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Obtaining More From the Electrical Chloride Test

by P. A. Claisse and T. W. Beresford

Synopsis: The electrical chloride test was developed some years ago and is carried out by driving chlorides through concrete samples using electric fields with high voltages up to 60 V. In the test, the total current passing through the sample in a few hours is used as an estimate of the transport properties of the chlorides in the concrete. This test has major advantages that it is rapid, and can be used insitu; and, it has been accepted by the ASTM. It has been criticised in the literature and has, for example, been found to give misleading results when pozzolanic materials are present. It has been pointed out by the author that if silica fume is added to the concrete, the current falls during the test. However, in plain concretes it normally rises.

This paper is based on the premise that the current test procedure only makes use of part of the available data. Therefore, it provides only part of the possible results for evaluation and analysis. By analysing the shape of the current-time curve, much more information about the constituents and properties of the concrete may be obtained. For the data presented in this paper, a large number of samples were tested and computer analysis of the shape of the current-time transients was used to identify the causes of the different attributes of the current-time transients. This analysis is of particular importance in Europe where new Eurocodes for cement permit addition of pozzolanic materials to almost all cements.

Keywords: Chlorides; concretes; diffusion; electrical properties; pozzolans.

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INTRODUCTION

Chloride movement through concrete has become a major concern, due to the corrosion of steel reinforcement by chlorides leading to premature damage to reinforced concrete structures. A test was developed(1) with the aim of predicting how concrete would behave with respect to the movement of chloride ions with time. It is known as the "rapid determination of chloride permeability of concrete" test. It was developed by Whiting(1). During this test, an external potential is applied to a concrete specimen, a cylinder 50 mm in length and 50 mm radius, with a solution of 0.5M sodium chloride on one side of the sample and 0.3M sodium hydroxide on the other. The electric potential applied is 60V. During the experiment, the current passed through is measured every 30 minutes. A greater amount of charge passing through the sample indicates a poor sample with respect to chloride movement. This is the ASTM C1220 test(2).

Some authors have cast doubt on the interpretation of the ASTM C1202 test results(3, 4). During the test a number of ions, in addition to chloride ions, are moving. They are all contributing to the overall current that is measured. It is even possible that other ions are contributing more than chloride. If this is the case, it may invalidate the results.

In an aim to generate a greater understanding of this test, some models have been developed. These are based around the Nernst-Planck equation(5). Both Andrade,et.al(6) and Luping and Nilsson(7) developed different models based around this equation with respect to the chloride ion. They both predict the rate at which the chloride ion will move through the concrete. They both have developed experiments to support their results.

Both these models concentrate on the chloride ion only. This makes it difficult to relate to the current versus time transients observed during the rapid test, where all ions present are contributing. The next stage is to introduce the effects of these other ions into the model to obtain a more complete picture of the flux of chloride ions, as well as the other ions that are participating.

The interaction between the ions has an important effect on the rate at which the chloride ion migrates. Local electric effects will influence each ion. Charge build-up causes voltages to be set

against that of the applied field, to stop unpaired positive and negative ions from occurring. The greater the applied voltage the further apart the ions can move, since the back voltage will have to equal the applied voltage before equilibrium is reached. A chloride ion can not move far through the concrete sample unless in its environment there is a counter ion, so that charge neutrality is maintained.

A numerical model has been designed to follow the course of four ions during the electrical test of ASTM C1202; and, to see how they combine to generate the current versus time plot observed experimentally. These four ions are sodium, chloride, potassium, and hydroxide. All are present in significant quantities at the start of the test. Therefore, all contribute to the observed current. At the start of the test the pore solution is assumed to have sodium, potassium, and hydroxide ions. Although other ions are present, these three are in the highest concentration and are also the three with the greatest diffusion coefficients. They will, therefore, contribute most to the current.

NUMERICAL MODEL

A computer model has been developed to simulate the generation of current during a standard electrical test. This programme is primarily dependent on two parts:

1. the movement of ions due to the effect of diffusion and the applied electric field; and,
2. the voltage correction.

