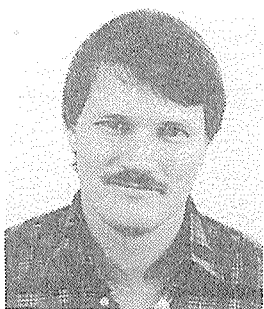


## ANALYSIS OF PORE SOLUTION SQUEEZED OUT OF CEMENT PASTE AND MORTAR



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Small bars made of cement paste and mortar, conditioned in various climates were after conditioning analyzed for the substances Cl and OH. The measurements were made on a pore solution which had been pressed out of these specimens. The results have been used to calculate the chloride bounding capacity and effective diffusion coefficients for different qualities.

Keywords: Chloride, bounding capacity, diffusion coefficients.

### 1 INTRODUCTION

A common cause for the initiation of corrosion in reinforcement in concrete is that the solution which surrounds the steel contains excessively high chloride concentrations. As a result of this, numerous researchers have studied how rapidly chlorides are transported into the concrete, which chloride concentrations have occurred in concrete damaged by corrosion etc. A study of the literature shows, for example, that widely varying values have been given for the maximum chloride content in concrete. These areas lie within a range of 30-30 000 mg/l, converted to concentration in pore solution. A closer study of the maximum values which can be tolerated shows that the minimum value specified comes from laboratory experiments where the corrosion study was carried out in saturated  $\text{Ca(OH)}_2$  solution. The largest values come from practical experience in cases where chloride has been mixed with the concrete, which has been surrounded by an indoor climate during the function period.

No uniform system for specifying chloride concentration in concrete has yet been established. The method most commonly adopted is to specify the chloride content as  $\text{Cl}^-$ /cement content,  $\text{CaCl}_2$ /cement content or  $\text{Cl}^-$ /concrete weight. The reason why these measuring systems are used is that the values can be obtained through a purely chemical analysis. This is not, however, the chloride content which surrounds the embedded steel

since a considerable proportion of it is bound chemically and physically in the concrete. For a specific chloride quantity per  $m^3$  concrete, the concentration in the pore solution will vary not only with the bound quantity but also with the porosity and the degree of filling of the pore system. A high level of porosity offers increased possibilities for dilution compared with a low level of porosity. When concrete is dried out, the concentration of all soluble substances in the pore solution is increased due to the lower degree of dilution. Furthermore, it seems reasonable to assume that the quantity of chloride bound in concrete is a function of the concentration in the pore solution, in other words the free chloride. The chemical composition for cement and aggregate, and the ageing of the concrete are also likely to play an important part here.

Consequently, the chloride quantity should be determined in such a way that the concentration in the solution which surrounds the embedded steel can be specified.

Measurements of the free chloride concentration in cement paste, mortar and concrete can be carried out, in the case of fully saturated specimens, by means of a pressure method which Longuet /1976/ and others have made use of. This method has been further developed by Rombén at the Cement and Concrete Research Institute in Stockholm in such a way that small mortar specimens (approx. 1 g) can be analyzed.

## 2 TEST METHOD

The equipment used for squeezing out pore solution from cement paste and mortar consisted of a tablet press in which a hole had been drilled in the lower mould unit to permit the pore solution to run out when the specimen was subjected to pressure, see FIG 1. Squeezing out pore solution from paste and mortar was relatively simple as long as the material had a capillary pore system which was filled with solution. It was difficult, on the other hand, to guide the solution along the correct path to the cup used for collecting the solution. All the seals, which consisted of teflon packing, consequently constituted important components in the equipment.

