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Experimental Studies Of The Chloride Permeability Of Concrete

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Abstract

The effects of concrete mix variables on chloride ion permeability were examined using three series of experiments, designed to identify those effects that are measured by the Rapid Chloride Permeability Test. Standard aggregates were used in one series of experiments, but specialized aggregates designed to illustrate the effects of the tortuosity of diffusion paths were used in the other two series. While the volume fraction of aggregate was found to dominate the resistance to chloride permeability, significant effects attributed to interfacial transition zones (ITZs) and tortuosity were also found, particularly for concretes with water-to-cement ratios less than 0.4.

1 Introduction

An important measure of concrete durability is the diffusivity of chloride ions. An understanding of the relationships between chloride ion diffusivity and concrete mix design is needed to develop durability-based mix design procedures. While significant research results have been reported towards enhancing this understanding [1, 2], much work remains to be done. In this paper, it is shown how a statistical approach can be used to develop an experimental program that investigates the aforementioned relationships. A preliminary interpretation of the experimental results is also presented.

1.1 Measurement of Chloride Diffusion Rates

A standard measure of chloride ion diffusivity is the Rapid Chloride Permeability Test (RCPT), in which ionic transport is accelerated by an applied electric field [3, 4]. RCPT exploits fundamental similarities between the transport of chloride ions by diffusion under concentration gradients and by conduction under potential gradients. The relationship between the diffusion and conductivity coefficients is given by the

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Nernst-Einstein relation [5]. Since the measurement of conductivity can be carried out in less time and with less complicated techniques than measurements of diffusion, conductivity measurements have been used to compare the chloride diffusivities of concrete of differing compositions.

In this work, the Rapid Chloride Permeability Test (RCPT) [6] was chosen as the technique for making these comparisons, after some modifications which are discussed below. Whiting [3] describes the development of the test method and its correlation to the 90-day ponding diffusion tests.

1.2 Chloride Diffusivity and Mix Variables

Since most aggregate is relatively impermeable to chloride ions, the ionic transport occurs through the cement phase surrounding the aggregate particles. Consequently, the permeability of the material is determined both by the microstructural properties of the cement phase and the mesostructural properties of the aggregate phase. The ionic transport through the cement phase occurs through a complex pore network and is controlled by the amount of evaporable water present in the paste, and the concentration of the mobile ions in the pore fluid [6]. Thus, for concrete made with ordinary portland cement, the mix parameter with a direct influence on the microstructural properties is the water-to-cement ratio. As for the concrete mesostructure, there are two mix parameters that are important. The relative proportions of different grades of aggregate and the shapes of the aggregate generate the network of permeable material, and potentially could be of use in designing concretes with low chloride permeability.

The interaction between the aggregate and the cement influences the transport properties of chloride ions by a combination of three basic mechanisms.

(1) **Dilution** Concretes with high volume fractions of aggregate would have less cement available in which transport could take place. This mechanism, in its simplest form, would induce a linear dependence of chloride permeability on the volume fraction of aggregate.

(2) **Tortuosity** As the volume fraction of aggregate increases, the paths that the chloride ions follow through the material become longer and more twisted in order to pass around the impermeable material. This phenomenon, known as tortuosity, has been studied in colloidal dispersions [7], catalysis [8], porous rocks [9], and in concrete itself [10, 11, 12]. Tortuosity effects would appear as a reduction in permeability below that expected from dilution alone. For spherical aggregate, Maxwell's theory shows that the rate of increase in tortuosity is larger at low aggregate volume fractions as compared with higher volume fractions. Thus, the combination of dilution and tortuosity would induce a decreasing,

yet concave effect of chloride permeability as the volume fraction of aggregate increases.

(3) **ITZ Effects** The interfacial transition zone (ITZ) is a thin layer of cement paste in contact with the aggregate particles, with higher porosity, conductivity and w/c ratio than the surrounding bulk cement paste [13]. The formation of the ITZ is due to the so-called wall effect during cement hydration and its thickness has been suggested to be in the 10-50 micron range. The higher permeability of the ITZ results in a higher permeability of the concrete. As the quantity of aggregate increases, the ITZ phases would be closer to each other, and an effect, which is similar but not identical to percolation, would occur resulting in markedly higher conductivities [14]. However, the greater w/c ratio of the ITZ implies that the surrounding matrix would have a w/c that is lower than what is anticipated in the original mix design. This would cause a reduction of permeability in concrete with a relatively large ITZ phase, as determined by the total surface area of the aggregate.

