Quantitative Studies of Chloride Permeability of Concrete

Research Report FHWA-RI-RTD-98-1

December 1998

by
John Walsh, Ph.D. Sr. Chemist, Michael Sock, Sr. Civil Engineer,
Jose Lima, Sr. Civil Engineer, Steven Quintin, Engineering Technician III,
and Joseph Fera, Engineering Technician III

Research
Technology
Development

Prepared for the
Rhode Island Department of Transportation
in Cooperation with the U.S. Department of Transportation
Federal Highway Administration

RHODE ISLAND DEPARTMENT OF TRANSPORTATION

William D. Ankner, Ph.D., Director
James R. Capaldi, P.E., Chief Engineer
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16. Abstract

Studies were undertaken to develop a quantitative determination of chloride ion permeability in concrete based upon measuring the chloride ion migration in the concrete. The intent was to modify AASHTO standard method T-277 to measure the amount of chloride ion which completely passed through a concrete specimen while simultaneously measuring total charge as normally performed by the method. Studies showed that more than 99% of the chloride ion does not pass completely through the concrete disk specimen, but instead, remains within the concrete disk. Evaluation of permeability by measurement of complete passage of chloride ion was therefore not feasible. However, measurement of the test cell chloride ion transferred into the concrete disk was found to be a means to evaluate chloride permeability of the concrete specimen. This enables the measurement of chloride ion permeability in grams of chloride rather than in colulombs of total charge. The studies showed that total charge as measured in the T-277 method is not due solely to chloride ion, but that the total charge is an accumulation of charges contributed to by a water electrolysis background charge, and charges due to presence of other ions in the test cell solutions. It was shown that based upon the amount of chloride ion transferred into the concrete disk, the total charge measured was always much greater than that possibly due to chloride ion alone. Based upon these findings, total charge is not a specific measure of chloride ion permeability. Measurement of chloride ion transferred into the concrete specimen appears to be a direct evaluation of chloride ion permeability of the concrete. It is actually a measure of the absorbance of chloride ion by concrete, and specifically defines the amount (by weight) of chloride ion taken-up by, or permeating into a concrete specimen.

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Executive Summary

Exposure of concrete structures to sea air, deicing chemicals and moisture causes intrusion of chlorides into the concrete. Some concretes are more susceptible to chloride intrusion than others and are at higher risk of chlorides reaching the reinforcing steel "rebars" within the concrete causing corrosion of the steel and subsequent deterioration of the concrete.

Concretes can be classified based upon their degree of chloride intrusion or chloride permeability. This is accomplished by using AASHTO Method T-277. The degree of intrusion or permeability is determined by measuring the total charge passed through a concrete sample in contact with a salt solution and subjected to an applied voltage for a set length of time. The measured total charge is used as a measure of the "Chloride Ion Permeability " of the concrete sample. The higher the total charge, then the higher the chloride permeability and more susceptible the concrete is to intruding chloride. This is the current "state of the art" test procedure for determining chloride intrusion or permeability of concrete.

After studying and attempting to use the total charge technique (AASHTO T-277), it was realized that a quantitative relationship between total charge and chloride permeability has never been established. It was realized that total charge could not be the result of chloride ions alone, and that charge was contributed to by other sources in the testing procedure.

The objective of this study was to develop a method for evaluating chloride permeability based upon the amount of chloride ion which enters into and migrates through a concrete specimen. This would be a specific and direct measure of chloride and chloride permeability. Chloride permeability could then be defined as "grams of chloride" instead of "total charge as coulombs" which most users don't comprehend. The study would also enable observing the physical and chemical processes occurring in the test cell.

The results show that total charge as measured in the T-277 Method is not due solely to chloride ion, but that total charge is an accumulation of charges contributed to by the electrolysis of water at the electrodes within the test cell, and charges due to the presence of other ions in the cell solutions and also in the concrete itself. Based upon these findings, total charge is neither a measure of chloride ion or, chloride ion permeability.

Studies also showed that chloride ion which enters the concrete specimen remains in the specimen and does not pass through the concrete. In fact, there appears to be little movement or migration of the chloride once inside the concrete. It was also found that five salts, all chloride ion free, when tested in the T-277 test cell, produced total charge equal to total charge obtained using sodium chloride as the cell standard test solution. Consequently, ions other than chloride readily produced charge and can easily contribute to total charge.

It was found that measurement of chloride ion which transfers out of the sodium chloride cathode cell reservoir and enters the concrete specimen is a direct measure of chloride ion intrusion or permeability of the concrete. A chemical method was developed for the measurement of the transferred chloride as grams of chloride. This provides an accurate evaluation of chloride permeability of concrete as grams of chloride, and which is independent of total charge and other interfering sources. Chloride permeability can now be defined quantitatively and meaningfully by weight of chloride intrusion into concrete.

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Abstract

Studies were undertaken to develop a quantitative determination of chloride ion permeability in concrete based upon measuring the chloride ion migration in the concrete. The intent was to modify AASHTO standard method T- 277 by measuring the amount of chloride ion which completely passed through a concrete specimen instead of measuring total charge as described in the method. Studies showed that more than 99% of the chloride ion does not pass completely through the concrete disk specimen, but instead, remains within the concrete disk. Evaluation of permeability by measurement of complete passage of chloride ion was therefore not feasible. However, measurement of the test cell chloride ion transferred into the concrete disk was found to be a means to evaluate chloride permeability of the concrete specimen. This enables the measurement of chloride ion permeability in grams of chloride rather than in coulombs of total charge. The studies also showed that total charge as measured in the T-277 method is not due solely to chloride ion, but that the total charge is an accumulation of charges also contributed to by a water electrolysis background charge, and charges due to presence of other ions in the test cell solutions. It was shown that based upon the amount of chloride ion transferred into the concrete disk, the total charge measured was always much greater than that possibly due to chloride ion alone. Based upon these findings, total charge is not a specific measure of chloride ion permeability. Measurement of chloride ion transferred into the concrete specimen appears to be a direct evaluation of chloride ion permeability of the concrete. It is actually a measure of the absorbance of chloride ion by concrete, and specifically defines the amount (by weight) of chloride ion taken-up by, or permeating into a concrete specimen.

Introduction

Chloride permeability of concrete is a significant factor in causing corrosion of reinforcing steel within the concrete. Permeability of chloride ions through the concrete to reach the steel often results in the formation of "rust", the main corrosion product of the steel rebars. The rust exerts large tensile forces due to volume changes on the surrounding concrete which causes internal fracturing as well as delamination and spalling of bridge decks.

It was realized early-on that prevention of chloride ion migration to the reinforcing steel surface would greatly reduce the corrosion problem. It was also apparent that a means for retarding and possibly preventing chloride ion migration was to incorporate materials within the concrete which would act as barriers to the chloride ions. Materials such as latex and other polymers, silica fumes, fly ash, and internally sealed concrete have been proposed and studied.

The remaining necessary requirement was a reliable test method to evaluate the effectiveness of such materials or to simply determine the chloride permeability of various concretes per se and possibly classify the concretes on the basis of permeability. The AASHTO standard test method T- 259, "Resistance of Concrete to Chloride Ion Penetration," was utilized for this purpose. This method involved salt ponding horizontal surfaces of concrete slabs of predetermined dimensions (size and thickness) with 3% by wt sodium chloride solution for 90 days. A chloride ion concentration profile was then carried out by measuring chloride ion concentrations at prescribed depths. The profile was used to determine the degree of chloride migration into the concrete sample. By this method, permeability was determined by the concentration of chloride measured.

Although the 90-day ponding test is a reliable and documented method, it has the disadvantage of being a very lengthy and time consuming procedure. Preparation of the concrete slabs, the 90-day ponding period and the necessity for chloride profiling analyses complicates and lengthens the permeability evaluation process. Consequently, an accelerated testing procedure was developed, namely, AASHTO Method T-277 entitled "Rapid Determination of the Chloride Permeability of Concrete". The title of this method was later changed to "Electrical Indication of Concrete's Ability to Resist Chloride". In this method an applied electrical voltage is used to cause rapid migration of chloride ions into the concrete sample thus enhancing the rate of chloride permeability and greatly shortening the testing procedure time.

The method consists of monitoring the amount of electrical current passed through a concrete specimen when one end of the specimen is immersed in a sodium chloride solution and the other end in a sodium hydroxide solution. A potential difference is maintained across the specimen for six hours. The periodically monitored electrical current is plotted against time, and the area under the curve is integrated to determine the total charge passed in coulombs during the six hour test period. Total charge passed (coulombs) is then related to chloride permeability. The greater the charge measured, then the greater the chloride permeability of the concrete.

By means of the rapid test method, total charge of known types of concrete have been determined, and a reference table established. Consequently, the measured total charge of an unknown concrete can be compared to those in the reference table for classification of the concrete, such as, a high, moderate or low water-cement ratio concrete, or a latex or polymer modified concrete etc.

After studying and attempting to use the rapid test method, it became apparent that it provided only general information regarding the relationship between total charge and permeability. A conclusive quantitative relationship between total charge and permeability has never been established. Moreover, total charge is not specific to chloride ion alone, but is the resulting charge caused by all the ions present in the test cell system. Sodium and hydroxyl ions are in abundance plus, ions from soluble salts in the concrete sample per se. All such ions contribute charge to the resulting total charge. Total charge is not indicative of chloride ion charge nor of chloride ion permeability. The rapid test lacks the necessary specificity to relate coulombs or charge caused by chloride ion to chloride permeability.

Since chloride ion was the species of interest and is relatively easy to quantitatively measure, it was decided to develop an analytical chemical means to measure the quantity of chloride which actually migrates in a concrete sample. This would enable defining chloride permeability of concrete in actual amounts of chloride (grams) which had migrated through the concrete. The ability to measure chloride permeability directly by grams of chloride would provide an absolute data value suitable for subsequent calculations by engineers which is not the case with measured total charge expressed as coulomb data.

The objectives of this work were first, to develop a chemical analysis to measure the amount of chloride ion that migrates through a concrete specimen, second, to establish a quantitative relationship between chloride ion migration and concrete permeability, and third, to establish reference data relating amount of chloride in grams, to degree of permeability similar to the table in AASHTO Method T-277 relating coulombs and permeability.

Experimental Procedures

Specimen Preparation -

Three batches of concrete were prepared using different water/cement ratios which were 0.40, 0.42, and 0.43 respectively. All other factors were held constant as possible (see Appendix A for mix design and batch test results). The batch using the middle water/cement ratio (0.42) was of larger amount than the other two. This allowed more permeability specimens to be fabricated as the bulk of the permeability test runs were made with specimens from this batch. Specimens were cast as 10 cm, (4.0 in.) diameter by 20 cm, (8.0 in.) long cylinders. Six disk specimens were used in a given test run. All were sliced from concrete cylinders from the same batch and mix design.

Slab specimens 34 cm, (13.5 in.) wide by 34 cm, (13.5 in.) long by 12 cm, (5 in.) thick were also cast from each batch and were fabricated with a dike using a Styrofoam spacer. This enabled creating a 26 by 26 by $2^1/_2$ cm, (10.2 by 10.2 by 1 in.) containment area. The concrete was marked as to which batch it was prepared from and was cured in a moist room for twenty-eight days.

Permeability specimens were made from the concrete cylinders by cutting the cylinders into 5 cm, (2.0 in.) thick disks. Three such disks were obtained from each cylinder. Two and one-half cm, (1.0 in.) was cut from both ends of each cylinder prior to cutting the three specimens from the remainder of the cylinder. Each specimen disk was marked with the batch and original location in the cylinder, that is, top, middle or bottom section.

Test Procedures -

1) Permeability Tests

The test procedure was run according to AASHTO Method T-277, "Electrical Indication of Concrete's Ability to Resist Chloride," with some apparatus modifications for the purpose of automating the test (see Appendix B for a description of the apparatus and equipment). Six sample cells were connected in parallel to two interface cards in a standard MS-DOS compatible computer. Once the sample cells were wired into the system and the control software program was started, the test was allowed to run with manual spot checks to insure proper operation. The 0.01 ohm shunt resistors specified in T-277 used to measure the current through the specimen cell were replaced with three ohm resistors to allow a voltage large enough to be detected by the interface cards. The current never rose above 0.2A. and the voltage loss relative to the sixty volts potential drop across the cell was considered to be negligible. The test run time as specified in T-277 was six hours.

The volume of the solution added to each cell reservoir was measured at the start and finish of each run. Chloride analyses of the cell solutions were also performed prior to addition to the cell reservoirs and after test completion. A time-study test of charge and chloride ion concentration variation with time was carried out in one of the test runs. Two milliliters of sodium chloride solution was removed from the reservoir of each cell at one-half hour intervals. Coulomb and chloride values were determined for each half-hour interval.

2) Concrete Disk and Slab Tests

Concrete disks from each run where a sodium chloride cell solution was utilized in the cathode cell were drilled in five places on the face of the disk which had been in contact with the sodium chloride solution. Each drilling location was first drilled to a depth of 0.64 cm, (1/4 in.) and the powdered sample discarded. The drilling was then carried on to a depth of 2.54 cm, (1 in.). These 2.54 cm, (1 in.) drillings at the five places were then combined and used for concrete disk chloride analyses.

Concrete slabs which were ponded in a 3% by wt. sodium chloride solution for 90 days as specified in AASHTO T-259 were drilled in five places at depths of 1.9 and 4.5 cm, (3/4 and $1^3/_4$ in.) The 1.9 cm, (3/4 in.) drillings were combined to form a single depth sample, and the 4.5 cm, ($1^3/_4$ in.) drillings combined to form the second depth sample. Each composite sample was analyzed for chloride. These samples were used to provide a chloride permeability profile for the concrete slab specimens and, also for comparison to chloride values obtained via the chloride permeability cell testing.

3) Chloride Analyses and Charge Measurements -

Chloride analyses for the cell solutions, concrete disks and slabs were carried out according to AASHTO T-260 method "Sampling and Testing for Total Chloride Ion in Concrete and Concrete Raw Materials", with some slight modifications to account for pH adjustments and appropriate dilutions. All cell solutions, even cathode cell solutions which were either neutral or slightly acidic prior to testing, became strongly basic after the six hour test runs. It was necessary to adjust to an acid pH before titrating with standard silver nitrate. Concrete powdered samples from the disk and slab specimens were extracted with hot nitric acid solutions as specified in T-277 to free chlorides from the concrete powders. After filtration, the resulting solution extracts were then titrated with silver nitrate. Silver nitrate titrations were carried out using an Orion 940 Autotitration System which determined titration end-point (ml) and grams of chloride ion present, and also provided a Gran-Plot titration curve of silver nitrate volume (ml) versus voltage (mv). A standard sodium chloride solution was titrated on a daily basis prior to sample titrations to insure accuracy and reliability of the instrument.

Charge measurements as coulombs were made during the permeability test runs by measuring current readings (amperes) every one second. Summing the ampere readings results in charge or coulombs at a given total test time. At the end of a six hour test run, the total charge passed through the cell is known and expressed as coulombs. These measurements, recordings and calculations were performed by the computer software program during and at the end of the test run.

Test Results

1) Current versus Time Studies -

For each of the six cells in every test run, amperage readings were taken at given time intervals during the six hour run. Plots of current (amperes) versus time (seconds) were made to observe the comparisons between cells within a given run, that is, current changes in each cell over the six hour period. These plots would further enable the comparison of currents between runs having the same cell solution systems and, also those of different solution systems.