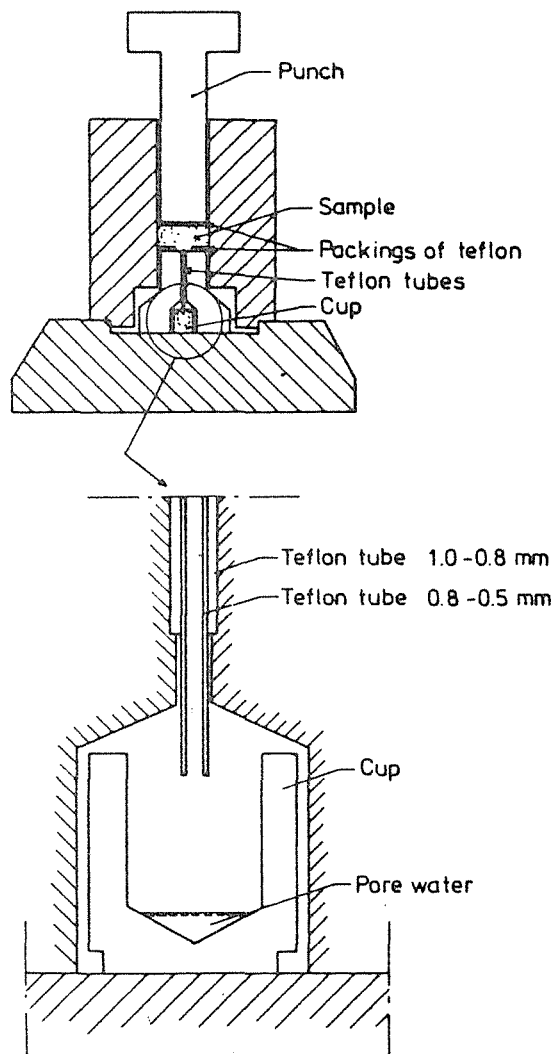


FIG 1. Equipment used for pressing out pore water in concrete.

The quantity of pore solution obtained from each pressing, from about 1 g paste or mortar, varied between 0 and 15  $\mu\text{l}$ .

Consequently, it was not possible to carry out the chemical analysis in the conventional manner by means of titration. Microtitration would, admittedly, have been possible but it was considered far too time-consuming. After various preliminary experiments, it was established that ion-selective chloride electrodes could be used, see FIG 2.

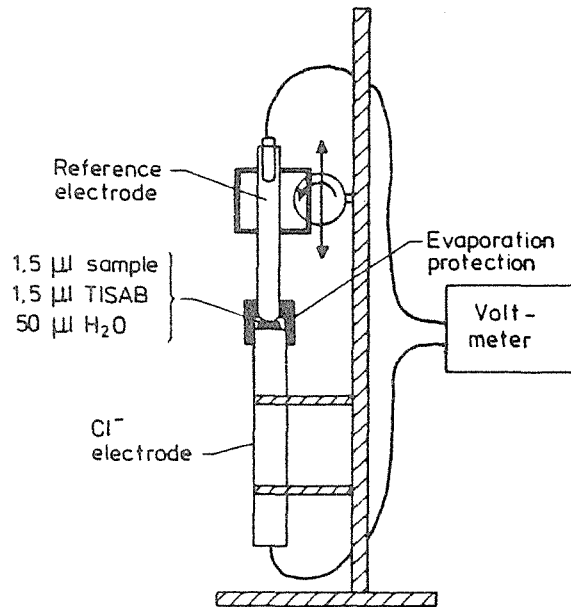


FIG 2. Analyzing equipment.

The specimens were cut by means of a guillotine to avoid disturbances in connection with sampling. Sawing out discs might have entailed a redistribution of the substances which occurred in the pore system due to the heat developed during sawing and a possible dilution of the pore solution with the cooling water.

An important question was whether or not the pressing operation would entail squeezing out more than the free chlorides only. Consequently, the concentration of chloride was measured in one specimen with a known chloride content after the solution had been squeezed out at a pressure varying between 100-800 MPa. No marked difference could be noticed in the chloride concentration during these measurements. Consequently, the method involving the squeezed out chloride solution was considered to be useful in this investigation of the pore solution in cement-based materials.

