the pH and the effect of chloride, while the released chloride moreover promotes the conduction of electric current.
- Concrete coming into contact with an environment containing Cl will absorb chloride by means of two mechanisms: if the surface of the concrete is dry, capillary absorption of the liquid containing the chloride will take place; after saturation, further penetration of chloride into the concrete will occur by diffusion in the aqueous phase of the concrete. Transfer of chloride by diffusion also occurs if the concrete was already wet at the time of coming into contact with it. During this diffusion the chloride is bound by the cement (chemically and by adsorption), depending on the degree of hydration of the cement. The rate of chloride penetration is highest in young mortar; with increasing hydration the diffusion of chloride diminishes until an equilibrium between combined and free chloride is attained. Under comparable conditions the penetration depth of chloride into blastfurnace cement mortar was always found to be smaller, by a factor ranging from 2 to 5, than into portland cement mortar.
- The overall conclusion therefore is that Cemij blastfurnace cement behaves, for practical purposes, considerably more favourably than portland cement in so far as contact with chlorides is concerned – both in the case where chloride is present from the beginning and where chloride-free concrete subsequently comes into contact with a liquid containing chloride. There is no known method for the direct determination of how much chloride is present as combined chloride. This can, however, be determined indirectly as the difference between the total quantity present and the quantity of free chloride. For the purpose of thus estimating the combined chloride it is also possible to make use of the adsorptive equilibrium existing between free and combined chloride, a relationship which is now tentatively known.