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**THE INFLUENCE OF CHLORIDES ON THE ALKALINITY OF CONCRETE**

by

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# THE INFLUENCE OF CHLORIDES ON THE ALKALINITY OF CONCRETE

## ABSTRACT

It is well known that under certain circumstances sodium chloride and calcium chloride can be found dissolved in the liquid phase of concrete. There have been a number of reports stating that these salts can produce reductions in concrete alkalinity. Furthermore, it has been suggested that the magnitude of the pH reduction is sufficient to enhance the influence of chlorides, one of the primary agents causing corrosion of concrete reinforcement. In this report the influence of NaCl, KCl and CaCl<sub>2</sub> additions on the pH of saturated Ca(OH)<sub>2</sub> solution, 0.04M KOH and cement-water extracts has been investigated experimentally and the results compared with calculated pH changes based on ionic equilibria and the theory of more concentrated electrolyte solutions. It was concluded that even when the liquid phase of concrete contained high salt concentrations the maximum pH reduction arising from this effect was only 0.5 pH unit and generally pH decreases were substantially less than this. This level of pH reduction is not likely to have a significant influence on the effectiveness of concrete as a protective cover for the steel reinforcement.

## 1. INTRODUCTION

It is well established that sodium and calcium chlorides are sometimes present in the liquid phase of concrete. These can originate from a variety of sources, namely:

- (1) deicing salts,
- (2) marine sprays,
- (3) marine aggregates, and
- (4) calcium chloride accelerator.

Sources 1–3 usually result in sodium chloride in the concrete while source 4 produces calcium chloride in the concrete pores.

There have been reports that both these salts, particularly calcium chloride, result in substantial reductions of concrete alkalinity.

This could be a problem of some severity and it has been suggested as one of the primary mechanisms by which chlorides cause corrosion of concrete reinforcement. If the pH of concrete with no dissolved chlorides falls below about 11.0 the passivity of the steel reinforcement is dissipated allowing the steel to corrode. In the presence of dissolved chlorides however, the critical pH below which steel corrodes is increased by an amount dependent on the chloride and hydroxyl ion concentration. Consequently if dissolved chlorides in concrete have the effect of reducing the pH in addition to initiating localised corrosion on breakdown of passivity, their deleterious effects would be of a much more serious nature and intensity than is commonly thought.

In this report the validity of a significant loss of concrete alkalinity from the presence of dissolved salts is questioned.

Concrete normally provides embedded steel with a high degree of corrosion protection since the liquid phase of concrete has a pH in the range 12.4 to 13.2. At this level of alkalinity steel is passivated, but the presence of aggressive anions or a decrease in pH can result in the failure of the passive film.

A number of papers<sup>1-5</sup> have reported the decrease in pH of calcium hydroxide solutions, used to simulate the liquid phase of concrete, resulting from the addition of calcium and sodium chlorides. Explanations for this phenomenon in terms of the common ion effect and the ionic equilibria of sparingly soluble salts have been suggested for the calcium chloride case, but no adequate explanation has been forthcoming for sodium chloride.

Berman<sup>1</sup> has reported a reduction in pH from 12.6 to 12.25 at 0.05M NaCl and to 12.15 at 1.0M NaCl. He also deduces from the measurements of Clear and Hay<sup>6</sup> and of Stratfull<sup>7</sup> that chloride concentrations in the range 0.4M to 4.0M are possible at the level of top reinforcement in a bridge deck treated with deicing salts. There are a number of other reports of excessively high chloride levels and low pHs in concrete usually resulting from marine exposure. Rosenqvist<sup>8</sup> reported pH values from concrete extracts no higher than 11.5 and in corroding regions values as low as 6-9 were obtained. These results were from a tropical concrete wharf where sea water was used for mixing water and pozzolanic material was added to the ordinary Portland cement. Two and ten per cent chloride<sup>9</sup> by weight of free absorbed water were observed in concrete bridge piles above and below the fluctuating water level and 14 per cent chloride<sup>10</sup> was observed in samples taken from the tidal zone at a distance of 75 mm below the concrete surface.

Of the various ions present in sea water it is thought to be the magnesium ions which have the most pronounced effect on the alkalinity due to the low solubility product of magnesium hydroxide. Calculations have demonstrated that an addition of 0.02M Mg<sup>2+</sup> results in a pH reduction of 12.6-9.5 while an addition of 1M Ca<sup>2+</sup> only causes a fall of pH from 12.6-11.3<sup>3</sup>.

It has already been stated that concrete normally has a pH in the range 12.4-13.2. There are a number of ways in which this pH can be lowered, namely:

- (1) by the addition of excessive pozzolanic material to the mix,
- (2) by carbonation,
- (3) by the ingress of salts and
- (4) locally, inside corroding pits.

Pozzolanic materials are added to portland cement to slow the rate of heat development during curing. However one of the undesirable side effects is that portland-pozzolana cements have various amounts of Ca(OH)<sub>2</sub> bound to the reactive siliceous materials and consequently in some cases it is conceivable that all the excess Ca(OH)<sub>2</sub> could be consumed with a resultant decrease in concrete pH.

Carbonation can reduce the pH of concrete to about 9, but normally this only occurs in the surface layer of the concrete to a depth of about 10 mm. Carbonation at deeper levels only occurs if the concrete is cracked or very permeable.

Localised reduction of pH in corroding pits results from the concentration of chlorides in the pit and subsequent hydrolysis leading to the formation of acidic conditions within the pit<sup>11</sup>.

The presence of salts in concrete can arise at the mix stage or from subsequent ingress from the environment. Consequently it can be seen from the above discussion, assuming pozzolanas are not used, that a general lowering of concrete pH could only result from the presence of salts. There is evidence that in marine conditions sea salts can penetrate good quality concrete up to depths of 100 mm in a relatively short period<sup>9,12</sup>(1 year) and evidently salt present at the mix stage will be uniformly distributed throughout the concrete.

Johnson and Grove<sup>13</sup> have shown that the solubility of calcium hydroxide increases as the concentration of potassium chloride increases but Berman<sup>1</sup> claims that this effect is more than counterbalanced by the reduction in  $\text{Ca(OH)}_2$  activity coefficient which results from the increase in ionic strength of the solution corresponding to the chloride additions.

To summarise, the only mechanism whereby the pH of concrete could be generally reduced, as opposed to localised reductions, is by the presence of dissolved salts in the liquid phase. The bulk of the evidence available suggests that significant pH lowering occurs if the salt concentrations in concrete rise above their normally low values, due to the application of deicing salts or exposure to marine environments. As the corrosion of reinforcement is enhanced at low pH and low  $\text{pCl}^-$  it is evident that if chlorides really do significantly lower concrete pH their effect would be conjoint in nature.

However some doubt still exists concerning the influence of chlorides, particularly sodium chloride, on the pH of concrete probably because no satisfactory explanation is available to explain the phenomena. It is hoped that the experimental results and discussion which follow will elucidate the position.

## 2. EXPERIMENTAL

The influence of the addition of sodium chloride, potassium chloride and calcium chloride on the pH of cement-water extracts, saturated calcium hydroxide, saturated calcium hydroxide + excess solid calcium hydroxide and 0.04M potassium hydroxide has been investigated.

### 2.1 Preparation of extracts and solutions

#### (i) *Cement-water extracts*

Ordinary Portland Cement (OPC) and distilled and deionized water were mixed together in a ratio of 1:1 by weight and stirred thoroughly at 10 minute intervals over a period of 2 hours hydration. The mixture was then filtered and the pH of the filtrate determined immediately and again after one week stored in an air tight flask.

#### (ii) *Saturated calcium hydroxide solution*

A stock solution was prepared using excess analar grade calcium hydroxide and distilled-deionized water. Samples were withdrawn from the stock solution and rapidly filtered to remove any undissolved  $\text{Ca(OH)}_2$  before transferring to tightly stoppered flasks.