### 3 PRODUCTION OF SPECIMENS, VALUES OF COMPONENT VARIABLES AND CONDITIONING

Bars with a diameter of 19.5 mm and a length of about 70 mm, made of mortar and paste, were cast with different W/C and cement types in accordance with Table 1. The casting was carried out in teflon moulds and with intensive external vibration.

All of the specimens were conditioned between 2 and 4 months in a saturated  $\text{Ca}(\text{OH})_2$  solution. During this time, specimens were sawn from the bars.

The experiments were of the type diffusion experiments. (Specimens in 3% NaCl-solution with one surface exposed)

The experiments were carried out in laboratory air with a temperature of  $20 \pm 2$  °C.

After the first curing period in saturated  $\text{Ca}(\text{OH})_2$  solution, the specimens were placed in three different humidity climates:

- continued curing in saturated  $\text{Ca}(\text{OH})_2$  solution
- 80% relative humidity, air free from  $\text{CO}_2$ .
- 50% relative humidity, air free from  $\text{CO}_2$

This conditioning continued for about a year. The specimens which had been subjected to drying out before the test were weighed both before and after the conditioning.

After this lengthy conditioning, the Portland cement and the slag cement specimens were regarded as having a similar degree of hydration for the various climates. This meant that the slower slag cement would not be less favoured in the experiments.

Table 1. Mix proportions and measured porosity for different mixes. The porosity was measured by means of weighing and drying out at 105°C on 5 specimens which had lain in a saturated  $\text{Ca}(\text{OH})_2$  solution for about 2 years. The consistence of these mixes varied from fluid to harsh. The compaction applied was, consequently, varied until fully satisfactory compaction had been obtained.

Cement type	Cement content <sub>3</sub> kg/m <sup>3</sup>	Paste	Mortar C: Sand (0-4 mm)	W/C	Porosity * %
Portland	1390	P	-	0.40	38.4 + 0.4
"	1090	P	-	0.60	50.3 ± 0.5
"	540	-	1 : 3	0.40	15.1 ± 0.8
"	480	-	1 : 3	0.60	22.5 ± 0.4
Slag **	1370	P	-	0.40	44.9 ± 0.4
"	530	-	1 : 3	0.40	16.8 ± 0.3
"	480	-	1 : 3	0.60	24.1 ± 0.6

\* The theoretically calculated porosity agreed with the real porosity within +2% units.

\*\* (70% slag, 30% Portland cement)

All surfaces not exposed were thoroughly insulated with epoxy and with an external protection.

Specimens in which chlorides were added to the fresh cement paste were also cast for comparison purposes with the values obtained from the diffusion and evaporation experiments. The chloride quantity was varied from 0-2.5%  $\text{Cl}^-$ /weight cement. Two different salts were used, KCl and  $\text{CaCl}_2$ .

It should be noted that experiments with specimens which had been dried out and included in the diffusion test consisted of a combined transport as a result of capillary suction and diffusion. These experiments are, however, called diffusion tests.

## 4 RESULTS

### 4.1 Free, bound and total chloride concentration

Test cores were taken from the 3% salt solution at various times. These cores were cut into discs. The pore solution which was squeezed out was analyzed for both  $\text{Cl}^-$  and  $\text{OH}^-$  in cases where the pore fluid was sufficient and for  $\text{Cl}^-$  only in cases where the quantity of pore fluid was small. Double determinations were carried out for most of the  $\text{Cl}^-$  measurements. The total chloride content was also measured in relation to the CaO quantity in most of the specimens. The quantity of chloride per cement quantity could thus be calculated in a conventional manner.

FIGS 3-7 show a mode of presentation where free chloride has been plotted as a function of the bound chloride per weight unit cement.

The factor  $k_d$  is a constant which specifies the quantity of free chloride in relation to the quantity of bound chloride per weight unit cement.

