Statistical Studies of the Conductivity of Concrete Using ASTM C1202-94

Sanjay S. Jaiswal[1], Jeffrey D. Picka[2], Takeru Igusa[3], Alan F. Karr[4], Surendra P. Shah[5], Bruce E. Ankenman[6], and Patricia Styer[7]

Abstract

The effects of concrete mix variables on durability are investigated by means of statistical techniques. A modified version of ASTM C1202 is used as an indirect measure of chloride diffusivity. Two series of experiments were designed to facilitate the statistical analysis of the mix variable effects. While standard aggregate grades were used in one experimental series, non-standard grades were developed in the other series to enhance the effects of the tortuosity of ionic flow. As expected, the volume fraction of aggregate was the dominant experimental factor in the conductivity test results. However, it was found that significant effects could also be attributed to interfacial transition zones and the tortuosity of ionic flow, particularly for concrete with water-to-cement ratios less than 0.4. Statistical methods were also used to evaluate the variability of the ASTM C1202-94 test results. Estimates were determined for the variance components associated with the test results for different depths within the cast concrete samples, from different samples made from the same batch of concrete, and from different batches of concrete of the same composition.

[1] Andersen Consulting, Chicago IL 60601
[2] Department of Mathermatics, University of Maryland, College Park MD 20742
[3] Department of Civil Engineering, Johns Hopkins University, Baltimore MD 21218
[4] National Institute of Statistical Sciences, Research Triangle Park NC 27709
[5] NSF Centre For Advanced Cement-Based MaterialsEvanston IL 60208
[6] Department of Industrial Engineering and Management Sciences, Northwestern University, Evanston IL 60208

[7] College of American Pathologists, Northfield IL 60093

1 Introduction

1.1 Conductivity as an Indirect Measurement of Chloride Diffusivity

The test ASTM C1202-94, also known as the Rapid Chloride Permeability Test, was originally proposed as a simple, indirect measure of chloride diffusivity in concrete. This test, which is essentially a conductivity test, has been criticized because of the severity of the experimental conditions and because of uncertainties about the relationship between the electrical conductivity and the chloride diffusivity of concrete. Nevertheless, the test is widely used in providing a rough assessment of the resistance of concrete to chloride attack.

Since the chloride diffusivity of concrete is a fundamental property relating to its durability, there has been intense interest in test methods that can evaluate this property. Recently, researchers have investigated the relationships between the test results of direct measures of chloride diffusivity, such as the 90-day ponding test AASHTO T 259, and test results arising from indirect measures of chloride diffusivity by electrical or electrochemical means, such as ASTM C1202-94 [1]. Andrade and Whiting [2] have investigated conventional concretes and have established a linear relationship between the diffusion coefficients determined from chloride concentration gradients produced by diffusion and those arising from an electrochemical driving force. Andrade [3] and Zhang and Gjörv [4] have shown that the basic physical mechanism behind conductivity tests such as ASTM C1202-94 is the migration of chloride ions through the pore structure in concrete. Thus, ASTM C1202-94 or variations of this method will remain important experimental tools for assessing concrete durability.

In this paper, statistical techniques are used to determine the effects of concrete mix variables on the relative conductivity to chloride penetration as measured by a slightly modified version of ASTM C1202-94. In addition to constructing basic models of the data, estimates were also made of the components of the variation of conductivity, most notably those associated with variation in properties between different batches of concrete of the same composition, between different cylinders of concrete cast from the same batch, and between different slices cut from the same cylinder.

1.2 Relationships Between Concrete Mix Variables and Conductivity

Researchers investigating the relationship between the cementitious properties of concrete and chloride diffusivity and conductivity have examined both the physical structure of concrete at scales ranging from large aggregate particles to nanoscale paste porosity and also the transport mechanisms ranging from the chemistry of the pore solutions to the validity of the Nernst-Einstein equation. In this paper, a three-phase model for concrete proposed by Garboczi *et al* [5] is considered. The first of the three phases is the aggregate, which in most cases is relatively impermeable to chloride ions. The cement paste is subdivided into the remaining two phases, the bulk paste and the interface transition zone (ITZ). The ITZ is a thin layer that forms a shell surrounding all aggregate particles and that has a thickness of 10-50 μm. The porosity, conductivity, diffusivity, and water-to-cement (w/c) ratio of the ITZ are all considered to be higher than those of the bulk paste [6].

For concrete made with ordinary Portland cement, the w/c ratio has the most significant effect on the diffusivity and conductivity of the bulk paste and ITZ phases at the microstructural scale. However, at the scale of a concrete specimen that is significantly larger than the largest aggregate within it, the size distribution and physical locations of the aggregate particles determine a complex geometry for the bulk paste and ITZ phases and consequently for the resulting paths of chloride ions. Thus, the concrete mix variables that could affect the averaged or effective chloride diffusivity (or conductivity) of a concrete specimen are the volume fraction and size distribution (grading) of the aggregate and the w/c ratio. These mix variables were used in the design and execution of both experimental programs that were undertaken.

To interpret the results of the experiments in terms of the interactions among the three phases of the model, the following mechanisms suggested by Garboczi *et al.* are examined. Based on the arguments referenced in the preceding section, conductivity will be used in the remainder of the paper under the assumption that it is a measure of chloride diffusivity and concrete durability.