Eleven permeability test runs were made consisting of six cells per run for a total of sixty-six concrete disk specimens tested for permeability studies. However, cell solutions were varied during certain runs in order to study the charge effects of salts other than sodium chloride. Most of the solution changes were made in the cathode cell by replacing the sodium chloride with another salt solution which did not contain chloride ion. In only two runs was the sodium hydroxide in the anode replaced and each time distilled water was used. In total, four runs were carried out using sodium chloride versus sodium hydroxide solutions, two runs using distilled water, first in the anode cell, and then in both cells i.e. cathode and anode simultaneously, and five other runs involving the use of a non-chloride containing salt solutions in replacement of sodium chloride in the cathode cell. The permeability test runs are summarized as follows:

Test Run	Test Cell Solution System		Table #	Figure #
1	Sodium Chloride vs. Sodium Hydroxide	(0.40 w/c)	1	1
2	" " "	(0.43 w/c)	2	2
3	" " "	(0.42 w/c)	3	3
4	" " "	(0.42 w/c)	4	4
5	Sodium Chloride vs. Water	(0.42 w/c)	5	5
6	Water vs. Water	(0.42 w/c)	6	6
7	Sodium Nitrite vs. Sodium Hydroxide	(0.42 w/c)	7	7
8	Sodium Nitrate vs. Sodium Hydroxide	(0.42 w/c)	7	8
9	Sodium Sulphite vs. Sodium Hydroxide	(0.42 w/c)	7	9
10	Sodium Sulphate vs. Sodium Hydroxide	(0.42 w/c)	7	10
11	Calcium Nitrate vs. Sodium Hydroxide	(0.42 w/c)	7	11

In general, the results showed that all of the cell systems caused current changes which increased moderately and eventually leveled off during the six hour test period. Systems with no chloride also developed current of varying amounts. Some amounts were greater than those of the sodium chloride systems. Systems containing water as cell solutions in one or both cells produced the smallest currents. However, the amounts were significant enough that they must be accounted for when designating the individual contributors to total current (and to total charge) of a test cell system.

Plots of current versus time for these cell systems are shown as follows: Figures 1 through 4 are plots for sodium chloride versus sodium hydroxide, Figures 5 & 6 are those of sodium chloride versus water in one case and water versus water in the other system. The water runs were made to obtain background current information regarding water because all of the cell solutions used are aqueous salt solutions. Figures 7 through 11 are plots for the five non-chloride salt solutions versus sodium hydroxide.

<u>Sodium Chloride vs. Sodium Hydroxide Cell Systems</u>

Current - Time Plots

Figures 1 & 2

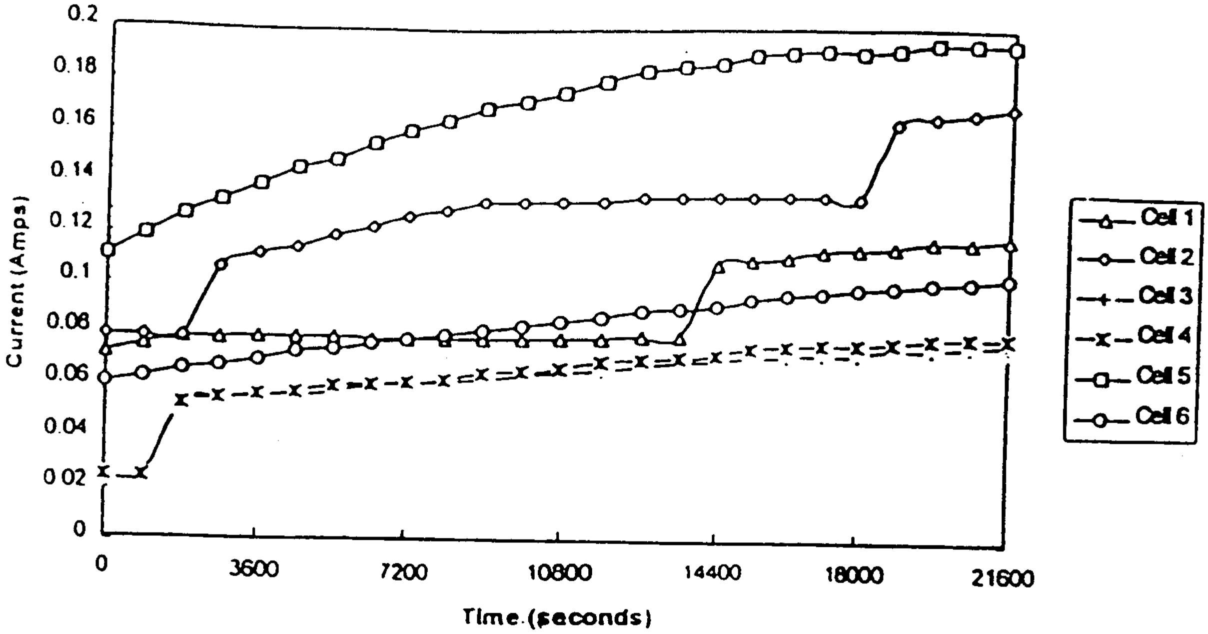

Figure 1 - Permeability Test Run One: NaCl to NaOH, w/c = 0.40

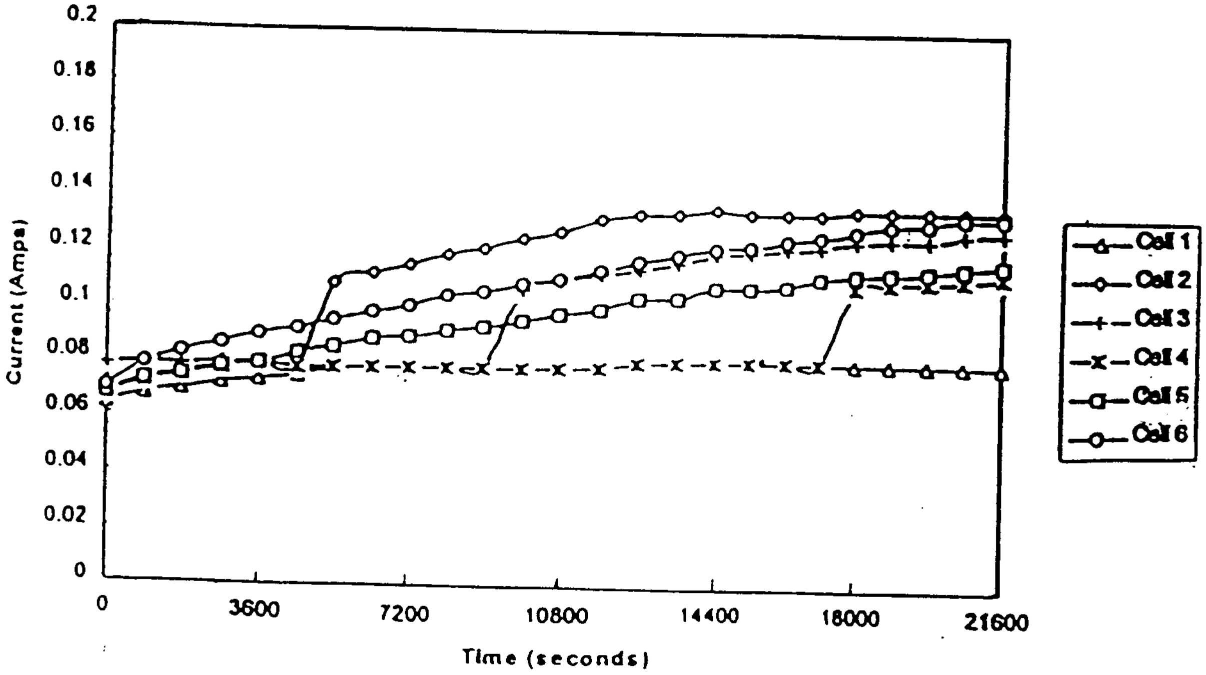

Figure 2 - Permeability Test Run Two: NaCl to NaOH, w/c = 0.43

Sodium Chloride vs. Sodium Hydroxide Cell Systems
Current - Time Plots
Figures 3 & 4

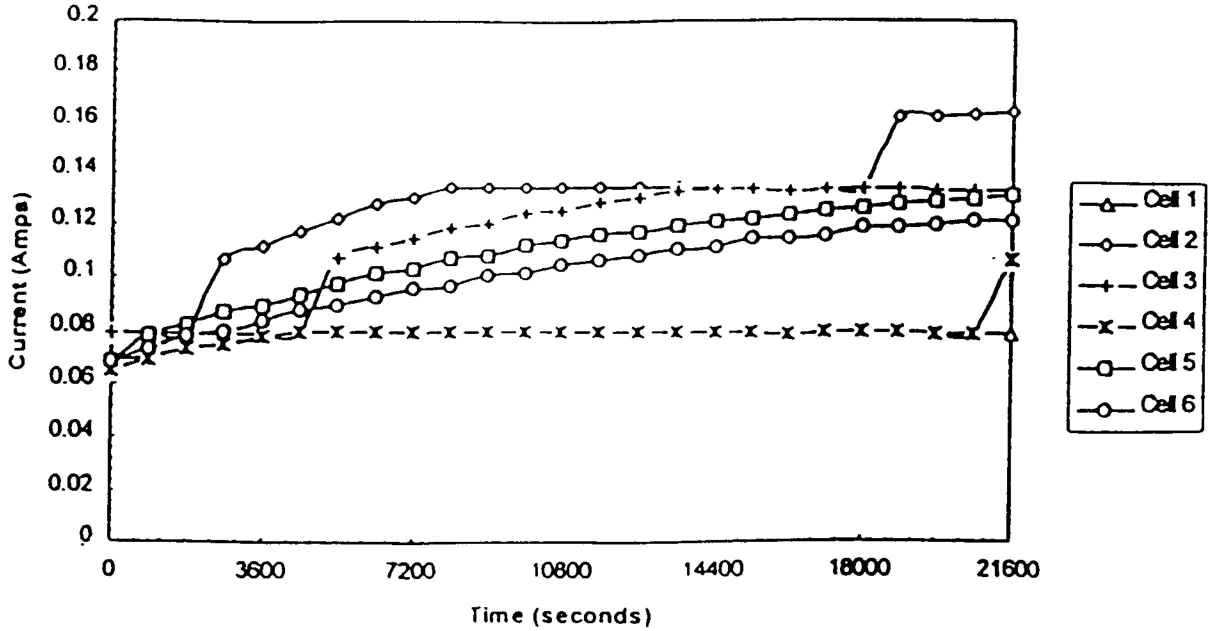

Figure 3 - Permeability Test Run Three: NaCl to NaOH, w/c = 0.42

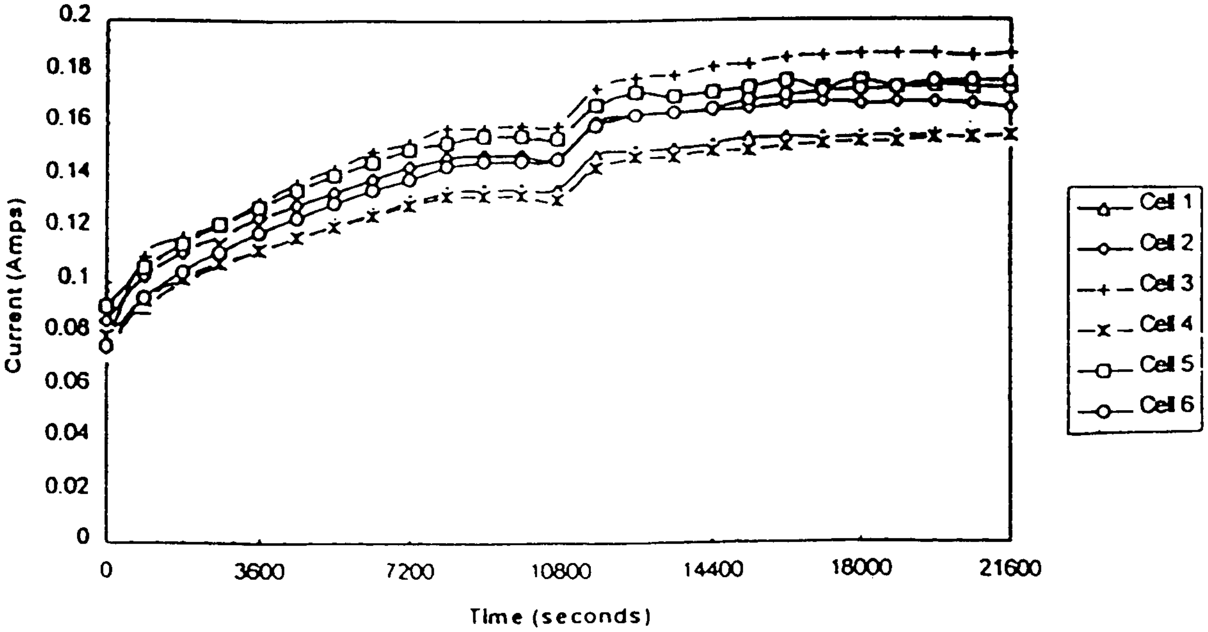

Figure 4 - Permeability Test Run Four: NaCl to NaOH, w/c = 0.42
[sampling of NaCl solution throughout run].