(iii) *Saturated  $\text{Ca}(\text{OH})_2$  solution + excess solid  $\text{Ca}(\text{OH})_2$*

Preparation was as for (ii) but without the filtration operation.

(iv) *0.04M potassium hydroxide*

This solution was prepared from analar grade potassium hydroxide and distilled-deionized water and stored in tightly stoppered jars. This concentration of potassium hydroxide has a similar pH to cement-water extract and saturated calcium hydroxide.

The three chlorides, sodium, potassium and calcium were added as solid analar grade  $\text{NaCl}$ ,  $\text{KCl}$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ .

Blank pH tests were carried out on all the solutions in the absence of chloride to check for any pH reduction due to dissolution of atmospheric carbon dioxide, although steps were taken to exclude it where appropriate. The pH of the solutions when exposed to the atmosphere was also measured. All measurements were carried out at ambient temperature, ie  $22^\circ\text{C} \pm 2^\circ\text{C}$  using a Pye model 290 pH meter with an accuracy of  $\pm 0.01$  pH unit. The pH was determined 2 hours and 1 week after solution preparation in each case.

### 3. RESULTS

The results are presented as graphs 1–11. Figures 1–3 and 5 show that the pH of cement-water extract or  $\text{Ca}(\text{OH})_2$  solution changes very little between 2 hours and 1 week which implies that the storage flasks were adequately sealed.

Sodium chloride additions up to 5 per cent by weight caused small reductions in pH (maximum 0.2 pH unit) of cement-water extracts and saturated calcium hydroxide solution (Figures 1 and 5).

Calcium chloride hexahydrate additions up to 10 per cent by weight resulted in small pH reductions of cement-water extract and saturated calcium hydroxide of maximum values 0.25 and 0.6 pH unit respectively (Figures 2 and 6).

Potassium chloride additions up to 5 per cent by weight resulted in small pH increases of cement-water extract and saturated calcium hydroxide solution of maximum value 0.15 pH unit (Figures 3 and 5).

In potassium hydroxide solution potassium chloride additions up to 5 per cent by weight produced a maximum pH decrease of 0.10 pH unit while calcium chloride hexahydrate additions up to 5 per cent by weight caused a maximum pH reduction of 0.5 pH unit (Figure 7).

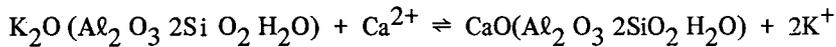
Blank tests on cement-water extract, saturated calcium hydroxide and 0.04M potassium hydroxide left exposed to the laboratory atmosphere for one week with no salt additions showed pH reductions in the range 0.2 to 0.3 pH unit.

Blank tests on cement-water extracts, saturated  $\text{Ca}(\text{OH})_2$  and KOH solutions stored in sealed flasks showed no change in pH after one week.



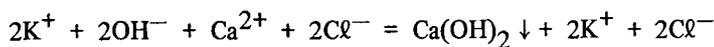
Consequently it is predicted that the addition of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  to calcium hydroxide solutions would result in a lowering of the pH. This is confirmed by the results shown in Figures 2 and 6. However the decrease in pH for a 10 per cent by weight addition of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  to a cement-water extract was 0.24 pH unit while the decrease for an equivalent  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  addition to saturated calcium hydroxide was 0.59 pH unit. The explanation for this phenomenon is pertinent to the circumstances prevailing in concrete. It has been accepted for some time that the liquid phase of concrete consists primarily of a saturated solution of calcium hydroxide with minor contributions to the alkalinity from potassium and sodium hydroxides which sometimes occur as oxides, in small quantities in cement. Peguin et al<sup>14</sup> have devised a technique for the extraction of the liquid phase of hardened concrete of any age by subjecting about 300 cm<sup>3</sup> of concrete to a pressure of 100–150 bars. The liquid extracted has been analysed to show how its constituents vary with concrete age. They have shown that very early in concrete existence the alkalinity is almost entirely due to calcium hydroxide but progressively potassium and sodium hydroxides become the chief source of alkalinity. At 28 days the contribution of calcium hydroxide is negligible and most of the alkalinity results from potassium hydroxide with a smaller contribution from sodium hydroxide. Of course, this will vary with the original composition of the cement although this is typical of OPC.

The mechanism for the progressive rise in KOH and NaOH at the expense of  $\text{Ca}(\text{OH})_2$  is probably as follows: the alkali metal compounds and the silica and alumina from the cement combine to form compounds analogous to natural zeolites which have typical base exchange properties thus:



From the above discussion it can be appreciated that the presence of calcium chloride in the liquid phase of concrete will result in a much smaller decrease in pH than would occur from an equivalent addition to calcium hydroxide since although  $\text{CaCl}_2$  can lower the pH of KOH solutions (see below) in concrete there would always be sufficient excess solid  $\text{Ca}(\text{OH})_2$  to replenish the hydroxyl ion concentration in solution. A cement-water mixture, extracted before setting, is an intermediate case.

It is however possible for the pH of alkali metal hydroxides to be reduced by the presence of calcium chloride. This occurs by a different mechanism summarised by the following equation:



Obviously pH reduction would only result when the  $\text{CaCl}_2$  addition is sufficient to exceed the solubility product of  $\text{Ca}(\text{OH})_2$ .

Tables 2 and 3 below compare the calculated reduction in pH for  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  additions to saturated  $\text{Ca}(\text{OH})_2$ , 0.04M KOH and cement-water extracts with the decreases in pH found experimentally (Figures 2, 6 and 7). The calculations were performed using the standard equations for the equilibrium solubility product of  $\text{Ca}(\text{OH})_2$  and the equilibrium ionization product of water.

**TABLE 2**

Calculated and experimental decreases in pH of Ca(OH)<sub>2</sub> and KOH solutions with added CaCl<sub>2</sub> 6H<sub>2</sub>O

CaCl <sub>2</sub> 6H <sub>2</sub> O concentration per cent by weight	Calculated - ΔpH	Experimental - ΔpH	Solution
0.4	0.00	0.05	0.04M KOH
0.5	0.03	0.06	
1.0	0.19	0.15	
2.5	0.37	0.32	
5.0	0.52	0.50	
0.5	0.06	0.12	Saturated Ca(OH) <sub>2</sub>
1.0	0.25	0.25	
2.5	0.42	0.35	
5.0	0.56	0.43	
10.0	0.70	0.61	

**TABLE 3**

Calculated and experimental decreases in pH of cement-water extracts with added CaCl<sub>2</sub> 6H<sub>2</sub>O

CaCl <sub>2</sub> 6H <sub>2</sub> O concentration per cent by weight	Calculated - ΔpH based on 0.04M KOH	Calculated - ΔpH based on sat Ca(OH) <sub>2</sub>	Experimental - ΔpH
0.5	0.03	0.06	0.04
1.0	0.19	0.25	0.08
2.5	0.37	0.42	0.15
5.0	0.52	0.56	0.19
10.0	0.70	0.70	0.25

The agreement of results in Table 2 is quite close and although the agreement in Table 3 is not so good this is to be expected since precise calculations cannot be made for cement-water extracts owing to the complex nature of the cement composition. The smaller than predicted pH decreases are probably the result of some of the CaCl<sub>2</sub> being converted to insoluble cement hydration products leaving a lower concentration in solution.

In conclusion it can be stated that calcium chloride does reduce the pH of the liquid phase of concrete by small amounts at high concentrations. At 5 per cent by weight CaCl<sub>2</sub> 6H<sub>2</sub>O pH reductions in the range 0.19 to 0.50 have been observed. CaCl<sub>2</sub> 6H<sub>2</sub>O solutions of higher concentration are unlikely to be found in the pores of concrete and although higher CaCl<sub>2</sub> concentrations have been reported it should be noted that they include both the CaCl<sub>2</sub> in solution and the CaCl<sub>2</sub> combined with C<sub>3</sub>A etc in cement hydration products which remain in the solid state. Remembering that concrete usually has a pH about 0.3 pH unit higher than sat Ca(OH)<sub>2</sub> solution the small pH reduction resulting from high calcium chloride concentrations is not significant in terms of corrosion of reinforcement.