> 1) **Dilution.** Since the aggregate is essentially impermeable to chloride ions, the bulk of the transport must occur in the cement and ITZ phases. In the absence of any other effects, conductivity should be proportional to the volume fraction of conductive phases present.
>
> 2) **Tortuosity.** The permeable phases are formed into a network structure that becomes more complex as the volume fraction of aggregate increases. The degree of complexity of this deformation is referred to as the tortuosity, and will depend on grading properties as well as the aggregate volume fraction. The effects of tortuosity have been studied in catalysis [7], in the flow through porous rocks [8], and in concrete itself [9,10,11]. Tortuosity effects reduce conductivity below that expected from dilution alone. For spherical aggregate, the conductivity predicted from Bruggeman's unsymmetrical effective medium theory [12] is proportional to the volume fraction of cement paste raised to the 1.5 power. This leads to a rate of increase in tortuosity that 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 conductivity as the volume fraction of aggregate increases.
>
> 3) **ITZ Effects**. Because the ITZ has a higher conductivity, this alone might increase the conductivity of a specimen. However, the greater porosity and w/c ratio of the ITZ imply that the bulk paste must have lower than expected porosity and w/c than would be expected from mix ratios, which means that the conductivity of the bulk paste could be reduced in concrete with a large surface area of aggregate. Counteracting this would be the effect of ITZ around different aggregates connecting with each other in a manner that is similar but not identical to percolation [13].

Garboczi and his colleagues [5] developed a physics-based, quantitative model for these mechanisms and compared their model results with experimental data for mortars and simulated data from a pixel-based computational model for concrete. In the present study, statistical techniques are used to design an experimental program and to develop a model for providing a complementary insight into the effects of the preceding three mechanisms. The comparison of the data from this study with the aforementioned physics-based model is being reported elsewhere [14].

2 Experimental Approach

2.1 Design of Experiments

A primary goal of this study is to examine the effects of the w/c ratio, the aggregate volume fraction and the aggregate size distribution on the conductivity of concrete. To achieve this goal, a systematic approach using the statistical design of experiments was used to plan, implement and analyze the results. The theoretical basis of this approach can be found in Cox [15]and Box *et al.* [16]; more applications-oriented accounts can be found in Mead [17] and Montgomery [18]. With this statistical approach, it was possible to maximize the information gained in experiments where resources were limited.

The resulting program consisted of two separate studies. The first employed a gapped grading, in order to examine a broad selection of different concrete mixes and to identify any relationships between these mix variables and conductivity. The second used a standard grading, in which the concrete was mixed according to standard concrete practice and its conductivity was related to more standard compositional variables. Since C1202-94 is sensitive to differences in pore solution chemistry, commonly used supplementary materials such as silica fume and fly ash were not used in any of the experiments.

2.1.1 Gapped Grading Study

In the first study, the values of the mix variables were determined using statistically based experimental design techniques in order to determine the dependence of conductivity on basic physical aspects of the concrete. For this reason, mixes were chosen whose mix variables spanned the entire range of plausible values. Many of these mixes were far from standard concrete in composition, but their presence in the study improved the quality of models for conductivity that could be fit to the data.

A gapped aggregate grading was used in the study in order to be able to identify the effect of tortuosity in the samples. This approach had been previously explored in a pilot study that is reported elsewhere [14]. The grading consisted of a single grading of river sand with a fineness modulus of 2.6, combined with a combination of river gravel that passed through 19mm sieves, but was retained in 9mm or 12mm sieves. Ordinary Type I Portland cement was used as the binder. The three experimental factors were:

(1) the w/c ratio: six equally spaced values between 0.3 and 0.6 were used;

(2) the aggregate volume fraction, defined as the volume of all aggregate divided by the total volume of concrete: six equally spaced values between 0.4 and 0.8 were used; and

(3) the coarse aggregate proportion, defined by

$$\text{coarse aggregate proportion} = \frac{\text{Volume of 12mm Coarse Aggregate}}{\text{Total Volume of 9mm and 12mm Coarse Aggregate}};$$
\label{eq:ap2}

six equally spaced values between 0 and 1 were used.

Each factor combination, defined by values for the w/c, coarse aggregate volume fraction, and coarse aggregate proportion chosen among the preceding levels, resulted in a uniquely defined concrete mix design. If all combinations of these levels had been used, there would have been 6^3=216 concrete mix designs. To reduce the experimental effort, 6^2=36 factor combinations were chosen by an algorithm that generated space-filling designs [19,20] so that they were evenly distributed among the 216 possible combinations in such a way that all 36 different combinations of coarse aggregate volume fraction and coarse aggregate proportion levels could be included. Since this procedure does not follow standard mix design criteria, many of the mix proportions resulted in concrete specimens with unusual characteristics such as extreme segregation or high unworkability.

Only one cylinder was cast and tested for each of the 36 factor combinations. Thus, 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.

2.1.2 Standard Grading Study

In this study, the mix proportions and aggregate grading were limited to those used in standard practice [21] in order to relate the conductivity to mix variables that are used in practice. River gravel and sand were used, with standard gradings as determined from the British Standard Code of Practice (BS 5328 - 1991) and McIntosh & Erntroy curves [21]. The three experimental factors and their levels were:

1) the w/c ratio (0.38, 0.45, 0.52);
2) the maximum aggregate size (9mm or 19mm); and
3) the grading of the coarse and fine aggregate (four standard grades for each maximum aggregate size).

To eliminate potential problems with segregation that were observed in the preceding study, the volume fraction of aggregate was chosen such that each concrete mix proportion had a constant moderate level of workability [21]. Ordinary Type 1 Portland white cement was used as the binder to facilitate optical image analysis. While image analysis was of great use in estimating volume fractions in gapped grading study samples that had undergone segregation, the use of standard concrete mixes prevented segregation in the standard grading study.

The total number of possible factor combinations is $2 \cdot 3 \cdot 4 = 24$. All of these were used, resulting in a full factorial experimental design. While this aspect of the statistical design of experiments was standard, the model for the error was not. In the standard model for the inherent random variability in an experimental test result, it is assumed that every observation of the conductivity consists of a simple function of the mix variables, plus a random error term having the same probability distribution in each test result. In this experimental series, the error terms which are inherently included in each conductivity test result would have the following three contributions, known as variance components:

1) The *batch-to-batch variance*, which describes the variability between different batches of concrete made according to the same mix design.

2) The *cylinder-to-cylinder* variance, which describes the variation between cylinders made from the same batch of concrete.