A factor which must be noted at this stage is that certain difficulties were encountered in squeezing out the pore solution from specimens with  $W/C = 0.40$  which had been hydrated during a lengthy period of time. This was particularly true of specimens which had already dried, in other words, in cases where the degree of water saturation was not maximum. It was probably possible to squeeze out only the water in the capillary pore in these specimens.

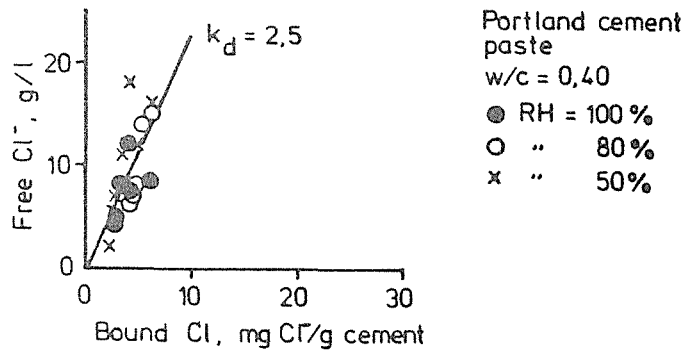


FIG 3. Measured free chloride concentration as a function of the bound chloride per weight unit cement.

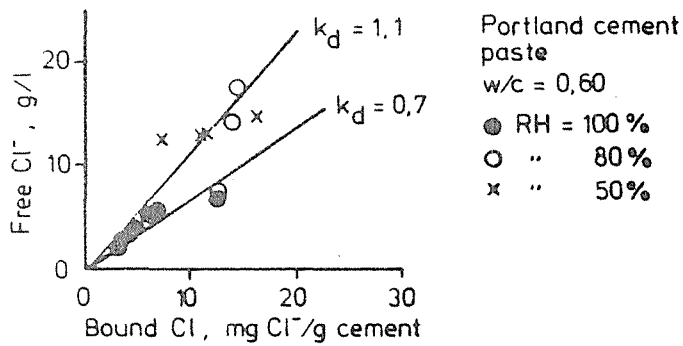


FIG 4. Measured free chloride concentration as a function of the bound chloride per weight unit cement.

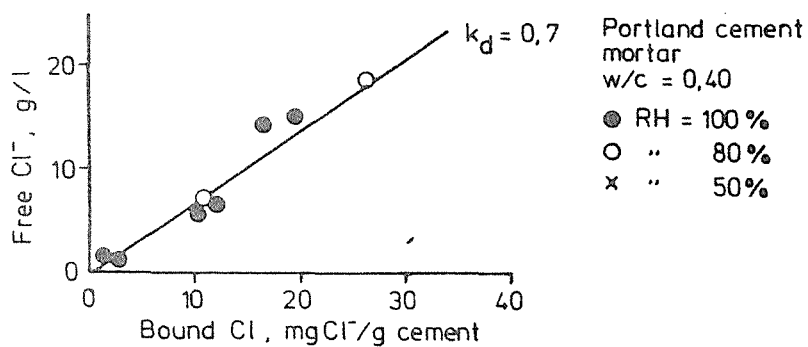


FIG 5. Measured free chloride concentration as a function of the bound chloride per weight unit cement.

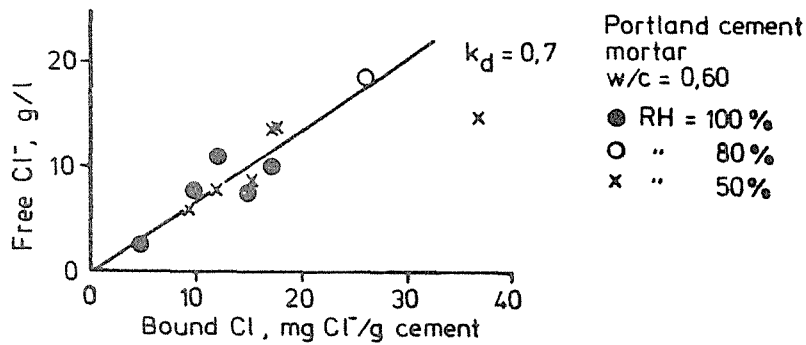


FIG 6. Measured free chloride concentration as a function of the bound chloride per weight unit cement.

