

1 **Modelling the Rapid Chloride Permeability Test**

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11
12 **Abstract.**

13 A computer model has been written to simulate the Rapid Chloride Permeability Test (RCPT)
14 described in ASTM C1202. The model represents the key processes of diffusion and
15 electromigration using standard equations but then maintains charge neutrality by modelling
16 changes to the voltage distribution. This method enables the model to predict current-time
17 transients similar to those recorded in experiments and it can then be used to obtain basic
18 parameters such as diffusion coefficients for tested samples by optimising to the observed data.
19 Experimental data showing a non-linear voltage distribution is presented together with model
20 results which show that the non-linearity has a significant effect on the current. Other predictions
21 from the model are compared with published data and shown to give good agreement.

22
23 **1. Introduction**

24
25 The Rapid Chloride Permeability Test (RCPT) was developed by Whiting (1) and has been
26 standardised as ASTM C1202-97 (2). This paper presents a computer model which is intended
27 to describe the test. The main objectives of the work are:

- 28 a. To make use of the shape of the current-time transient which is recorded every time the test is
29 carried out.
30 b. To enable the test to differentiate between different factors which might cause higher or lower
31 charges to be recorded. For example a sample with a low initial concentration of hydroxyl ions

1 (which might be caused by the use of a pozzolanic material in the concrete) might give a low
2 result and be confused with a sample with a low chloride diffusion coefficient.

3 c. To obtain the chloride diffusion coefficient from the test to permit comparison with other
4 tests.

5 d. To provide a scientific explanation for the results from the test.

6
7 The key phenomenon which is proposed in this work is the non-linearity of the voltage
8 distribution during the test. It is proposed that a linear voltage drop through the sample is not
9 maintained throughout the test and experimental observations are presented to support this
10 theory.

11

12 **2. The Physical Processes**

13

14 2.1 The transport processes.

15 The significant transport processes which take place during the test are diffusion and
16 electromigration.

17

18 In the diffusion process the dissolved ions move through the water at a rate determined by the
19 concentration gradient. The flow per second per unit cross sectional area of the solid (the Flux, J)
20 is given by Fick's law (3) which is shown in equation [1].

21

$$22 \quad J = \varepsilon D \frac{dC}{dx} \quad \text{mol/m}^2/\text{s} \quad [1]$$

23

24 where

25 ε is the porosity,

26 D is the intrinsic diffusion coefficient in m^2/s and

27 C is the ionic concentration in the pore fluid in mol/m^3 .

28 x is the distance in m.

29

30
31 Electromigration is caused by the applied voltage. If an electric field is applied across the solid the
32 negative ions will move towards the positive electrode (3).

33

34 The flux due to electromigration is given by equation [2]:

1

$$J = \frac{\varepsilon D z E C F}{RT} \quad \text{mol/m}^2/\text{s} \quad [2]$$

3 where

4 z is the valency of the ion

5 F is the Faraday constant = 9.65×10^4 Coulomb/mol

6 E is the electric field in volts/m

7 R = 8.31 J/mol/°K

8 T is the temperature in °K

9

10 2.2. Adsorption

11 The transport processes are restricted by adsorption in which a linear isotherm is assumed, i.e. a
 12 fixed proportion of the ions in any part of the barrier are adsorbed onto the matrix and will not
 13 move. The use of a non-linear isotherm could improve the accuracy of the results but it would
 14 require substantially more input data to define the isotherm for each type of mixture.

15

16 To describe these processes two different ionic concentrations must be defined (4):

17

18 C kg/m³ is the concentration of ions per unit volume of liquid in the pores. These ions will pass
 19 through the barrier under the influence of the physical transport processes. The concentration per
 20 unit volume of the solid will be εC where ε is the porosity.