Water Cell Systems
Current - Time Plots
Figures 5 & 6

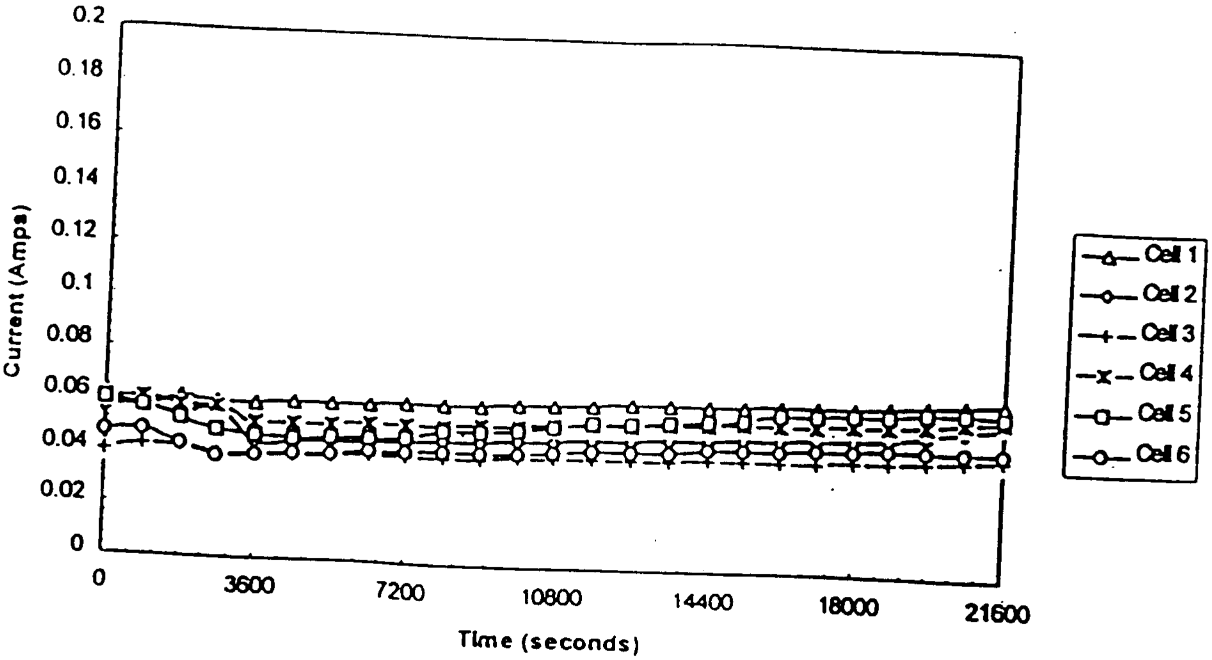

Figure 5 - Permeability Test Run Five; NaCl to H_2O, w/c = 0.42

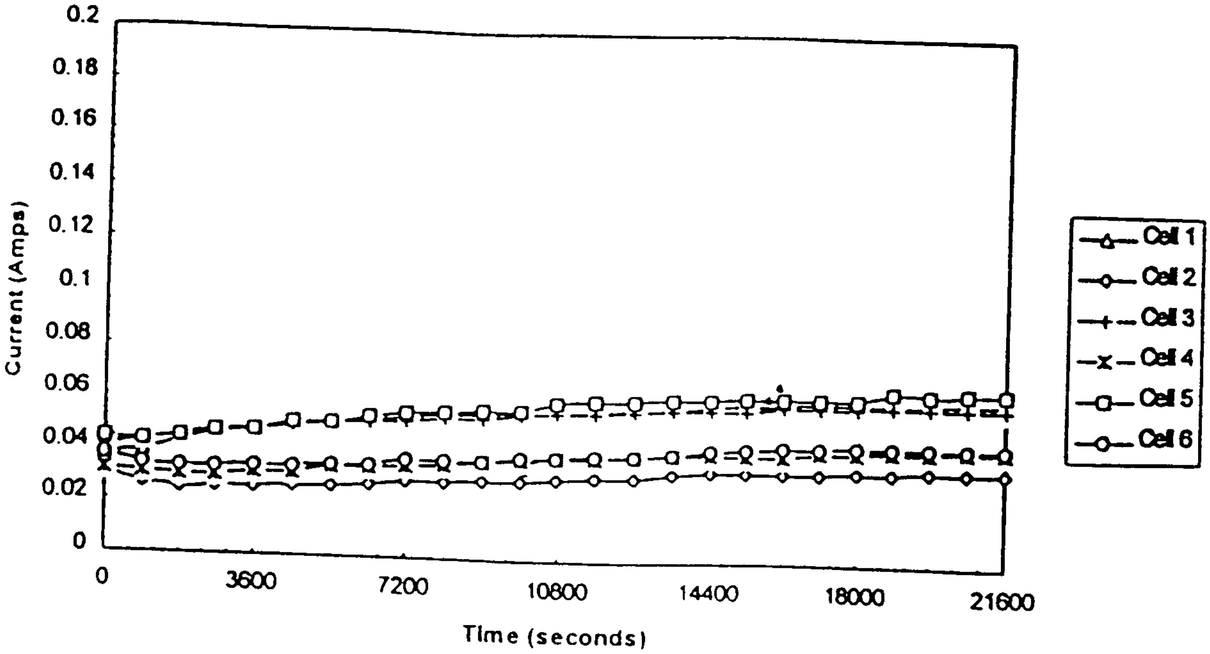

Figure 6 - Permeability Test Run Six; H_2O to H_2O, w/c = 0.42

Non-Chloride Salts vs. Sodium Hydroxide Cell Systems

Current - Time Plots

Figures 7 & 8

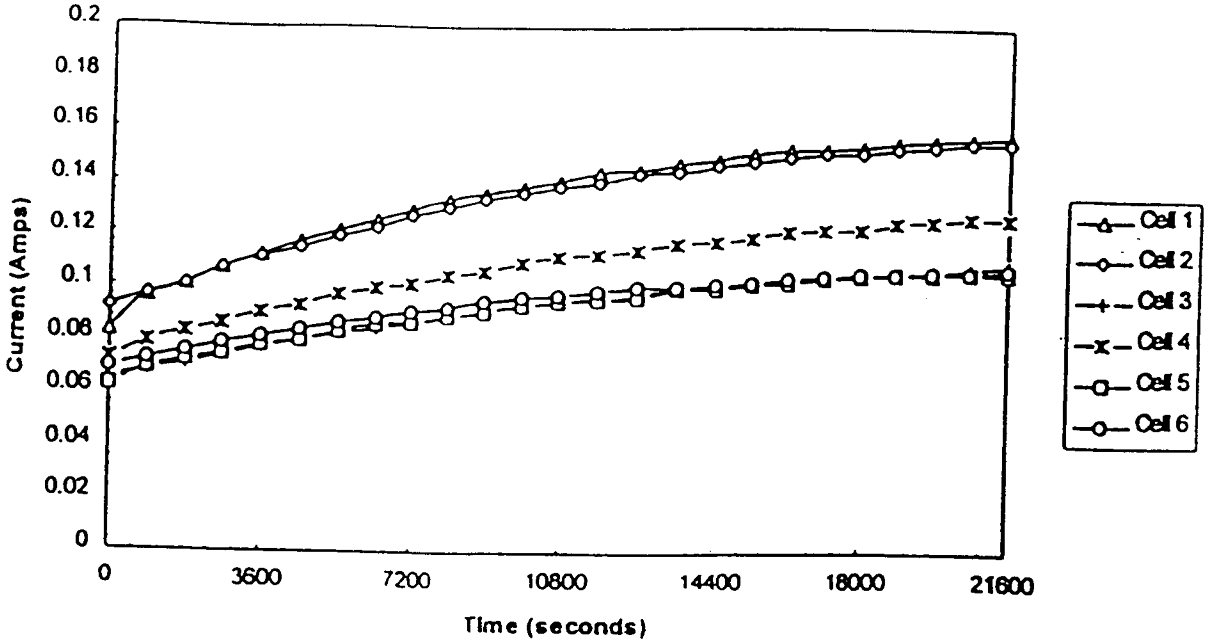

Figure 7 - Permeability Test Run Seven; $NaNO_3$ to NaOH, w/c = 0.42

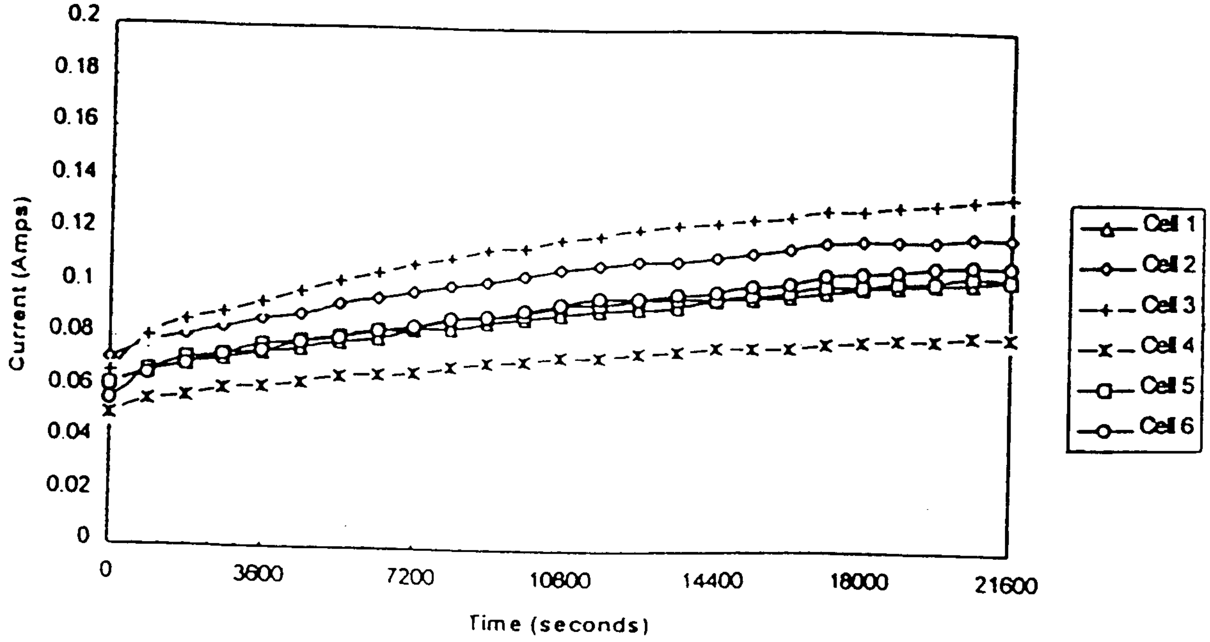

Figure 8 - Permeability Test Run Eight; $NaNO_3$ to NaOH, w/c = 0.42

Non-Chloride Salts vs. Sodium Hydroxide Cell Systems

Current - Time Plots

Figures 9 & 10

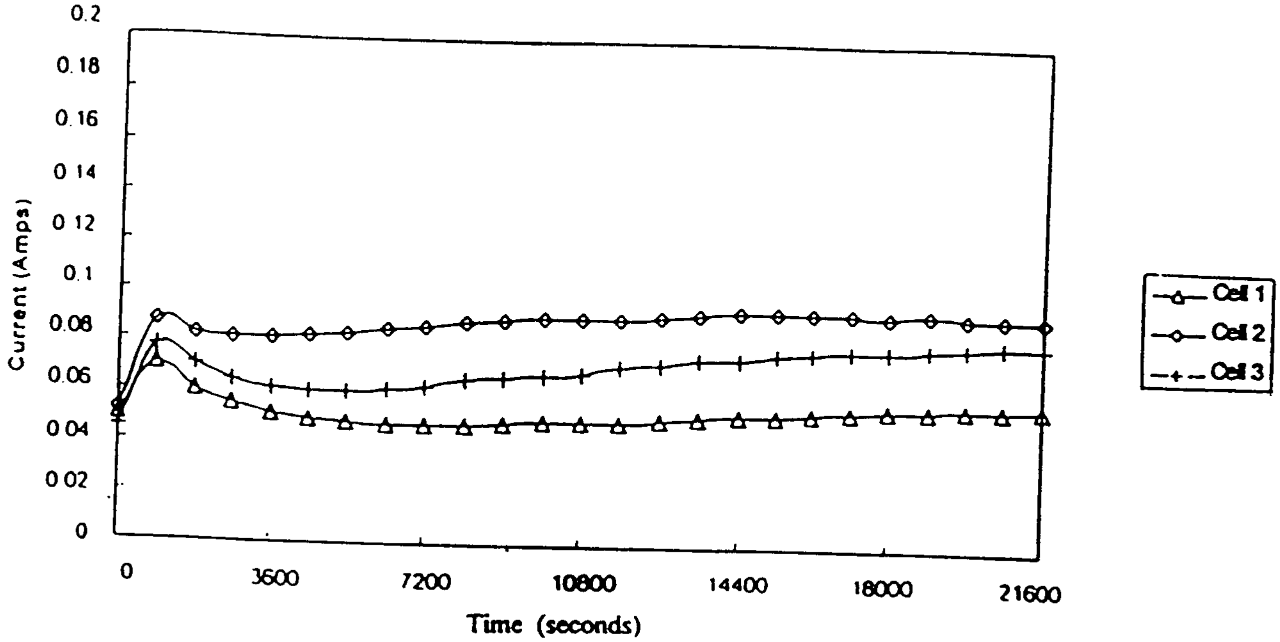

Figure 9 - Permeability Test Run Nine: Na_2SO_4 to NaOH, w/c = 0.42

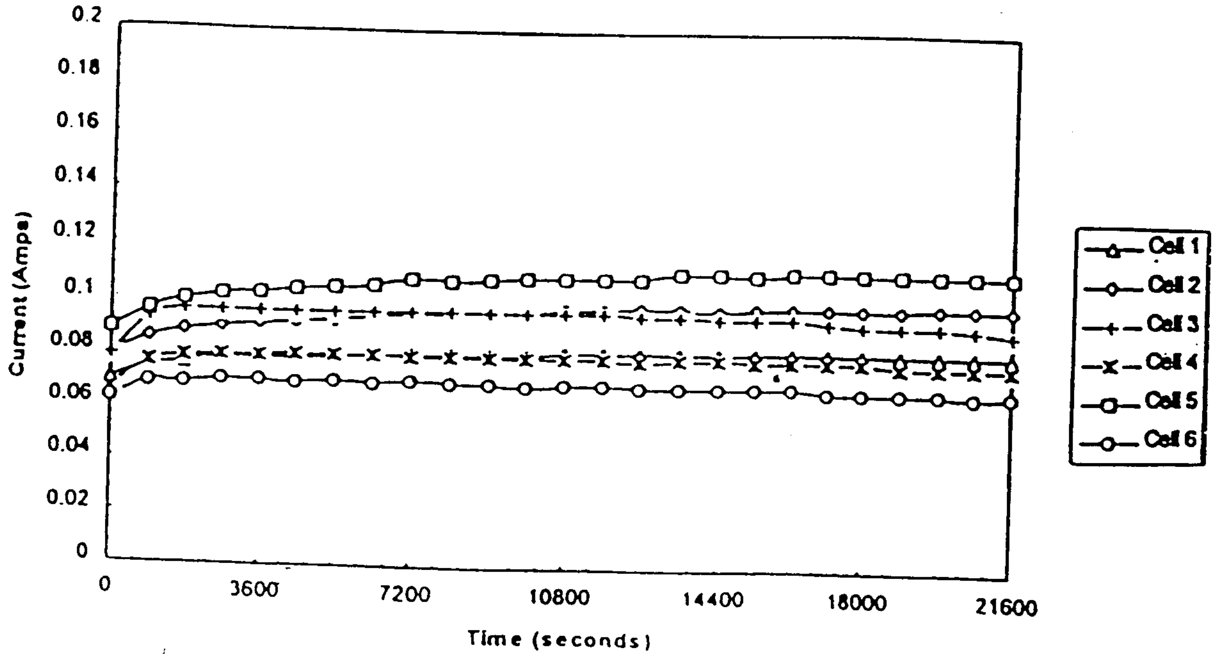

Figure 10 - Permeability Test Rim Ten: Na_2SO_4 to NaOH, w/c = 0.42

Non-Chloride Salts vs. Sodium Hydroxide Cell Systems
Current - Time Plots
Figure 11

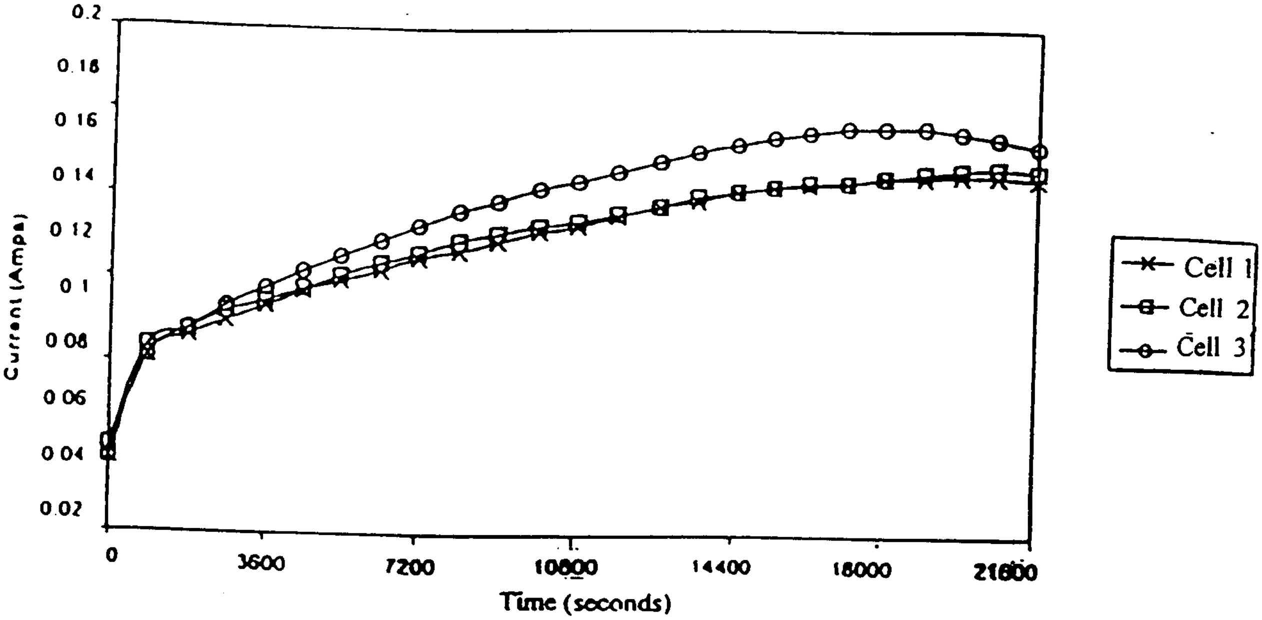

Figure 11 - Permeability Test Run Eleven: $Ca(NO_3)_2$ to NaOH, w/c = 0.42

Observations of the current versus time studies are summarized as follows:

* *The individual test cells did not pass the same amounts of current.* Currents varied moderately from cell to cell even under the same experimental conditions.