Garboczi and his colleagues [15] developed quantitative models for these mechanisms, and compared the model results with experimental data for relatively simple mortars and simulated data from a pixel-based computational model for concrete. The purpose of the present study is to develop an experimental program, using statistics-based experimental design methods, to obtain sets of permeability data which may provide further insight into the effects of the preceding three mechanisms. A summary of the statistics-based experimental program, resulting data, and a preliminary analysis are presented herein. Although these data has been compared with predictive models of permeability [16], further study is needed to explain the complex interaction between the mechanisms.

1.3 Experimental Program

The experiment program consisted of three studies. Each study built upon techniques and observations developed in the previous study.

1.3.1 Pilot Study: Spherical Aggregate in Paste

In order to be able to distinguish between the effects of dilution and tortuosity, the initial series of experiments used alumina spheres as aggregate, with cement paste providing the matrix. Two sizes of alumina spheres were used in order to alter the tortuosity of the matrix without affecting the volume fraction of aggregate.

1.3.2 General Study: Statistically Designed Concrete Mixes

Owing to difficulties with the alumina ball aggregate from the pilot study, a gapped grading of aggregate [17] that was geometrically similar to the alumina balls was used in combination with a mortar. To provide as much information as possible concerning the effect of mix variables on chloride permeability, the values of the mix variables were determined using statistically based experimental design techniques. This approach resulted in some mix designs that fell outside the standard mix designs used in practice.

1.3.3 Specific Study: Standard Concrete Mixes

In the specific study, the mix designs were limited to standard mix designs at a constant, moderate level of workability [17]. Furthermore, the study was statistically designed to estimate all of the possible sources of permeability variation that might occur in concrete preparation, as explained in the next section. The materials used were chosen to allow the optimal use of image analysis techniques, which proved to be vital in extracting information from the data in the general study.

2 Experimental Technique

Statistical concepts were used in the planning stage, during implementation and in the final analysis of the results in order to make best use of the available information. With these techniques, it was possible to maximize the information gained in experiments where resources were limited.

2.1 Design of Experiments

Since the effects of the concrete mix variables on permeability were of primary interest, these variables were used as the experimental factors. In the pilot study, standard experimental designs were used to determine the levels for the factors for each specimen and to block the experiment, i.e. assign specimens to mix batches. The theoretical basis of this procedure can be found in Cox [18] and Box *et al.* [19]; more applications oriented accounts can be found in Mead [20] and Montgomery [21]. In the specific study, a significantly larger number of factors and levels were of interest. To keep the total number of specimens at a manageable size, it was necessary to use a non-traditional experimental design based on the work of Ankenman *et al.* [22].

2.1.1 Pilot Study

The pilot study involved a very simple two-factor experiment. These factors were:

(1) Volume Fraction of alumina balls, defined as

$$VF = \frac{\text{Volume of 6mm } \phi \text{ and 12mm } \phi \text{ alumina balls}}{\text{Total volume of concrete}}$$

(2) Relative proportion of coarse aggregate, defined as

$$AP = \frac{\text{Volume of 12mm } \phi \text{ Alumina Balls}}{\text{Volume of 6mm } \phi \text{ and 12mm } \phi \text{Alumina Balls}}$$

Only two levels of each factor were considered, making a total of four combinations of the two. The materials were chosen specifically so that AP and VF could be estimated from the samples after destruction of the matrix in a oven. Two cylinders were made for each combination of factors, and three slices were cut from each cylinder.

2.1.2 General Study

The intent of this study was to examine chloride permeability for a broad range of concrete mixes. This was achieved by including an additional experimental factor and increasing the number of levels for each factor from two to six, so that six different volume fractions were used instead of the original two. In addition, standard coarse aggregate was used in place of the alumina. A gapped grading was used for the coarse aggregate, made by combining what was retained in the 9mm and 12mm sieves in one of six fixed ratios. These particular sizes were chosen on account of their being similar in size to the alumina balls used in the pilot study.