21

22 C_s kg/m³ is the total concentration (including adsorbed ions) per unit volume of the solid. The
 23 ions which are adsorbed onto the solid will not move. The capacity factor is defined as [3]

24

$$\alpha = \frac{C_s}{C} \quad [3]$$

27 The apparent diffusion coefficient D_a, which is measured if total concentrations rather than
 28 solution concentrations are measured, is related to the intrinsic diffusion coefficient by equation

29 [4]

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$$\frac{\alpha}{\varepsilon} = \frac{D}{D_a} \quad [4]$$

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2.3 Voltage Correction

The flux in equation 2 has a term in it for the electric field E. This will arise both from the applied voltage and the distribution of charged ions in the sample.

The field caused by the applied voltage will be uniform across the sample. At the start of the experiment all of the ions will be in pairs with no net charge but as soon as, for example, a chloride ion migrates into the sample without its sodium pair it will create a field E which will cause a potential difference (5) given by equation [5]

$$V = \int E dx \quad \text{Volts} \quad [5]$$

This will distort the uniform voltage drop caused by the applied potential.

The effect of the field will be to inhibit further migration of ions causing any more build-up of charge. In this way Kirchoff's law will take effect and the current into any point within the sample will equal the current out of it. In the solutions at either end of the sample neutrality will be maintained by ion generation and removal at the electrodes.

The change in voltage will be a direct effect of different ionic concentrations in the sample. Soon after the start of the test there will be chloride ions in one side of the sample and sodium in the other side. The regions with these ions in them will have different resistivities due to the different mobilities of the different ions thus the system is equivalent to three different resistances in series. The voltage drop will depend on the size of each resistance and will not be uniform across the sample.

At the start of the test there is assumed to be virtually no chloride in the sample. When the voltage is applied the chloride ions will start moving into it. If they are to be responsible for the measured current they will be moving without the sodium anions. The rate at which they can flow in will be determined by the number of charge carriers (primarily hydroxyl ions) already available in the sample to carry the current forward to the anode. This concentration of existing charge carriers may be measured as the resistivity of the sample as discussed above. Clearly if there are no existing charge carriers in the sample (i.e. it is an insulator) no current will flow and chloride will only penetrate by diffusion.

1
2 Yu et al. (6) have carried out experimental measurements of ionic diffusion at an interface
3 between chloride-free and chloride-containing cementitious materials. They observed that the
4 chloride ions obeyed Fick's law but the hydroxyl ions distributed themselves to preserve charge
5 balance. This movement would have been caused by an electric field established by the chloride
6 ions and is the mechanism proposed in the present work.

7
8 **2.4 Temperature Calculation**
9 When the current flows it will cause Ohmic heating in the sample. This is regularly observed
10 during the experiments. The heat will be lost at a rate which is approximately proportional to the
11 temperature difference between the sample and room temperature.

12
13 **3. The computer model.**

14
15 **3.1 Transport Calculations.**
16 The model works by repeated application of equations 1 and 2 through time and space. The sizes
17 of the steps of time and space are set by continuously reducing them and checking that the solution
18 remains constant. In particular the time step is reduced sufficiently to ensure that the concentration
19 does not change by more than 10% during any time step. The calculations are carried out for ions
20 in solution and at the end of each time step they are re-distributed using the capacity factor to
21 calculate adsorption.

22
23 **3.2 Voltage changes.**
24 These effects are applied within the model by distorting the voltage and checked by ensuring that
25 charge neutrality is maintained throughout the sample at all times. This is clearly not possible if
26 only one ion type is being considered and all therefore of the migrating ions are considered
27 together. The initial concentrations in the sample must be equal for anions and cations and if the
28 data does not comply with this requirement the model will not run.

29 Ion generation and removal at the electrodes is represented in the model by assuming that the
30 ions being generated and removed are always hydroxyl ions. This assumption is probably most
31 accurate at the cathode where hydroxyl ions are produced together with some hydrogen gas. At
32 the anode hydroxyl ions are removed and the resulting oxygen may be used in corrosion of the
33 electrode, but checks on the sensitivity of the model have shown that this will not cause a
34 significant error.