3) The *slice-to-slice variance*, which describes the variation between slices cut from the same cylinder.

A physical interpretation of these three variance components is given in the discussion of results in Section 3.2.

Since each of the variance components defined above could appear in test samples taken from a large structural member, the standard grading study was designed so that all three components could be estimated. If all three components had been estimated for each of the 24 concrete mixes used in the experiment, then it would have been necessary to make at least two batches for each mix and at least two cylinders from each batch, resulting in $24 \cdot 2 \cdot 2 = 96$ specimens. To reduce the experimental effort, it was decided that for each mix, 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 experimental procedure would lead to a 50% reduction of the number of tests while still allowing estimates of the variance components to be made from a reasonable number of observations. The details of this experimental design are given in Ankenman *et al.* [22], while general discussions of this type of model are given in the books by Scheffé [23] and Searle *et al.* [24].

2.2 Materials and Procedures

The concrete specimens were 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 slices. These slices were labeled Top, Middle, and Bottom, relative to the orientation in which the cylinder was cast. The casting dates for each concrete mix proportion were chosen randomly before the start of the experiments. This was to ensure that the environmental and other conditions on the day of casting or testing as well as any inexperience on the part of the experimenters in early testing would not be confounded with the conductivity results for the various concrete mix proportions. The cylinders were cured underwater for 28 days before being subjected to the conductivity test.

In the study of gapped graded concrete, four cylinders were cast for each composition. Three cylinders were used for compression tests while the fourth was sliced and subjected to the conductivity test. In the study of standard-graded concrete, six cylinders were made from each batch, with three reserved for compression tests and one or two retained as replacements. Initially, an experimental design criterion was used to divide the twenty-four compositions into two groups of twelve. For one group, two batches were made and six cylinders cast from each batch. From each of these batches, one cylinder was selected for the conductivity test. For the other twelve compositions, only a single batch was made, but two cylinders were subjected to the conductivity test. In several cases, extra batches of concrete were made for some compositions when time allowed. For each tested cylinder, the Top and Bottom slices were subjected to the conductivity test.

2.3 The Rapid Chloride Permeability Test

In the ASTM C1202-94 conductivity test, a 60V DC voltage is maintained across the 50mm thick specimens held between a pair of electrolyte-filled cells for 6 hours, and the total charge passed is recorded. Four pairs of cells were used, and the specimens were randomly assigned to these cells, so as to ensure that any effects associated with a specific cell would not confound any specific composition or cylinder location effects. Feldman *et al.* [25] have shown that the initial current during the first few seconds of the test may lead to a more accurate measure of conductivity. This is particularly true for specimens with high conductivity, where the severity and duration of the electric field could heat and damage the concrete. The initial current was used as the measure of concrete conductivity in the gapped grading study, while the total charge accumulated over 6 hours was used in the standard grading study. Figure 1 shows the very strong linear relationship between initial current and accumulated charge for the standard grading study.

2.4 Image Analysis

Since the concrete mix proportions in the gapped grading study do not follow standard mix design criteria, it is not surprising that significant segregation was observed in many of the specimens. Thus, the aggregate volume fraction for a given batch would not be a reasonable estimate of the aggregate volume fractions of the slices of the cylinders cast from the batch. To obtain more accurate estimates of the aggregate volume fraction, images of each face of each slice were digitized and analyzed using stereological procedures. Details of these procedures are given in a separate paper [26].

3 Results and Discussion

The results from both studies illustrated the same basic behaviour. Permeability was consistently found to be most strongly influenced by the volume fraction of aggregate, but the gapped and standard grading 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 Gapped Grading Study

The data from the gapped grading study, shown in Figure 2, clearly indicate a non-linear dependence on aggregate volume fraction (*VF*). The linear regression model with interaction terms which best fits these data is given in Table 1. This model reveals a dependence of the conductivity not only on the coarse aggregate proportion (*AP*) and the water-to-cement ratio (*w/c*), but also on their interactions. This model can be considered to be purely statistical since the mathematical form of the model was not derived from equations of physics. For sake of comparison, a physics-based model based on two-phase unsymmetric effective medium theory in which log(initial current) is linearly related to log(1-VF) was also fit to the data. The coefficients of this model were determined by linear regression. It was found, however, that the physics-based model does not capture the non-linear relationship between the volume fraction and the initial current as closely as the statistical model in Table 1. As will be seen below, the physics-based model provides a good fit for the results from the standard grading study. This may be related to the use of gapped aggregate in the gapped grading study.

The interaction between the coarse aggregate proportion and the other two variables is illustrated in Figure 3 for four different extreme values of w/c and the course aggregate proportion. Several interesting trends are shown by these plots.

- For small values of the coarse aggregate proportion in which all of the coarse aggregate is of the smaller of the two sizes used, higher w/c values result in substantially higher conductivity (Figure 3, upper left). This is expected, since increasing the w/c is expected to increase the conductivity of the bulk paste.

- For high values of the coarse aggregate proportion in which all of the coarse aggregate is of the larger of the two sizes used, the w/c has very little effect on the conductivity (Figure 3, upper right). This implies that the larger aggregate is associated with some mechanism that counteracts the difference in the conductivity of the bulk paste. This may be an ITZ effect, or an unmeasurable effect relating to bleeding or segregation in the non-standard concrete mixes.

- For low w/c, increasing proportion of the larger size of coarse aggregate increases the permeability (Figure 3, lower left). This could be attributed to difference in the structures of the ITZs in the two samples, but might also be related to the change in the relative volume of ITZ present. By decreasing the size of the largest aggregate, the amount of ITZ increases since this increases the surface area of the aggregate. This may reduce the w/c content of the bulk paste to a larger degree than would occur with the large aggregate. Both of the suggested mechanisms would counteract any tortuosity effect.

- For high w/c, the effect of aggregate size is the reverse of what is seen in the case of low w/c (Figures 3, lower right). 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.