Part 1 is the basis of the numerical model. The movement of the ions is determined by their diffusion coefficients. This in turn is determined through the use of the Nernst-Planck equation. Part 2 controls the movement of the ions with respect to the local environment. In the local region, charge build-up must be controlled. Internally, the ions will only move so far away from each other under the effect of the external electric field until the voltage resulting from their distance apart brings them again closer together, or a new ion partner is found. If there is too much charge build-up the system corrects itself back within the constraints established before continuing.

The Nernst-Planck equation used is(5):

$$J_i = -D_i \left[\left(\frac{\partial c_i}{\partial x} \right) - c_i z_i \frac{FE}{RT} \right] \quad (1)$$

where the various parameters are:

J_i = the flux of species i ($\text{mol m}^{-2} \text{s}^{-1}$)

D_i = the diffusion coefficient for species i ($\text{m}^2 \text{s}^{-1}$)

c_i = concentration of species i (mol m^{-3})

x = the distance travelled (m)

z_i = the charge of species i

F = Faraday's constant (C mol^{-1})

E = electric field (V m^{-1})

R = gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)

T = temperature (K)

In the model, this equation is split into two parts, Part 1 is:

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$$J_1 = -D_i \left(\frac{\partial c_i}{\partial x} \right) \quad (2)$$

This is Fick's first law for one-dimensional flux. The flux with respect to diffusion is evaluated and then taken on to the second part of the equation which evaluates the migration with respect to the externally applied electric field. Part 2 is:

$$J_2 = -D_i \left(c_i z_i \frac{F}{RT} \frac{\partial \phi}{\partial x} \right) \quad (3)$$

where $\frac{\partial \phi}{\partial x} = -E$. The two flux values are then combined to give the total flux.

Part 2 of the model is based around maintaining the charge balance in accordance with Kirchhoff's law(8). If there is charge build-up, the model then corrects itself and then re-evaluates the flux. If it is still not within the specified range, the model will loop around again. This will continue until the specified charge balance is maintained, in this instance the maximum net charge is limited to 10^{-7} Coulombs. The direction of the flux of each specific ion which will move is determined by the charge on each ion, either +1 or -1, multiplied by the voltage. This works by correcting the voltage, effectively removing any build up of charge. This reflects the physical situation in which the charge which builds-up will be dissipated by the distortion to the electrostatic field that it causes; i.e., by distorting the linear voltage drop across the sample.

The model works by splitting the sample into N slices. Each slice is of equal length except the two slices nearest the two reservoir solutions at either side of the sample. These two slices are half the thickness of the others. The flux is worked out individually for diffusion and migration for each slice. At the end of each cycle, the current is added for each ion and the total current, and then printed and displayed graphically.

The required input information is:

1. the diffusion coefficients of each ion(sodium, potassium, chloride, and hydroxide).
2. reservoir concentrations(sodium chloride solution and the sodium hydroxide solution at either side of the sample).
3. ionic concentrations of the pore solution(sodium and potassium hydroxide).

RESULTS

The numerical model is able to generate results that are in the same range of current values obtained experimentally, Fig 1. It is possible, from the model, to see which ion is dominating the current at each point in the current versus time chart. All of the rapid test experiments give a current versus time chart which rises to a maximum and then decays until the end of the test. It is observed, from Fig 1, that the true shape of the current-time transient could not be always observed in the 360 minutes recommended in the ASTM C1202(2). The test was, therefore, conducted for 1000 minutes. The potential applied was 40V. Fig

2 shows typical results for a portland cement/fly ash sample. The current was measured every 5 minutes.

The computer/numerical model requires information with respect to the concentration of ions within the sample as well as the concentration of the sodium hydroxide and sodium chloride solutions. Results have been reported by several authors with respect to the concentration of ions present in concrete pore solution(9, 10). An estimate is made for each sample. The diffusion coefficients are estimated from the paper by Page,et.al(11). Their values for chloride were used initially in this project. The other diffusion coefficients were extrapolated from their relationship in aqueous conditions(12).

