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AN INVESTIGATION OF EXPERIMENTAL METHODS USED TO DETERMINE FREE AND TOTAL CHLORIDE CONTENTS

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ABSTRACT

The free chloride content in cement pastes may be assessed by analysing the pore solution expressed under pressure using a pore press, or achieving an equilibrium between a known external solution and the pore solution, while the total chloride content is commonly determined using acid soluble extraction. A comparison of these techniques indicates that loosely bound chloride is released during pore solution expression under pressure and this may result in a significant overestimation of the free chloride content. Chloride binding relationships determined in this manner may produce errors when used in modelling chloride transport as the expressed pore solution concentration can be significantly greater than that in the contaminating solution. Furthermore acid soluble extraction may underestimate the total chloride content. The use of ultrasonic treatment to accelerate the achievement of equilibrium also results in the release of loosely bound chloride which in turn limits the chloride taken up by such samples.

Introduction

The determination of the degree of chloride binding in concrete is of significant interest as it strongly affects the rate of chloride ingress,(1, 2). Two suggested methods aimed at determining the free chloride level involve either expressing the pore solution from a cement or mortar sample by applying pressure using a pore press(3), or achieving an equilibrium between an external solution of known concentration and the pore solution(4, 5). In the first case the free chloride concentration is given by its concentration in the expressed solution. In the second case it is given by the concentration of the external storage solution. The free chloride content expressed by weight of cement may then be calculated using the free water content, often assumed to be equal to the evaporable water content.

Other methods of assessing the free chloride content are based on mixing powdered samples with a solvent and measuring the amount of chloride passing into solution. These are

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prone to errors resulting from the reversible nature of some binding reactions. Thus the soluble chloride measured is dependent on test variables such as the agitation time of the powder/solvent mixture(6). Pore solution expression under pressure has been shown to be significantly more accurate than some of these extraction techniques(7).

The use of the pore press is well established and much data has been acquired in this manner(1, 8, 9). It has however been noted that this technique may overestimate the free chloride levels and the free chloride levels determined may be 20% higher than the true values(7). Other reported data have surprisingly produced expressed pore solution concentrations which were twice that in the surrounding contaminating solution(10). The use of the pore press also presents difficulties when applied to concrete and elaborate specimen preparation techniques dealing with the presence of coarse aggregate particles(11) may further impair the accuracy of the method in these circumstances.

It has also been noted that the determination of the total chloride content using acid soluble extraction may be inaccurate. While the quantity of chloride extracted increases with the nitric acid concentration and temperature, even aggressive conditions such as boiling nitric acid, may result in less than 90% of the total chloride being determined(12). Similar inaccuracies are also present in other reported data at low chloride contents(13).

The equilibrium method has been used to produce standards for the assessment of other methods and is therefore considered to be fairly accurate(7). However it has the disadvantage of being time consuming. Up to 1 year has been required to achieve equilibrium on cement paste samples which were 10 mm thick(14). To accelerate the method it has been suggested that samples could be coarsely ground(4, 5). This is however likely to increase the active surface area available for binding and allow further hydration which in turn may affect the accuracy of the method.

This work on chloride binding provides further evidence of the errors which may result when pore solution expression under pressure is used in the determination of the free chloride content and acid soluble extraction is used to assess the total chloride content. Furthermore, the novel use of ultrasonic treatment of samples stored in a chloride solution as an alternative method of accelerating the ingress of chloride is examined. This will agitate the pore solution and is thus expected to hasten the achievement of equilibrium or steady state conditions.

Experimental Methods

Cylindrical cement samples of w/c 0.5 were cast in 49 mm diameter moulds which were then sealed and rotated slowly for 24 hours to prevent segregation. The oxide composition of the cement and its calculated Bogue composition is given in Table 1. After 28 days curing at

TABLE 1

Oxide and Bogue Composition of the Cement

Oxide Composition									Bogue Composition			
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	Ig. Loss	C_3S	C_2S	C_3A	C_4AF
64.7	20.7	4.6	3	1	0.13	0.65	3	1.3	62.2	12.4	7.12	9.12

22°C the samples were removed from the sealed moulds, sliced into 5 mm thick discs and stored in saturated lime water for 1 week. The evaporable and non-evaporable water was then determined by heating to 105°C and 1050°C and the remaining discs from each casting were stored in sealed containers holding 0.132 l of storage solution. The storage solution initially contained 0.135M sodium chloride (NaCl) and 0.3M sodium hydroxide (NaOH).

