



# Effect of CaCl<sub>2</sub> and NaCl additions on concrete corrosivity

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## Abstract

In addition to breaking down the passive film on embedded steel, the level of chloride content in concrete also influences the electrical resistivity of the concrete and, hence, the kinetics of the reinforcement corrosion, as long as the corrosion process is under resistance control. While there is general agreement in the literature that the binding of chlorides in concrete is higher when CaCl<sub>2</sub> is added to the fresh concrete, in comparison with NaCl, the effect of different chloride sources on the concrete resistivity is not so well known.

To quantify the effect of different types of chloride source on the concrete corrosivity, different mortars with OPC and 0.50 w/c were prepared, and various amounts of CaCl<sub>2</sub>, NaCl and NaOH were added to the fresh mixtures. The corrosivity was primarily tested by measurements of electrical resistivity and acid capacity.

The paper summarizes the results of the study regarding the effect of both the type and amount of chloride source on concrete corrosivity. © 2004 Elsevier Ltd. All rights reserved.

*Keywords:* Admixtures; Chlorides; Corrosion; Electrical resistivity; Acid capacity

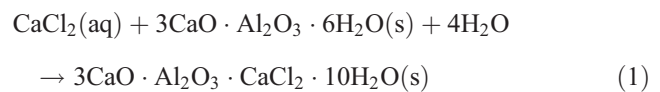
## 1. Introduction

Portland cement concrete normally provides both a very good chemical and physical protection to all embedded steel. The chemical protection is primarily provided by the high-alkaline nature of the pore water (pH 13.0–13.5), where the steel becomes electrochemically passivated. In addition, a physical protection is provided by the concrete, either by retarding or preventing the penetration of aggressive species like chlorides or carbon dioxide to the steel/concrete interface.

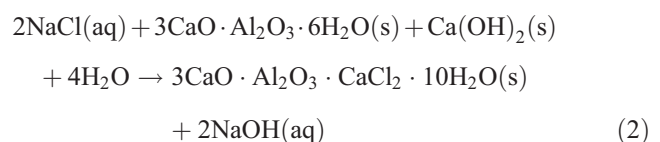
When chlorides penetrate concrete, some of it is bound either in the form of Friedel's salt (3CaO · Al<sub>2</sub>O<sub>3</sub> · CaCl<sub>2</sub> · 10H<sub>2</sub>O) or physically adsorbed to the amorphous calcium silicate hydrates (CSH). Thus, it is only the remaining free chlorides that represent a risk for depassivation and corrosion of the steel. This risk is best expressed in terms of the chloride to hydroxyl ion concentration [Cl<sup>-</sup>]/[OH<sup>-</sup>] in the pore solution [1].

For accelerated-corrosion testing on embedded steel in concrete, chlorides are often added to the fresh concrete mixture. For this purpose, sodium chloride is mostly used as

a chloride source, although calcium chloride is also being applied. When chlorides are added to the fresh concrete mixture, however, the cement paste system may be affected, and this may also affect the testing conditions for the accelerated testing. While there is general agreement in the literature that the binding of chlorides in concrete is higher when CaCl<sub>2</sub> is added to the fresh concrete in comparison with NaCl [2–6], the effect of different chloride sources on the concrete resistivity is not so well known. The presence of additional ions, such as Na<sup>+</sup> or Ca<sup>2+</sup>, may also influence the chloride binding [7]. Friedel's salt is formed from calcium aluminate hydrate and a soluble chloride source after:



or



From the above equations, it can be seen that the addition of sodium chloride to the fresh concrete will increase the pH,

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and this effect is well documented in the literature [8]. It is also well documented that an increased alkalinity will activate the cement hydration and will give a more dense paste structure with smaller pores compared with that of nonactivated cements [9]. As part of a more comprehensive research program [10], it was of interest to study the influence of  $\text{CaCl}_2$  and  $\text{NaCl}$  additions on concrete corrosivity for embedded steel. This was primarily carried out to quantify the effect of increased alkalinity in the pore solution on chloride binding.

## 2. Experimental

While McCarter et al. [11] monitored the development of electrical properties (conductance, capacitance, etc.) to study the early hydration of cement paste systems, Reddy et al. [12] applied acid neutralization capacity measurements to quantify the inhibitive properties of concrete and to determine the pH-dependent solubility of chlorides in concrete. Both of these techniques were used in the present experiments. Electrical resistance measurements were used to follow the hydration process, while acid capacity titration, in combination with chloride measurements using a  $\text{Cl}^-$ -sensitive electrode, was used to determine the acid capacity and amount of bound chlorides as a function of ambient pH level.

Mortar specimens were produced by mixing one part of OPC with three parts of sand, using a water-to-cement ratio (w/c) of 0.50. The mortar was mixed for 3 min in a Hobart mixer and then poured into polyethylene (PE) moulds, where four equidistant pins of stainless steel, for resistance measurements, were also installed. Finally, the moulds were sealed with a PE cover (Fig. 1). In addition to  $\text{CaCl}_2$  and  $\text{NaCl}$ ,  $\text{NaOH}$  was also added to the fresh mortar for comparison, all of which were added in two levels of concentration (Table 1).