The current into the sample is the same as the current out of the sample, Kirchhoff's law(8). The current is controlled by the concentration of ions and by the diffusion coefficients. As the concentration outside the samples is constant, in every experiment, it is the concentration of ions within the sample at the start of the experiment, and the diffusion coefficients of all ions involved, that is of most importance. The pore solution of concrete is made up of mostly potassium, sodium and hydroxide ions. After 180 days, typical concentrations are shown in Table 2.

A comparison of the experimental results with portland cement, w/c = 0.3, 28 day wet cure, at a potential of 40V was made. This experiment was performed in triplicate, so the comparison is made against three sets of experimental results, Fig 1. In order to simulate the action of hydroxide ions dissolving into the pore solution, high values of the total hydroxide ions in the sample were used, Table 1. The actual starting concentrations in the pore solution are shown in Table 3. In order to maintain charge neutrality in the sample sodium was dissolved into the pore solution as the ion partner for the hydroxide ions. As can be seen from Fig 1, these values used in Table 1 give a comparable current with the experimental results. Fig 3 shows the total current from the computer model and how each of the four ions contribute to the total. As can be seen, the initial rise in current is due to hydroxide ions dissolving into the sample. Once the maximum current is reached the current decays, with the decrease in current from the hydroxide ion, as now more hydroxide ions are leaving the sample than are dissolving into the pore solution. The potassium, sodium, and chloride ions both have lower diffusion coefficients than hydroxide, so move slower than the hydroxide, and contribute less to the current.

After 1000 minutes, the computer model predicts that the hydroxide ion concentration has dropped significantly, Figs 3 and 4. However, it still dominates the total current. It is worth noting that the chloride current is now very similar to the hydroxide ion and if the test is to continue for a greater amount of time that a minimum might occur. After this then the current would be dominated by the chloride ion. The chloride concentration profile is shown in Fig 5. Figs 6 and 7 show how the potassium and sodium ions concentration changes during the test. These ions

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have to be present to maintain electric neutrality. As the chloride ion concentration increases towards the end of the test, so does the sodium ion concentration. The potassium ion concentration changes in a similar manner to the hydroxide ion, only at a slower rate, since its diffusion coefficient is lower, and in the opposite direction.

The value of the chloride diffusion coefficient is higher than those that are found from measurement by other authors(13). This is expected, since these will normally be measured from diffusion tests, where the chloride ion is normally partnered with a slower moving sodium ion. If these values are used in the numerical model then the current observed, for these concentration values, is smaller.

During the experimental work so far carried out by ourselves, a maximum in the current versus time transient has always been observed. This point during the numerical model is when the hydroxyl ions are leaving the sample at a greater rate than they are dissolving into the pore solution. Feldman et al(14), noted a rise in current towards the end of their tests, though they operated at 60V, not 40V as in our experimental work. This suggests that if our experiments ran for a longer duration that the current would rise. This is observed by the model. If the hydroxide ion does not dissolve into the pore solution as the pH falls, then this phenomena occurs well within the duration of the test, typically after 500 minutes.

It was assumed the highest hydroxide ion concentration in the pore solution that could be used was 320 mol m^{-3} . This value was suggested by Taylor(9) for hydroxyl concentration in pore solution of samples 180 days old. When this value was used, the diffusion coefficients were adjusted so that the current is in the same range as the experimental currents. This made no significant difference, as the hydroxide ion still left the sample within the duration of the test, with the current rising at roughly the same time.

It is assumed that calcium hydroxide is dissolving into the pore solution, forming calcium chloride and sodium hydroxide, as the pH drops. This explain why it seems to take longer for hydroxide ions to become depleted experimentally than is proposed by the computer model when this is not considered. Experimentally the pore solution is being continually re-filled with hydroxide ions. When the point comes where all the calcium hydroxide has dissolved into the pore solution the current may then rise, as was noted by Feldman et al (14), and chloride ion then approaches its drift velocity.