(2) Potassium chloride and sodium chloride

Superficial examination would suggest that neither of these salts should affect the pH of Ca(OH)<sub>2</sub>, KOH, cement-water extracts or concrete. However, there have been a number of reports<sup>1,3,4,5,10</sup> of sodium chloride producing significant decreases in pH of alkaline media. The influence of potassium chloride on these media does not appear to have been investigated.

Certainly it can be stated that neither NaCl or KCl could have any influence on the pH of these media as a result of common ion effects. However, in the absence of a reasonable explanation for pH reductions caused by NaCl, the validity of this phenomenon has been in doubt even though it has been widely reported. In this report NaCl has caused reductions in pH, maximum value 0.2 pH unit at high concentrations while KCl has caused increases in pH, maximum value of 0.15 pH unit. These effects can be explained by the following argument:

(a) KOH solution

As the ionic strength of an electrolyte increases so the ability of the ions in that solution to act independently of each other is reduced. This has the effect of reducing the effectiveness or activity of each ion; this is summarised in the relationship between concentration and activity

$$\text{ie } [\text{OH}^-] \times f_- = a_{\text{OH}^-} \quad \dots \dots \dots (2)$$

where  $[\text{OH}^-]$  = concentration of  $\text{OH}^-$

$$f_- = \text{activity coefficient of } \text{OH}^-$$

and  $a_{\text{OH}^-}$  = activity of  $\text{OH}^-$

In general, if very concentrated solutions are neglected, the activity coefficient of an ion in solution decreases with increasing concentration. Now the precise definition of pH is

$$\text{pH} = -\log_{10} a_{\text{H}^+} \quad \dots \dots \dots (3)$$

and the activity of hydrogen ions is directly related to the activity of hydroxyl ions. This has two effects (i) the pH of KOH solutions is generally less than predictions based on the concentration, except in very dilute solutions when the activity coefficient is unity and (ii) even dilute solutions of KOH can show a pH reduction when the presence of other salts increases the ionic strength of the solution. This is the result of equations of the type

$$\log f_{\pm} = -A |z_+ z_-| I^{1/2} \quad \text{for dilute solutions } I < .01 \quad \dots \dots \dots (4)$$

$$\text{and } \log f_{\pm} = \frac{-A |z_+ z_-| I^{1/2}}{1 + BdI^{1/2}} \quad \text{for more concentrated solutions} \quad \dots \dots \dots (5)$$

- where  $f_{\pm}$  is the activity coefficient
- $z_+, z_-$  are the valencies of the constituent ions
- $I$  is the ionic strength of the solution
- $A, B$  are constants
- $d$  mean effective diameter of the ions

$$I = \frac{1}{2} \sum m_i z_i^2 \dots \dots \dots (6)$$

$m_i$  is the molality and the summation is carried over each ionic species in solution.

These equations show that increasing ionic strength lowers the activity coefficient of KOH and hence the pH.

Consequently the addition of NaCl or KCl to the 0.04M KOH solution should cause a reduction in the  $a_{OH^-}$  and hence the pH. It is difficult to estimate the actual decrease in pH in solutions which are not reasonably dilute because the theory of concentrated solutions is very complex and has not been quantitatively established (see Appendix). However by using equation (5) and (6) above the addition of 5 per cent by weight NaCl and KCl to 0.04M KOH should result in pH reductions of approximately 0.15–0.20.

Another factor which must be considered is the sodium ion error which is associated with normal glass electrodes in the presence of sodium ions. For example a solution 0.5M  $Na^+$  will result in the normal glass electrode measuring too low by 0.3 pH units at a pH of 12<sup>15</sup>.

The results obtained in the current examination show that 5 per cent by weight additions of KCl and NaCl result in pH decreases of 0.12 and 0.35 pH units respectively (Figure 7). This is in reasonable agreement with the forecast pH changes.

If it is assumed that the alkalinity of concrete is due mainly to alkali metal hydroxide then the experimental and theoretical factors discussed above indicate that the presence of KCl or NaCl in high concentrations would produce a decrease in pH not exceeding 0.2 pH unit, which is barely significant.

**TABLE 4**  
Calculated pH changes resulting from salt additions to 0.04M KOH

Solution composition	Ionic strength (I)	$f_{\pm}$ KOH	$-\Delta pH$
0.04M KOH no salts	0.04	0.85 <sup>16</sup>	0.06
0.04M KOH + 5 per cent NaCl	0.89	0.56	0.25
0.04M KOH + 5 per cent KCl	0.70	0.60	0.22
0.04M KOH + 10 per cent NaCl	1.74	0.52	0.28
0.04M KOH + 10 per cent KCl	1.36	0.54	0.27
—	0.10	0.76	0.12
—	0.50	0.63	0.20
—	1.0	0.56	0.25
—	5.0	0.45	0.34

Table 4 shows the predicted pH changes resulting from additions of NaCl and KCl to 0.04M KOH calculated using equations 2, 3, 5 and 6.

(b)  $\text{Ca(OH)}_2$  solution (saturated)

The situation in this medium is somewhat different to that in potassium hydroxide since the activity of hydroxyl ions is controlled by the equilibrium solubility product relationship of the sparingly soluble  $\text{Ca(OH)}_2$ .

As with KOH the addition of KCl and NaCl increases the ionic strength of the solution which results in a decrease in activity coefficient of the hydroxyl ion. However from the strict definition of solubility product

$$K = a_{\text{Ca}^{2+}} \cdot a_{\text{OH}^-}^2 = [\text{Ca}^{2+}] f_{\text{Ca}^{2+}} \cdot [\text{OH}^-]^2 f_{\text{OH}^-}^2 \dots \dots \dots (7)$$

it can be seen that in order to maintain K constant any decrease in  $f_{\text{Ca}^{2+}}$  and  $f_{\text{OH}^-}$  must be counter-balanced by corresponding increases in  $[\text{Ca}^{2+}]$  and  $[\text{OH}^-]$ .

Consequently the theory predicts that additions of NaCl and KCl should have no effect on the pH of saturated  $\text{Ca(OH)}_2$  if excess solid  $\text{Ca(OH)}_2$  is in contact with the solution. Obviously if excess solid were not available the solution would become unsaturated and the pH would decline correspondingly. The theory also predicts that the solubility of  $\text{Ca(OH)}_2$  will increase with addition of salts. The validity of this effect has been conclusively proved by experiment<sup>13</sup> for a variety of different salts and concentrations.

The experimental results from the current investigation broadly confirmed this picture. The additions of KCl (Figure 5) had little effect on the pH resulting only in barely significant increases. The pH decrease on adding NaCl (Figure 4) can be assigned to the sodium ion error inherent in glass electrodes. The absence of excess solid  $\text{Ca(OH)}_2$  resulted in a larger pH decrease, as predicted (Figure 4). However in concrete excess  $\text{Ca(OH)}_2$  is almost certain to be available hence NaCl and KCl additions would not be expected to result in pH decreases, even if the alkalinity of concrete was due primarily to  $\text{Ca(OH)}_2$ .

(c) Cement-water extracts

It has already been shown that the alkalinity of cement-water extracts of 2 hours age results from a combination of  $\text{Ca(OH)}_2$  and alkali metal hydroxides<sup>14</sup>. The theory discussed above indicates that additions of NaCl and KCl to saturated  $\text{Ca(OH)}_2$  + excess solid  $\text{Ca(OH)}_2$  should have no influence on pH while similar additions to 0.04M KOH should result in very small pH reductions. Consequently for the cement-water extracts, additions of NaCl and KCl would not be expected to change the pH except possibly for a marginal decrease. The experimental results (Figures 1 and 3) showed a pH increase of 0.1 and decrease of 0.15 respectively for 5 per cent additions of KCl and NaCl. The decrease in pH arising from NaCl can probably be attributed to the sodium ion error of the glass electrode. There is no satisfactory explanation of the pH increase resulting from KCl additions although the numerical value of the increase was very small.