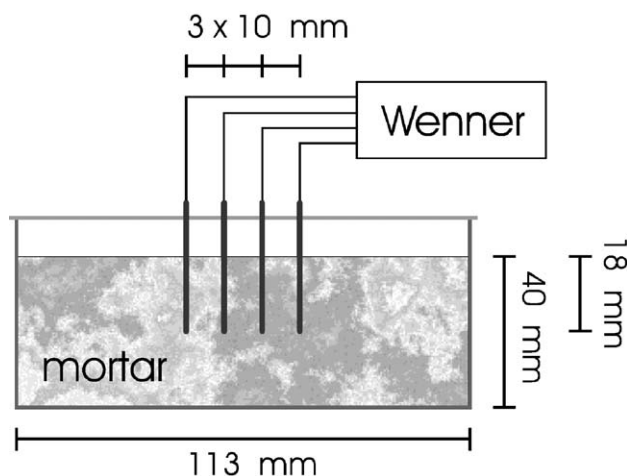


Fig. 1. Experimental set-up for monitoring of electrical resistance during hydration.

Table 1

Admixtures added to the fresh mortar

Number of specimens	$\text{CaCl}_2$ [mol/kg cement]	$\text{NaCl}$ [mol/kg cement]	$\text{NaOH}$ [mol/kg cement]
3	0	0	0
3	0.25	0.5	0.5
3	0.75	1.5	1.5

The electrical resistance, which was measured by connecting a Wenner device to the four pins, was monitored over a period of approximately 60 days. The Wenner method involves passing an alternating current between the outer pair of the four pins and measuring the voltage drop between the inner pins. The resistivity obtained from the Wenner device is given by:

$$R = 2\pi a \frac{U}{I}$$

$U/I$  is the measured resistance and  $a$  denotes the pin spacing. After 60 days, the samples of crushed and pulverized mortar were prepared, and a series of suspensions was produced by initially adding 50 ml deionised water to 10 g of pulverized sample. Every 5th minute, 1.5 molar nitric acid was then added, in steps of 0.5 ml. The mixture was stirred permanently using a magnetic stirrer. The chloride concentration of the solution was determined by an  $\text{Ag}/\text{AgCl}$  electrode, which had been calibrated for solutions in the pH range of 7 to 13. At the end of the 5-min stirring periods, both pH level and the chloride concentration were determined.

## 3. Results and discussion

### 3.1. Electrical resistivity

As shown in Figs. 2 and 3, the electrical resistivity typically decreased during the first few hours until a minimum was reached; it then rapidly increased as the cement setting started. The initial decrease in resistivity can be related to the early period of cement hydration, during which, both calcium and hydroxyl ions are steadily being dissolved [13]. This increased amount of dissolved ions is obviously causing a decrease in resistivity. When a critical amount of calcium and hydroxyl ions is formed, however, a rapid crystallisation of CH and CSH takes place and, as a result, a rapid increase of resistivity also does take place. After a few weeks of further hydration, the resistivity is only slowly increasing. Mainly, two characteristic times,  $t_1$  and  $t_2$ , in the hydration process can be observed in the log–log presentation, representing the change of curvature of the S-shaped curve. For the OPC-mortar without any admixture,  $t_1=6.5$  h and  $t_2=9.5$  days were observed (Fig. 2A).

As discussed by McCarter et al. [11] the change of conductance is associated with increased rigidity and den-

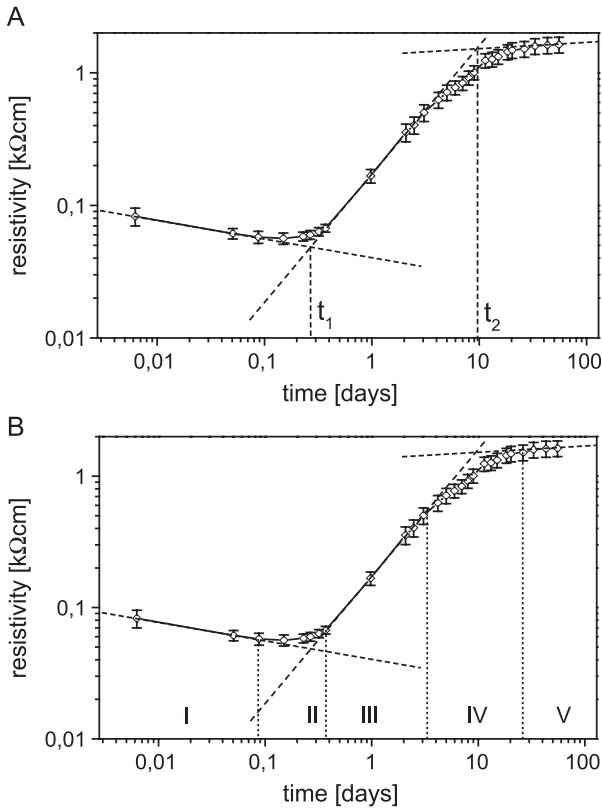


Fig. 2. (A) Relationship between resistivity and hydration time in mortar without any admixture. (B) Characteristic regions in the relationship between resistivity and hydration time.

sity of the mixture. From the shape of the conductance time curve, five distinct regions were introduced in analogy with isothermal conduction calorimetry studies: preinduction period (I), dormant period (II), acceleratory period (III), acceleration period (IV) and a diffusion-controlled period (V). A similar presentation is shown in Fig. 2B, from where it can be seen that in Period I:  $\log \rho$  decreases linearly with  $\log t$  from 0 to 2 h; Period II:  $\log \rho$  changes from linearly decreasing to linearly increasing with  $\log t$  from 2 to 9h; Period III:  $\log \rho$  is increasing linearly with  $\log t$  from 9 to 80 h; Period IV:  $\log \rho$  levels out with  $\log t$  from 80 h to 26 days; and Period V: almost no change of  $\log \rho$  takes place after a period of 26 days.