The concentration profile for chloride depth in the sample is shown in Fig 5. In this instance the computer model represented 10 slices/cells ($N = 10$). The concentration of four slices is shown in Fig 5. Taking Slice 4, which is 19.5 mm into the sample from the sodium chloride reservoir, the concentration varies as shown in Fig 8. The concentration is well below 500 mol m^{-3} , 0.5 mol l^{-1} , the sodium chloride concentration at the start of the test. The concentration in cell 1 is the greatest. Once chloride enters

each cell of the sample its concentration rises before levelling off. It then rises slowly until the end of the test. In cell 10 the initial concentration is zero, and remains this way during the first 80 minutes. So the initial current in this cell has nothing to do with chloride.

If the hydroxide ion concentration is considered, Fig 4, it can be seen in cell 10 the concentration rises. The hydroxide ions entering cell 10 is greater than the hydroxide ions leaving cell 10. After 400 minutes, the hydroxyl concentration in cell 10 is nearly double its value at the start of the test. This is due to hydroxide ions migration from the other 9 cells towards the anode in the sodium hydroxide reservoir. To get to the anode these hydroxide ions must pass through cell 10. It is unlikely the pH has dropped in cell 10, it has probably risen, so no hydroxide will have dissolved into the pore solution by the end of the test.

The role of adsorption and reaction of the ions to take them out of solution is important(15). Adsorption will effectively reduce the diffusion coefficient. Estimating the diffusion coefficient without an adsorption parameter will give a low result. Any reaction that the ions undergo, that takes those ions out of solution, will have a more serious effect on the current. Chloride ions are known to form chloroaluminate within concrete(16). Removal of chlorides from solution will reduce the amount of current in the system. However, each site can only take an ion out of solution once. So on complete reaction of all available sites, their effect on current will disappear.

The effect of adsorption and reaction have not yet been included in the computer model. Despite this, the model still behaves satisfactorily, and gives results that compare favourably with the experimental data presented. If they were included the diffusion coefficients used in the model would have to increase.

This type of modelling could be applied at a building/construction site. Having gathered a set of data, the model could then best fit the curve generated experimentally. The diffusion coefficients which can then be derived give far more direct information on the potential durability of the concrete.

If this test was used insitu, from the techniques developed by Whiting(1), the power of a modern computer would be more than adequate to optimise the observed current-time transient output from the model and give direct results on the basic properties of the concrete. Thus, for example, if the concrete contained a pozzolanic material, then the reduced current resulting from the depletion of hydroxide ions caused by the pozzolanic reaction would not be confused with a reduction in chloride diffusion.

CONCLUSIONS

The computer model presented offers the opportunity to obtain more from the electrical test, such as:

1. The diffusion coefficients of the major ions.
2. Predicted concentration of chloride ions at various penetration depths.

3. The transference number (the amount to the total current that each ion supplies individually) of each ion with respect to the overall current observed.

If the hydroxide ion concentration is considered, Fig. 4, it can be seen in cell 10 the concentration rises. The hydroxide ion entering cell 10 is greater than the hydroxide ion leaving cell 10. After 400 minutes, the hydroxyl concentration in cell 10 is nearly double its value at the start of the test. This is due to hydroxide ions migrating from the other 9 cells towards the anode in the sodium hydroxide reservoir. To get to the anode these hydroxide ions must pass through cell 10. It is unlikely the cell has dropped to cell 10. It has probably risen, so no hydroxide will have been driven into the pore solution by the end of the test.

The rate of adsorption and reaction of the ions to take them out of solution is important (15). Adsorption will effectively reduce the diffusion coefficient. Estimating the diffusion coefficient without an adsorption parameter will give a low result. Any reaction that the ions undergo, that takes them out of solution will have a more serious effect on the current. Chloride ions are known to form chloro-complexes with copper (16). Removal of chloride from solution will reduce the amount of current in the system. However, each ion can only take an ion out of solution once. An complete transfer of all available ions, their effect on current will disappear.

The effect of adsorption and reaction have not yet been included in the computer model. Despite this the model still behaves satisfactorily, and gives results that compare favourably with the experimental data presented. If they were included the diffusion coefficients used in the model would have to increase.