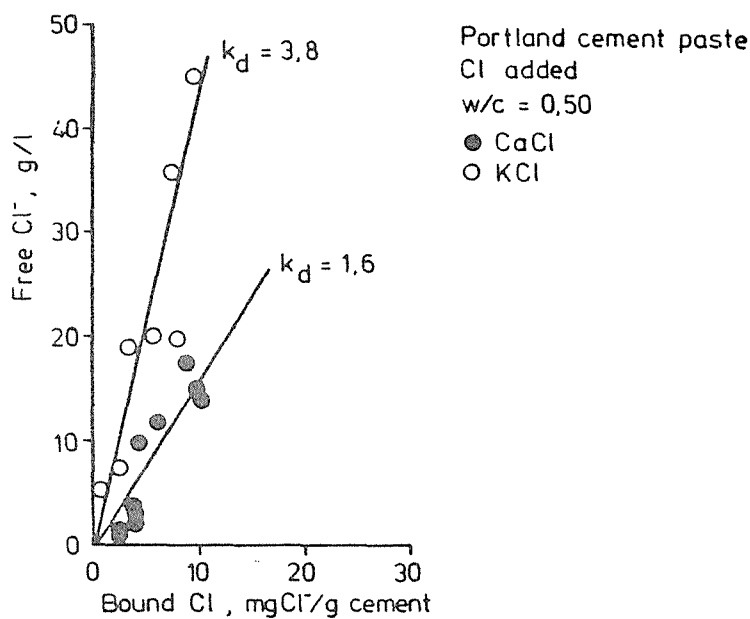


FIG 7. Measured free chloride concentration as a function of the bound chloride per weight unit cement.

#### 4.2 Diffusion with chemical reaction

It was assumed in the introduction that chlorides are, in some way, partly eliminated from the diffusion process. In the simplest case, where a chemical reaction and a physical adsorption consume chlorides immediately and where the free concentration,  $c_{\text{free}}$ , is directly proportionate to the bound concentrations,  $c_{\text{bound}}$ , according to the following equation:

$$c_{\text{bound}} = R \cdot c_{\text{free}}$$

where R is a constant.



The diffusion equation becomes, in one dimension:

$$\frac{\partial c_{\text{free}}}{\partial t} = D \frac{\partial^2 c_{\text{free}}}{\partial x^2} - \frac{\partial c_{\text{bound}}}{\partial t}$$

where  $t$  = time

$x$  = distance

This equation is the same as the pure diffusion equation if  $D$  is constant:

$$\frac{\partial c_{\text{free}}}{\partial t} = \frac{D}{R + 1} \frac{\partial^2 c_{\text{free}}}{\partial x^2}$$

where the constant  $D/(R + 1) = D_{\text{eff}}$ , effective diffusion coefficient.

In these tests and in the processing of the results, it has been assumed that the transport has followed the abovementioned equation in those cases in which the specimens were conditioned at 100% RH.

The effective diffusion coefficient has been calculated with the aid of concentration profile curves in accordance with FIG 8, where the measurement results have been plotted.

It can be seen from this figure that  $D_{\text{eff}} \cdot t/l^2 = 0.05$  to  $0.07$  for the plotted specimen, Portland cement mortar,  $W/C = 0.6$  and 71 days exposure. The effective diffusion coefficient lies between the values 7 to  $10 \cdot 10^{-12} \text{ m}^2/\text{s}$ .

Sometimes the specimens which have been taken have been so thick that the effective diffusion coefficient was difficult to determine. Consequently, the limits where the coefficient should lie have been specified for all the measurement batches.