1
2 3.3 Temperature
3 This effect has been included in the code with a constant of proportionality for the heat loss
4 which was determined from experimental observations of the peak temperatures.
5

6 3.4 Optimisation.

7 The model which is outlined above would be useful for calculating the current transient for a
8 sample for which all of the physical properties were known. In practice the opposite is required;
9 the current transient is observed and the properties of the sample must be calculated from them.
10 This can be done by a process of optimisation. Repeated modelling is carried out and the
11 properties are adjusted to give a transient which is as close to the experimental values as
12 possible. Unfortunately the properties cannot be considered sequentially for this. For example it
13 is not possible to optimise the chloride diffusion and then go on to optimise the hydroxyl ion
14 concentration because this will give a different minimum for the chloride diffusion. Thus the
15 different properties must be optimised together.

16 The optimisation has been the process which has delayed the use of this model. The authors
17 previously presented the basic method (7) but were unable to apply it due to the limited capacity
18 of the computers generally available at the time. With a modern standard desk-top computer
19 three properties may be optimised in a few hours. This may be seen as locating a single
20 minimum point in the three dimensional space created by these three variables.
21

22 3.5 Methods used in the work presented in this paper.

23 For the work that is presented here the migration of four ions has been considered: chloride,
24 hydroxyl, sodium and potassium. Each of these is defined by three variables, a diffusion
25 coefficient, a capacity factor and an initial concentration in the sample. It has been noted above
26 that the computers which were used were capable of optimising three of the resulting 12
27 variables which define the system. In effect nine variables must be set and the remaining three
28 are calculated. For the present work the hydroxyl and chloride diffusion and initial concentration
29 of hydroxyl ions were optimised. Table 1 shows the initial values of the variables.

30 When the initial concentration of one ion in the system was increased in order to optimise the
31 solution it was necessary to balance this with a counter-ion to maintain neutrality. When the
32 chloride was increased the counter-ion was assumed to be sodium but when the hydroxyl was
33 increased an immobile anion was introduced to represent a net charge on the matrix.
34

1 **4. Experimental methods.**

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3

4 Mixes were cast to the proportions shown in Table 2 and cured in water for 28 days.

5

6 The testing was carried out using apparatus which was similar to that described in ASTM but
7 with the following specific differences:

8 1. The end-volumes were larger at 0.8 litres, compared with typical volumes of 0.2 litres for the
9 standard apparatus.

10 2. The experiment was run at 40 Volts.

11 3. The samples were run for 1000 minutes (17 hours). These longer runs typically give far
12 greater changes in current during the test than are normally observed during a six hour test.

13 4. The cells were designed to give access to the top of the sample (8). For some samples this
14 was used to establish a salt bridge by drilling 4mm diameter holes in the samples and installing a
15 flexible plastic pipe containing 0.1M potassium chloride. The other end of the pipe was placed
16 in a beaker with a reference electrode.

17 The computer modelling was carried out using code written in Visual Basic running as a macro
18 in Microsoft Excel on a standard desk-top computer.

19

20 **5. Model Validation.**

21

22 5.1 An Analytical Solution

23 Luping and Nilsson (3) presented an integrated solution to equations 1 and 2 which gives the
24 concentration of chloride ions at different times.

25

26
$$c_{cl.} = \frac{c_o}{2} [e^{ax} \operatorname{erfc}\left(\frac{x + aDt}{2\sqrt{Dt}}\right) + \operatorname{erfc}\left(\frac{x - aDt}{2\sqrt{Dt}}\right)]$$

27 where

28
$$a = \frac{zFE}{RT}$$

29 and c_0 is the concentration at the surface (in the reservoir).