This type of modelling could be applied at a wide range of conditions. Having gathered a set of data, the model could then be used to generate experimental data. The diffusion coefficients which can then be derived give far more direct information on the physical properties of the concrete.

If this test was used mainly from the techniques developed by White (1), the power of a modern computer would be most fully adequate to optimize the observed concentration transient output from the model and give direct results on the basic properties of the concrete. Thus, for example, if the concrete contained a particular material, then the reduced current resulting from the depletion of hydroxide ions could be the primary reaction would not be confused with a reaction in chloride diffusion.

CONCLUSIONS

The computer model presented offers the opportunity to obtain more than the electrical test, such as:
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2. Predicted concentration of chloride ions at various penetration depths.

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TABLE 1—VALUES USED IN MODEL FOR COMPARISON OF PORTLAND CEMENT MORTAR SAMPLES

Ion	Diffusion Coefficient ($\text{m}^2 \text{s}^{-1}$)	Sodium Chloride (mol m^{-3})	Sample (mol m^{-3})	Sodium Hydroxide (mol m^{-3})
Hydroxide	8.5×10^{-11}	0	1200	300
Chloride	3.03×10^{-11}	500	0	0
Sodium	1.89×10^{-11}	500	1122.4	300
Potassium	2.53×10^{-11}	0	77.586	0

TABLE 2—AFTER 180 DAYS, TYPICAL CONCENTRATIONS FOR PASTES OF PORTLAND CEMENT OF W/C = 0.5(8)

0.5(8)

Ion	Concentration
OH^-	0.32 mol l^{-1} (320 mol m^{-3})
Na^+	0.08 mol l^{-1} (80 mol m^{-3})
K^+	0.24 mol l^{-1} (240 mol m^{-3})

TABLE 3—PORE SOLUTION CONCENTRATIONS AT THE BEGINNING OF THE ELECTRICAL TEST

Ion	Pore Solution Concentration (mol m^{-3})
Hydroxide	103.45
Chloride	0
Sodium	25.86
Potassium	77.59

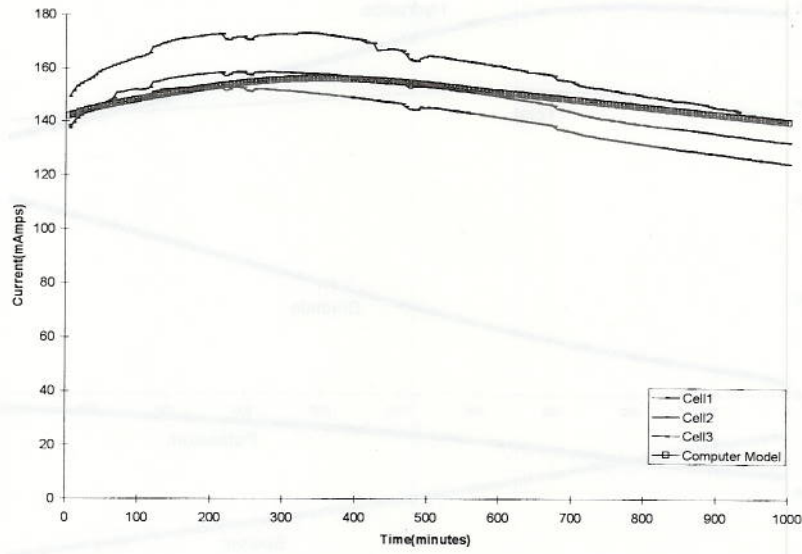


Fig. 1—Comparison of the computer model versus experimental results on portland cement, w/c = 0.3, 28 day cure. Applied potential is 40V