Although physics-based models based on two-phase effective medium theory indicate that the conductivity should be independent of effects from aggregate size, these models may not be applicable to the concrete used in either study on account of the high volume fractions of aggregate that were used and the absence of any ITZ effects from these theories.

3.2 Standard Grading Study

For the standard grading study, the relationships found were more complex. The use of standard gradings eliminated the segregation that made some gapped grading study specimens excessively permeable, but this also had the effect of confounding the volume fraction and coarse aggregate proportion effects that were differentiated in the gapped grading study.

In this study, the physics-based model fits the data better than the purely statistics-based model with interaction terms. The statistically determined coefficients for the physics-based model are given in Table 2 below. Given the dramatic effect of w/c in the results from the gapped grading study and the differences in the degree of hydration in low w/c and high w/c cements, separate models were fit for each of the values of w/c. Plots of these equations for each w/c ratio are given in Figure 4.

Four major observations can be made on the basis of this fit.

- The physics-based model can be fit to these data, and the purely statistical model that fit the gapped grading study results does not fit here as well. The difference may be related to the grading of the coarse aggregate, and the effects that the gap in grading has on the ITZ structure of the material.

- The models for the w/c=0.45 and w/c=0.52 concretes are almost vertical translates of each other, and can also be modeled using straight lines with statistically indistinguishable slopes. This suggests that the effect of bulk matrix conductivity is independent of that of the volume fraction of aggregate. The slope in the case of w/c=0.45 match the theoretical result of 3/2, which was obtained by Maxwell for the dilute limit [27].

- The model for w/c=0.38 lies below those for the other two w/c ratios. If the same dependence on w/c had been found in all three cases, the concrete with w/c=0.38 would have higher conductivity at low volume fractions. The concrete with small volume fractions that was used in this study has more small aggregate in its gradings than does the concrete with large volume fractions of aggregate, and this may be responsible for the difference. Since the gapped grading study suggested that there was no interaction between the dependence of conductivity on volume fraction and its dependence on the grading, this change in slope would be consistent with the effects seen when the coarse aggregate proportion was increased in the gapped grading study.

- Close examination of the relationship between the volume fraction of aggregate and the conductivity suggests that if the maximum aggregate size is small, the slope of the relationship increases with increasing volume fraction. This could be the result of a tortuosity effect that is not present or not detectable when the larger maximum size of aggregate is used. This slight curvature is not statistically distinguishable, and so is not included in the models used here.

The sizes of the variance components were estimated by two different methods, based on the model chosen for the standard grading study data. The method of moments was used to find estimates of the components based on a model fit by least squares regression, as discussed in Searle *et al.* [24]. While this method is easy to implement, it has the disadvantage that it can produce negative variance estimates. Further, the initial model fit is not necessarily correct, since it assumes that all the observations are independent and this assumption contradicts the existence of the variance components. If a different estimation method, known as the EM (expectation-maximization) algorithm [24], is used, then these problems can be avoided. This method is more difficult to implement, but as seen from Table 3, the variance component estimates are very close to the method of moments estimates. The coefficients fit using the EM algorithm are also close to those found by a conventional least squares fit, which suggests that the results from both simpler analyses are good in spite of the underlying assumptions for those methods not being fully satisfied.

The variance components can be interpreted as follows. The *batch-to-batch variance* is caused by differences in mixing, pouring, and other processes associated with the production of each batch of concrete. This variance component would be associated with the differences in conductivity in different regions of a slab poured from different batches of concrete having the same mix design. The *cylinder-to-cylinder variance* is caused by the fact that the aggregate size and shape distribution in a given batch of concrete would differ from the aggregate size and shape distribution of each cylinder cast from the batch. This variance component would reflect the variation in conductivity between closely spaced cores in a large slab. The *slice-to-slice variance* includes all other sources of variability such as the measurement variability associated with the ASTM C1202-94 conductivity test, the variability of aggregate size and shape distribution in different slices cut from the same cylinder, and any unexplained sources of variation. The intensity of the electric field used in the ASTM C1202-94 conductivity test has been reported to produce irreversible changes in the microstructure of concrete and possibly may also induce cracks in the specimen. This was confirmed in the experiments, since some specimens were visibly deteriorated and had to be discarded. As a consequence, measurements could not be repeated on individual slices. Statistically, this implies that the measurement error and the variation caused by physical differences between slices cannot be separately estimated. If an alternative test were used that could be replicated on an individual slice, then a fourth variance component could be used to separate the measurement error from the slice-to-slice variation.

The variance component estimates suggest that all of the three components are non-negligible. The slice to slice component is the largest, but also includes measurement error as well as the effects of variation in aggregate composition. The batch-to-batch variation is roughly the same size, indicating that the differences between batches made with the same grading cannot be ignored, especially as the cylinder-to-cylinder variation is considerably smaller. This suggests that there may be variations in properties in concrete slabs fabricated from multiple batches of concrete that would be greater than local variation.

4 Conclusions and Summary

The most basic conclusion that can be drawn from these studies is that the conductivity of concrete depends primarily on the amount of cement present in which chloride ion transport can take place. This is expressed through the dominance of the aggregate volume fraction in the models fit.

Secondly, the size distribution of the aggregate has an effect on the conductivity of concrete, particularly when low w/c ratio cements are used. This effect may be related to the interfacial transition zone, and it has an effect on the functional form of the dependence of conductivity on volume fraction.

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. This would suggest that if samples are taken from large structural members for conductivity tests, then the samples should be taken far enough apart to ensure that they came from different batches of concrete.

Finally, the analysis of the variance components also indicates that variations associated with the conductivity test mostly likely accounts for less than a third of the total variability of the conductivity. The randomness of concrete, resulting from spatial and material variations at the specimen, inter-batch, and intra-batch levels for the same mix design, may well account for at least two thirds of the total variability of conductivity. This implies that the spatial and material variability of concrete would result in spatially localized weaknesses with respect to transport properties that may cause a concrete member to be less durable than what would be predicted using average properties.