From this discussion it is possible to elucidate some of the unexplained results from the literature on this topic.

- (i) The most common confusion arises from the frequent addition of salts to saturated  $\text{Ca(OH)}_2$  with no excess solid phase present<sup>1,3,4</sup>. Consequently salts which influence the hydroxyl ion concentration by the precipitation of hydroxide, eg  $\text{MgCl}_2$  can cause substantial decreases in pH of the order of 2 pH units for a 0.2M  $\text{Mg}^{2+}$  solution. However these circumstances are not relevant to concrete,

where excess solid  $\text{Ca(OH)}_2$  is almost certain to be present. A number of reports neglect to mention whether excess solid phase is present.

- (ii) Nearly all the work on the influence of alkali metal salts on the pH of solutions simulating the liquid phase of concrete has involved  $\text{NaCl}$ <sup>1,3,4,5</sup>. Although this compound may be frequently found in concrete it is not the most suitable for measurements of small pH changes owing to the inherent error of glass electrodes used in alkaline solutions containing sodium ions.
- (iii) The source of alkalinity in concrete is widely ascribed to  $\text{Ca(OH)}_2$ <sup>1,3,4,5</sup> whereas closer examination reveals that this assumption is at the least an oversimplification and at worst incorrect. Consequently interpolation of results in  $\text{Ca(OH)}_2$  solution to concrete can be misleading and is only really justified in circumstances where the cement contains no alkali metal oxides or when the added salt precipitates a significant proportion of the hydroxyl ions from the KOH.
- (iv) There have been a number of reports of very high chloride contents of concrete. pH reductions resulting from similar salt contents in saturated  $\text{Ca(OH)}_2$  solution have then been interpolated to concrete<sup>1,3</sup>. This is manifestly incorrect since the pH reduction applies to dissolved salt while the concrete chloride content includes both freely dissolved chloride and chloride combined with  $\text{C}_3\text{A}$  etc, as insoluble complexes. The latter generally predominates.

One reporter<sup>1</sup> was so concerned at the pH decreases he observed that it was suggested that alkalis such as sodium hydroxide and barium hydroxide should be added to the cement to achieve a higher initial pH. Although this is quite feasible, in concrete it would have a number of unfortunate side effects, eg a substantial loss in strength<sup>17,18,19</sup>.

It is hoped that this discussion will have emphasised two points:

- (1) The shortcomings in interpolating pH changes resulting from the addition of one salt (usually  $\text{NaCl}$ ) to one alkali (usually  $\text{Ca(OH)}_2$ ) to the situation in the liquid phase of concrete. For example  $\text{NaCl}$  and  $\text{Ca(OH)}_2$  are certainly not the only constituents of the liquid phase of concrete and pH measurements on alkaline solutions containing  $\text{Na}^+$  are subject to the sodium ion error of the glass electrode.
- (2) Regardless of the source of concrete alkalinity the addition of  $\text{NaCl}$ ,  $\text{KCl}$  or  $\text{CaCl}_2$  results only in very small pH reductions even at improbably high salt contents. In the most extreme case the pH decrease from this effect will not exceed 0.5 pH unit and in most cases will be much smaller.

## 5. ACKNOWLEDGEMENTS

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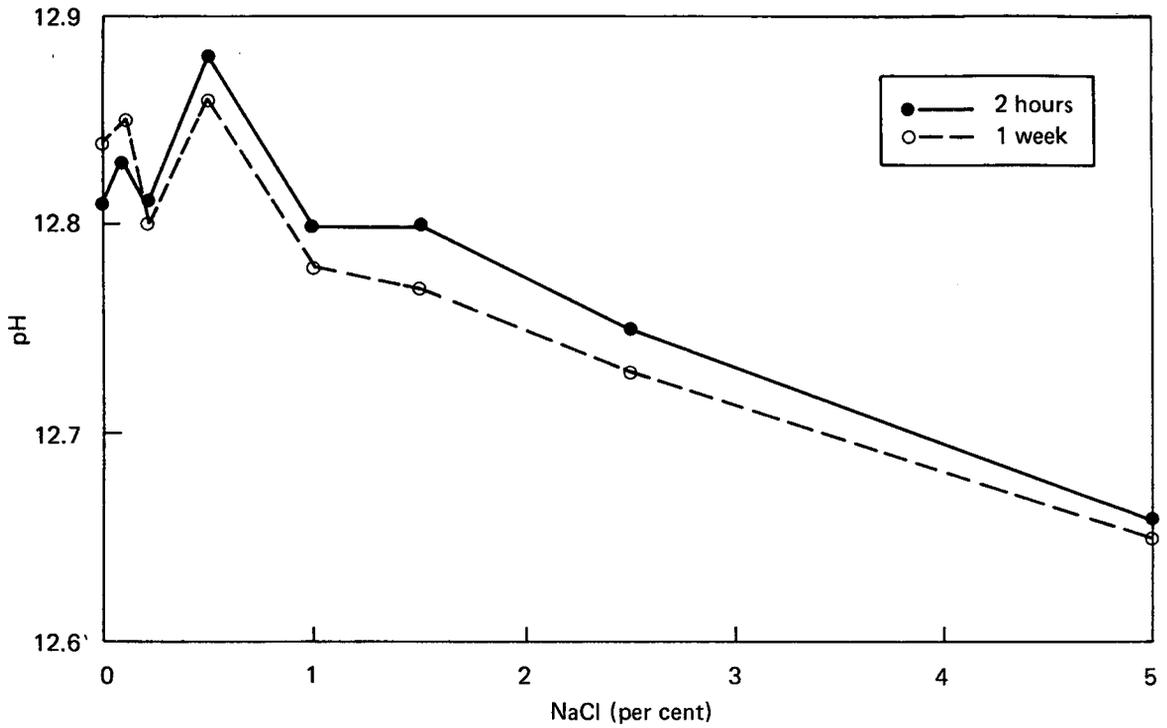