The three experimental factors used were:

(1) The volume fraction of aggregate (VF).

(2) The water-to-cement ratio (WC).

(3) The proportion of coarse aggregate, as defined by

$$AP = \frac{\text{Volume of 12mm } \phi \text{ Coarse Aggregate}}{\text{Volume of 9mm } \phi \text{ and 12mm } \phi \text{ Coarse Aggregate}} \quad (1)$$

If the experimental design procedure for the pilot study had been used, $6^3 = 216$ different combinations of the factors would have been required. To reduce the experimental effort, a subset of 36 possible combinations was taken, using algorithms for space-filling designs [23]. This reduction was implemented through the ACED algorithm [24] in such a way that all $6^2 = 36$ different combinations of AP and VF levels were included, and so that these combinations were evenly spread out among the 216 possible combinations. Due to the wide variability of the mix designs, some of the resulting concrete specimens exhibited unusual characteristics such as extreme segregation or high unworkability. Also, only one cylinder was tested for each of the 36 combinations, and so it was not possible to statistically model the inherent random variability in the experimental results. It was decided that at this stage, the information gained from examining the 36 combinations of mix variables was more important than the information which would be gained from modeling the inherent variability.

2.1.3 Specific Study

In this study, standard mix designs using standard aggregate gradings were used. The three experimental factors were:

(1) The maximum aggregate size (9mm sieve or 19mm sieve).

(2) The water-to-cement ratio (0.38, 0.45, 0.52).

(3) The grading of the coarse and fine aggregate (four standard grades for each maximum aggregate size).

The volume fraction of aggregate was chosen such that each concrete mix had a constant moderate level of workability [17]. The total number of possible factor combinations is $2 \times 3 \times 4 = 24$, and all 24 of these combinations were used in a full factorial experimental design. While this aspect of the experimental design was standard, the model for the error was not. In the standard model for the inherent random variability in an experimental trial, it would be assumed that every observation of the permeability consisted of a simple function of the mix variables, plus a random error term having the same distribution in each trial. In the case of this experiment, the error terms would have three contributions, known as variance components.

(1) The variation between batches, caused by differences in mixing, pouring, and other processes associated with the manufacture of each batch of concrete. This will be designated as the *batch-to-batch variance.*

(2) The variation between the cylinders, caused by each one getting a different sample of the aggregate size and shape distribution out of the batch. This will be designated as the *cylinder-to-cylinder variance.*

(3) The measurement variability of the RCPT, the variability of aggregate content in different slices cut from the same cylinder, and any unexplained sources of variation. These components cannot be

separated from each other, and will be known as the *slice-to-slice variance.*

All of these variance components would appear in the test of a core taken from concrete poured in the field, and so it is necessary that all of these variance components be estimated. Because the destructive nature of the RCPT made estimation of measurement error impossible, it was not possible to use experimental design methods to isolate this component from the slice-to-slice variation within each cylinder.

To estimate all three variance components for each of the 24 concrete mix designs, it would be necessary to make at least two batches for each mix and at least two cylinders from each batch, resulting in $24 \times 2 \times 2 = 96$ specimens. In order to reduce the experimental effort, it was decided that for each composition, either two batches would be made with a single cylinder tested from each, or a single batch would be made and two cylinders from that batch would be tested. As long as the batch-to-batch and cylinder-to-cylinder variances were unaffected by the composition, this would lead to a reduction of the number of tests by 50% while still allowing estimates of the variance components from a reasonable number of observations. The details of this design are given in Ankenman *et al.* [22], while general discussions of this type of model are given in the books by Scheffé [25] and Searle *et al.* [26].

2.2 Materials and Procedures

The concrete was cast in 100mm diameter x 200mm high cylindrical molds. The specimens were stored under water until testing to reduce shrinkage. At the time of testing, the top and bottom 25mm of the cylinders were cut off and discarded to reduce edge effects. The remaining 150mm of each cylinder was cut into three 50mm thick disks. These slices were labeled Top, Middle, and Bottom, relative to the orientation in which the cylinder was cast. All tests occurred on random days chosen before the start of the experiment so as to ensure that the atmosphere on the day of the test or any inexperience on the part of the experimenters in early testing would be confounded with the results for a particular composition of concrete.