* *Water as both anode and cathode solutions produced a significant amount of background current* which will contribute appreciably to total charge, and must be accounted for when measuring current and total charge of salt solutions.

* *Type of anode solution has marked effect on current in sodium chloride cathode systems.* Sodium hydroxide as anode solution caused a two-fold increase in current with sodium chloride systems as compared to water as the anode solution.

* *Non-chloride salts as cathode solutions produce currents as readily and abundantly as chloride salts.* Nitrate-nitrite, and sulphate-sulphite salts gave about the same degree of currents as the chlorides. Calcium salts gave the highest currents of all the salts tested.

In addition, the plots reveal several points of more specific interest as follows:

* The divalent *cation,* calcium (Ca^{+2}), in a cell solution gave high currents, even greater than when chloride ions were present.

* The divalent *anions* did not all cause the same degree of current. Nitrate/nitrites cause larger currents than sulphates/sulphites.

* The current versus time plots for the two water system runs (NaCl vs. H_2O and H_2O vs. H_2O, Figures 4 & 5) were very close and similar despite the fact that chloride ion was present in one of the systems.

* In contrast, NaCl vs. NaOH cells gave much higher currents than the water systems apparently due to the presence of sodium hydroxide as the anode solution rather than water.

The results indicate that ions other than chloride contribute to total current (and to total charge), and the contribution varies with ion type, that is, anion versus cation and with the ionic charge (valence) of the ion.

2) Permeability Test Studies -

a) Sodium Chloride vs. Sodium Hydroxide Cell Systems

Sodium Chloride was the cathode solution and sodium hydroxide the anode solution for four test runs of NaCl vs. NaOH cell systems. The grams of chloride in the initial 3% by wt NaCl cell solution and also any minute amount of chloride in the initial 0.3N NaOH cell solution was determined by silver nitrate titration prior to the test run. The volumes of the cell solutions were measured before and after the runs. After the six hour test, the grams of chloride in both cell solutions were again determined by titration. In this manner, the grams of chloride transferred out of the NaCl compartment and also the grams of chloride entering the NaOH compartment were determined. The charge passing through the system was measured in real time via computer during the run, and the total charge was determined upon termination of the run. Four runs with six cells each enabled twenty-four NaCl vs. NaOH cell solution systems to be studied. Permeability test data for the four runs are shown in Tables 1, 2, 3, & 4.

Table 1. Chloride Permeability Test Data:

Run #1 NaCl vs. NaOH
0.40 w/c

Test Cell #	Gram Cl Transferred	Gram Cl To Disk	Gram Cl To NaOH Cell	% Cl To Disk	% Cl To NaOH Cell	Coulombs Passed
1	0.4655	0.4641	0.0014	99.69	0.31	1878
2	0.5301	0.5296	0.0005	99.91	0.09	2660
3	0.3624	0.3595	0.0029	99.21	0.79	1315
4	0.3640	0.3580	0.0061	98.35	1.66	1373
5	0.7121	0.7115	0.0007	99.91	0.09	3488
6	0.4131	0.4126	0.0005	99.88	0.12	1756
Max	0.7121	0.7114	0.0061	99.91	1.66	3488
Min	0.3624	0.3580	0.0005	98.35	0.09	1315
Avg	0.4745	0.4726	0.0021	99.50	0.51	2078

Table 2. Chloride Permeability Test Data:

Run #2 NaCl vs. NaOH
0.43 w/c

Test Cell #	Gram Cl Transferred	Gram Cl To Disk	Gram Cl To NaOH Cell	% Cl To Disk	% Cl To NaOH Cell	Coulombs Passed
1	0.5023	0.5003	0.0020	99.59	0.41	1610
2	0.6107	0.6094	0.0014	99.78	0.22	2431
3	0.5157	0.5133	0.0024	99.53	0.47	2101
4	0.4352	0.4349	0.0003	99.92	0.08	1736
5	0.5594	0.5593	0.0002	99.97	0.03	1999
6	0.5797	0.5794	0.0003	99.94	0.06	2266
Max	0.6107	0.6094	0.0024	99.97	0.47	2431
Min	0.4352	0.4349	0.0002	99.53	0.03	1610
Avg	0.5338	0.5328	0.0011	99.79	0.21	2024

Table 3. Chloride Permeability Test Data:

Run #3 NaCl vs. NaOH
0.42 w/c

Test Cell #	Gram Cl Transferred	Gram Cl To Disk	Gram Cl To NaOH Cell	% Cl To Disk	% Cl To NaOH Cell	Coulombs Passed
1	0.3952	0.3951	0.0002	99.96	0.04	1625
2	0.5727	0.5722	0.0005	99.92	0.08	2650
3	0.5118	0.5113	0.0005	99.90	0.10	2397
4	0.4359	0.4359	0.0000	100.00	0.00	1633
5	0.4674	0.4671	0.0003	99.93	0.07	2276
6	0.5071	0.5066	0.0005	99.90	0.10	2105
Max	0.5727	0.5794	0.0005	100.00	0.10	2650
Min	0.3952	0.3951	0.0000	99.90	0.00	1625
Avg	0.4817	0.4814	0.0003	99.94	0.06	2114

Table 4. Chloride Permeability Test Data:

Run #4 NaCl vs. NaOH
0.42 w/c

Test Cell #	Gram Cl Transferred	Gram Cl To Disk	Gram Cl To NaOH Cell	% Cl To Disk	% Cl To NaOH Cell	Coulombs Passed
1	0.6830	0.6819	0.0011	99.84	0.16	2790
2	0.7985	0.7975	0.0009	99.88	0.12	3049
3	0.7886	0.7871	0.0001	99.80	0.20	3361
4	0.6790	0.6778	0.0011	99.84	0.16	2759
5	0.7015	0.7010	0.0004	99.94	0.06	3183
6	0.6609	0.6603	0.0006	99.91	0.09	3032
Max	0.7985	0.7975	0.0011	99.94	0.20	3361
Min	0.6609	0.6603	0.0001	99.80	0.06	2759
Avg	0.7186	0.7176	0.0007	99.87	0.13	3029

Results of the permeability test studies are summarized as follows:

* *The amounts of chloride ion transferred out* of the individual NaCl cathode cell compartments were not the same. The amounts varied between each of the six cells within a given test run and also between runs. See Figure 12.

* *The total charge or coulombs produced* by the respective cells was not the same for each cell. Total charge varied per cell as did chloride ion transfer out of the NaCl compartment of the cell. See Figure 13.

* *Chloride ion transfer and total charge (coulombs) varied in phase within each cell.* Meaning as one increased or decreased so did the other. See Figure 14.

* *Plotting chloride ion transfer concentration and total charge versus cell numbers* gives two plots which are almost parallel indicating some possible quantitative relationship. See Figure 15.

* *A quantitative relation is further indicated* when chloride ion transfer concentration is plotted directly versus total charge. In this case an almost linear plot is obtained. See Figure 16.

* *The amounts of chloride ion reaching the NaOH anode compartment* after passing through the concrete disk sample were extremely small, usually only a few milligrams, and varied considerably. In some cases no chloride ion reached the NaOH compartment. On average only 0.22 % of the migrated chloride ion reached the NaOH anode. See averages in Tables 1 to 4 under % Cl to NaOH Cell columns.

* The amount of chloride remaining in the concrete disk sample after six hours testing was determined by difference. Simply, the amount of chloride reaching the NaOH anode was subtracted from the amount transferred out of the NaCl compartment. It was calculated that about 99.78% of the transferred chloride ion remained in the concrete disk specimens and did not reach the NaOH compartment. See averages in Tables 1 to 4 under % Cl to Disk columns.

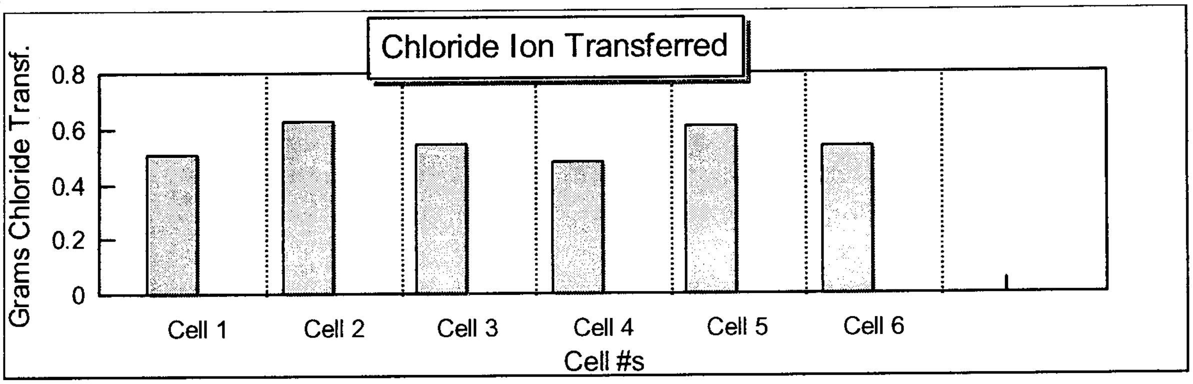

Figure 12. Variation of amount of chloride ion transferred out of each cell during six hour run.

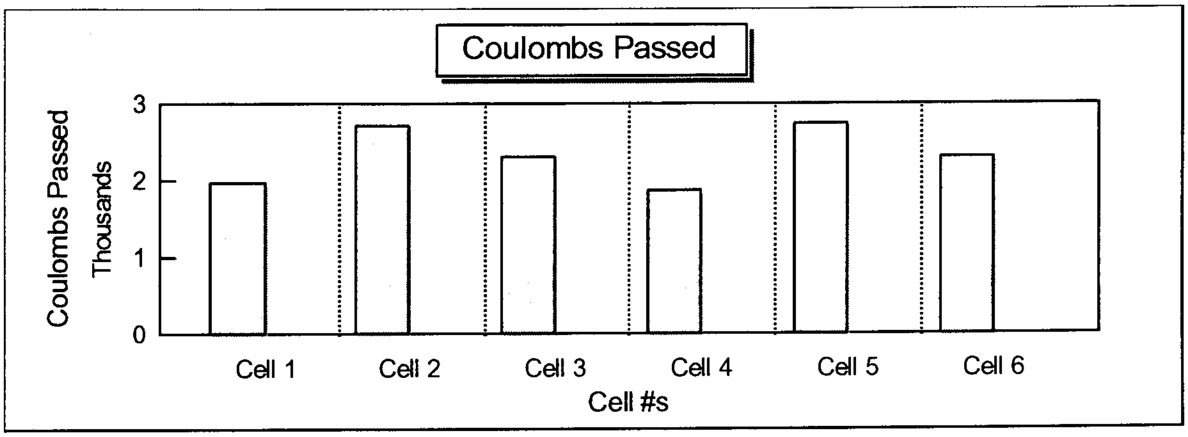

Figure 13.. Variation of amount of charge (coulombs) passed by each cell during six hour test run.

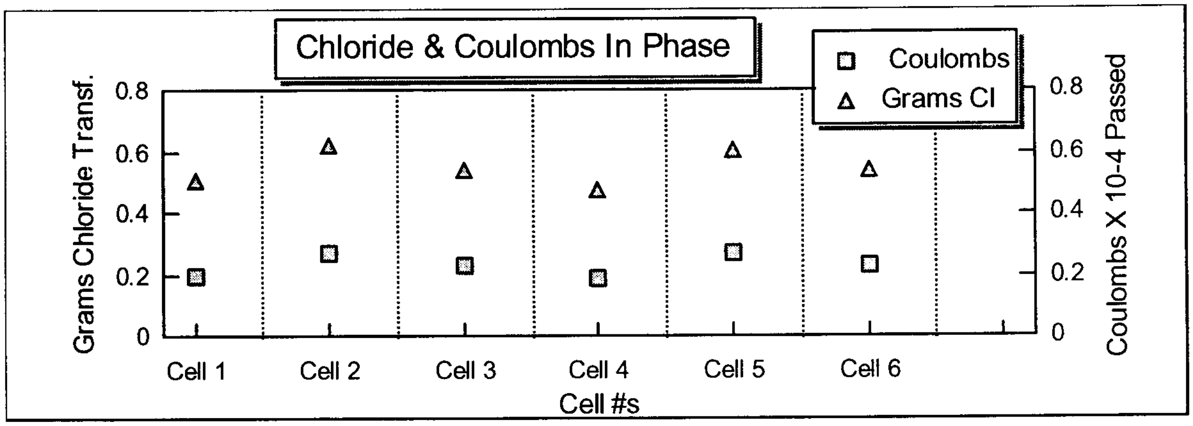

Figure 14. Amount of chloride ion transferred and amounts of coulombs passed vary in phase in each cell.

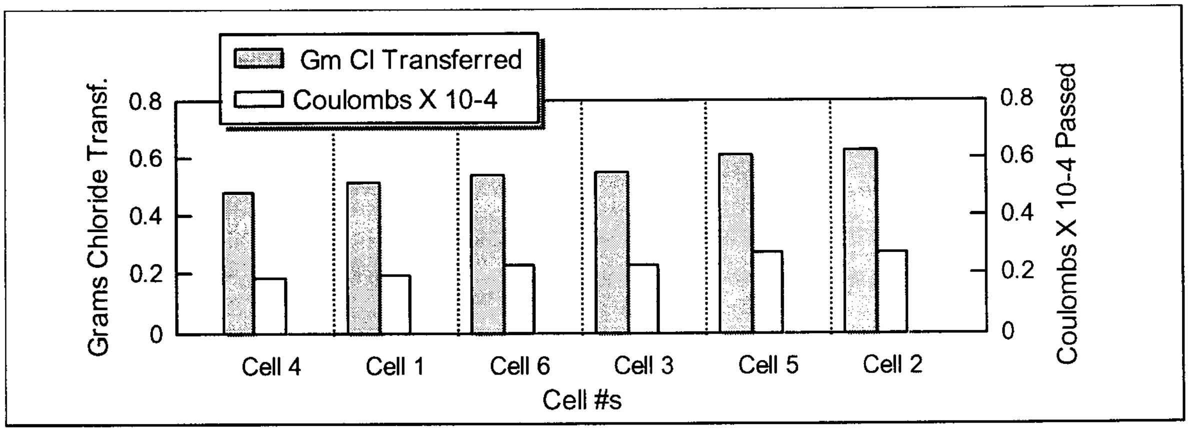

Figure 15. Chloride ion transfer increase compared to corresponding total charge (coulombs) increase gives two almost parallel plots.