Fig. 1 THE VARIATION OF THE pH OF CEMENT-WATER EXTRACT WITH ADDED NaCl

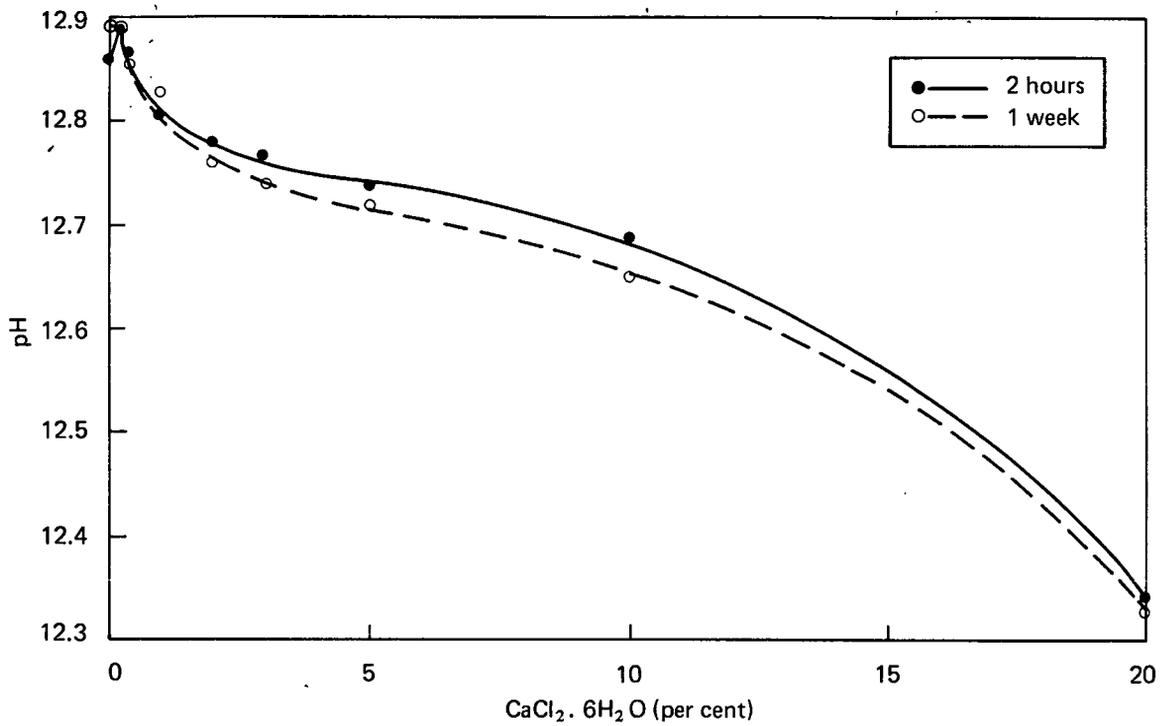


Fig. 2 THE VARIATION OF THE pH OF CEMENT-WATER EXTRACT WITH ADDED CaCl<sub>2</sub> · 6H<sub>2</sub>O