For the specimens with mineral admixtures, it can be seen from Fig. 3A–C that the shape of the  $\log \rho \log t$  curves changes significantly.

These results clearly demonstrate that the early development of electrical resistivity in the fresh mortar (preacceleration period) is a clear function of the concentration of admixture in the mixing water. Since the total charge density in the mixing water is the same both for  $\text{CaCl}_2$ ,  $\text{NaCl}$  and  $\text{NaOH}$ , the resistivity should be similar for the three types of admixtures. From Fig. 4, which shows the resistivity values 1 h after casting for different  $\text{Cl}^-$  and  $\text{OH}^-$  concentrations, the observed resistivities are, in fact, of similar values.

Since the time of setting depends on the amount and type of dissolved ions, different durations of the preaccelerating phase are expected for the different samples.  $\text{CaCl}_2$  is known to be a set accelerator [14] and, hence, an increased amount of calcium chloride should give a shorter preaccel-

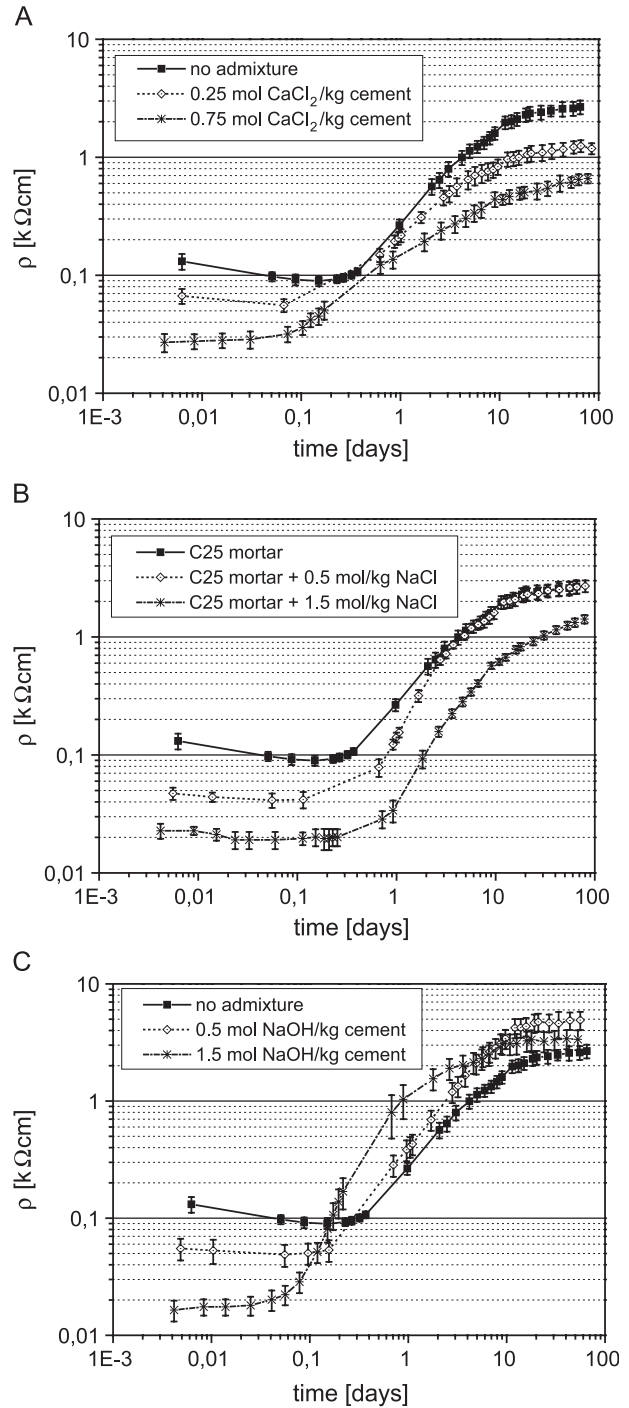


Fig. 3. (A) Development of resistivity for samples containing various amounts of  $\text{CaCl}_2$ . (B) Development of resistivity for samples containing various amounts of  $\text{NaCl}$ . (C) Development of resistivity for samples containing various amounts of  $\text{NaOH}$ .

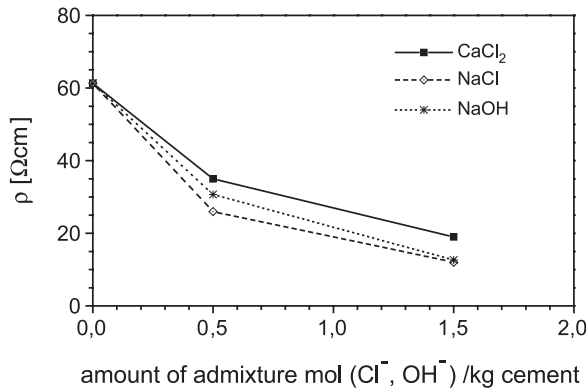


Fig. 4. Resistivity values as a function of admixture concentration observed 1 h after casting.