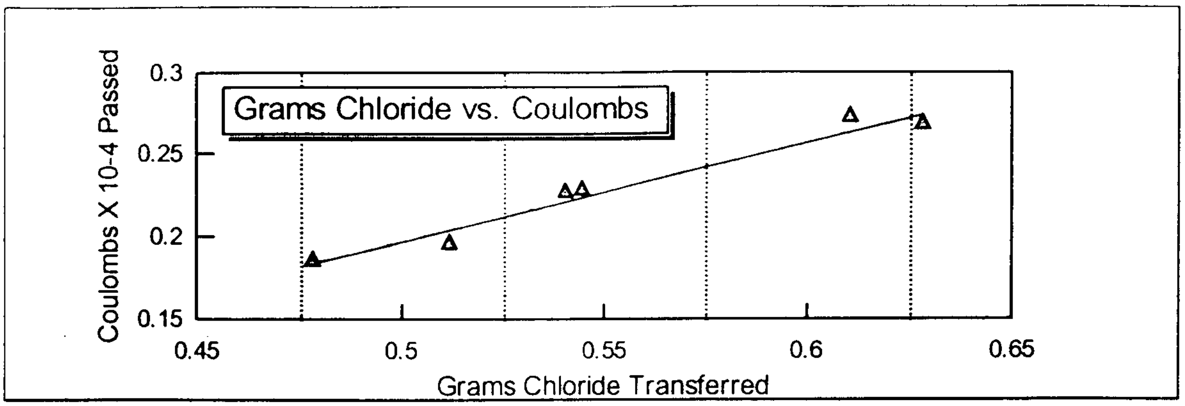

Figure 16. Quantitative relationship between grams chloride ion transferred and coulombs passed through system.

b) Aqueous Cell Solution Studies

Two runs were carried out in which water was used as a cell solution. In one run, water was placed in the anode cell to replace NaOH. In the other run, water was placed in both the anode and cathode cells instead of NaOH and NaCl respectively. Table #5 shows the data for Run #5 which is the NaCl vs. H_2O system. Table #6 displays data for Run #6 which is the H_2O vs. H_2O system. These runs were carried out as previously described, wherein, the determination of chloride ion concentrations was made on both cell solutions (anode & cathode) before and after the test runs.

Table 5. Chloride Permeability Test Data:

Run #5 NaCl vs. H_2O
0.42 w/c

Test Cell #	Gram Cl Transferred	Gram Cl To Disk	Gram Cl To NaOH Cell	% Cl To Disk	% Cl To NaOH Cell	Coulombs Passed
1	0.2992	0.2991	0.0002	99.97	0.05	1255
2	0.2367	0.2364	0.0003	99.87	0.13	1088
3	0.2205	0.2202	0.0003	99.86	0.14	870
4	0.2639	0.2637	0.0002	99.94	0.06	1129
5	0.2672	0.2670	0.0002	99.94	0.06	1132
6	0.1835	0.1832	0.0003	99.83	0.17	918
Max	0.2992	0.2991	0.0003	99.97	0.17	1132
Min	0.1835	0.1832	0.0002	99.83	0.05	870
Avg	0.2452	0.2449	0.0003	99.90	0.10	1065

Table 6.

Run #6 H_2O vs. H_2O
0.42 w/c

Test Cell #	Gram Cl Increase In H_2O Cell (-)	Gram Cl Increase In H_2O Cell (+)	Coulombs Passed
1	0.0001	0.0001	1136
2	0.0001	0.0002	643
3	0.0001	0.0006	1125
4	0.0000	0.0002	778
5	0.0000	0.0004	1188
6	0.0001	0.0002	948
Max	0.0001	0.0006	1188
Min	0.0000	0.0001	643
Avg	<0.0001	0.0003	969

Results of these two aqueous cell systems are summarized as follows:

For Sodium Chloride vs. Water Cell System -

* The amount of chloride ion transferred out of the cathode NaCl cell was very much less with H_2O as the anode cell solution compared to the chloride transferred out when NaOH was the anode solution. Only about one-half the amount of chloride was transferred when using H_2O. The average chloride ion transfer with H_2O was 0.25 g while with NaOH it was 0.55 g. See Figure 17.

* The average charge (coulombs) passed through the six cells was approximately one-half that obtained with NaOH as the anode solution. The average value was 1065 coulombs with H_2O compared to 2311 coulombs with NaOH. See Figure 18.

* The amount of chloride (grams) transferred out by each of the six cells was reasonably close and a plot of charge versus chloride concentration gave an approximate straight line. See Figure 19.

* The amount of chloride ion transferred to the anode (H_2O cell) was extremely small and almost constant , that is, almost the same amount by each of the six cells. The average value was 0.0003 g Cl passed through. See Table 5.

* In brief, replacing NaOH by H_2O as the anode solution resulted in less overall cell activity, such as less chloride ion transferred out, less chloride reaching the anode, and less total charge being generated in the cell system. However, the relative amount of chloride remaining in the concrete disk was about the same as found for NaOH anode solutions, that is about 99.90 %. See Table 5.

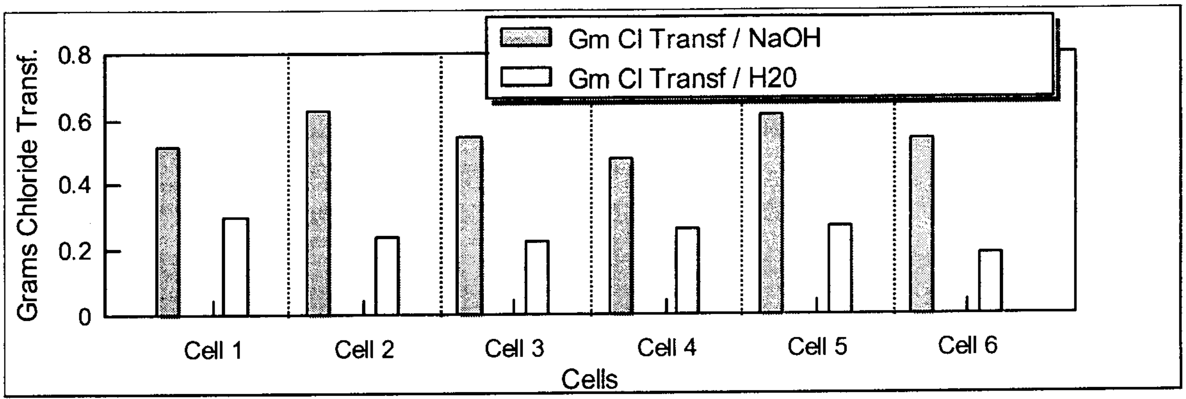

Figure 17. Comparison of amounts of chloride transferred with NaOH as the anode solution to the amounts of chloride with H_2O as anode solution.

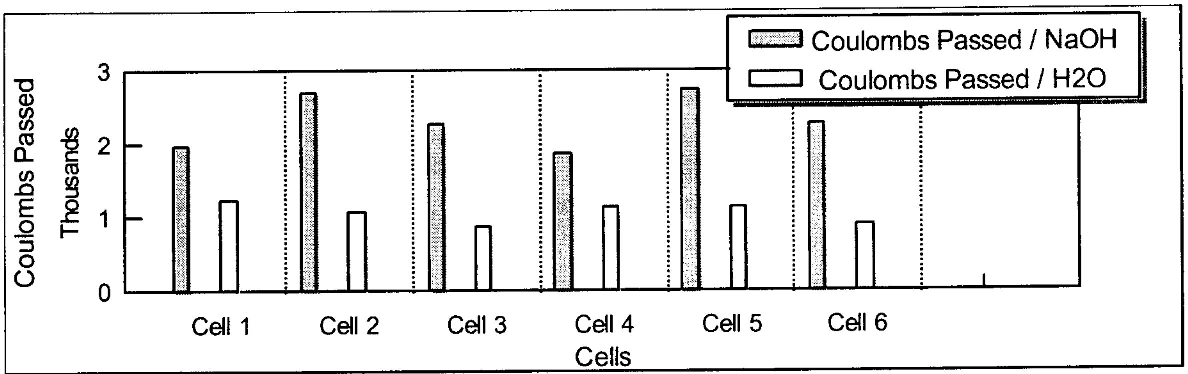

Figure 18. Comparison of amounts of coulombs passed with NaOH as the anode solution to the amounts of coulombs with H_2O as anode solution.

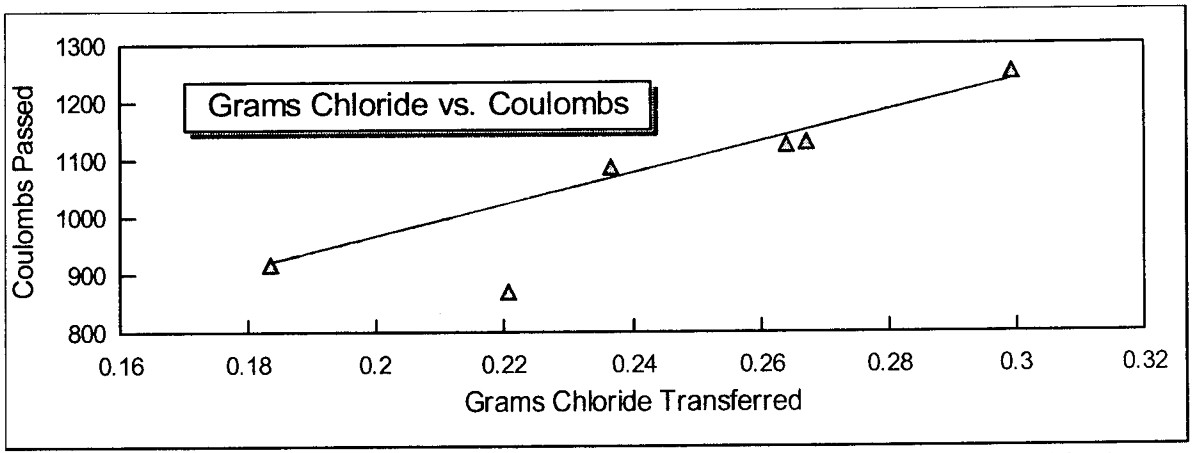

Figure 19. Quantitative relationship between grams chloride ion transferred and coulombs passed for the NaCl vs. H_2O system.

For Water vs. Water System -

* Because there was no chloride ion present in this system, chloride ion transfer or migration was not an issue. Total charge was the experimental value of interest.

* An appreciable amount of charge was developed. The six cells gave an average total charge of 969 coulombs as shown in Table 6. These results are similar to those obtained with the NaCl vs. H_2O system which had an average value of 1065 coulombs total charge. See Table 5.

* The background charge of approximately one thousand coulombs (969 av.) found in the all-water system is significant. It is equivalent to 91% of the average total charge obtained with the NaCl vs. H_2O system where chloride ion was present at a 3% by wt concentration.

* It should also be noted that any ionic chemical species acquired from the concrete disk sample via contact with the cell solutions would also contribute to generation and passage of charge. Although distilled water was used as the cell solutions in both cells and the initial pH was about 6 to 7 (almost neutral), by the end of the test run, the cathode cell water was strongly basic and the anode side slightly acidic.

* These observations indicate possible reactions occurring within each cell compartment, and probably at cathode and anode electrodes.

For the H_2O vs. H_2O system, the charge produced in each cell varied as was the case with the other systems. This is indicated in Figure 20. Comparison of charge (coulomb) data for the three cell systems, that is, NaCl vs. NaOH, NaCl vs. H_2O and H_2O vs. H_2O are presented in Figure 21. Figure 21 shows that with NaOH as the anode cell solution the amount of charge passed is greatest. It also indicates that the total charge and charge developed within each cell are reasonably close for NaCl vs. H_2O and H_2O vs. H_2O systems, that is, the two systems having H_2O as the anode cell solution. It appears that the presence of chloride ion with H_2O did not have the same effect on charge development as took place with chloride ion and NaOH in the NaCl and NaOH system having NaOH as the anode cell solution.

Figure 21 also shows the distribution of charge within each of the six cells for the three systems. It is readily seen that the greatest concentration of charge is in the NaCl vs. NaOH system. The other two systems have much less charge generated and their charge data are relatively close. As mentioned previously, the average total charge for the H_2O vs. H_2O was 969 coulombs compared to 1065 coulombs for NaCl vs. H_2O. The average total charge for NaCl vs. NaOH was 2311 coulombs. For all three systems, the charge produced in each cell within a given system varied. This is indicated in Figure 21.

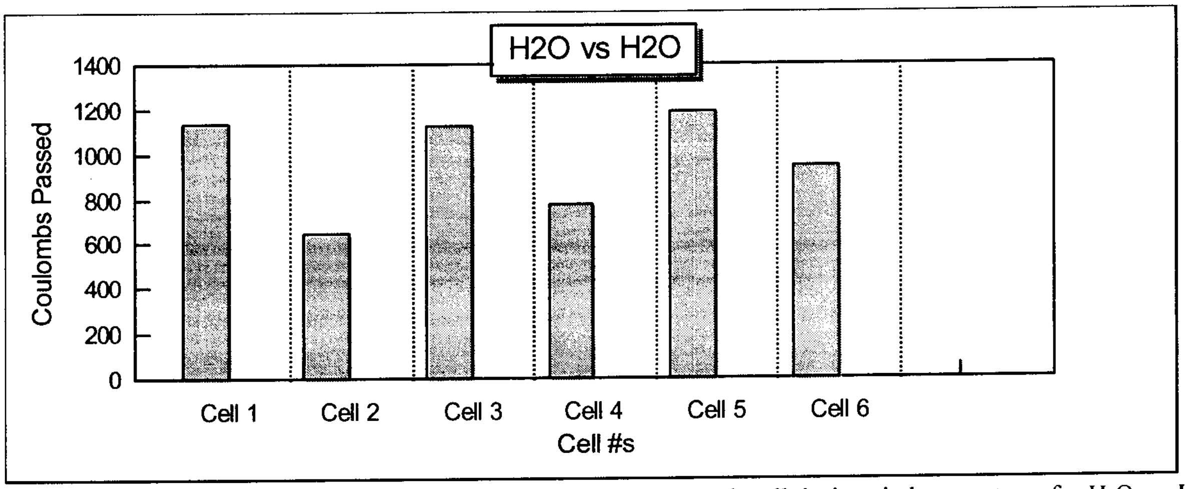

Figure 20. Variation of amount of charge (coulombs) passed by each cell during six hour test run for H_2O vs. H_2O system.