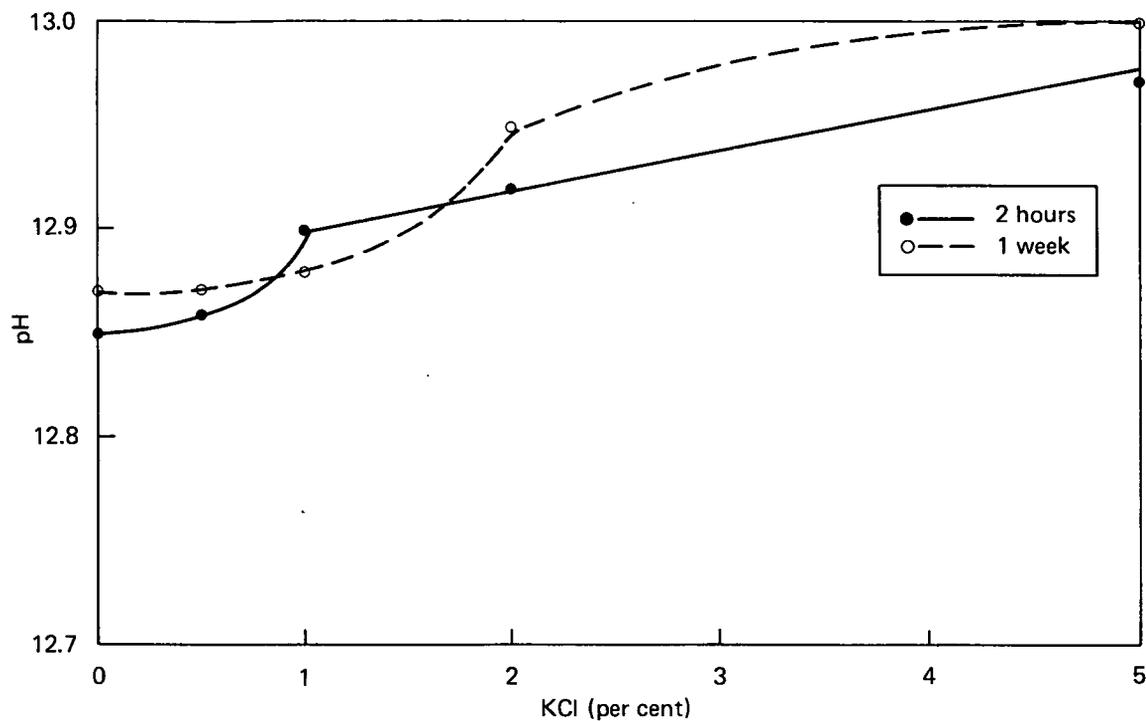


Fig. 3 THE VARIATION OF THE pH OF CEMENT-WATER EXTRACT WITH ADDED KCl

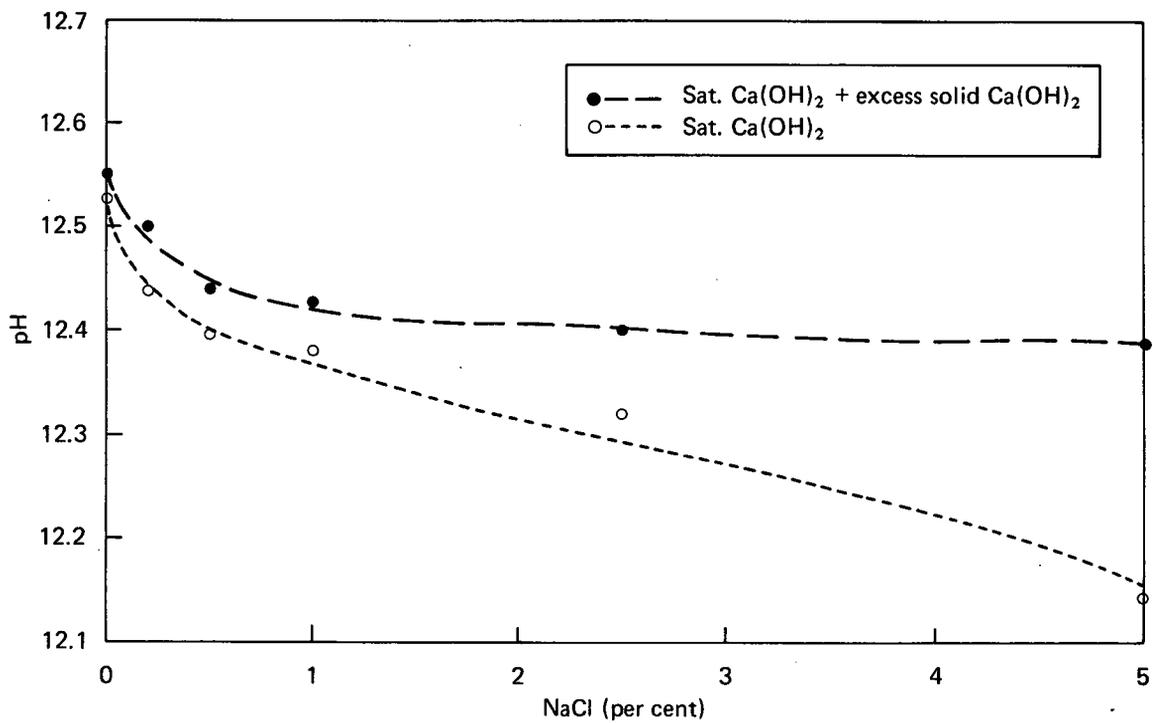


Fig. 4 THE VARIATION OF THE pH OF SATURATED  $\text{Ca(OH)}_2$  SOLUTIONS WITH ADDED NaCl

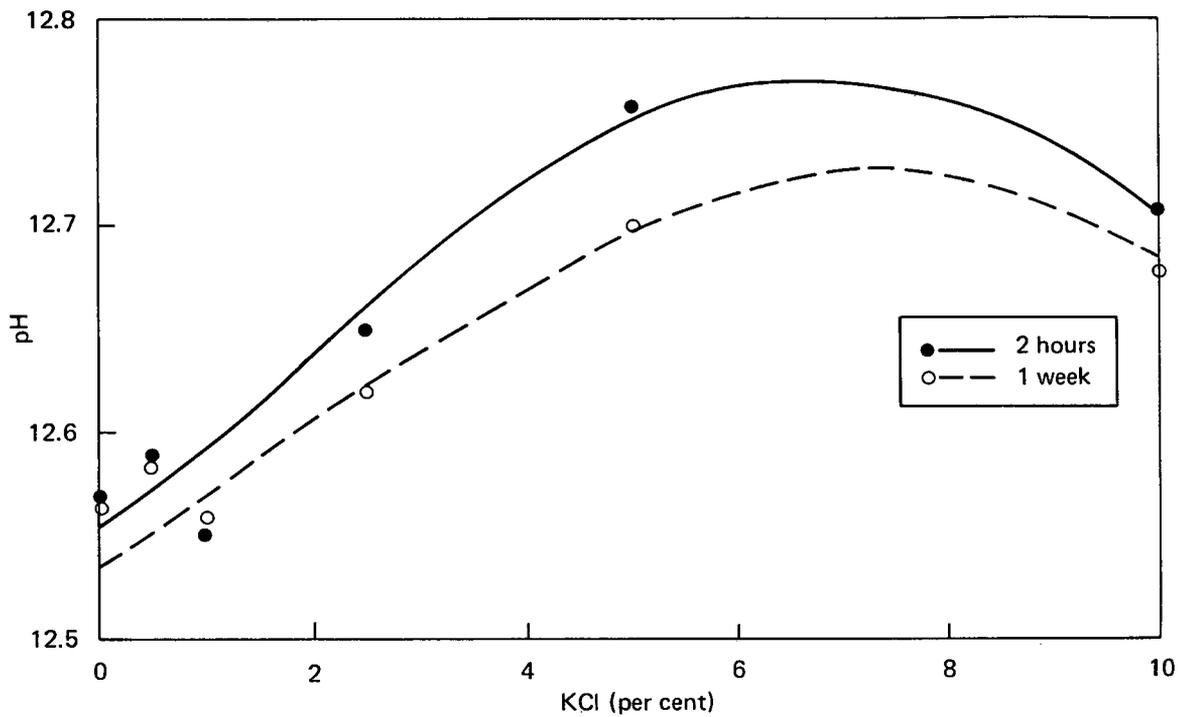


Fig. 5 THE VARIATION OF THE pH OF SATURATED  $\text{Ca(OH)}_2$  SOLUTION WITH ADDED KCl

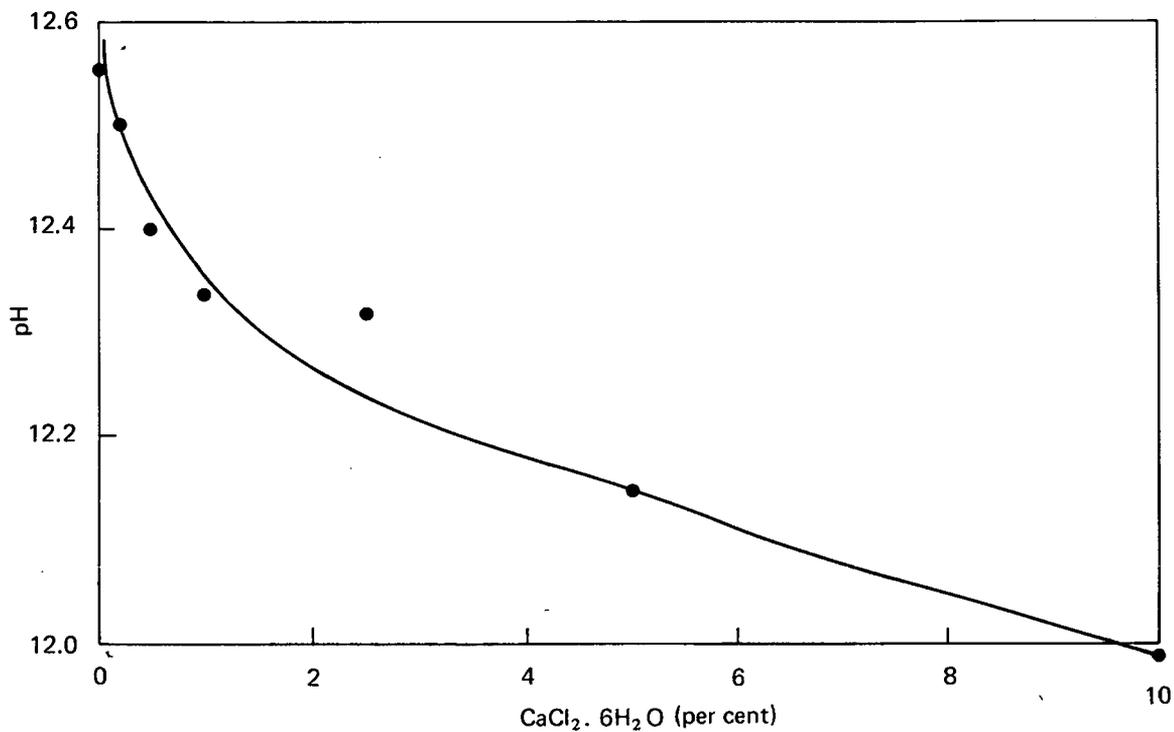


Fig. 6 THE VARIATION OF THE pH OF SATURATED  $\text{Ca(OH)}_2$  SOLUTION WITH ADDED  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

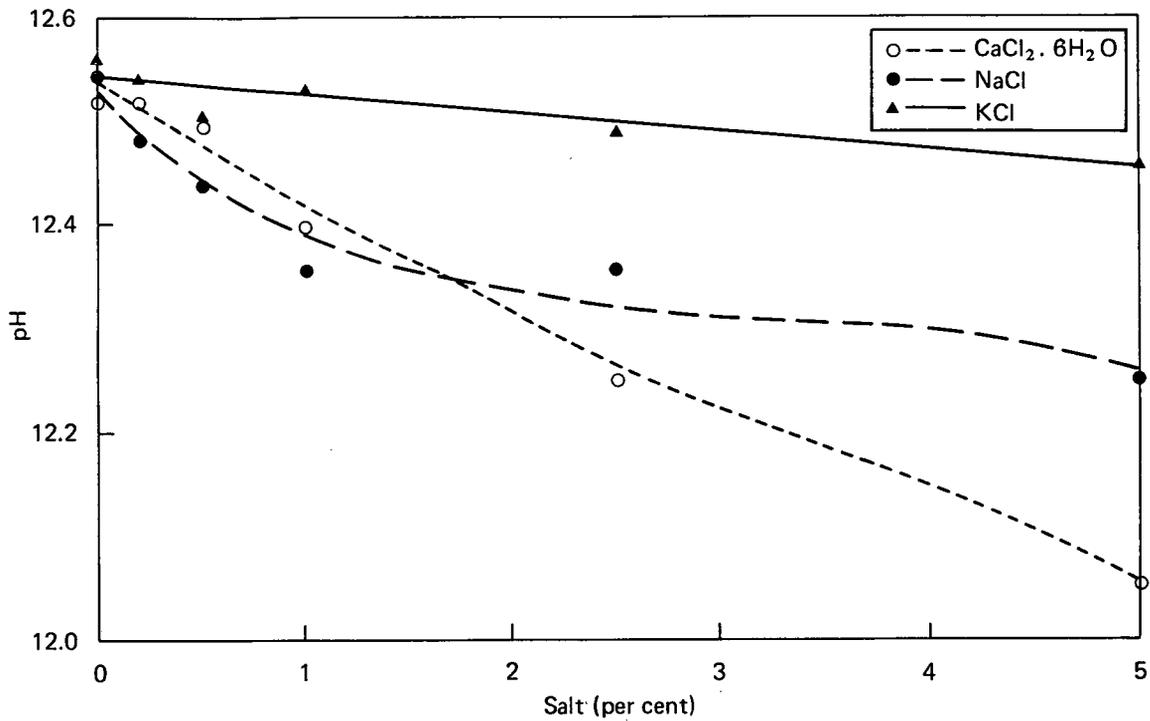


Fig. 7 THE VARIATION OF THE pH OF 0.04M KOH WITH KCl, NaCl AND CaCl<sub>2</sub>·6H<sub>2</sub>O ADDITIONS