Acknowledgments

This research was funded by the grants DMS-9313013 and DMS-9208758 from the National Science Foundation to the National Institute of Statistical Sciences. The apparatus for the RCPT was constructed by Steve Albertson and John Chirayil of the NSF Centre for Advanced Cement-Based Materials.

References

[1] ASTM C1202-94. *Standard test method for electrical indication of concrete's ability to resist chloride ion penetration*, 1996.

[2] C. Andrade and D. Whiting. A comparison of chloride ion diffusion coefficients derived from concentration gradients and non-steady state accelerated ionic migration. *Materials and Structures*, 29 (1996) 476-484.

[3] C. Andrade. Calculation of chloride diffusion coefficients in concrete from ionic migration measurements. *Cement and Concrete Research*, 23 (1993) 724-742.

[4] T. Zhang and O.E. Gjörv. Effect of Ionic Interaction in Migration Testing of Chloride Diffusivity in Concrete. *Cement and Concrete Research*, 25 (7) (1995) 1535-1542.

[5] E.J. Garboczi, L.M. Schwartz, and D.P. Bentz. Modeling the Influence of the Interfacial Zone on the DC Electrical Conductivity of Mortar. *Journal of Advanced Cement-Based Materials* 2 (1995) 169-181.

[6] K.L. Scrivener and K.M. Nemati. The percolation of pore space in the cement paste/aggregate interfacial zone of concrete. *Cement and Concrete Research* 26 (1996) 35-40.

[7] R.K. Sharma, and D.L. Cresswell. Effective Diffusion Coefficients and Tortuosity Factors for Commercial Catalysts. *Industrial and Engineering Chemical Research* 30 (1994) 1428-1433.

[8] M. Sahimi. *Flow and Transport in Porous Media and Fractured Rock* (VCH, Weinheim,1995)

[9] C. Hall. Barrier Performance of Concrete: A review of fluid transport theory, Materials and Structures. *RILEM TC-146: Tightness of Concrete with Respect to Fluids.* (RILEM, Paris, 1994) 291-306.

[10] S.P. Shah and K Wang. Microstructure, Microcracking, Permeability, and Mix Design Criteria of Concrete. *Fifth International Conference on Structural Failure, Durability and Retrofitting* (Singapore, 1997).

[11] D.P. Bentz, E.J. Garboczi, and E.S. Landgren. Multi-scale Microstructural Modeling of Concrete Diffusivity: Identification of Significant Variables. *Cement, Concrete, and Aggregate*s 20(1) (1998) 129-139.

[12] D.A.G. Bruggeman Berechnung verchiender physikalischer konstanten von heterogenen substanzen *Ann. Physik* 24 (1935) 636-679.

[13] S.S. Jaiswal, T. Igusa, P. Styer, A.F. Karr, and S.P. Shah. Influence of microstructure and fracture on the transport properties of cement-based materials. *Proceedings of the International Symposium on Brittle Matrix Composites 5*, A.M. Brandt, V.C. Li, and I.H. Marshall editors. (BIGRAF-Woodhead, Cambridge, 1997)

[14] S.S. Jaiswal. *Effect of Aggregates on Chloride Conductivity of Concrete: An Experimental and Simulation Approach*. Ph.D. thesis, Northwestern University,1998.

[15] D.E. Cox, *Planning of Experiments* (Wiley, New York, 1958)

[16] G.E.P. Box, W.G. Hunter, and J.S. Hunter. *Statistics For Experimenters* (Wiley, New York, 1978)
[17] R. Mead. *The Design of Experiments* (Cambridge University Press, Cambridge, 1988)

[18] D.C. Montgomery. *Design and Analysis of Experiments* (Wiley, New York, 3rd Edition, 1991)

[19] M.E. Johnson, L.M. Moore, and N.D. Ylvisaker. Minimax and maximin distance designs. *Journal of Statistical Planning and Inference* 26 (1990) 131-148.

[20] W.J. Welch. ACED Software. Technical report, National Institute of Statistical Sciences, 1995.

[21] A.M. Neville. *Properties of Concrete* (Longmans, London, 4th Edition, 1996)

[22] B.E. Ankenman, J.D. Picka, H. Liu, and A.F. Karr. A Class of Experimental Designs for estimating a response surface and variance components. *Technometrics* (under review).

[23] H. Scheffé. *The Analysis of Variance*, (Wiley, New York, 1959)

[24] S.R. Searle, G. Casella, and C.E. McCulloch. *Variance Components*, (Wiley, New York, 1992)

[25] R.F. Feldman, G.W. Chan, R.J. Brousseau, and P.J. Tumidajski. Investigation of the Rapid Chloride Permeability Test. *ACI Materials Journal* 91 (2) (1994) 246-255.

[26] T. Igusa, S.S. Jaiswal, A.F. Karr, J.D. Picka, and S.P.Shah. Quantitative Description of Coarse Aggregate Volume Fraction Gradient. *Cement, Concrete, and Aggregates* (under review)

[27] J.C. Maxwell. *Treatise on Electricity and Magnetism*. (Oxford University Press, Oxford, 3rd Edition, 1892) 435-441.