2.2.1 Pilot Study

The cement paste was prepared by mixing ordinary Type 1 Portland cement and water, in a water/cement ratio of 0.3. No sand was used. Alumina balls were mixed into the cement to yield four batches, from each of which two cylinders were cast. The concrete was cured for 90 days on average before being tested.

At the end of the experiment, exact determinations of the AP and VF for each cylinder were made by destructively firing the samples in a oven until only the refractory alumina balls were left intact. This procedure gave exact measurements of these quantities, which would not have been available had not the aggregate been capable of surviving the destruction of the cement.

2.2.2 General Study

For these experiments, ordinary Type 1 Portland cement was used as the binder, and river gravel and sand were used for the aggregate phase. The sand had FM = 2.6. The coarser aggregate was chosen from that which was retained by the 9mm and 12mm sieves, and the contents of each sieve were mixed so as to give the appropriate AP as defined by (1). Four cylinders were cast for each composition, three of which were used for compression tests while the fourth was sliced and subjected to the RCPT. Once mixed, the cylinders were cured underwater for 28 days before being subjected to the RCPT.

2.2.3 Specific Study

For these experiments, ordinary Type 1 Portland white cement was used as the binder. This differed from the general study, where ordinary gray cement was used, but the cement was chosen so that it had substantially the same chemical and transport properties as the cements used in the previous studies. River gravel and sand were used, but instead of the gapped aggregate of the previous phase, standard gradings as determined from the British Standard Code of Practice (BS 5328 - 1991) and McIntosh & Erntroy curves [17] were used. The eight gradings used were divided into two groups of four, with the maximum aggregate size being that retained by a 19mm sieve for one group, and retained in a 9mm sieve in the second. The cement was mixed with water-cement ratios 0.38, 0.45, and 0.52, and all 24 combinations of gradings and w/c ratios were used. Six cylinders were made from each batch, with three reserved for compression tests and one or two retained as replacements. Initially, an experimental design criteria was used to divide the twenty-four compositions into two groups of twelve. For one group, two batches would be made and six cylinders cast from each batch. From each of these batches, one cylinder would be selected for the RCPT. For the other twelve compositions, only a single batch would be made, but two cylinders would be subjected to the RCPT. In several cases, extra batches of concrete were made for some compositions when time allowed.

The concrete was cured underwater for 28 days. Only the Top and Bottom slices were subjected to the RCPT.

2.3 The Rapid Chloride Permeability Test

The RCPT, whose standard procedure is given in ASTM C1202-94 [6], is widely used as a measure of the durability of concrete against chloride ion ingress. Since the test is sensitive to differences in pore solution chemistry and therefore exaggerates the effectiveness of supplementary cementing materials in reducing permeability, commonly used supplementary materials such as silica fume and fly ash were not used.

In the standard RCPT, a 60V DC voltage is maintained across the 50mm thick specimens, with measurements being taken of the average current during the first 15 seconds of the test, and of the total charge passed through the specimen over a 6 hour period. However, it has been stated that this relatively high voltage may lead to irreversible changes in the microstructure of concrete and possibly cracking. Visible degradation of the concrete was observed in some specimens in all three studies, which prevented the repeated testing of individual slices that would have been required for estimation of the measurement error associated with the RCPT. The degradation manifested itself quite clearly in the general study, where certain highly permeable specimens had greater than expected values for the final charge, given the initial current. When the observations in which the total charge exceeded 10,000 coulombs were excluded, the relationship between initial current and final charge was practically indistinguishable from that found in the data from the specific study. Therefore, the initial current was used in the analysis of the general study.

Slices were assigned to the four available cells randomly, so as to ensure that any effects associated with a specific cell would not confound any specific composition or cylinder location effects.