Since several specimens were taken from the same quality but at different points in time and since the specimens have a different lengths, several values were received for the same test unit.

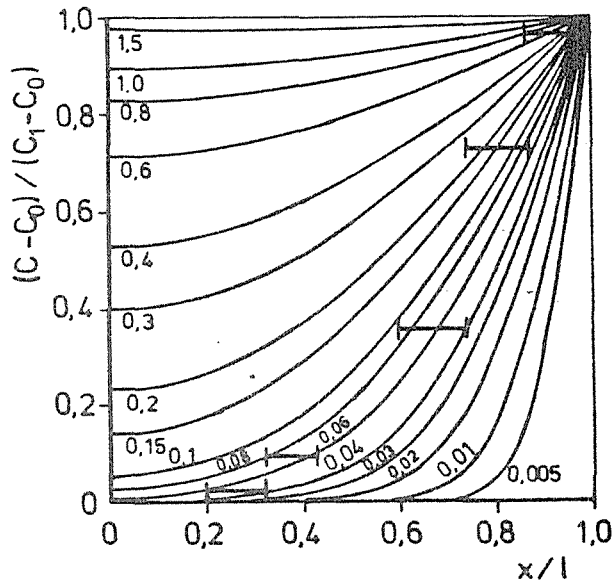


FIG 8. Concentration distributions at various times in the sheet  $-1 < x < 1$  with initial uniform concentration  $c_0$  and surface concentration  $c_1$ . Numbers on curves are values of  $Dt/l^2$ .

The results have been compiled in Table 2, which also indicates the varying ranges.

A concentration profile was obtained in a number of specimens which did not agree with the relation which had been assumed, Fick's diffusion with a bound chloride quantity which was directly proportionate to the free chloride concentration. In cases of this type, the innermost parts of the specimens have been used when calculating  $D_{\text{eff}}$  since the coefficient became greatest there. Sometimes too low a concentration was obtained in the surface layer in relation to the mathematical calculation. This was probably due to a measuring error, perhaps as a result of an error in the sampling volume during the analysis. It should be noted in this context that the concentration in the surface layer became higher in a number of cases than the value which was theoretically possible.

In order to shed light on the effects of capillary suction on chloride solution, FIG 9 present measured concentration profiles for specimens which were partly permitted to dry out compared with specimens which were kept saturated with moisture all the time.

Table 2. Calculated effective diffusion coefficients from measured free chloride concentrations in mortar and paste.

Cement type	Paste/Mortar	W/C	Porosity (%)	$D_{eff}$ ( $m^2/s \cdot 10^{-12}$ )
Portland	Paste	0.40	38	1 - 10
"	"	0.60	50	3 - 14
"	Mortar	0.40	15	0.8 - 5
"	"	0.60	23	4 - 12
Slag	Paste	0.40	45	0.3 - 0.7
"	Mortar	0.40	17	0.6 - 1
"	"	0.60	24	0.5 - 1

## 5 Discussion and summary of results

### 5.1 Free, bound and total chloride

The results can be summarized as follows:

- o Chlorides were bound to a greater extent in the mortar which was used compared with the cement paste, for example, FIGS 3 and 5. This applied particularly to the less permeable paste with W/C = 0.40. The reason may have been that the less permeable paste did not have the same accessibility for chlorides as mortar had. A lengthier exposure time might have entailed a higher degree of binding in the low permeable paste.
- o The quantity of chlorides bound in Portland cement products is, in the case of lengthy exposure times, independent of whether the chlorides were added during mixing or if they were later transported into the material. This can be regarded as correct since the chemical equilibriums are gradually stabilized, unless the reactions are irreversible and possible only during the hydration of the cement - assumptions not supported by the test.