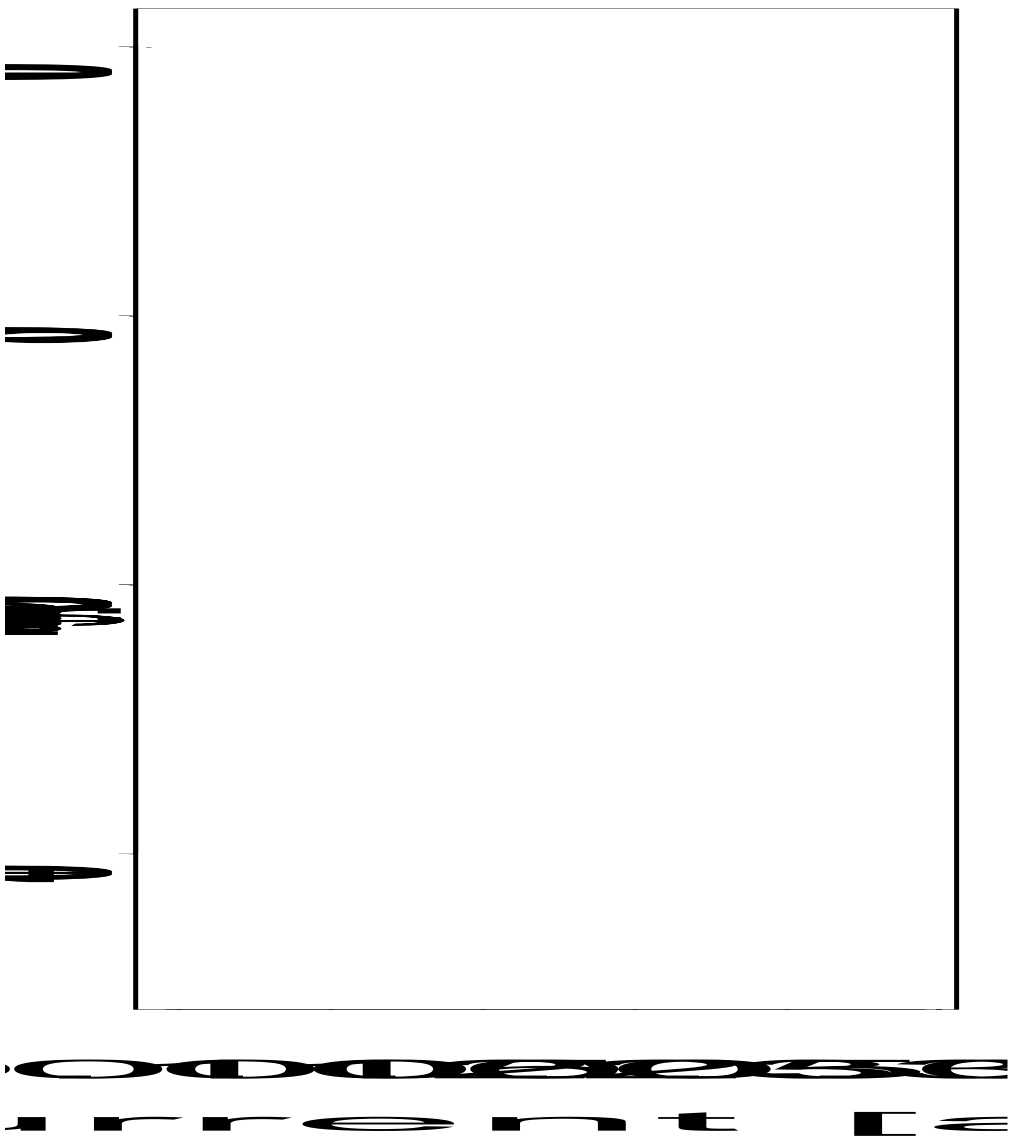
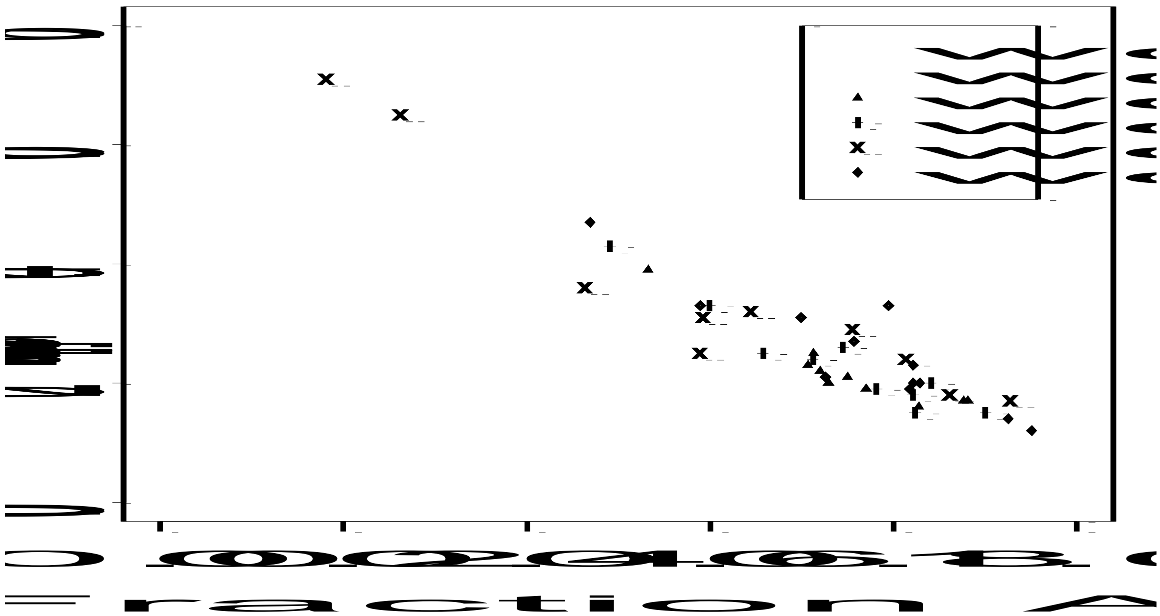


Figure 1: Dependence of final accumulated charge after six hours of testing on initial current passed through sample during the first 15 seconds of the conductivity test.