30

31 This may be differentiated to give the current:

32

$$I = FADc_0 a \left[\frac{2}{\beta \sqrt{\pi}} e^{-\left(\frac{\alpha}{2} - \frac{\alpha^2}{\beta^2} - \frac{\beta^2}{16}\right)} + \frac{1}{2} \operatorname{erfc}\left(\frac{\alpha}{\beta} - \frac{\beta}{4}\right) \right]$$

2 Where:

3 $\alpha = ax$

4 $\beta = 2a\sqrt{Dt}$

5 This equation only applies to a single ion. The model was checked against the equation but this
6 was only possible after disabling the voltage correction, temperature change routines and
7 changes to the concentrations in the reservoirs which are not included in the analytical solution.

8 With these precautions exact agreement was obtained.

9

10 5.2 Fitting the Data.

11 It has been observed that optimising with three variables will normally give the model sufficient
12 degrees of freedom to calculate a good theoretical fit to experimental data sets. Figure 1 shows
13 the model fit to the data for mix A. This was obtained by optimising to the experimental results.
14 The obtained intrinsic diffusion coefficients were 7.8×10^{-11} for hydroxyl and 2.9×10^{-10} for
15 chloride and the initial concentration of hydroxyl ions was 245 mol/m³. It may be seen that the
16 model is able to give a good fit to the shape of the curve. Figure 1 also shows the effect of
17 modelling the system with a linear voltage drop and it may be seen that the effect is significant.

18

19 5.3 Effect of hydroxyl ion concentration.

20 Figure 2 shows the predicted effect of the hydroxyl ion concentration on the initial, final and
21 average results. Typically this concentration would be most affected by the addition of
22 pozzolanic materials that would deplete the free lime during hydration. Sugiyama (9) has
23 observed that the initial current is far more significantly affected by this concentration than the
24 final current and it may be seen that this observation is well predicted by the model.

25

26 5.4 Chloride Profiles.

27 Figure 3 shows chloride concentrations predicted by the model at different times and compares
28 them with those found experimentally by different authors. For this modelling the volume of the
29 input reservoir was increased to reduce predicted changes in concentration. It may be seen that
30 the model predicts a small build-up of chlorides just below the surface that has not been
31 observed but the shape of the main part of the curve follows the observations.

1
2 5.5 Salt-Bridge measurements.
3 Figure 4 shows the current-time transient for a sample of mix B. The fit to this curve was
4 obtained with intrinsic diffusion coefficients of 1.65×10^{-11} for hydroxyl and 4×10^{-11} for
5 chloride and the initial concentration of hydroxyl ions was 90 mol/m³. Figure 5 shows the
6 voltage distribution across the sample after 6 hours indicating the predicted values and two
7 measurements made on replicate samples. It may be seen that the deviation from a linear voltage
8 drop is small but reference to Figure 4 shows that it has a very significant effect on the current.

9
10 5.6 Effect of sample length.

11 Figure 6 shows the predicted effect of changing the sample length. It may be seen that it is non-
12 linear with a greater increase in charge passing at shorter lengths. This effect was observed by
13 Abou-Zeid (11) for all of a number of series of samples tested.

14

15 **6. Discussion.**

16

17 Figures 7 and 8 show the predicted relationship between the measured charge passing and the
18 diffusion coefficients for sodium and chloride. This basic relationship would be expected and
19 has been observed by Yang(12) and others. Comparing these with figure 2 it may be seen that it
20 is indicated that a high initial current shows a high hydroxyl concentration, a high average current
21 (i.e. a current that increases and then falls) shows a high chloride diffusion and a more uniform
22 trend shows high sodium diffusion. For observed data these trends could be analysed using the
23 optimisation programme.