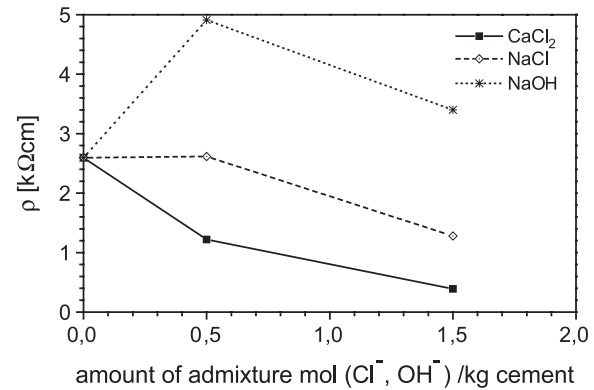


Fig. 6. Resistivity after 56 days of hydration as a function of admixture concentration.

erating period. Sodium hydroxide is known to be an activator [15,16] and, hence, a shorter preacceleration period should also be expected.

From Fig. 5, it can be seen that additions of CaCl<sub>2</sub> and NaOH give a similar decrease of the dormant period for equinormal concentrations, while the addition of NaCl gives a retardation of the cement hydration. Thus, it appears that only calcium and hydroxyl ions have an accelerating property, while the chloride ions do not have this ability. It appears that the mechanism of OH<sup>-</sup> dissolution after Eq. 2 is too slow for decreasing the dormant period.

The compressive strength of concrete also increases with increased concentration of sodium hydroxide [6]. Since the addition of NaOH gives a finer pore network, both an increased compressive strength and electrical resistivity can be expected.

The final concrete resistivities observed after a period of 56 days are shown in Fig. 6, from which it can be seen that the samples with NaOH gave the highest electrical resistivity. Thus, at an amount of 0.5 and 1.5 mol/kg, the resistivity was approximately 100% and 30%, compared with that of the reference sample, respectively. For the CaCl<sub>2</sub>, however, the resistivity decreased by approximately

50% and 85% for additions of 0.5 and 1.5 mol/kg (as Cl<sup>-</sup>), respectively.

The difference in resistivity for mortar with NaCl compared with that of CaCl<sub>2</sub> may be explained by the formation of NaOH, according to the reaction in Eq. 2. The increased alkalinity is responsible for a denser pore structure, which apparently is overweighing the increased ionic concentration of the pore water. While an addition of 0.5 mol/kg Cl<sup>-</sup>, in the form of CaCl<sub>2</sub>, reduced the resistivity by 50%, no change for an addition of 0.5 mol/kg NaCl was observed. In addition, for an addition of 1.5 mol/kg, the resistivity for NaCl remained much higher than for the equinormal addition of CaCl<sub>2</sub>. According Ref. [8], the OH<sup>-</sup> concentration in the pore water reaches a maximum for Cl<sup>-</sup> addition, as NaCl, of approximately 1.25% by weight of cement, which corresponds to approximately 0.35 mol NaCl/kg cement.

### 3.2. Acid neutralization capacity

To provide a basis for further discussion of Eq. 2, the alkalinity of the mortar samples was determined by measuring the acid neutralization capacity. The initial pH of the

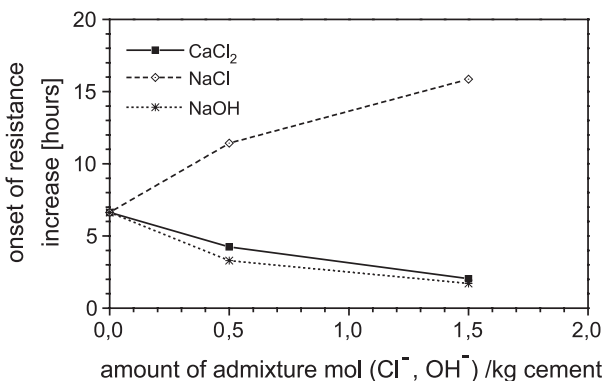


Fig. 5. Onset time ( $t_1$ ) for the increase of resistance as a function of admixture concentration.

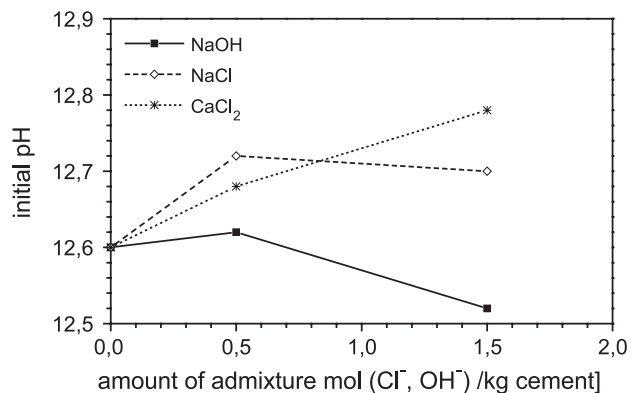


Fig. 7. Initial pH as a function of admixture.

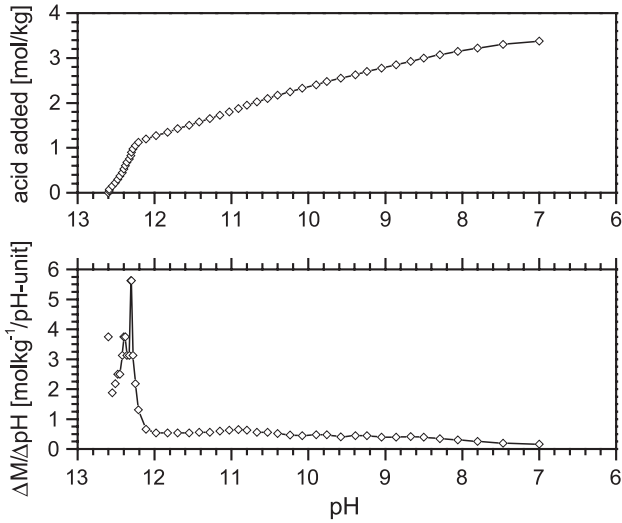


Fig. 8. Titration curve for a mortar sample without any admixture and the first derivative of the same.

suspensions of the pulverized samples, which was supposed to be equal to the pH of the pore water, clearly depended on the type of admixture. Both NaOH and NaCl increased the pH, in agreement with the reaction in Eq. 2, while CaCl<sub>2</sub> appeared to decrease the pH (Fig. 7).