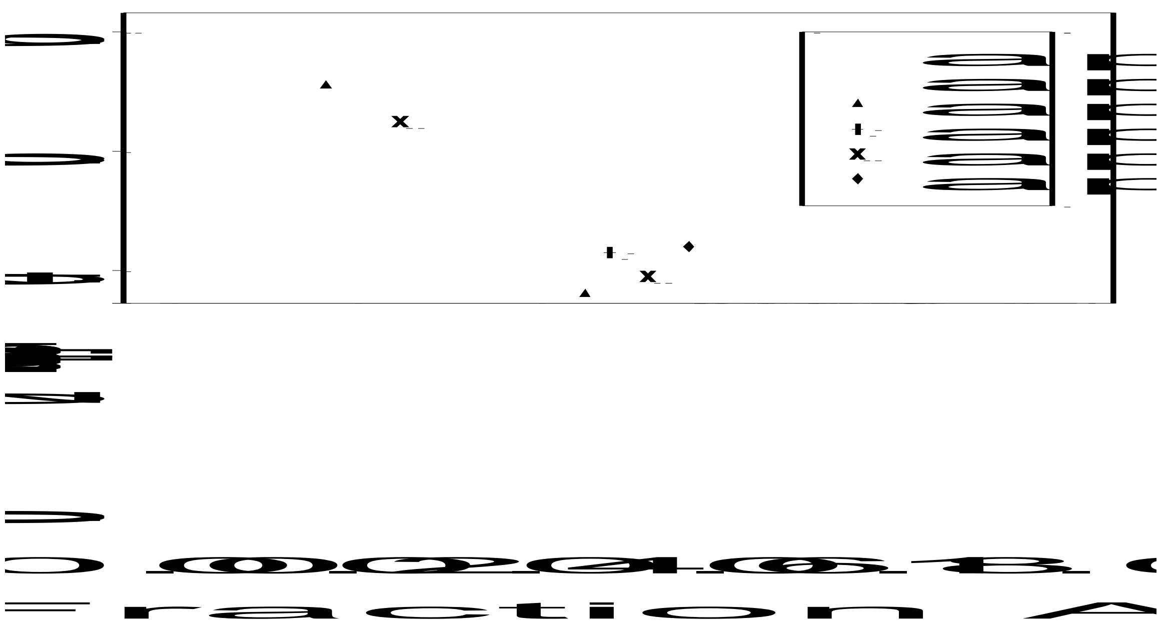


Figure 2: Data for the gapped aggregate study, showing primary dependence of initial current on volume fraction of aggregate and the effects of aggregate proportion and w/c ratio.

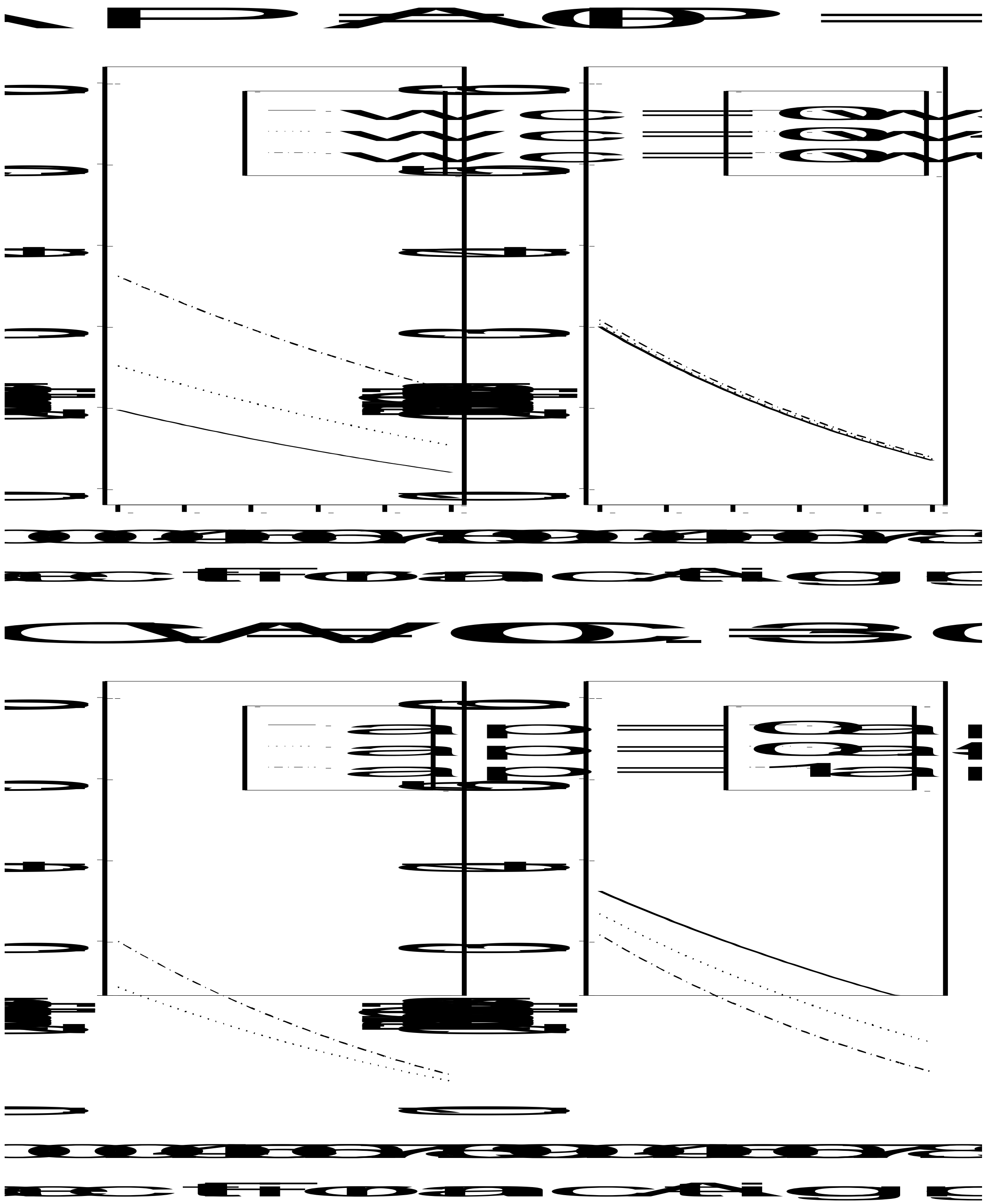


Figure 3: Fitted model for specific study. The top two plots fix the aggregate proportion at two extreme values and show the effect of changing the water-to-cement ratio, while the bottom two plots fix the water-to-cement ratio at two extreme values and show the effects of the aggregate proportion.