24 Figure 9 shows the predicted voltage at the mid-point of the sample at the end of the test as the
25 different variables are changed. This voltage would be 20 Volts in a linear voltage distribution.
26 It may be seen that measuring this would yield very useful data for the model to work with and
27 could separate out different phenomena. Pre-saturating the sample with chlorides is predicted to
28 have a very significant effect by reducing the resistivity across all of it except a small region near
29 the anode where the ions are depleted. The hydroxyl ion concentration may be seen to have a
30 significant effect on the mid-point voltage with a change from below 20V to above 20V as the
31 concentration increases. If a concrete sample is being tested and it gives a low Coulomb value
32 this could be caused by a low chloride diffusion coefficient but it could also be caused by the use
33 of a pozzolanic material to deplete the hydroxyl ions. Measuring the mid-point voltage could

1 differentiate between these two effects and determine whether the sample was as good as the
2 Coulomb value indicated. It is suggested that drilling a small hole and measuring this voltage
3 on a spare channel in the data-logger would not add significantly to the cost of these tests but
4 could yield very useful data for analysing the results.

5 All of the results reported here were taken over a test period of 17 hours. It is suggested that this
6 increased time adds significantly to the value of the data. Permitting the reservoirs
7 concentrations to change (by limiting their volume) will also cause the current to change more
8 during the test and give a clearer “signature” to show the properties of the sample being tested.

9

10 **7. Conclusions.**

11

12 1. The voltage drop across samples in the RCPT is not linear and the non-linearity has
13 significant effects on the results.

14 2. The test can be modelled to give realistic solutions using a computer simulation.

15 3. It is indicated that to obtain maximum information the test should be run for as long as
16 possible, the reservoirs should be limited and the voltage at the centre of the sample should be
17 recorded with a salt-bridge in a drilled hole.

18 4. Measuring the mid-point voltage could differentiate between samples which have low
19 Coulomb values due to low chloride diffusion and those where the low value has been caused by
20 ion depletion in a pozzolanic reaction.

21

22 **8. References**

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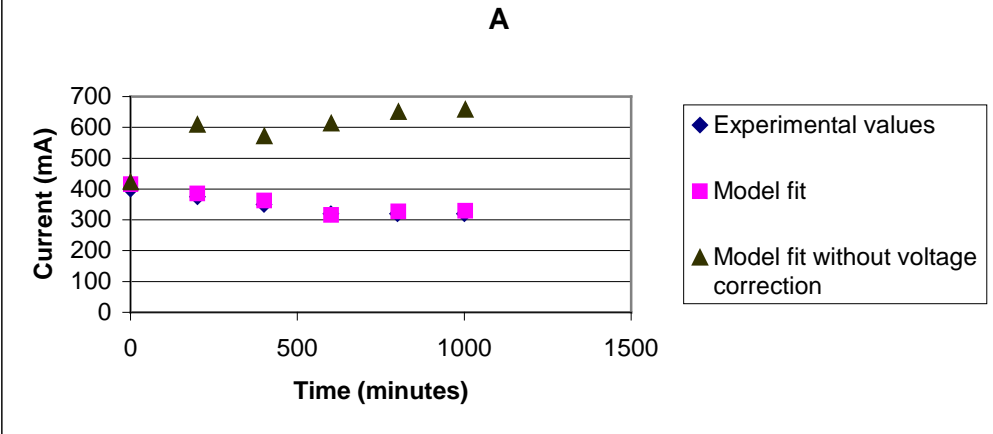
Table 1. Values for variables at start of run in base case prior to optimisation to fit experimental data.

Ion	Valence z	Intrinsic Diffusion Coefficient D m ² /s	Concentration C mol/m ³ (in liquid)			Capacity Factor
			negative reservoir	in sample	positive reservoir	
hydroxyl	-1	1.65E-10	0	275	300	0.2
chloride	-1	6.00E-10	500	0	0	2
sodium	1	4.00E-10	500	138	300	0.2
potassium	1	9.00E-11	0	137	0	0.2
anion	1	0	0	0	0	0.1