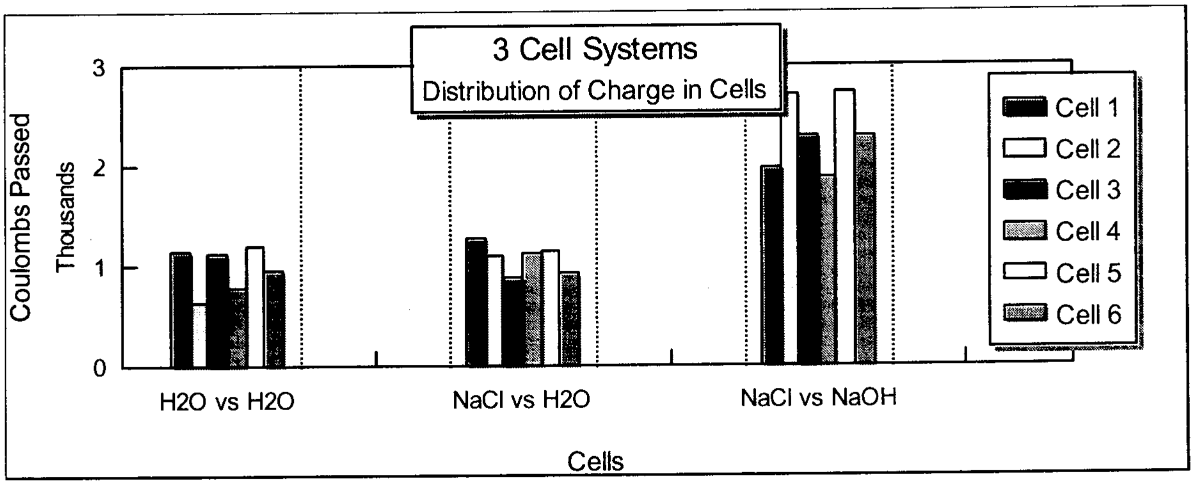

Figure 21. Distribution of charge (coulombs) within each cell for the three systems during six hour test run.

c) Non-Chloride Salts as Cell Solutions

Five salts, none of which contained chloride ion were studied as cathode cell solutions in place of sodium chloride. Sodium hydroxide was still used as the anode cell solution as in previous runs. The purpose was to observe how much charge was passed by sodium salts consisting of anions other than chloride. The salts were 3% by wt solutions of sodium nitrite ($NaNO_2$), sodium nitrate ($NaNO_3$), sodium sulphite (Na_2SO_3), sodium sulphate (Na_2SO_4), and calcium nitrate ($Ca(NO_3)_2$). The total charge data for these salts are given in Table 7. It should be noted that the nitrite (NO_2^-) and nitrate (NO_3^-) ions are univalent negative ions similar to chloride ion (Cl^-), while sulphite (SO_3^{-2}) and sulphate (SO_4^{-2}) ions are divalent negative ions, and calcium ion (Ca^{++}) is a divalent positive ion used to replace sodium ion (Na^+) which is a univalent positive ion. Therefore, this study involved ions of higher negative valence than chloride, and also a single ion of higher positive valence than sodium.

Table 7. Five Non-Chloride Salts Total Charge Data:

Total Charge Passed (Coulombs)

Cell #	Run #7 Sodium Nitrite $NaNO_2$	Run #8 Sodium Nitrate $NaNO_3$	Run #9 Sodium Sulphite Na_2SO_3	Run # 10 Sodium Sulphate Na_2SO_4	Run # 11 Calcium Nitrate $Ca(NO_3)_2$
1	2803	1829	1095	1646	3605
2	2761	2153	1836	1962	3667
3	1904	2375	1463	1946	4049
4	2231	1492	------	1616	------
5	1898	1876	------	2215	------
6	1951	1902	------	1410	------
Max	2803	2375	1836	2215	4049
Min	1898	1829	1095	1410	3605
Avg	2258	1938	1465	1799	3773

For Run #9 sodium sulphite (Na_2SO_3) and Run #11 calcium nitrate ($Ca(NO_3)_2$), only three test cells were available and used during these runs.

Results of the five different salt cell systems are summarized as follows:

* Sodium nitrate ($NaNO_3$) and sodium nitrite ($NaNO_2$) salts gave similar charge values with the nitrite ion (NO_2^-) salt being slightly higher. The measured charge for both salts was as much as the charge found with sodium chloride solutions where chloride ion was abundantly present.

* Sodium sulphate and sodium sulphite salts gave slightly lower charge values than the nitrite / nitrate salts. Although the average charge measured (coulombs) was somewhat less than that with chloride salts, the amount of charge was significant because of the fact that no chloride was present.

* Calcium nitrate salt gave the highest charge values of the five salts, even greater than any charge obtained with any of the 3% by wt sodium chloride test runs.

* All five, chloride free salts generated significant charge. The amount of charge produced varied with the kind of salt, that is, type of anion or cation and with valence. Charge was not a function of chloride ion presence.

The distribution of total charge in each of the six cells for the five non-chloride salts is shown in Figure 22. Also shown for comparison is the charge distribution for NaCl. It can be observed that the sodium nitrite / nitrate salts pass about the same amount of charge as NaCl, and that calcium nitrate charge exceeds that of NaCl.

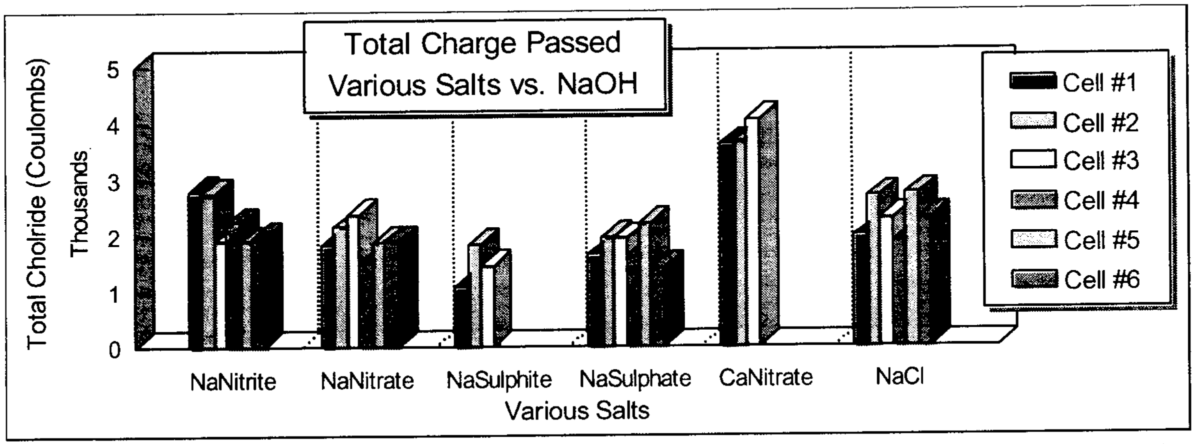

Figure 22. Total charge passed by each of six cells of the various salts used as cathode solutions versus NaOH solution.

The average total charge passed by the five salts are compared to that of NaCl and to the H_2O vs. H_2O system in Figure 23. Again it is evident that the amount of charge associated with the sodium nitrite / nitrate salts is similar to that of NaCl, and that calcium nitrate charge exceeds NaCl charge. Of additional importance is the fact that Figure 23 shows that the total charge passed in the H_2O system is appreciable (~ 1000 coulombs). This is important because the H_2O vs. H_2O system has no chloride ion and no other types of ionic species to transport charge. However, it causes a background charge of approximately 1000 coulombs which is included in total charge measurements. This background charge is pertinent to a specific concrete sample and may vary from sample to sample.

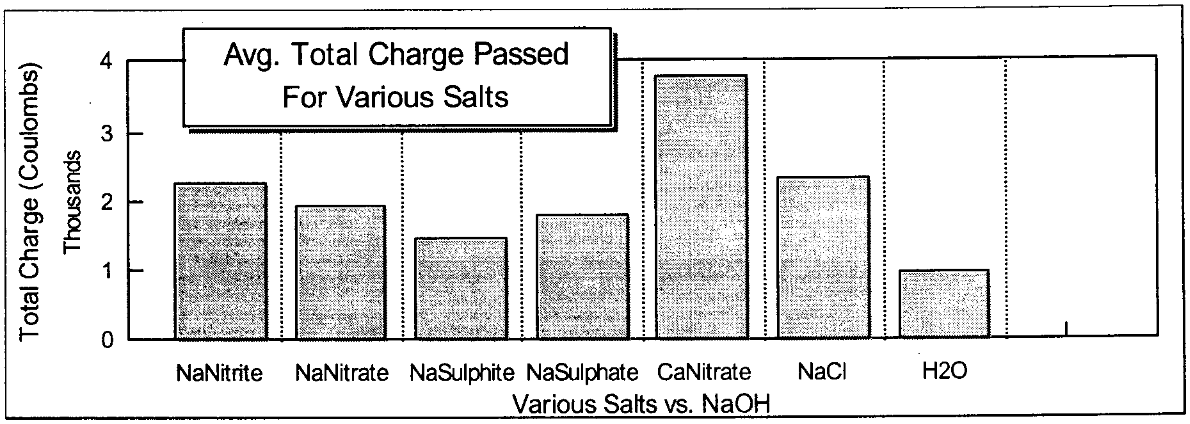

Figure 23. Averaged total charge passed by each of the five non-chloride salts vs. NaOH during a six hour test run. NaCl vs. H_2O, and H_2O vs. H_2O systems averaged total charges passed are included for comparison.

d) Permeability Time Studies

A time-study test of charge and chloride ion concentration variation with time was carried out using a NaCl vs. NaOH cell solution system. Small aliquots (2 ml) of sodium chloride solution were sampled from the reservoir of each cell at one-half hour intervals. Twelve samples were taken from each of six cells over a period of six hours resulting in a total of seventy two samples for chloride analyses. The data obtained from the six cells during this single test run were averaged together and the results are tabulated in Table 8.

The average data were obtained by combining the data for a given one-half hour time interval for each of the six test cells and calculating the average value. For example, at the first one-half hour, the data for total charge in each of the six test cells was combined and averaged. This was done for each one-half hour period over the six hour test run resulting in twelve data points for each parameter measured (12 data points for total charge, 12 for total chloride etc.).

Table 8. Total Charge and Chloride Ion Time Study Data:

Time Hours	Gm Cl Transfer at 1/2 hr./ ml	Total Gm Cl Transferred	Total Charge Passed (clb)
1/2	0.0006	0.0978	273.3
1	0.0009	0.1467	490.0
1 1/2	0.0012	0.1956	726.8
2	0.0016	0.2608	980.1
2 1/2	0.0021	0.3423	1241.5
3	0.0025	0.4075	1509.1
3 1/2	0.0032	0.5216	1799.5
4	0.0032	0.5216	2094.9
4 1/2	0.0036	0.5868	2395.5
5	0.0040	0.6520	2698.0
5 1/2	0.0047	0.7661	3003.1
6	0.0051	0.8313	3153.6
Max	0.0051	0.8313	3153.6
Min	0.0006	0.0978	273.3
Avg	0.0027	0.4442	1697.1

In Table 8, the second column (Gm Cl Transfer per 1/2 hr. / ml) lists data for the amount of chloride ion transferred at each 1/2 hour interval per milliliter of NaCl cathode compartment solution. These values multiplied by the volume of NaCl solution (163 ml.) used in the cell compartment resulted in the total grams of chloride transferred for each 1/2 hour interval. The total grams are listed in the third column (Total Gm Cl Transferred).

The fourth column (Total Charge Passed) presents data for the total charge accumulated or the sum of the one-half hour charge values up to that time of the six hour test run. Data in the fourth column was determined by the computer monitoring the test run.

Results of the time-study of charge and chloride ion variation are summarized as follows:

* Charge (coulombs) measured at one-half hour intervals plotted against time gave practically a straight line plot indicating a possible linear relationship of charge with time for the existing testing conditions. See Figure 24.

* Grams of chloride ion transferred out of the NaCl cathode compartment at one-half hour intervals plotted against time gave nearly a straight line plot indicating a possible linear relationship of amounts of chloride transferred with time under the same testing conditions. See Figure 24.

* Consequently, plotting grams of chloride ion transferred against charge passed for one-half hour intervals during the six hour test run also produced an almost linear plot. This of course indicates some quantitative relationship between chloride ion transfer and charge passed. See Figure 25.

* These results agree with those previously obtained with Test Runs 1, 2, 3, & 4 which were also NaCl vs. NaOH cell systems and showed the same relationships between charge, chloride ion and test run time.

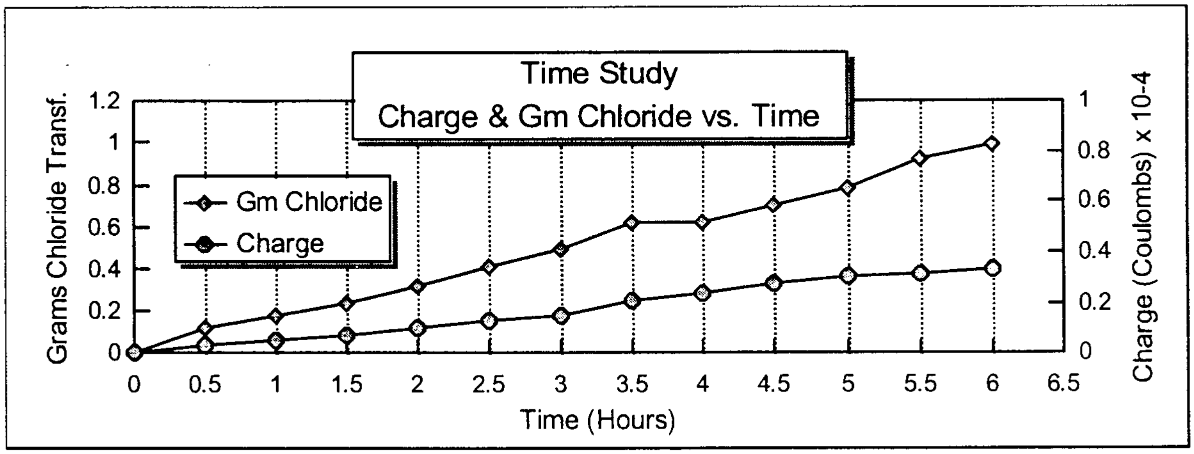

Figure 24. Total charge (coulombs) measured per one-half hour intervals and total grams chloride ion measured per one-half hour intervals during six hour test run.

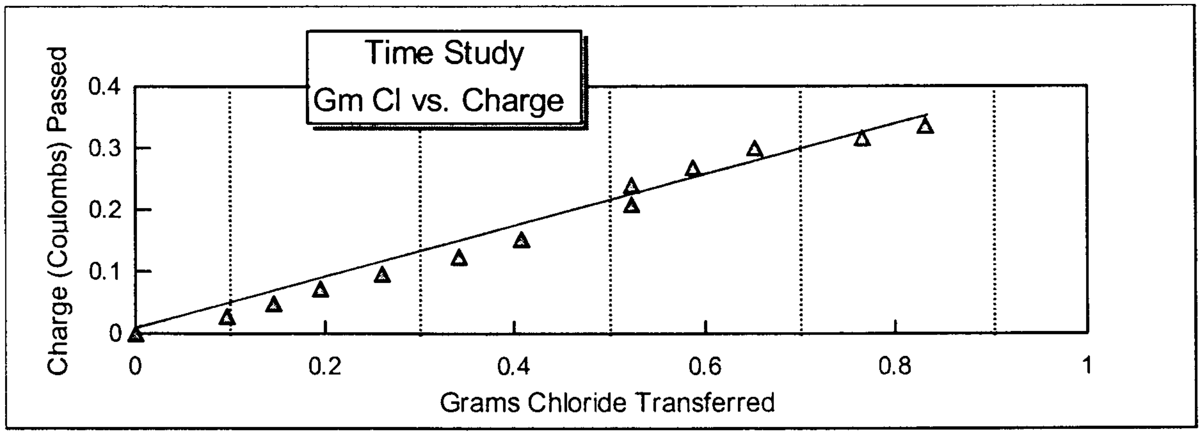

Figure 25. Quantitative relationship between grams chloride ion transferred and charge passed per one-half hour intervals during six hour test run.