Fig. 8. shows the acid neutralization titration curve for a mortar sample without any admixture and the first derivative of the same. Since the solid solution equilibrium of Ca(OH)<sub>2</sub> has a pH of approximately 12.5, it is assumed that the acid used to reduce the pH from its initial value to a value of 12.5 was consumed by the soluble hydroxides NaOH and KOH in the pore water. According to Glass et al. [17], the range of 12.5–12.0 can be attributed to the neutralization capacity of Ca(OH)<sub>2</sub>. In addition, according to the literature, the equilibrium pH of the solid-solution equilibrium for CSH may vary between 12.3 and 9.2 [18], while for the Friedel’s Salt, it is approximately 12.0 [19]. Since the conditions of the titrations performed in the present work were not steady state, the range of the acid neutralization capacity of both

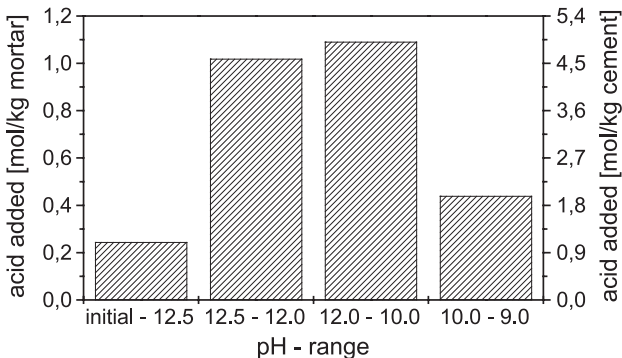
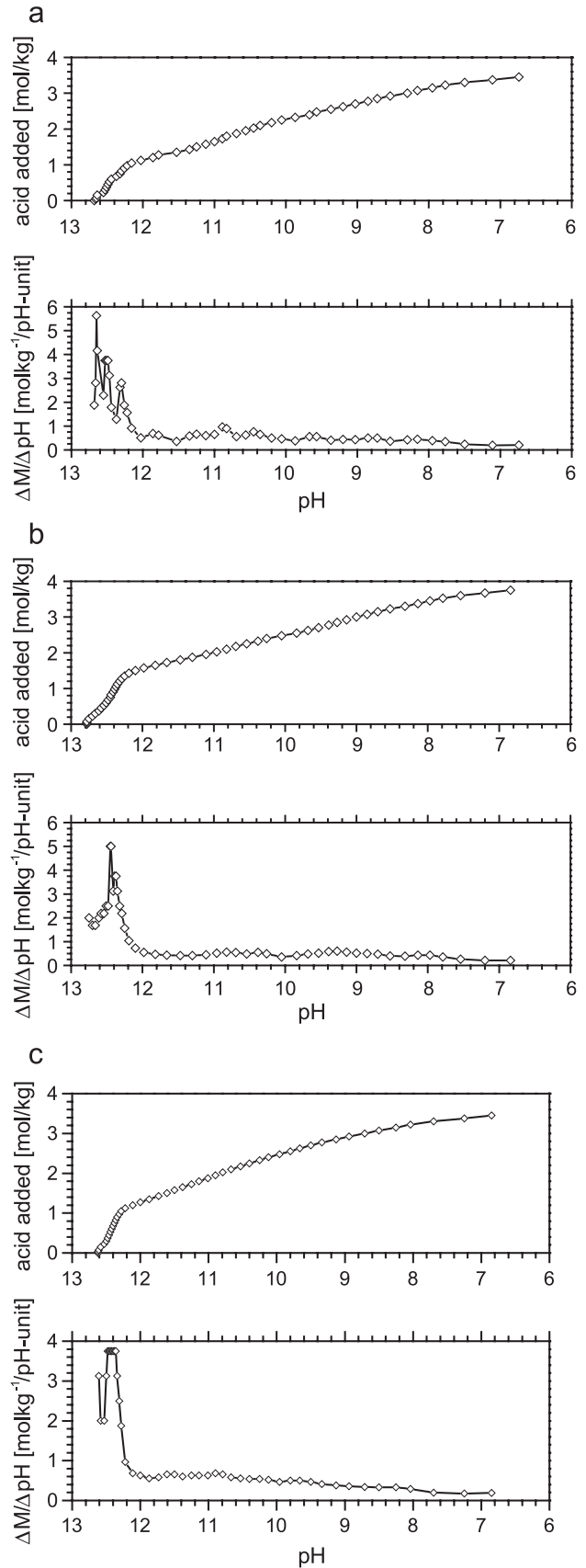


Fig. 9. Distribution of acid added to the four pH ranges for mortar without any admixture.