- o The quantity of bound chloride is dependent on which salt the concrete is exposed to, see FIG 7.  $\text{CaCl}_2$  gives a larger quantity of bound chloride than does KCl. This can also be explained chemically. The positive ion Ca changes over on release from  $\text{CaCl}_2$  to  $\text{Ca(OH)}_2$  and is precipitated due to the fact that the solution is already supersaturated. KCl changes over to KOH, which is not precipitated and which therefore counteracts continued chloride binding.
  
- o Bound chloride in relation to free chloride can be independent of the W/C for mortar if the bound chloride is counted per weight unit cement, see FIGS 5 and 6. A higher cement content per  $\text{m}^3$  concrete would thus give increased corrosion protection in chloride environments. This has been well known since concrete of a higher quality has always been selected in environments of this type.

## 5.2 Chloride diffusion in concrete

The values measured for the effective diffusion coefficient for chloride in concrete are between 3 and 5 times the power of 10 lower than for chloride in pure water. This can be regarded as theoretically correct since the solid phase in concrete prevents chlorides from being transported through the material. Furthermore, the channel system which exists in concrete is complex and gives a meandering path for the transport of the chlorides. These two factors should reduce the transport rate by about 3 times the power of 10. This has also been measured for many different substances in concrete. The permeability of the material is further increased by its ion-changing capacity. It should be noted here that although the slag cement specimens appear to have a lower absorption capacity of chlorides compared with Portland cement, the material is up to 10 times less permeable than the Portland cement specimens. The pore system is probably so designed that the large chloride ions can only utilize a small part of the pore system during their transport in the slag cement specimens or else the chemical composition is such that the chlorides are weakly repellent to the material.

Furthermore, the slagcement specimens were not as sensitive to W/C with regard to the value of the effective diffusion coefficient.