3) Concrete Disks & Slab Studies -

a) Concrete Disk Specimens

Attempts were made to analyze the concrete disk specimens used in the NaCl vs. NaOH cell studies for chloride content. Acquiring this data would enable a material balance accountability of the total amount of chloride ion in a given cell system. Quantitatively, grams of chloride transferred out of the NaCl cathode compartment should equal the sum of chloride that passed through the concrete disk to reach the NaOH anode compartment and the amount of chloride that remained within the disk. Several attempts to achieve an experimental material balance were unsuccessful because accurate determination of chloride remaining in the concrete disks was difficult. The difficulty was that the chloride which passed from the NaCl cathode compartment into the disk was not uniformly distributed through out the disk specimen. Instead, the chloride was concentrated on the face-side of the concrete disk which was in actual contact with the NaCl solution.

Initial attempts to determine chloride in the disks was carried out by taking samples at several locations and at a given depth on the face-side of the disk. This resulted in very high chloride values when compared to calculated amounts determined by the difference between the chloride transferred out of the NaCl compartment and the chloride reaching the NaOH anode compartment.

Another attempt was made to determine the chloride in the disks by depth profiling. One disk from each of three runs (Runs #1,2, & 3) was sampled in this manner using profiling depths of 2.54, 3.81, and 5.08 cm (1, $1^1/_2$ and 2 in.) on the face-side of the disk in contact with the NaCl cathode solution. This gave three samples from each disk for chloride analyses. The results are shown in Table 9. The summary at the bottom of the table compares the chloride values obtained by difference calculation, and by profile disk sampling. The calculation values are considered to be the accurate because they were determined by the difference of two experimental data values which are easily accessible and reliably accurate. The profiling results are reasonably close in comparison to the calculated difference values, but really not suitable for an acceptable material balance. See Figure 26 for examples of disk profiles.

Table 9.

Concrete Disk Chloride Determinations
Three Disk Profiling Samples
Disks From Runs #1, 2, & 3

Disk ID	Profile Depth (cm -- in.)	Chloride Found (%)	Total Disk Weight (grams)	Total Chloride Found In Disk (grams)
Run #1 Cell #2				
L1B	2.54 -- 1.0	0.0497	970.47	0.4823
L1B	3.81 -- 1.5	0.0154	970.47	0.1495
L1B	5.08 -- 2.0	0.0104	970.47	0.1009
Run #2 Cell #2				
H1B	2.54 -- 1.0	0.0141	998.53	0.1408
H1B	3.81 -- 1.5	0.0171	998.53	0.1707
H1B	5.08 -- 2.0	0.0109	998.53	0.1088
Run #3 Cell #5				
M2B	2.54 -- 1.0	0.0196	1005.58	0.1971
M2B	3.81 -- 1.5	0.0117	1005.58	0.1177
M2B	5.08 -- 2.0	0.0059	1005.58	0.0593

Summary:

Run # & Disk ID	Total Chloride In Disk By Difference (grams)	Total Chloride In Disk By Profiling (grams)
#1 L1B	0.5296	0.7327
#2 H1B	0.6094	0.4203
#3 M2B	0.4671	0.3741

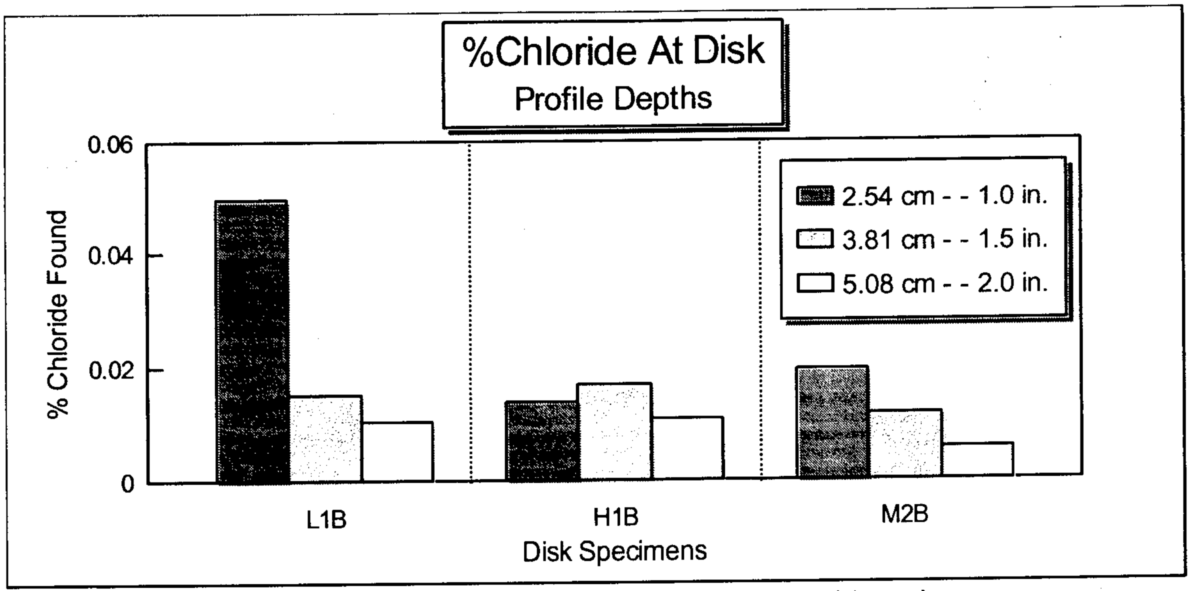

Figure 26. Amounts of chloride found at various profile depths of concrete disk specimens.

b) *Concrete Slab Specimens*

Concrete slabs which had been ponded in a 3% by wt sodium chloride solution for 90 days as specified in AASHTO T-259 method were drilled in five places at depths of 1.91 and 4.45 cm ($^3/_4$ and 1$^3/_4$ in.). The 1.91 cm ($^3/_4$ in.) drillings were combined to form a single depth sample, and the 4.45 cm (1$^3/_4$ in.) drillings were combined to form the second depth sample. Each composite sample was analyzed for chloride. A total of twelve slabs were prepared, each having two composite depth samples giving 24 samples for chloride analyses. The results are presented in Table 10. As observed with the concrete disk profile testing, the deeper depths showed much less chloride than those near the surface of the slab. See Figure 27.

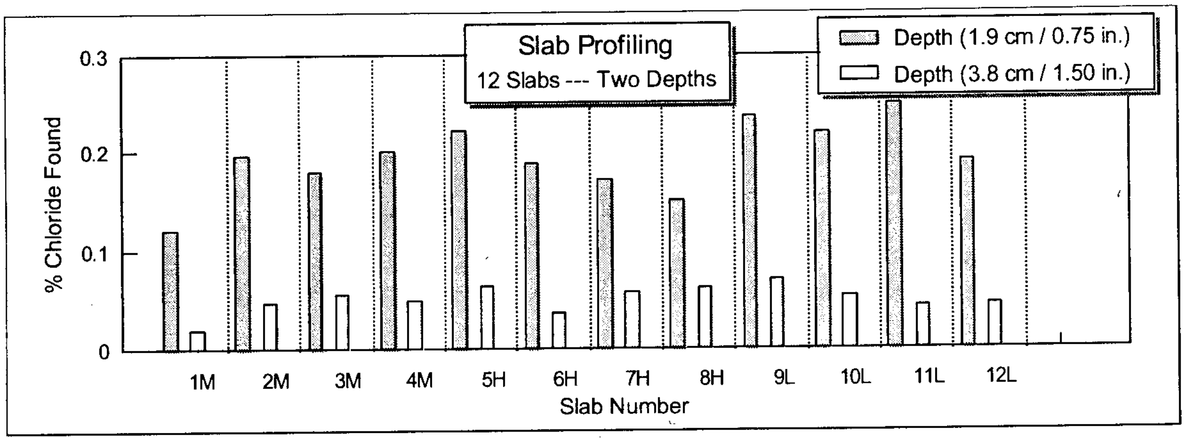

Figure 27. Percent chloride found in slab ponding samples at two profile depths.

However, comparing chloride penetration of the disk specimens used in the permeability cells to chloride penetration of the ponding slabs, it is seen that penetration is significantly greater with the slabs. At a profile depth of 3.81 cm ($1^1/_2$ in.) chloride penetration in the slabs was about five times greater than in the disks. This was the only profiling depth (3.81 cm or $1^1/_2$ in.) consistent in the disks and slabs, and therefore was used for the comparison. See Figure 28. Perhaps this large difference was to be expected because the chloride solution was in contact with the concrete slabs for much greater length of time (90 days) than the chloride solution used with the disks (six hours). This finding might give rise to question how effective is the applied voltage (60 volts) used to cause rapid migration of chloride ion in the permeability test method.

Comparison of disks at 2.54 cm (1 in.) depth to slabs at 1.9 cm (0.75 in.) indicated the slabs to contain about eight times more chloride than the disks. While this is not really a fair comparison because of depth differences, it does show the comparison trend to be consistent with that found at equal depths of 3.8 cm (1.5 in.) The increased difference from five to eight times is probably influenced by the surface salt effects with the slabs and the longer contact time the slabs had with the salt solutions.

Table 10 Concrete Slab Chloride Determinations
Slab Ponding Samples

Slab ID	Sample Depth cm	------ in.	Gram Chloride Found	% Chloride Found
High w/c (0.43)	1.91	0.75	0.0009	0.1843
"	3.81	1.50	0.0009	0.0557
Med w/c (0.42)	1.91	0.75	0.0008	0.1746
"	3.81	1.50	0.0004	0.0431
Low w/c (0.40)	1.91	0.75	0.0011	0.2239
"	3.81	1.50	0.0006	0.0529

The data in Table 10 are the averages of three sets of slabs at three different w/c ratios, (0.43, 0.42 & 0.40) Each w/c ratio set had four slabs and samples taken at two profile depths (1.91 & 3.81 cm) or (0.75 & 1.50 in.) per slab. *Grams Chloride Found & % Chloride Found* values given in the table are averages of four slab measurements.

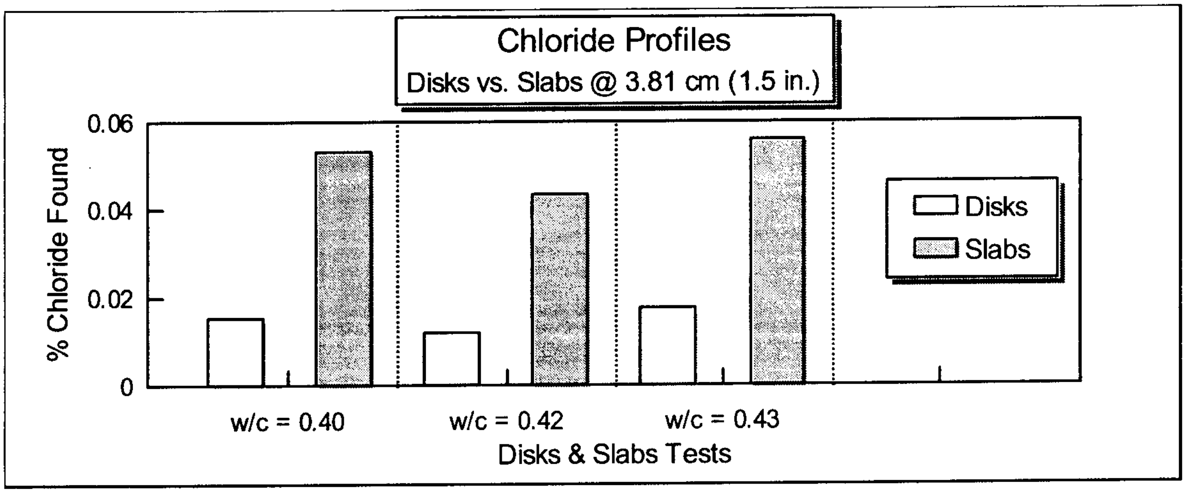

Figure 28. Comparison of chloride penetration in test cell disks to penetration in ponding slabs at 3.81 cm (1.5 in.) profile depth.

<u>Results of disk and slab studies are summarized as follows:</u>

* Chloride ion which had entered the disks was concentrated on the face-side of the disk in contact with the sodium chloride solution in the cathode compartment. The chloride was non-uniformly distributed throughout the disk.

* A material balance accountability of chloride ion in a given cell system requires determination of total chloride ion content in the disk. Because of the non-uniform distribution, the analysis for chloride ion in the disk requires pulverizing the entire disk which on the average weighed approximately 1000 grams. This is a tedious task when testing 72 disks.

* Chloride profile analyses of the disks per se, without pulverizing, did not result in accurate disk chloride content values to enable an acceptable material balance of chloride.

* Comparison of chloride ion profile analyses of the slabs to that of the disks used in the permeability cells, showed that chloride ion penetration is significantly greater with the slabs.

* Greater chloride ion profile results with the slabs may be due to the much greater length of time the slabs are in contact with the 3% by wt sodium chloride ponding solution. This again gives rise to question how effective is the applied voltage (60 volts) used to cause rapid migration of chloride ion in the permeability test method.

Discussion

(1) - *Current versus Time Studies* --

Tests carried out using multiple cells under carefully controlled experimental conditions in an effort to reduce variability showed that the currents varied moderately between the individual cells. As a result, the amount of total charge passed by each of these cells over a six hour test period was also found to be different. All six disk samples in a test run were sliced from concrete cylinders cast from the same batch of concrete of known mix design. It is unlikely that these differences could have been due to the concrete disk samples not being of uniform chemical composition. It is possible, however, that the cylinders were not of uniform structural composition. Although the same chemistry was present, there were physical structural differences within the disk samples, such as voids, air pockets, capillary channels, crevices etc. which could hasten or restrict the passage of ions transporting charge (current) in solution.

Aqueous cell systems consisting of water as the cathode and/or the anode solutions produced the lowest currents of all the cell systems studied. NaCl vs. H_2O (Run #5) and H_2O vs. H_2O (Run #6) illustrate this behavior. Both systems have water as the anode solution instead of sodium hydroxide. Lower currents resulted because the totally ionized NaOH solutions were replaced with H_2O which is only about 1×10^{-5} % ionized. There are significantly much less ions in the water solutions to carry current.

In contrast, comparing the cathode solutions in the same two systems (Runs 5 & 6), the completely ionized sodium chloride salt solution (NaCl vs. H_2O Run #5), produced only slightly higher currents than the H_2O vs. H_2O system (Run #6) which had no strongly ionized salt solutions in either the anode or cathode compartments. One would have expected Run #5 with an abundance of free Na^+ and Cl^- ions to exhibit the greater currents. It is apparent that the type of anode solution has significant effects on production of current in sodium chloride cathode systems.

The five chloride-free salts used as cathode solutions in place of sodium chloride produced currents of similar magnitude as sodium chloride. Calcium nitrate gave currents larger than those of the sodium chloride systems. This serves to point out that chloride ion is not the sole or even the dominant ion for producing current and hence for producing total charge. Current and charge are dependent upon the type of ions and the number of ions (concentration) in the system, that is, in both the anode and cathode compartments. Current and charge are therefore, a function of all the ions present in the cell system and not uniquely to chloride ion.