2.4 Image Analysis

In the pilot and general studies, the use of gapped aggregates resulted in segregation when the fresh concrete was vibrated in order to remove air voids. In the pilot study, destruction of the matrix in a oven allowed precise measurements of VF and AP to be made for each sample, but such an analysis was not possible in the general study. There, stereological procedures were used to estimate volume fractions from estimates of the total area of the faces of a slice of concrete that were contained in aggregate. Without such estimates, the effects of segregation would have rendered it impossible to obtain any information about permeability from the general study. Details of the procedure are given in a separate paper [27].

3 Results and Discussion

The results from all three studies illustrated the same basic behaviour. Permeability was consistently found to be most strongly determined by the volume fraction of aggregate, but the general and specific studies both illustrated the potential importance of ITZs and of dilution. In each case, the models were valid within the range of the data, but should not be extrapolated beyond it.

3.1 Pilot Study

The pilot study produced results which were suggestive, but which could not be generalized to the behaviour of real concrete. Electron microscope observations of the cement-alumina sphere interface revealed the presence of calcium carbonate, which is not in general seen at aggregate/cement interfaces. Even so, there was a non-linear dependence between accumulated charge and volume fraction that was concave, indicating that at the higher volume fractions, the concrete was more permeable than would be expected if the permeability was solely affected by dilution. This concavity is in agreement with the combination of dilution and tortuosity effects as described in Section 1.2. The model that best fit these data is given in Figure 1.

This model was extremely sensitive to the presence of one particular observation, which came from a top slice that had an unusually low AP value and an unusually high permeability. Once it was removed, any dependence on AP became statistically insignificant. For spherical aggregate without ITZ in a homogeneous matrix (such as cement paste), Maxwell's theory shows that AP does not affect permeability at fixed volume fractions. This may explain the behaviour in the pilot study.

3.1.1 General Study

For the results from the general study, the same non-linearity was found in the dependence of permeability on volume fraction, but in this case there was also a dependence on the water-to-cement ratio (WC) and on the aggregate proportion (AP). The initial current was used in place of the accumulated charge, as described in Section 2.3. The data are given in Figure 2 , while the model that best fit these data is given in Table 1.

As with the model in the pilot study, the model that best fit these data was concave, which can be attributed to a combination of dilution and tortuosity effects. The effects of AP and WC were considerably more complex, owing to the interaction between these two factors. Four major characteristics of this rela-

Table 1: Model For General Study Data

$$\log(\text{initial current}) = -1.3208 - 1.5072VF + 1.5624AP + 2.0267WC - 1.9381(WC)(AP) - 0.9286(VF)(AP)$$

Degrees of Freedom	56
Multiple R-Squared	0.8768

tionship are illustrated by the plots in Figure 3. This model would apply to gapped aggregate concrete of the type used in this experiment, as long as the WC was between 0.3 and 0.6 and the VF was between 0.4 and 0.9. Extrapolating beyond these limits would not be advisable.

- For small values of AP (all 9mm sieve aggregate), higher WC results in substantially higher permeability (Figure 3a). This characteristic can be attributed to the effect of WC on the permeability of the cement matrix phase.
- For high AP (all 12mm sieve aggregate), WC has very little effect on the permeability (Figure 3b). This implies that there must be an effect for high AP which counteracts the WC effect. Since the effects are essentially independent of the w/c ratio, this suggests that an ITZ effect or an unmeasurable effect due to bleeding or segregation might be responsible.
- For low WC, increasing the AP increases the permeability (Figure 3c). This can be attributed to two possible effects. At a given aggregate volume fraction, decreasing the AP results in higher surface areas, which yields a larger volume of ITZ. Since the ITZ draws water from the cement phase, the WC of the cement phase is less than the mix design, thereby reducing the permeability. The relation is the opposite to what might be explained by a tortuosity effect, and so ITZ transport may also be involved.
- For high WC, the effect of AP is the reverse of what is seen in the case of low WC (Figures 3d). This may be explained by the increase in tortuosity with increasing aggregate size, but may also involve unobservable segregation effects that affect the more segregation-prone high-w/c mixes.

The expected insignificance of AP predicted by Maxwell's theory which seemed relevant to the pilot study is not applicable to the general or specific studies because of the non-homogeneous nature of the mortar phase and because of the relative importance of the ITZ.