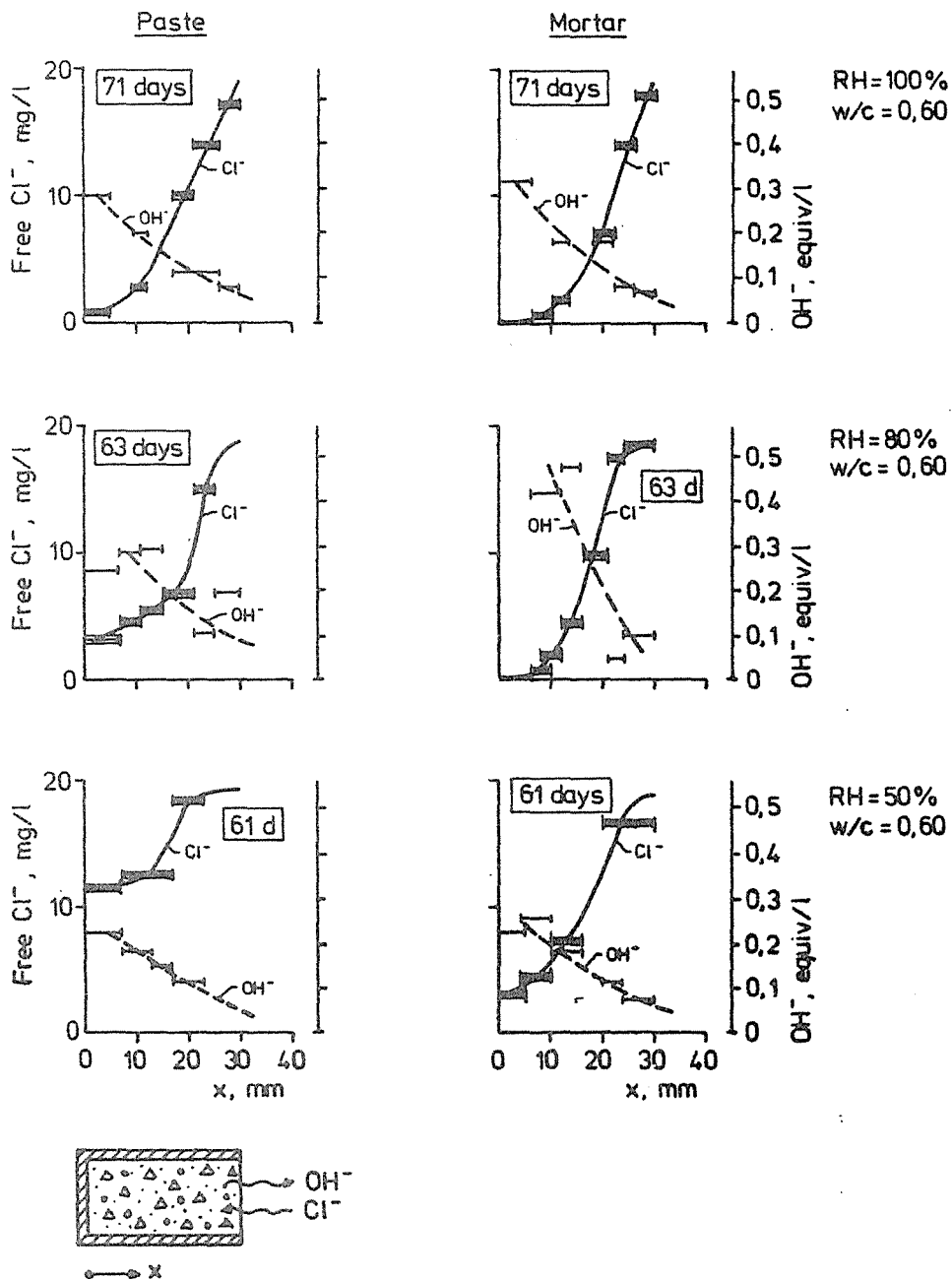


FIG 9. Measured  $\text{Cl}^-$  and  $\text{OH}^-$  concentration in squeezed out pore solution

In other respects, the measured values can be said to correspond to expectations and to show satisfactory agreement with previous experience, see, for example, Short and Page /1981/.

Tests with specimens which had partly dried out show that a capillary suction rapidly transports chlorides into concrete. A marked effect is obtained as the result of drying out in 50% relative humidity compared with drying out in 80% relative humidity. The exposure time is, however, very short, approximately 70 days, and only one moistening operation, in a salt solution, occurred in the experiment. This is very different from practical structures which may be constantly moistened and dried out.

As was the case for the absorption results, a cement mortar gave lower chloride concentrations compared with the paste specimens. The explanation is that paste binds smaller quantities of the mortar according to the results in the preceding section.

The hydroxide concentration in the specimens after the experiments was affected very little, on the other hand, by drying out. It should be noted, however, that the specimens were dried out in air free from  $\text{CO}_2$ . The explanation for this may be that the liquid which flowed in at the start of the test had the opposite direction to the  $\text{OH}^-$  which was diffusing out. Furthermore, it should be mentioned that the solution in which the specimens were stored became basic fairly rapidly.

The measured values for the  $\text{OH}^-$  concentration which are presented have the same order of size as the theoretically calculated values if one assumes that almost all the K and Na which occurs in the cement is dissolved in the pore solution.

## 6 SUMMARY

Small bars made of cement paste and mortar, conditioned in various climates were after conditioning analyzed for the substances Cl and OH.

The measurements were made on a pore solution which had been pressed out of these samples.

The results have been used to calculate the chloride bounding capacity and effective diffusion coefficient for different qualities.

The relation between free chloride in pore solution (g/l) and bound chloride per cement weight (g Cl<sup>-</sup>/ kg cement) amounted to about 0.7 for mortars with a W/C-ratio between 0.4 and 0.6.

The effective diffusion coefficient for chloride ions in mortar varied from 0.8 to 12 m<sup>2</sup>/s x 10<sup>-12</sup>, for samples made of ordinary Portland cement (Slite) and from 0.5 to 1 m<sup>2</sup>/s x 10<sup>-12</sup>, for samples made of slag cement.

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