Table 2: Mixes used for experimental work

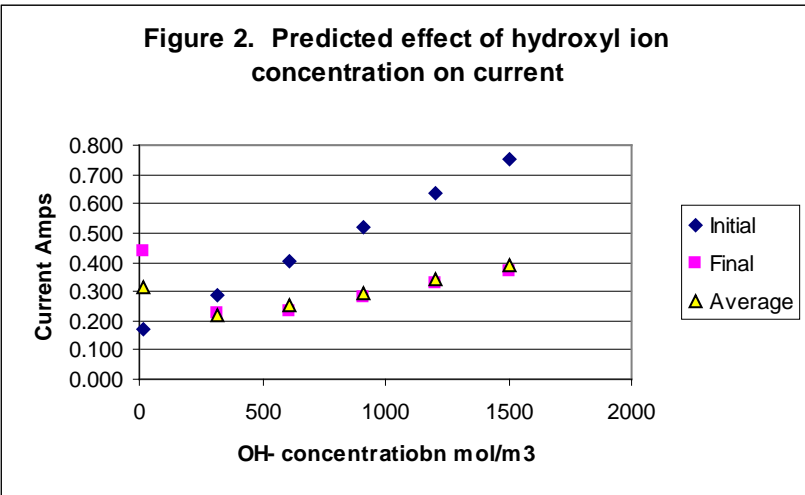
Mix	GGBS/cement	Water/cementitious	Sand/cementitious	Superplasticiser/cementitious
A	-	0.7	1.5	-
B	0.25	0.3	2.6	0.013

Figure 1. Example of model fit by optimisation for mix



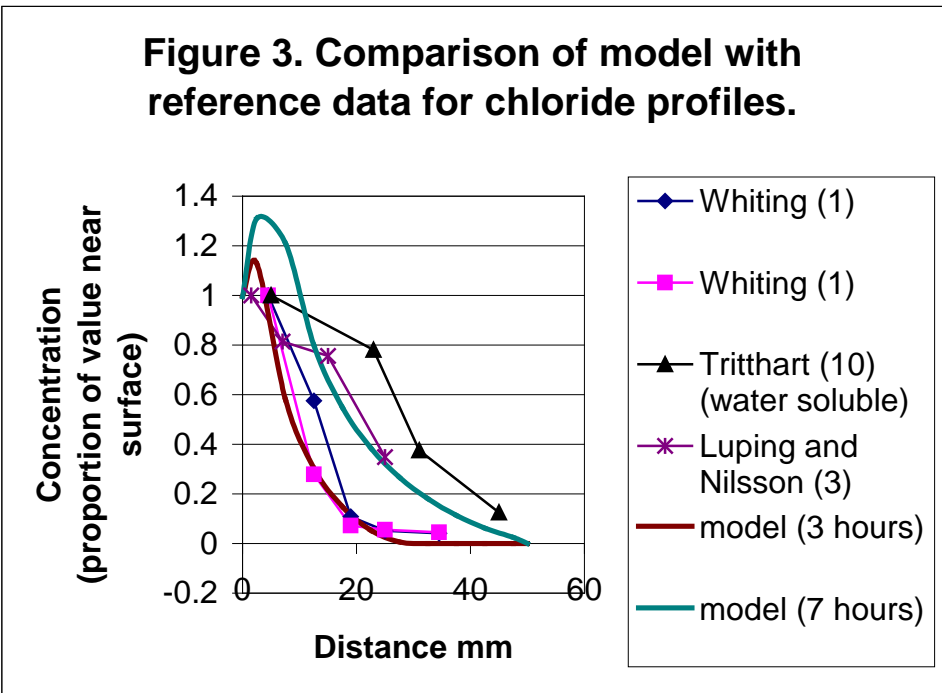
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Figure 2. Predicted effect of hydroxyl ion concentration on current