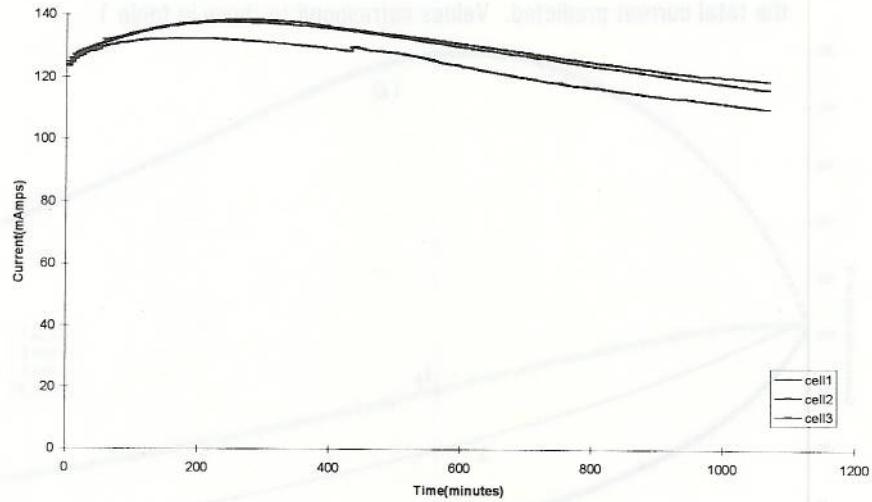


Fig. 2—Experimental results for the electrical test of portland cement/fly ash, w/c = 0.3, 28 day cure. Applied potential is 40V

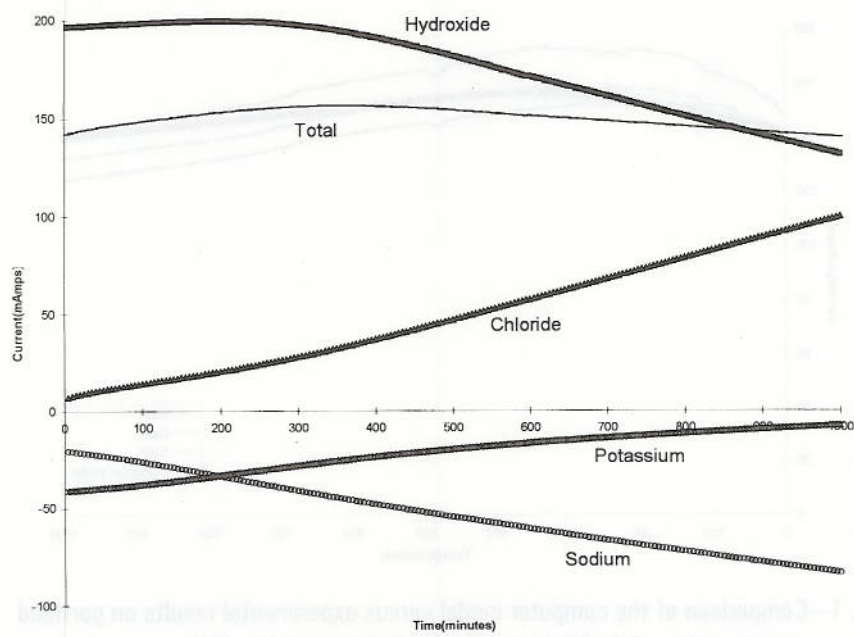


Fig. 3—From the computer model, the current predicted for all four ions compared to the total current predicted. Values correspond to those in table 1