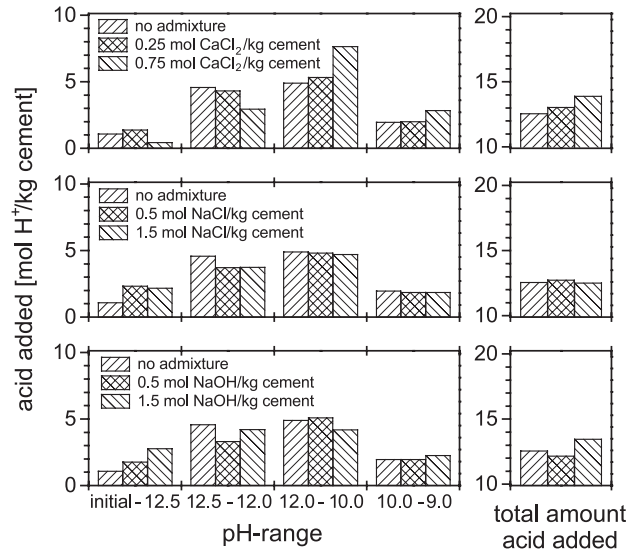
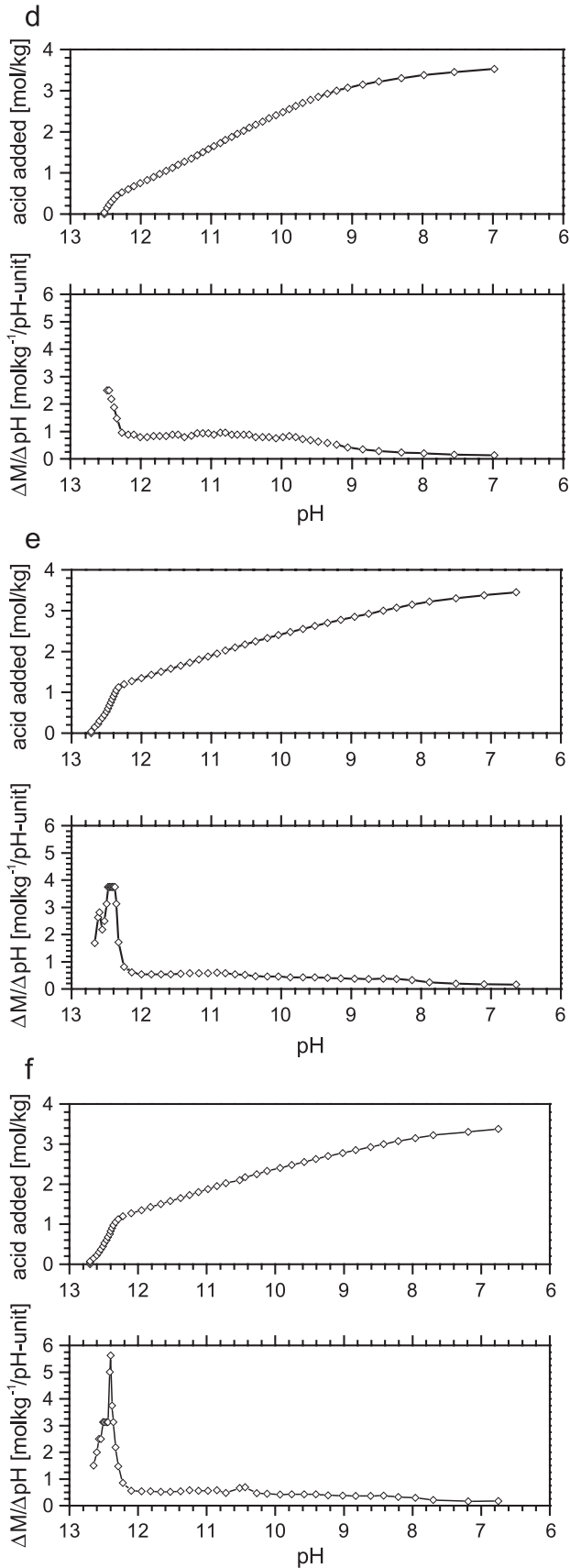


Fig. 11. Acid capacity for the various pH ranges of samples containing different amounts and types of admixtures.

the CSH and the Friedel’s Salt may represent a pH range of 12–10, while the pH range 10–9 may represent a “rest-capacity” of the system.

Fig. 9 shows the distribution of the acid added to the four pH ranges for the mortar without any admixtures. The acid added to reduce the pH from 12.5 to 12.0 means that approximately 2.3 mol or 170 g Ca(OH)<sub>2</sub> were formed per kg cement, which accounts for the strongest resistance of the mortar against acidification. Since a cement paste based on OPC, and cured for a period of 3 to 12 months, forms a calcium hydroxide content of typically 15–25% [20], this explains the high ability of an OPC to protect embedded steel against corrosion. For the CSH, approximately 4.9 mol acid (H<sup>+</sup>) per kg cement were needed to reduce the pH from 12 to 10, which also represents a strong resistance against acidification.

Fig. 10 shows the acid neutralization titration curves for the mortar with NaOH, CaCl<sub>2</sub> and NaCl, where the shapes of the curves are relatively similar with that of the mortar without any admixture. Only for the mortar with 1.5 mol CaCl<sub>2</sub>, the slope is somewhat reduced at higher pH levels.