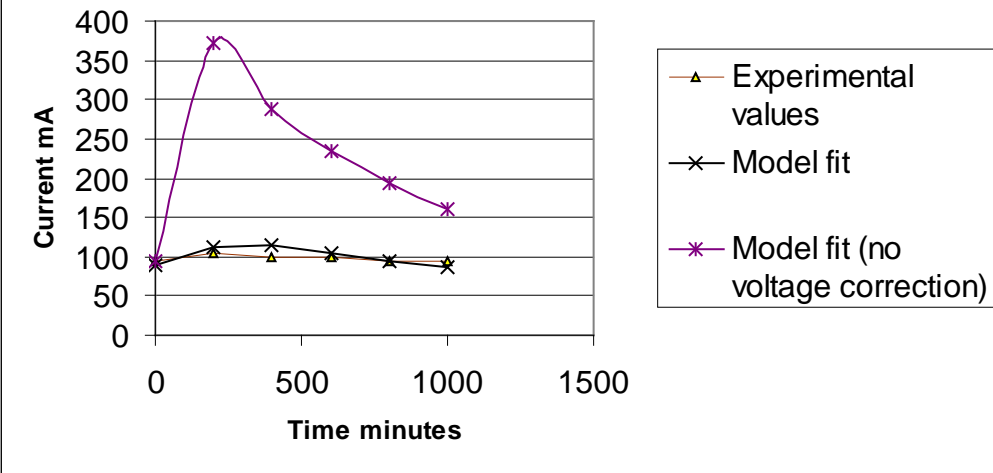
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Figure 3. Comparison of model with reference data for chloride profiles.



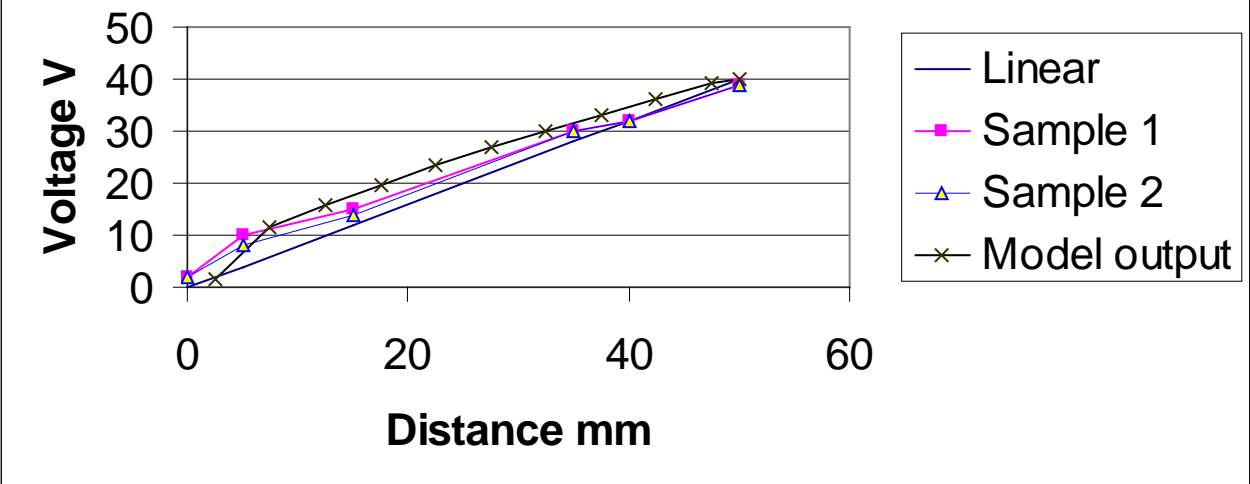
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Figure 4. Model fit to current transient for mix B