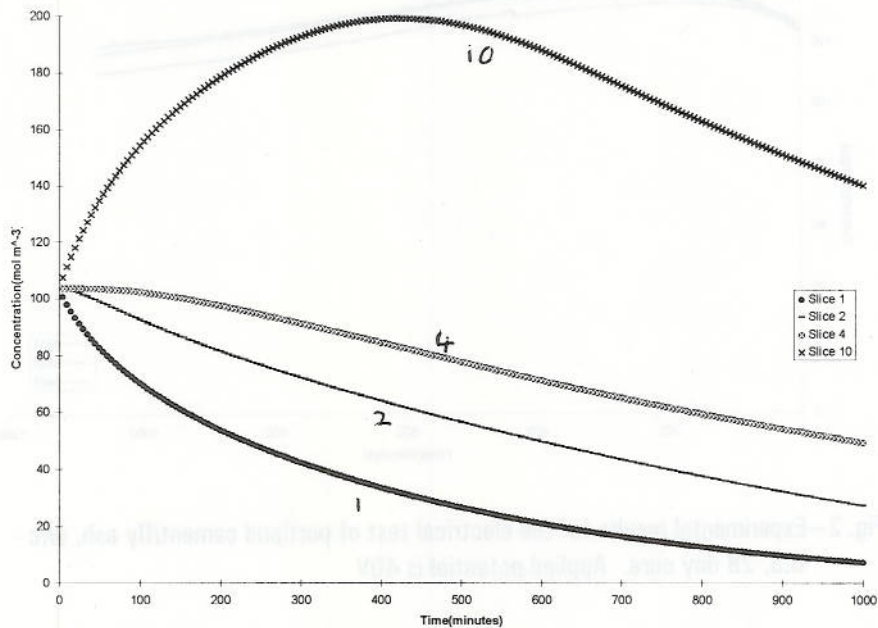


Fig. 4—Hydroxide concentration in slice 1, 2, 4, and 10, when N=10, for the computer model using values in table 1 (slice 1 is nearest NaCl solution)

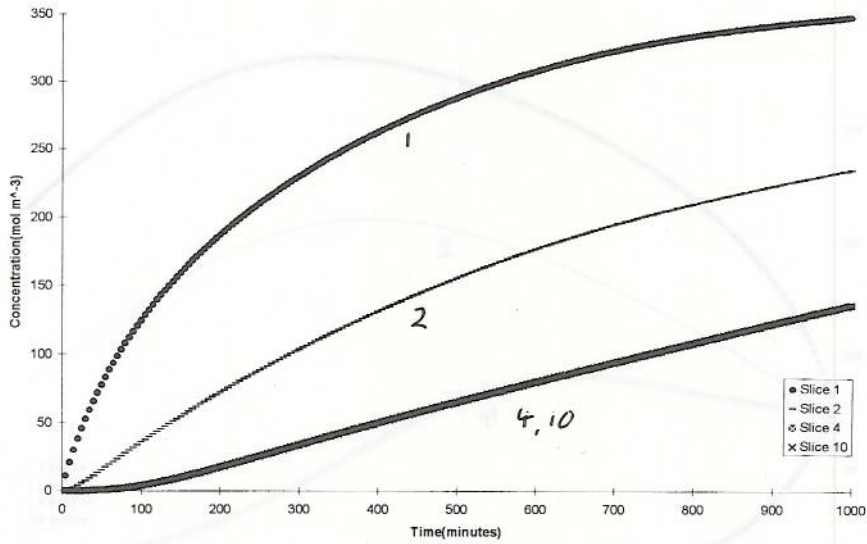


Fig. 5—Chloride concentration in slice 1, 2, 4, and 10, when $N=10$, for the computer model using values in table 1 (slice 1 is nearest NaCl solution)

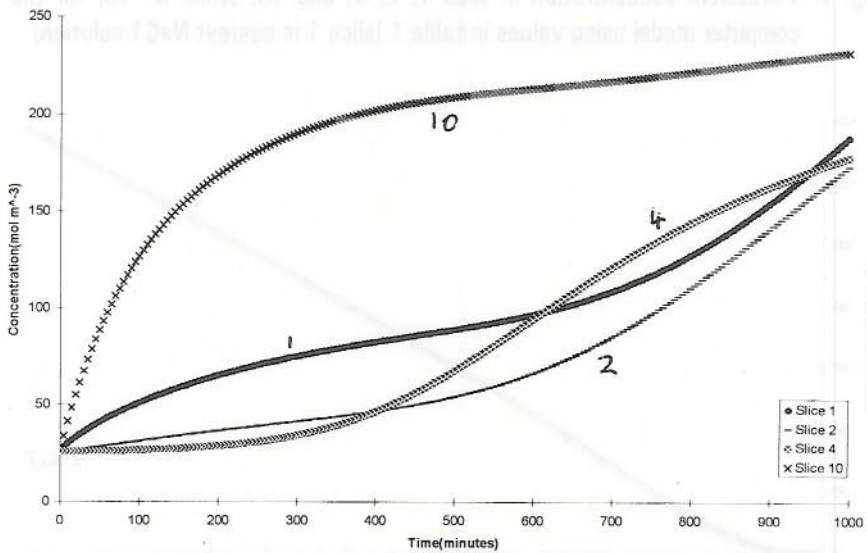


Fig. 6—Sodium concentration in slice 1, 2, 4, and 10, when $N=10$, for the computer model using values in table 1 (slice 1 is nearest NaCl solution)