Fig. 10. (a) Titration curve for mortar with 0.5 mol NaOH per kg cement and first derivation of the same (values in mol/kg mortar). (b) Titration curve for mortar with 1.5 mol NaOH per kg cement and first derivation of the same (values in mol/kg mortar). (c) Titration curve for mortar with 0.25 mol CaCl<sub>2</sub> per kg cement and first derivation of the same (values in mol/kg mortar). (d) Titration curve for mortar with 0.75 mol CaCl<sub>2</sub> per kg cement and first derivation of the same (values in mol/kg mortar). (e) Titration curve for mortar with 0.5 mol NaCl per kg cement and first derivation of the same (values in mol/kg mortar). (f) Titration curve for mortar with 1.5 mol NaCl per kg cement and first derivation of the same (values in mol/kg mortar).

In Fig. 11, the total picture is given of the amount of acid required to reduce the pH from the initial to 12.5, from 12.5 to 10.0 and from 10.0 to 9.0 for all types of admixtures investigated.

3.3. Comparison of CaCl<sub>2</sub> and NaCl

From the above results, it can be seen that additions of both CaCl<sub>2</sub> and NaCl released chlorides into the solution as the pH was successively reduced. For both types of admixture, most of the chlorides were released already when the pulverized mortar samples were mixed with pure water. For the sample with CaCl<sub>2</sub>, the chloride release was proportional to the pH reduction in the range from pH 12.5 to 11.0. At pH 11, no further chlorides were released, as the pH was lowered. This

was a stage where the theoretical chloride content was approximately 0.33 mol/kg mortar, calculated from the amount of chlorides added (Fig. 12a). For the sample with NaCl, the chloride release stopped at pH 12.55, and it appeared that the chlorides were increasingly rebound until a pH of 12.3 was reached. At this point, the chlorides were continuously released until a pH of 11.5, where no significant amount of chlorides was further dissolved (Fig. 12b).

The binding of chlorides appeared to be of a different quality for CaCl<sub>2</sub> and NaCl. In the case of CaCl<sub>2</sub>, a pH reduction to approximately 11 was needed to release all the bound chlorides, while in the case of NaCl, all the chlorides were released at higher pH values (above 11.5). It appeared that the CaCl<sub>2</sub> containing mortar was less prone to release the chlorides due to carbonation than the

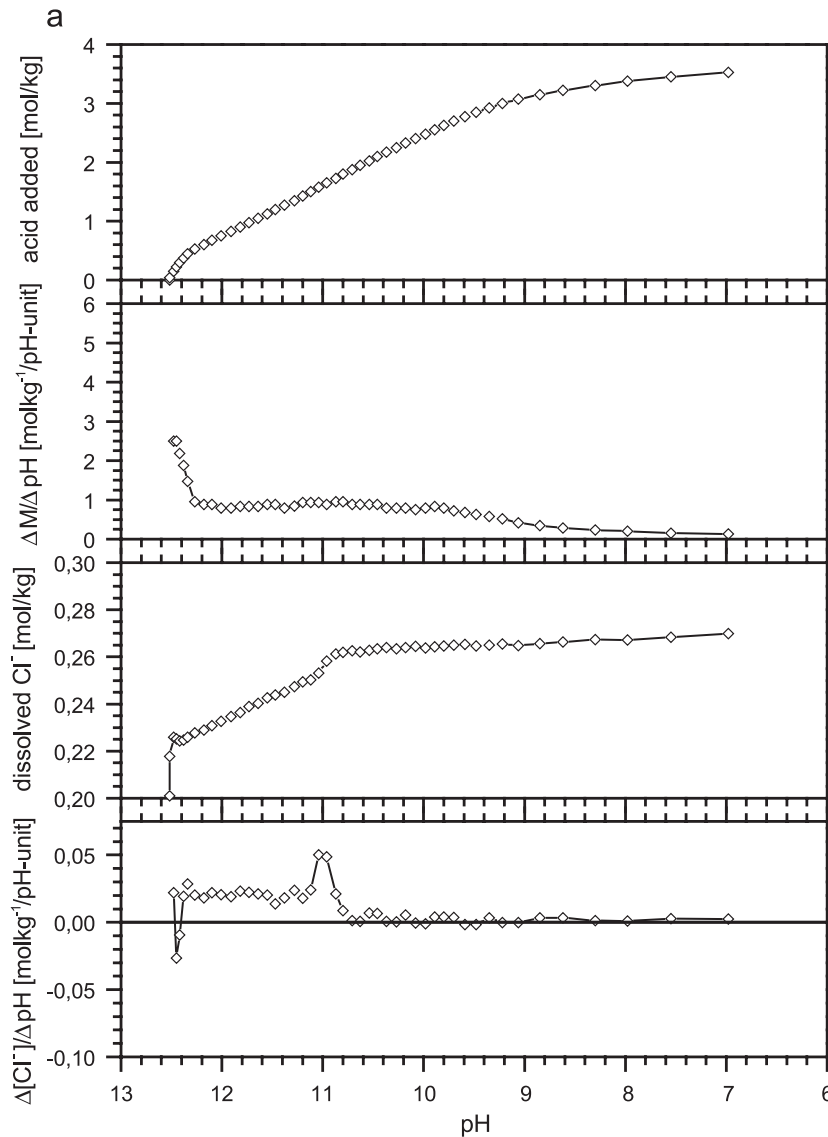


Fig. 12. (a) Acid capacity titration combined with potentiometric chloride measurement for a mortar sample containing 0.75 mol CaCl<sub>2</sub> per kg cement (0.33 mol Cl<sup>-</sup>/kg mortar). (b) Acid capacity titration combined with potentiometric chloride measurement for a mortar sample containing 1.5 mol NaCl per kg cement (0.33 mol Cl<sup>-</sup>/kg mortar).