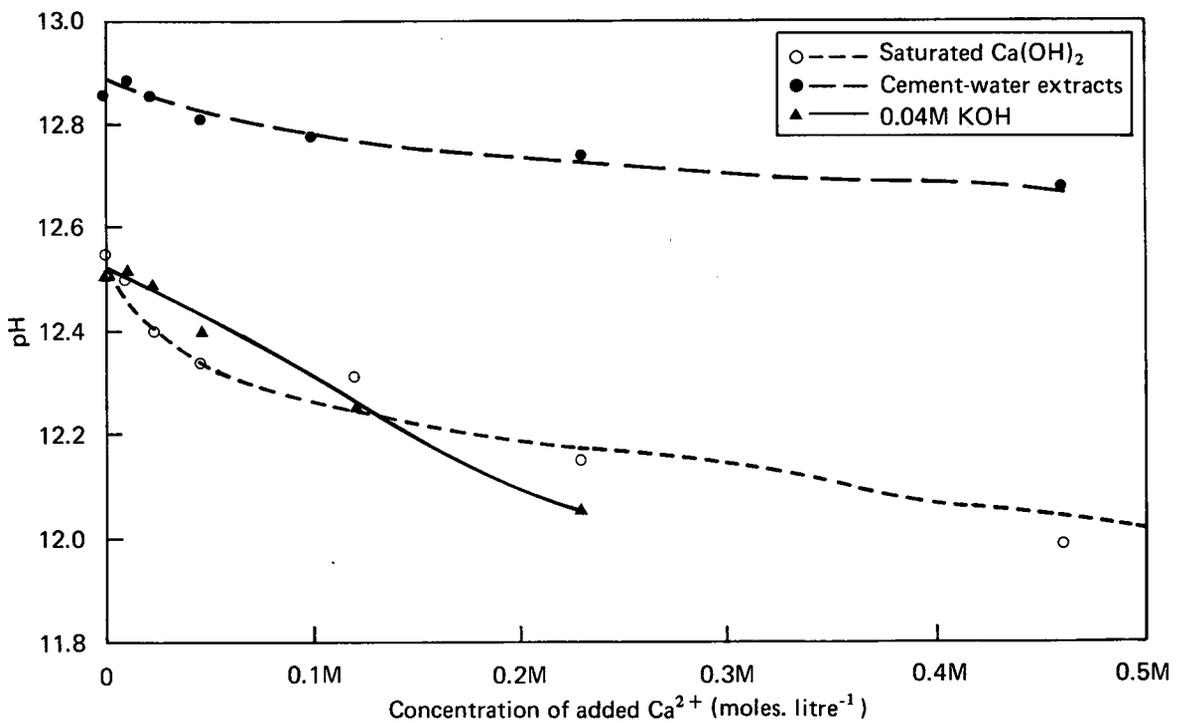


Fig. 8 THE INFLUENCE OF CaCl<sub>2</sub> ADDITIONS TO THREE DIFFERENT ALKALINE SYSTEMS

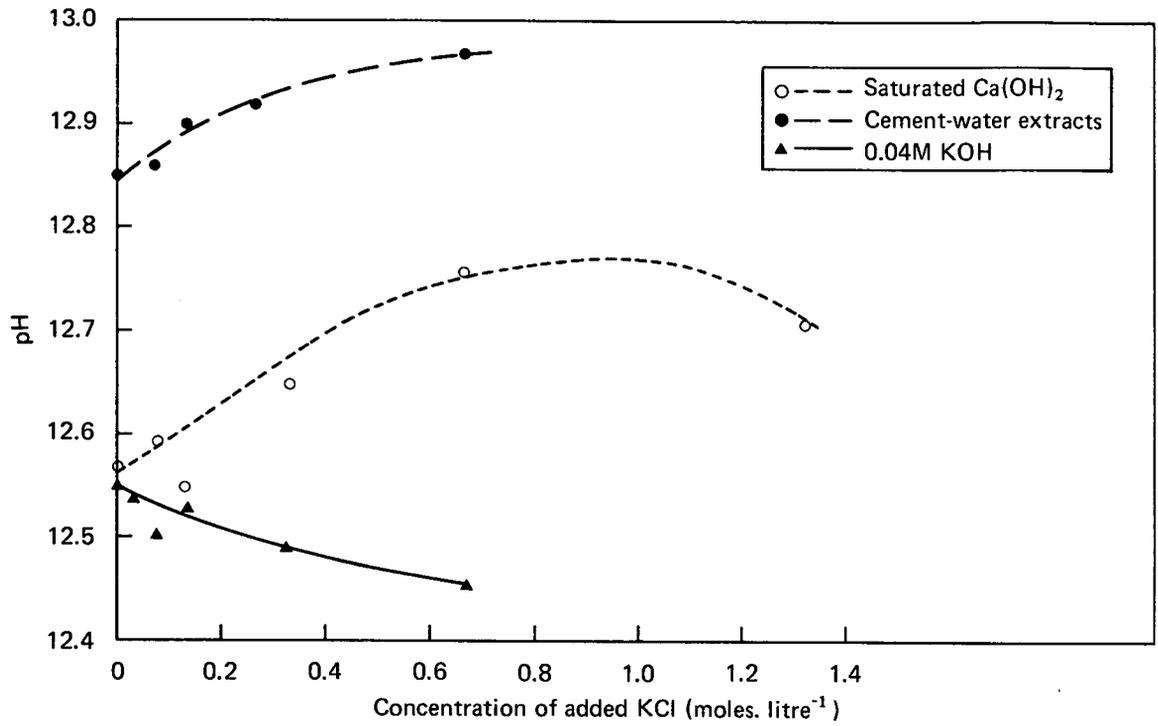


Fig. 9 THE INFLUENCE OF KCl ADDITIONS ON THE pH OF THREE DIFFERENT ALKALINE SOLUTIONS

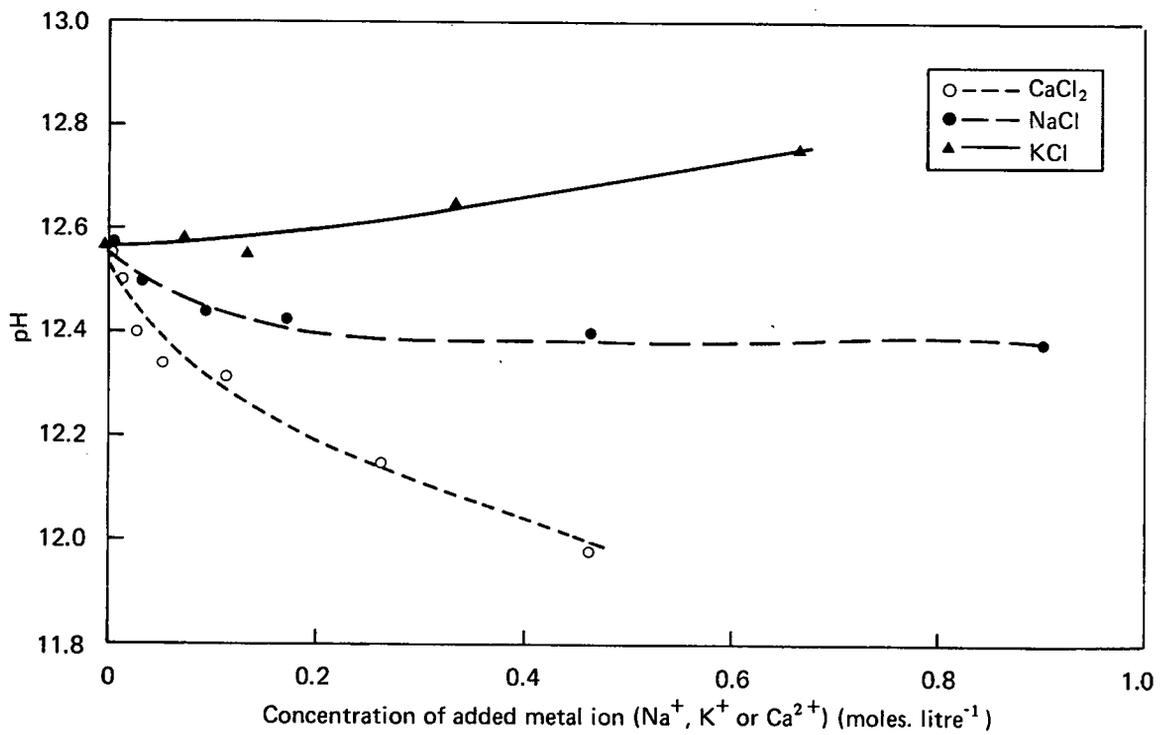
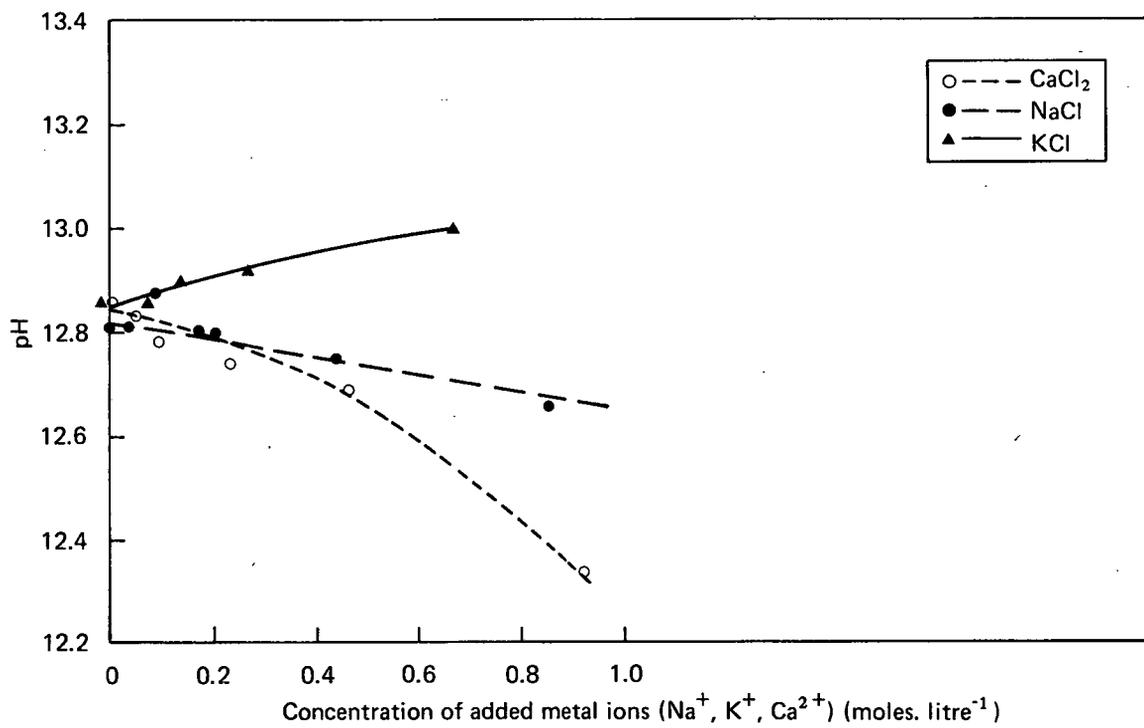


Fig. 10 THE INFLUENCE OF KCl, NaCl AND CaCl<sub>2</sub> ADDITIONS ON THE pH OF SATURATED Ca(OH)<sub>2</sub> SOLUTION



**Fig. 11 THE INFLUENCE OF NaCl, KCl AND CaCl<sub>2</sub> ADDITIONS ON THE pH OF CEMENT-WATER EXTRACTS**

## 7. APPENDIX

### THEORIES OF ELECTROLYTE SOLUTIONS

The Debye-Huckel theory of dilute electrolyte solutions assumes that strong electrolytes are completely dissociated into ions. Electrical interactions between the ions can lead to deviations from ideal behaviour. In order to calculate the equilibrium properties of solutions it is necessary to determine the excess free energy resulting from these ion based electrostatic interactions. This excess free energy is obtained by calculating the average electrical potential,  $E$ , of a given ion due to all the other ions in the solution. Once  $E$  has been established, the energy required to charge the ions reversibly to this potential can be determined. This is effectively the free energy due to electrostatic interactions which is related to the activity coefficient as a measure of the deviation from ideality. The ideal condition holds at infinite dilution when each ion can act independently of all the other ions in the solution, ie there are no electrostatic interactions.

At infinite dilution ions are distributed completely randomly and there is no net electrostatic interaction since attractive forces would be completely balanced by repulsive forces. At higher concentrations this situation is not likely to be found in practice since a negative ion is always more likely to be found in the vicinity of a positive ion rather than another negative ion. This results in an ordering of the ions in solution. However thermal motions prevent a complete ordering and the final result is a dynamic equilibrium between electrostatic interactions tending to produce an ordered structure and kinetic collisions tending to destroy them.

This type of argument led to the development of the Debye-Huckel limiting law

$$\log f_{\pm} = -A \left| z_+ z_- \right| I^{1/2}$$

This law however applies to dilute solutions only,  $I < 0.01$ .