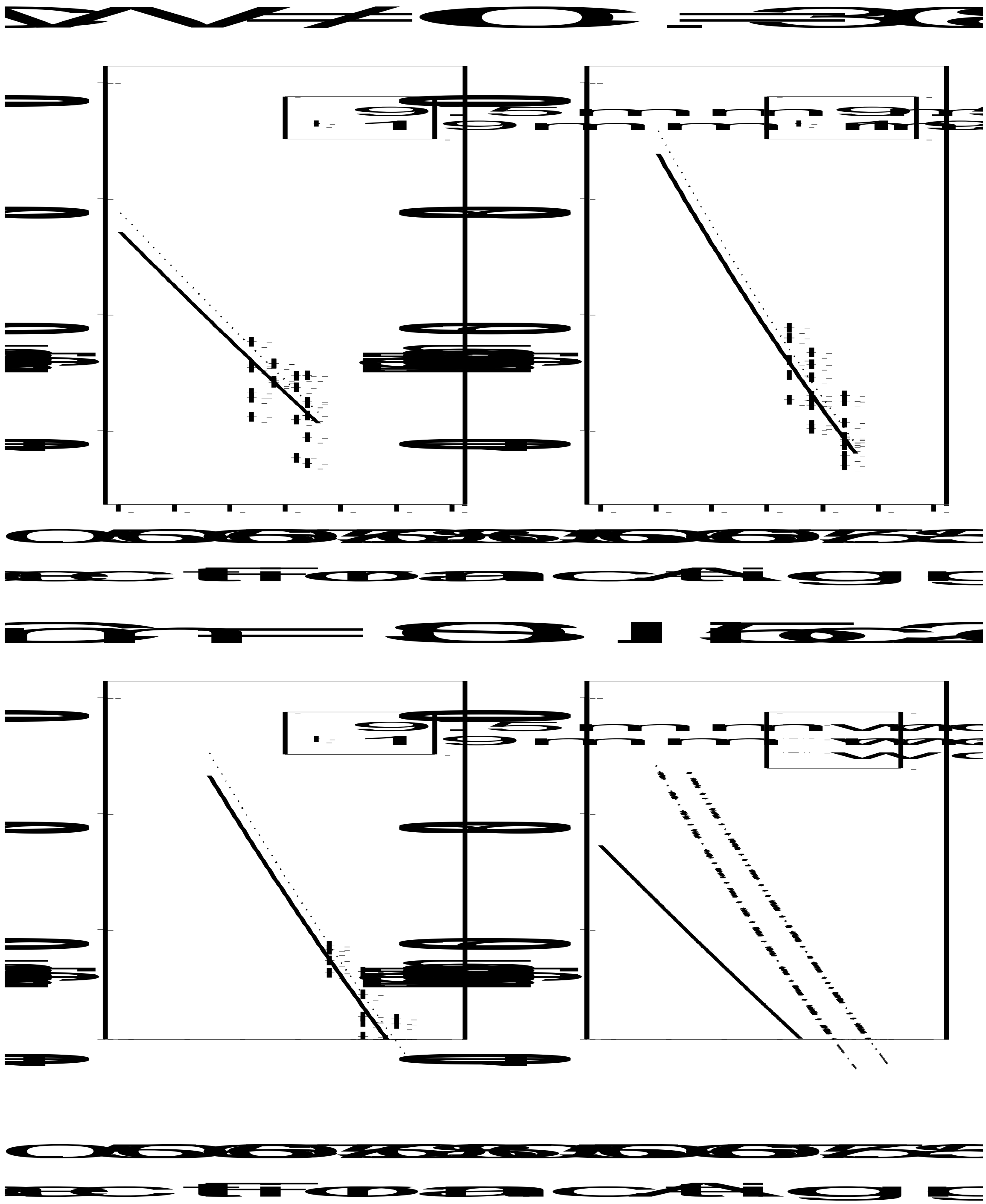


Figure 4: Dependence of final charge on volume fraction in standard aggregate study for each of the water/cement ratios. Solid lines indicate effect on bottom slices, dotted lines indicate effect on top slices. Note the slight curvature present in the samples with 9.5 mm maximum aggregate size. All three bottom slice models are shown together in the last plot in order to indicate relative position.

Table 1: Model For Gapped Grading Study Data

$$\log(\text{initial current}) = -1.84 - 0.99\,VF + 1.24\,AP + 2.03(w/c) - 1.94(w/c)(AP) - 0.61(VF)(AP)$$

Degrees of Freedom: 56
Multiple R-Squared: 0.8768

Table 2: Model For Standard Grading Study Data

$$\log(\text{final charge}) = 9.84 + 1.16\log(1-VF) \qquad W/C=0.38$$

$$= 10.46 + 1.50\log(1-VF) \qquad W/C=0.45$$

$$= 10.37 + 1.31\log(1-VF) \qquad W/C=0.52$$

Degrees of Freedom & 113
Multiple R-Squared & 0.8771

Table 3 : Variance Component Estimates

Variance Component	Standard Deviation Estimate [Method of Moments] (Coulombs)	Standard Deviation Estimate [EM Algorithm] (Coulombs)
batch-to-batch	0.052	0.049
cylinder-to-cylinder	0.028	0.025
slice-to-slice	0.062	0.073