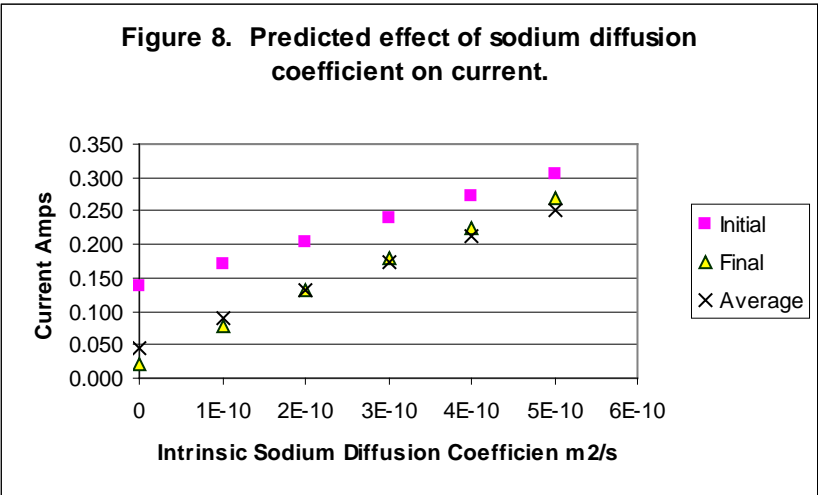
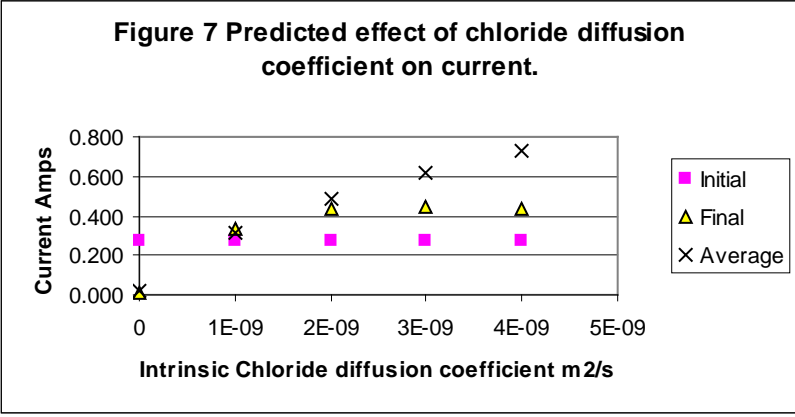
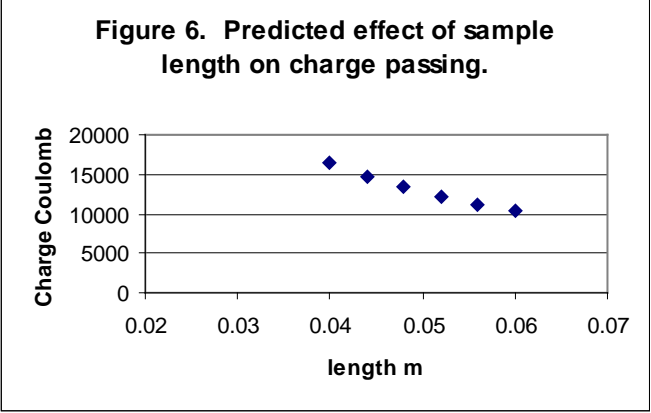
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Figure 5. Experimental and theoretical voltage distribution for mix B

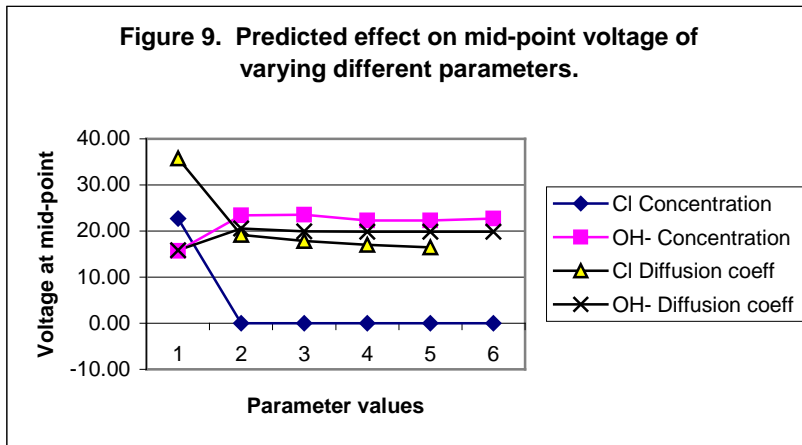


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