Five of the containers were subjected to ultrasonic treatment by placing them in an ultrasonic bath (DAWE Sonicleaner type 6444A) for 2 periods of 30 minutes each per day on five days of the week. At intervals containers holding both the ultrasonically treated and untreated samples were removed for analysis. One additional set of discs was stored normally while another was subjected to ultrasonic treatment for a period of 45 days. The treatment regime was then swapped and, after a further 15 days, samples were removed for analysis.

The acid soluble chloride was determined on one disc. This was ground, treated with boiling nitric acid and filtered to remove a grey residue which was washed. The pore solution in the remaining disks was expressed under pressure using a pore press as previously described(8). The acid soluble chloride together with the chloride content of the expressed pore solution and the storage solution were analysed by potentiometric titration against silver nitrate.

Results

The evaporable water content of the samples determined from the weight loss occurring at 105°C after they had been stored in lime water for 7 days was 40% by weight of cement while the non-evaporable water content determined at 1050°C was 18%. The determination of the non-evaporable water content took into account the ignition losses.

The time dependence over a sixty day period of normal storage (no ultrasonic treatment) of the chloride content in the expressed pore solution and external solution as well as the acid soluble chloride content is given in Table 2. As the result of variations in the sample weights, the initial chloride content available for contamination varied when expressed per unit weight of cement although the variation between samples subjected to the same treatment is small.

The acid soluble chloride content increased while the storage solution concentration decreased consistently over this period with no evidence that an equilibrium or steady state condition had been reached. With the exception of the anomalous behaviour between 28 and 60 days, the chloride concentration in the expressed pore solution also exhibited a general increase to values significantly higher than the external storage solution concentration.

TABLE 2
Results Obtained on Samples Subjected to Normal Storage

Storage Duration (days)	Sample Weight (wet) (g)	External Solution			Pore Solution Cl^- Concentration		Acid Soluble Cl^- (% cement)	Calculated Total Cl^- (% cement)
		Initial Cl^- (% cement)	Final Cl^- (mole/l)	Final Cl^- (% cement)	(mole/l)	(% cement)		
7	159.13	0.63%	0.059	0.27%	0.040	0.057%	0.32%	0.35%
14	157.62	0.63%	0.053	0.25%	0.051	0.072%	0.37%	0.38%
28	156.95	0.64%	0.050	0.23%	0.064	0.091%	0.39%	0.40%
60	157.24	0.63%	0.048	0.23%	0.062	0.087%	0.41%	0.41%

TABLE 3
Results Obtained on Samples Subjected to Ultrasonic Treatment

Storage Duration (days)	Sample Weight (wet) (g)	External Solution Initial Cl⁻ (% cement)	External Solution Final Cl⁻ (mole/l)	External Solution Final Cl⁻ (% cement)	Pore Solution Cl⁻ Concentration (mole/l)	Pore Solution Cl⁻ Concentration (% cement)	Acid Soluble Cl⁻ (% cement)	Calculated Total Cl⁻ (% cement)
7	173.16	0.58%	0.056	0.24%	0.050	0.071%	0.30%	0.34%
14	169.57	0.59%	0.052	0.22%	0.051	0.072%	0.35%	0.36%
28	172.33	0.58%	0.051	0.22%	0.052	0.074%	0.34%	0.36%
45	170.48	0.59%	0.051	0.22%	0.051	0.073%	0.34%	0.37%
60	170.98	0.58%	0.050	0.22%	0.052	0.074%	0.34%	0.37%

Table 3 gives the results obtained when the samples were ultrasonically treated. After 14 days the chloride concentration of the external storage solution and the expressed pore solution as well as the acid soluble chloride content stabilised. The chloride concentration of the expressed pore solution was marginally higher than the storage solution concentration after longer storage periods, although this difference may be insignificant. The acid soluble chloride levels were significantly lower than the maximum achieved in the absence of treatment. This would partly result from a reduction in the available chloride per unit weight of cement in the case of the samples which were ultrasonically treated as these samples weighed typically 8.6% more than the untreated samples.