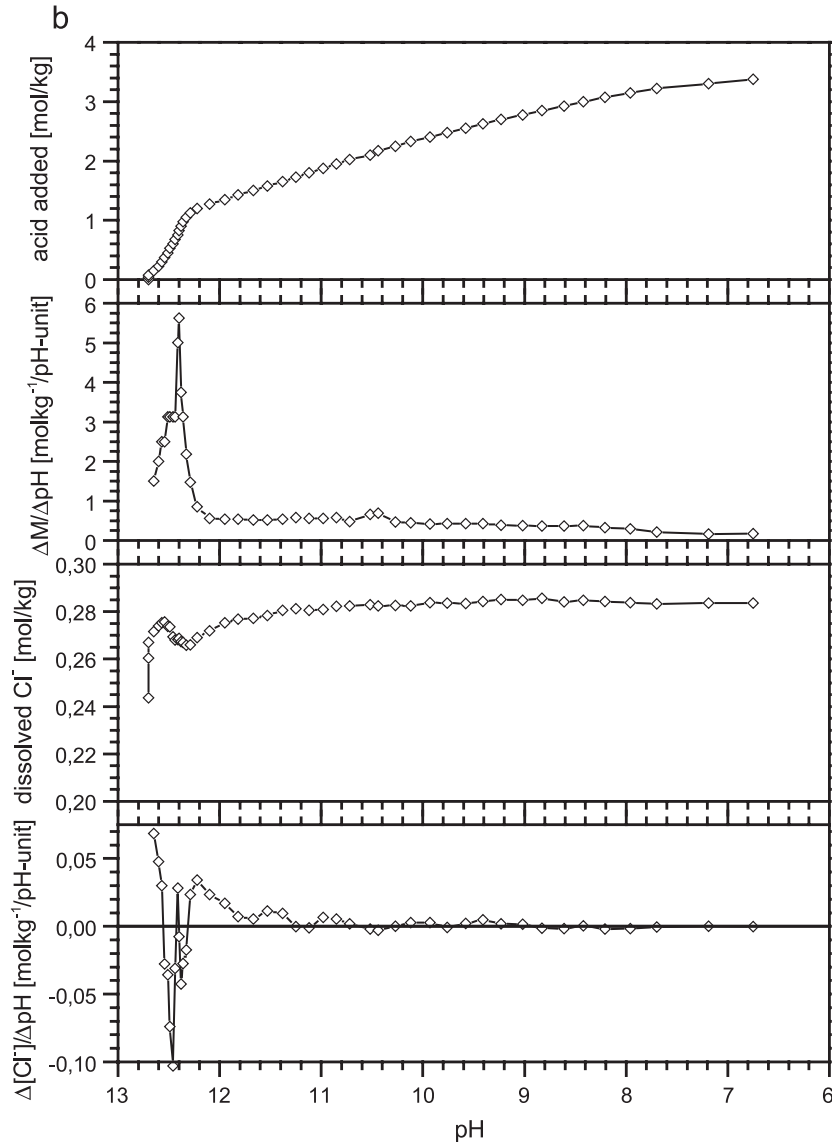


Fig. 12 (continued).

NaCl containing mortar. Both for NaCl and CaCl<sub>2</sub>, however, the amount of acid to reduce the pH to 11.5 was approximately the same, with 7.1 and 7.2 mol H<sup>+</sup>/kg cement, respectively. In both cases, this is assumed to be due to carbonation.

#### 4. Conclusions

By adding various amounts of chlorides to fresh mortar prepared with OPC and 0.50 w/c, it was observed that NaCl as chloride source gave a higher pH and, hence, a less corrosive [Cl<sup>-</sup>]/[OH<sup>-</sup>] ratio in the pore water compared with CaCl<sub>2</sub> as chloride source. The addition of NaCl also did give a higher electrolytic resistivity of the mortar by a factor of 2 to 2.5 compared with that of CaCl<sub>2</sub>. As a result, the effect of NaCl added to fresh cement mortar appears to

give much less corrosive conditions than that of CaCl<sub>2</sub>. It was further observed that:

1. When CaCl<sub>2</sub> was added to the fresh mortar:
  - The amount of dissolved hydroxyl ions or pH level was reduced.
  - The acid capacity for Ca(OH)<sub>2</sub> or amount of Ca(OH)<sub>2</sub> was decreased.
  - The acid capacity for CSH and/or Friedel's Salt was increased.
2. When NaCl was added to the fresh mortar:
  - The amount of dissolved hydroxyl ions or pH level was increased.
  - The acid capacity for Ca(OH)<sub>2</sub> or amount of Ca(OH)<sub>2</sub> was decreased.
  - No change in acid capacity for CSH and/or Friedel's salt was observed.



3. When NaOH was added to the fresh mortar:
  - The amount of dissolved hydroxyl ions or pH level was increased.
  - The change in acid capacity of Ca(OH)<sub>2</sub> was not clear.
  - The change in acid capacity for CSH was not clear.
4. Since concrete is more permeable than mortar for the same w/c ratio, the observed effects of the various chloride additions would probably be even more distinct in concrete than in mortar. Therefore, if NaCl or CaCl<sub>2</sub> is added to fresh concrete as a chloride source for accelerated corrosion testing of embedded steel, the different effects of these admixtures both on the chemical and physical properties of the concrete should be considered.

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