3.1.2 Specific Study

For the specific study, the relationships found were more complex. The use of standard gradings eliminated the segregation that made some specimens excessively permeable, and also confounded the effects of VF with the AP effects that had been seen in the general study. As a result, the relationships between mix variables and permeability are slightly different from what was seen in the pilot and general studies.

The model that best fit these data is given in Figure 4 below. Given the dramatic effect of WC on the results in the general study and the differences in structure between low WC and high WC matrix phases, one model was fit for each of the values of WC. Plots of these lines and the data from the specific study are also given in Figure 4. Four major characteristics of this relationship are illustrated by these plots.

- The first major difference between the specific study and the previous two studies is the general linear trend in the permeability. This behavior can be explained in terms of the dependence on AP noted in the general study. For the specific study, low volume fractions corresponded to gradings with roughly lower proportions of larger-sized aggregate. In the general study, this is quantified by a lower AP which resulted in a general reduction in permeability. For the specific study, this would cause a flattening of relationship at low volume fractions, and thus produce a linear relationship

- The line fit for $WC = 0.38$ is significantly lower than those for the higher WC, which is expected from the effect of WC on the permeability of the cement matrix phase. However, the models for $WC = 0.45$ and $WC = 0.52$ were statistically indistinguishable from each other. Thus, at the higher WC, the effects of ITZ appears to counteract the effect of WC.

- The fitted lines for $WC = 0.45$ and $WC = 0.52$ are almost parallel, but have steeper slopes than the line fit for concrete with $WC = 0.38$. This may be related to an ITZ effect, or may be related to the presence of unhydrated cement in the concrete with $WC = 0.38$.

There are also features of these data which are suggestive, but which are not statistically significant in all cases, as illustrated in Figure 5. First, for all three WC ratios, the concrete which had a maximum aggregate size of 9mm produced permeabilities whose average behaviour was concave. This may be because of increased conductivity associated with closer spacing of the ITZ phases and a reduced rate of increase of the tortuosity effect at higher aggregate volume fractions. This behaviour was not seen in the concretes having maximum aggregate size of 19mm, but for one of those concretes (with $WC = 0.52$, Figure 5b), there was a suggestive upturn for the concrete with $VF = 0.8$. This could be caused by a significant increase of the ITZ effect due to percolation, but it could also be explained by chance variation. The data at $VF = 0.8$

came from two different batches of concrete, while the data at $VF = 0.79$ came from two cylinders cast from the same batch of concrete. It is not possible to establish if this upturn is due to the difference in variability or due to an actual physical effect.

The sizes of the variance components were estimated by using a model that fit individual lines for different WC values, but which also included factors that were not found to have effects significantly different from zero. The method-of-moments estimators for variance components [26] were used to construct rough estimates of these components, which are given in Table 2.

Table 2 : Variance Component Estimates

Variance Component	Standard Deviation Estimate (Coulombs)
batch-to-batch	275
cylinder-to-cylinder	177
slice-to-slice	318

The relatively large size of the slice-to-slice component may be due to gravity effects during curing such as segregation of the large aggregate and some bleeding of curing water. More precise estimates of the variance components will require the use of a more complicated model for fitting the data.

4 Conclusions and Summary

As a result of these three studies, three basic conclusions could be drawn.

First, the chloride permeability of concrete depends primarily on the amount of cement present in which chloride transfer can take place. This is expressed through the dominance of the volume fraction in the models fit. The aggregate proportion effects in the general study and the effect of grading in the specific study suggest that tortuosity and ITZ structure both influence chloride permeability. If the conditions which produce the apparent reduction in ITZ effect in the general study were found, then it would be possible to produce mixes with improved chloride resistance.

Second, no clear effects from percolation of ITZs were observed. These might have been observed in one case, but the effect was not very large. The relationship between grading, tortuosity, matrix permeability and ITZ structure permeability appears to be complex. The results of the general and specific studies will be useful in developing models that may eventually explain these relationships.

Third, the components of variation in the specific study are all of roughly the same order of magnitude, although the cylinder-to-cylinder variation is smaller than the other two. The use of larger samples would reduce many of these components, since larger samples contain more similar distributions of aggregate size and shape.

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