The total chloride content of the samples can be calculated by assuming that it is equal to that removed from the storage solution. The results are given in Tables 2 and 3. It may be noted that the calculated total chloride content was consistently higher than the measured acid soluble chloride content. In the case of ultrasonically treated samples this difference, expressed as a percentage of the calculated total, was typically 7.4% while a smaller difference of typically 4.1% was observed on untreated samples.

The effect of ultrasonic treatment (UT) after a period of normal storage (NS) and normal storage after a period of ultrasonic treatment is given in Table 4. It can be seen that, when compared with 60 days of normal storage, 45 days of normal storage followed by 15 days of ultrasonic treatment results in more chloride remaining in the external solution, a lower acid soluble chloride content and an expressed pore solution concentration close to that of the storage solution. Similarly, when compared with 60 days of ultrasonic treatment, 45 days of ultrasonic treatment followed by 15 days of normal storage results in less chloride remaining in the external solution, more acid soluble chloride and an expressed pore solution chloride concentration above that of the storage solution.

TABLE 4
Results Obtained on Samples Subjected to Period of Normal Storage and Ultrasonic Treatment

Treatment	Sample Weight (wet) (g)	External Solution Initial Cl⁻ (% cement)	External Solution Final Cl⁻ (mole/l)	External Solution Final Cl⁻ (% tot. Cl⁻)	Pore Solution Cl⁻ Concentration (mole/l)	Pore Solution Cl⁻ Concentration (% tot. Cl⁻)	Acid Soluble Cl⁻ (% cement)	Acid Soluble Cl⁻ (% tot. Cl⁻)
45NS+15UT	166.36	0.60%	0.051	37.98%	0.051	12.12%	0.36%	59.71%
45UT+15NS	169.22	0.59%	0.049	36.29%	0.056	13.31%	0.35%	59.80%
60 NS	157.24	0.63%	0.048	35.76%	0.062	13.72%	0.41%	64.50%
60 UT	170.93	0.58%	0.050	37.29%	0.052	12.59%	0.34%	58.54%

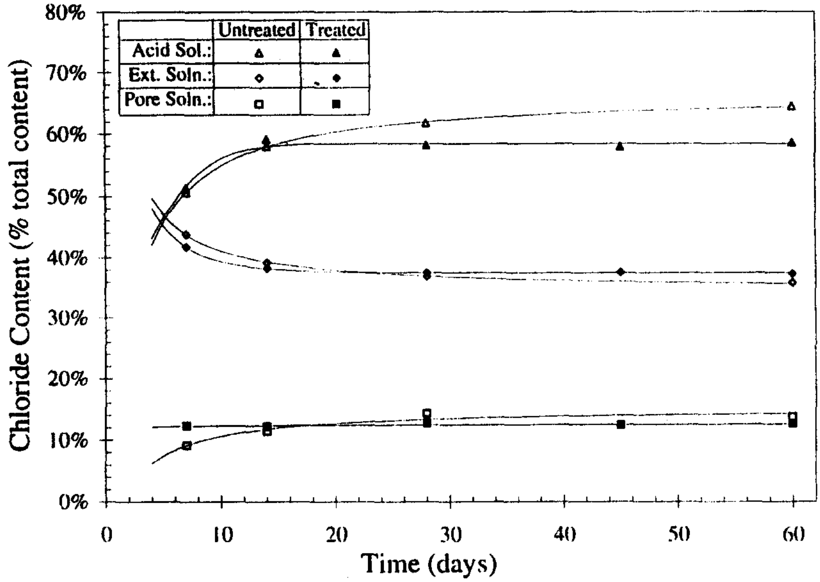

FIG. 1.

The acid soluble, storage solution and expressed pore solution chloride content of the ultasonically treated and untreated samples presented as a percentage of the total chloride in the system.

Discussion

The acid soluble, storage solution and expressed pore solution chloride content of ultrasonic treated samples is compared with untreated samples in Fig.1. To minimise the effect of the variation in initial sample weights, the plotted values are presented as a percentage of the total chloride in the system (the initial chloride content of the storage solution) expressed relative to the cement weight. As expected ultrasonic treatment significantly reduces the time required to achieve equilibrium or steady state conditions. However, while it initially results in the more rapid removal of chloride from the storage solution, after 28 days higher acid soluble and expressed pore solution chloride contents as well as lower storage solution chloride contents were observed in the absence of treatment. In all cases more than 50% of the initial chloride content of the storage solution was taken up by the samples.