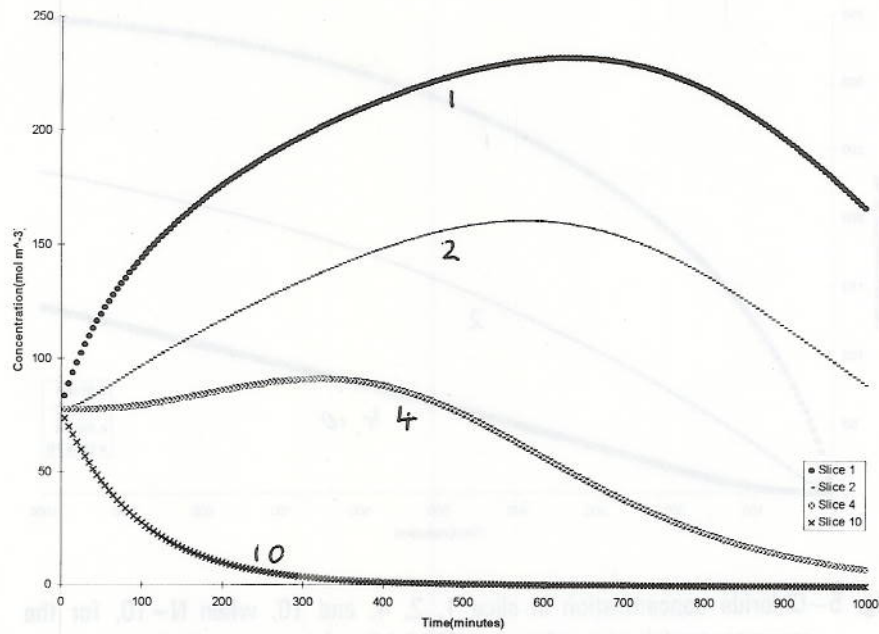


Fig. 7—Potassium concentration in slice 1, 2, 4, and 10, when $N=10$, for the computer model using values in table 1 (slice 1 is nearest NaCl solution)

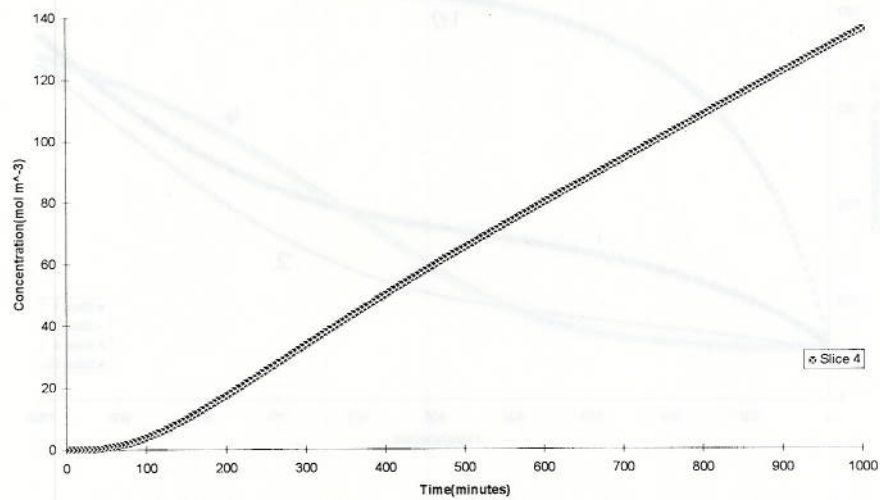


Fig. 8—Chloride concentration predicted by the computer model with values as in table 1 for slice 4 (19.5 m deep into sample from sodium chloride solution)