The theory of more concentrated solutions is one of the major unsolved problems in physical chemistry because the mathematics becomes increasingly complex as divergence from extreme dilution increases. The reasons for this problem can be summarised thus: the dissociation of a hypothetical molecule AB requires the separation of the oppositely charged ions  $A^+$  and  $B^-$ . The electrostatic attractions between typical ions decrease only slowly with distance so that some association still exists at a separation of several molecular diameters. Another factor opposing complete dissociation is the extremely high rate of dissociation and reformation of molecules from ions in solution. Consequently the mean lifetime of a dissociated ion is very short,  $\sim 10^{-10}$  sec and in this time span an ion is much more likely to recombine with an ion of opposite charge than to become completely dissociated.

In more concentrated solutions it is postulated that ion-pairs are formed by electrostatic attraction. The probability of ion-pair formation increases with decreasing solvent dielectric constant and ionic radius. This ion-pair formation results in the decrease in the activity coefficient with consequent influence on ionic equilibria. The repulsive forces between ions at close separation also become important as the solution concentration increases and results in decreasing electrostatic interactions. The actual ionic radius is significant in more concentrated solutions. Debye and Huckel adapted their initial theory which assumed the ions were point charges, taking the actual ionic size into account. The relationship between activity coefficient and ionic strength which resulted is

$$\log f_{\pm} = \frac{-A |z_+ z_-| I^{1/2}}{1 + BdI^{1/2}}$$

which applies to solutions of somewhat greater concentration than the limiting law.

## ABSTRACT

**The influence of chlorides on the alkalinity of concrete:** P R VASSIE: Department of the Environment Department of Transport, TRRL Laboratory Report 915: Crowthorne, 1979 (Transport and Road Research Laboratory). It is well known that under certain circumstances sodium chloride and calcium chloride can be found dissolved in the liquid phase of concrete. There have been a number of reports stating that these salts can produce reductions in concrete alkalinity. Furthermore it has been suggested that the magnitude of the pH reductions is sufficient to enhance the influence of chlorides, one of the primary agents causing corrosion of concrete reinforcement. In this report the influence of NaCl, KCl and CaCl<sub>2</sub> additions on the pH of saturated Ca(OH)<sub>2</sub> solution, 0.04M KOH and cement-water extracts has been investigated experimentally and the results compared with calculated pH changes based on ionic equilibria and the theory of more concentrated electrolyte solutions. It was concluded that even when the liquid phase of concrete contained high salt concentrations the maximum pH reduction arising from this effect was only 0.5 pH unit and generally pH decreases were substantially less than this. This level of pH reduction is not likely to have a significant influence on the effectiveness of concrete as a protective cover for the steel reinforcement.

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