The calculated total chloride contents (Tables 2 and 3) suggest that total chloride is underestimated when determined by acid extraction. As noted in the introduction, similar observations have previously been reported(12, 13). These may partly be due to errors associated with the method, such as the loss of vapour borne chloride on exposing the sample to boiling nitric acid. Other possible explanations include adsorption of some chloride onto the walls of the storage container and the retention of some strongly bound chloride in the insoluble residue filtered out prior to the determination of the chloride content. The difference between ultrasonically treated and untreated samples may be attributed to the retention of more strongly bound chloride in the insoluble residue after treatment. This explanation would also partly account for the large difference in acid soluble chloride content between the treated and untreated case after correcting for the variable initial sample weights in Fig.1. However the range of differences, particularly in the case of the normal storage results (Table 2), suggests that further work is needed to confirm this.

The high chloride concentrations in the expressed pore solution after normal storage, which in many cases were higher than the storage solution concentrations (Table 2), confirms similar observations previously reported(7, 10). This probably results from the release of loosely bound chloride when the pore solution is expressed. After 60 days normal storage, the expressed pore solution concentration was 30% above the storage concentration and is likely to increase when an equilibrium or steady state condition is reached.

When compared with normal storage, ultrasonic treatment results in a significant reduction in the difference in chloride concentrations in the expressed pore solution and the storage solution (Table 3). Further confirmation of this is provided by the data given in Table 4. It is postulated that this results from release of loosely bound chloride during treatment effectively preventing the sum of the loosely bound plus free chloride content, which would be present in the expressed pore solution, from rising above that in the storage solution. This reduction in the level of effective chloride binding when the samples are subjected to the ultrasonic treatment would also explain the differences in the expressed pore solution, storage solution and acid soluble chloride contents after 60 days storage in Fig.1.

It is evident from the above discussion that ultrasonic treatment will have limited practical use in accelerating the equilibration process due to its direct effect on chloride binding. It may also promote hydration and affect the microstructure of the sample which in turn will also influence the binding capacity of the sample tested. However the data in Table 4 indicates that even after a period of ultrasonic treatment, a period of normal storage will result in the concentration of the expressed pore solution rising above that of the external solution. The only reasonable explanation for these findings at present is that both pore solution expression under pressure and ultrasonic treatment result in the release of loosely bound chloride.

The difference between the results of the equilibrium method and those of the pore solution expression method will be determined by the ratio of loosely bound chloride relative to that in the pore solution. This will depend on factors such as the cement type and pore solution chloride concentration. For example an effective restriction in the number of binding sites may result in a smaller difference between the storage solution and the expressed pore solution concentration as the chloride concentration increases. Such factors may give rise to a range of differences between the equilibrium and pore solution expression methods.

In the above discussion chloride has been classified as being free if its concentration in the pore solution cannot exceed that of the storage solution, loosely bound if it is released into the pore solution expressed under pressure, bound when it is not released by pore solution expression and perhaps strongly bound when it is not released by acid extraction. All forms of chloride binding will affect chloride ingress through their effect on the concentration gradients in the pore solution. Thus binding isotherms determined by pore solution expression under pressure may result in some inaccuracies when used in modelling chloride transport as the expressed pore solution concentration can have values greater than the external solution concentration. It has however been noted that bound chloride may still present a corrosion risk(10, 15) and thus techniques which permit the determination of various degrees of binding may prove to be useful.

Conclusions

Pore solution expression under pressure results in the release of some loosely bound chloride which in turn may result in an overestimation of the level of free chloride. Failure to take this loosely bound chloride into account may result in errors when using the resulting binding relationship to model chloride transport.

Acid soluble extraction may underestimate the total chloride content of samples. Possible reasons for this include errors associated with the method as well as its failure to release all strongly bound chloride.

Ultrasonic treatment of samples accelerates the ingress of chloride and the achievement of equilibrium or steady state conditions. However it also releases loosely bound chloride which results in a lower total chloride content for a given concentration of the source of chloride.

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