(2) - Permeability Test Studies --

a) Sodium Chloride versus Sodium Hydroxide Systems:

NaCl vs. NaOH is the standard cell solution system used to evaluate concrete permeability. The objective of studying this system was to measure the amount of chloride ion which transferred from the sodium chloride cathode compartment, passed through the concrete disk and finally reached the sodium hydroxide anode compartment. It was presumed that the chloride ion measured would be an accurate measure of the chloride permeability of the concrete in terms of grams chloride which actually passed through the concrete disk. It was also assumed that chloride ions carrying current had to reach the sodium hydroxide anode compartment in order to complete an electrical circuit and generate charge.

Results showed that only an extremely small fraction of the chloride ion (0.22%) which leaves the sodium chloride compartment actually reaches the sodium hydroxide compartment, and that more than 99% remains in the concrete disk. Therefore, because chloride ion does not pass through the concrete in substantive amounts, one cannot measure chloride transferred into the sodium hydroxide anode compartment as such to determine its concrete permeability. Although very little of the chloride ion reached the sodium hydroxide anode compartment, a large amount of total charge was generated. This finding conflicts with the presumption that chloride ion must reach the anode in the sodium hydroxide compartment in order to generate charge.

A significant result of these studies is that the data show a quantitative relation between the amount of chloride ion transferred out of the sodium chloride compartment and the total charge generated. As chloride ion transferred out increases, total charge increases. This relation exists even though practically all of the chloride ion remains within the concrete disk and never reaches the sodium hydroxide compartment. This means the chloride ion per se does not carry electrons to the anode compartment and generate charge. There is some other mechanism or process responsible for causing total charge. It appears that the chloride ion need only to migrate out of the sodium chloride compartment and into the concrete disk to enhance the ability to transport charge.

Measurement of chloride ion transfer would be a direct measure of *chloride permeability of concrete* or *of chloride penetration of concrete.* The measurement could also be expressed as *the resistance of concrete to chloride* or *the absorbance of chloride by concrete.* Regardless of which interpretation is used, the experimental measurement is grams of chloride which is specific to chloride ion, and is very accurate and reproducible. In comparison, total charge is not specific to chloride, its measurement has poor reproducibility and also, total charge can change as the concrete ages. In addition, total charge is measured in electrical units (coulombs) which are not as clear and practical to work with as grams. For example, try converting 1000 coulombs to pounds of chloride per cubic yard (lb./yd^3). On the other hand, conversion of a thousand grams of chloride to pounds per cubic yard is easier.

It should be noted that total charge is contributed to by all of the ionic species present. It is actually a measure of the electrical conductivity of concrete and as such can be indicative of, or be a measure of *concrete total ionic permeability* but it is not specifically a measure of chloride ion permeability. Chloride ion actually exhibits very little permeability of concrete. Determination of chloride ion migration requires direct measurement of the ion and cannot be done by charge measurements in the presence of other ions.

In addition to the experimental evidence that there is extremely little chloride ion migration through the concrete, theoretical explanations can also account for total charge not being solely related to chloride ions. One of the basic principles in electrochemistry is that in solutions, current or charge is carried by the migration of all ions in the solution, both anion (-) and cation (+). The cell solutions in the NaCl vs. NaOH system consists of sodium (Na^+), hydroxyl (OH^-) and hydrogen (H^+) ions in addition to the chloride ions which also carry current and, therefore, contribute to total charge. The amount of current or charge contributed by any particular ion depends upon its valence (Na^+, Ca^{+2}), concentration, and ionic mobility in the solution. It is readily seen that total charge is a function of several factors and not just chloride ion related. It is also possible for additional ions to be solubilized or extracted from the concrete disk specimen by the cell solutions. These additional solubilized ions would also contribute to total charge.

b) <u>Aqueous Cell Solution Systems:</u>

(Sodium Chloride vs. Water System) -

In one aqueous system, the sodium hydroxide solution in the anode compartment was replaced with distilled water while sodium chloride solution was still used in the cathode compartment. This partially aqueous system (NaCl vs. H_2O) exhibited decreased current chloride ion transfer and decreased chloride at the anode compared to sodium hydroxide as the anode solution For the six cells tested, the average total charge generated was 1065 coulombs. This is only 46% of the average amount of 2311 coulombs found with sodium hydroxide as the anode solution. Percentage wise, the amount of chloride remaining in the concrete disks was about the same as found for the sodium hydroxide anode solutions, that is, greater than 99.0%.

(Water vs. Water System) -

In the other aqueous system, both the sodium chloride cathode solution and the sodium hydroxide anode solutions were replaced with distilled water forming a total water cell system, (H_2O vs. H_2O). Because there was no chloride ion present, the only experimental value measured was total charge which gave an average value of 969 coulombs for the six cells in the system.

Results of the two aqueous cell systems illustrated several points. First, the effect on chloride ion transfer and upon total charge by the *type of anode compartment solution.* Sodium hydroxide solution is totally ionized (100% ionized) compared to distilled water which is only about 1 x 10^{-5} % ionized. The sodium hydroxide solution had considerably more ions available to carry current and develop greater total charge. Consequently, the NaCl vs. NaOH systems gave greater total charge than NaCl vs. H_2O systems. The type of anode solution is important, in particular, the ionic nature and ionic strength of the solution.

Secondly, it is somewhat unexpected that the total water system (H_2O vs. H_2O), produced an average total charge (969 coulombs) close to the average total charge (1065 coulombs) given by the sodium chloride versus water system (NaCl vs. H_2O). The water system had neither chloride ions nor appreciable amounts of any other kind of ions to carry current and generate charge. However, the mechanism of total charge generation not only involves migration of ions to carry current, but also involves *the electrolysis of water* at each of the two electrodes in the cell system.

Electrolysis of water occurs at the cathode electrode and the anode electrode in their respective compartments. Electrolysis of water at the cathode results in the formation of hydrogen gas (H_2) and hydroxyl ion (OH^-). The chemical reaction for this process is shown as $2H_2O + 2e^- = H_2 + 2OH^-$. At the anode, oxygen gas (O_2) is formed and hydrogen ions (H^+). The process is shown as, $2H_2O = O_2 + 4H^+ + 4e^-$. Each of these electrode reactions produces charge in their respective cell compartments which contributes to the total charge of the cell system. Consequently, in the total water system, which has no chloride ion and very little free ions, there is developed an appreciable total charge. This charge due to the electrolysis of water is *present in all aqueous salt cell systems as background charge.*

Evidence of the water electrolysis reactions actually occurring at the two electrodes was observed in each of the eleven test runs carried out during these studies. Over the eleven test runs, all of the cathode compartment solutions (NaCl) were initially at neutral pH = 7. After the six hour test run, all eleven cathode solutions were strongly basic at pH values of 9 or 10. This was most likely due to the formation of basic hydroxyl ions (OH^-) due to electrolysis at the cathode electrode. Six of the anode compartments (H_2O) were initially near neutral at a pH ~ 6, and after the six hour test run, all six were slightly acidic at pH values near 5. Formation of acidic hydrogen ions (H^+) due to electrolysis at the anode electrode was probably the cause. The other five sodium hydroxide anode compartments were initially very strongly basic at pH of 10 to 12 and the formation of hydrogen ions by electrolysis was not sufficient enough to change the solution pH to acidic. The pH of these solutions remained basic, but at a lower pH of 8 to 9.

c) *Non - Chloride Salts as Cell Solutions*:

Five chloride-free salt solutions were tried as cathode compartment solutions to replace the standard sodium chloride solution. All five salts generated an appreciable total charge without the presence of chloride ion. Four of the salts retained sodium as the cation, but the chloride anion (Cl^-) was replaced by nitrite (NO^-_2), nitrate (NO^-_3), sulphite (SO^{-2}_3), and sulphate (SO^{-2}_4) anions. The fifth salt contained neither sodium as cation, nor chloride as anion. This salt was calcium nitrate $Ca(NO_3)_2$ consisting of Ca^{+2} cation and NO^-_3 anion.

The four different anion salts gave average total charge values that were relatively close to that of the standard NaCl vs. NaOH systems. Calcium nitrate salt gave total charge values significantly greater than the standard. Changing from a univalent sodium cation (Na^+) to a double valent calcium cation (Ca^{++}) resulted in a large increase of charge. For example, sodium nitrate ($NaNO_3$) developed an average charge of 1938 coulombs, while the calcium nitrate salt ($Ca(NO_3)_2$) gave 3773 coulombs average charge.

The amount of current carried by an individual ion (anion or cation) is dependent upon its valence, concentration and its velocity or mobility in solution. This is easily shown by comparing the two salts calcium nitrate and sodium nitrate. Ca^{++} is divalent and Na^+ univalent, they are at equal concentrations, and each has about the same mobility in solution. NO^-_3 in each salt is univalent, and has the same mobility, however, there are twice as many NO^-_3 ions in calcium nitrate than in sodium nitrate. The net result is that calcium nitrate causes greater charge because it has a cation of higher valence and an anion at higher concentration.

The purpose of the non-chloride salt study was to show that such salts would also produce significant charge and convey the fact that the presence of their ions in standard cell systems (NaCl vs. NaOH) would also contribute to and effect total charge. Again, total charge is not due to chloride ion alone.

d) *Permeability Time Study:*

Initially, it was assumed that chloride ion transferred out of the sodium chloride cathode compartment, passed through the concrete disk and entered the sodium hydroxide anode compartment. A study of charge and chloride ion transfer variation with time was planned with the intent to observe erratic or non-linear changes, or possibly reaching maximum or limiting values of either charge or chloride ion transfer. Neither of these events occurred, but instead was found, a linear relation between charge and time, a linear relation between chloride ion transfer and time and also a linear relation between charge and chloride ion transfer with time.

Data obtained with the time studies gave a more precise and correct representation of the on-going processes within the test cells than the data obtained by measuring total charge and chloride transfer at the end of the six hour test runs. This can be observed by viewing and comparing plots of the two different kinds of data sets. Data acquired after the six hour tests (as in Runs #1 through #4, NaCl vs. NaOH systems) resulted in plots indicating that each of the six cells did not generate the same total charge or transfer out the same amount of chloride ion. Total charge and chloride ion transfer were variable, but in phase with one another. Also, the plot of total charge versus chloride ion transfer was not obviously linear, but appeared to be approaching linearity. In comparison, time study data produced plots that were consistent and uniform, and exhibited apparent linearity in every case. There was no doubt that cell charge and chloride ion transfer changes with time were in phase and linear.

The reason for the differences was that comparisons made after the six hour test runs were based upon a single data measurement of charge and chloride ion for each of the six cells in a given test run. These plots simply showed that each of the six cells did not generate the same total charge or transfer out the same amount of chloride ion over the six hour period. With the time study run, twelve measurements of charge and chloride ion were taken over six hours in the same cell, and the single averaged data of the twelve measurements plotted for each cell. Consequently, changes or variations in charge or chloride ion were averaged out, and the resulting plots were more consistent and uniform.

The time-study results agreed with those previously obtained with sodium chloride versus sodium hydroxide cell systems (Runs #1, 2, 3, & 4) which were not time-study tests, and showed the same linear relationships between charge, chloride ion and time. This further supports the measurement of chloride ion transfer as a means to directly measure chloride permeability of concrete and other parameters such as chloride penetration, resistance of concrete to chloride and absorbance of chloride by concrete.

(e) - Application of Faraday's Law -- Relation of Electrical Charge and Chemical Changes of Ions In Solution:

Faraday's Law best explains the relationship of electrical charge and ions in solution. It can be applied to these studies to illustrate the relationship between total charge and chloride ion and other ions also present in solution. The Law describes chemical changes of substances which result when an electrical current is passed through a solution. These changes occur at the solution electrodes and are caused by electrical charges at the electrodes. The law states that one Faraday of charge consists of 96,485 coulombs and will chemically change one mole of singly charged anions or cations at an electrode. Applying this principle to the chloride ion, one Faraday of charge (96,485 coulombs) will chemically change or react with one mole of chloride ion or with 35.5 grams of chloride ion. One mole of chloride ion (Cl^-) = 35.5 grams.

Knowing this relationship one can convert coulombs to grams of an ionic species, that is, convert electrical units to grams, or grams to electrical units, coulombs. Faraday's Law can be applied to the results and data of the current studies to explain and substantiate several experimental findings.

For example:

1) <u>Determination of the amount of total charge actually resulting from chloride ion alone</u>:

The average chloride ion transfer for the four sodium chloride versus sodium hydroxide runs was 0.5522 grams. The average total charge measured was 2311 coulombs. Knowing the grams of chloride ion transferred and applying Faraday's Law, one can calculate the possible maximum amount of charge that can be generated by this amount of transferred chloride. This is shown as follows:

By Faraday's Law: 96,485 coulombs ~ one mole Cl^- = 35.5 gram Cl^-

$$\frac{\text{wt. per mole Cl}}{\text{96,485 coulombs}} = \frac{\text{grams Cl transf}}{\text{coulombs generated}}$$

$$\frac{\text{35.5 grams}}{\text{96,485 coulombs}} = \frac{\text{0.5522 grams}}{\text{coulombs generated}}$$

$$\text{coulombs generated} = \frac{0.5522 \text{ x } 96{,}485}{35.5} = 1500 \text{ coulombs}$$

As shown here, only 1500 coulombs were possible for generation by the transfer of 0.5522 grams of chloride ion. Actually, 2311 coulombs were measured. *This means that 811 coulombs came from some sources <u>other than chloride ion.</u>* The average background charge due to water electrolysis (969) could easily account for the excess charge.

2) <u>To illustrate that chloride ions do not have to pass through concrete disk sample to generate charge</u>:

Repeating the same calculation but using the grams of chloride ion that actually reached the sodium hydroxide anode (0.0011 grams), would result in a possible total charge of only 3.0 coulombs. *These calculations indicate that the transferred chloride ions <u>do not have to pass through the concrete disk</u> and reach the sodium hydroxide anode compartment in order to generate charge.*

3) *Faraday's Law and Linearity of Charge and Chloride Ion Transfer:*

To illustrate the validity of the linearity of charge variance with chloride ion transfer, Faraday's Law was applied to the experimentally measured chloride ion transfer data obtained in the time-study run The amounts of charge that could be theoretically generated based upon the amount of chloride ion actually transferred were calculated according to Faraday's Law. The data are shown in Table 11. The calculated theoretical charge values and the measured charge values were plotted against the measured chloride ion transfer data. Figure 29 shows the two plots (theoretical charge and actual charge versus grams chloride ion transfer). The theoretical plot is linear and the actual plot is very near linear. The actual charge plot has a greater slope due to higher charge values not caused by chloride ion transfer, but caused by the migration of other ions (Na^+, & OH^-).

Table 11. Theoretical Charge Data Calculated By Applying Faraday's Law:

Time Hours	Avg. Gram Cl Transferred	Actual Coulombs (Measured)	Theoretical Coulombs (Calculated)
½	0.0978	273.3	320.7
1	0.1467	490.1	407.4
1½	0.1956	726.8	521.1
2	0.2608	980.1	702.6
2½	0.3423	1241.5	910.1
3	0.4075	1509.1	1052.4
3½	0.5216	1799.5	1288.1
4	0.5216	2094.9	1285.9
4½	0.5868	2395.5	1408.5
5	0.6521	2698.1	1584.1
5½	0.7661	3003.1	1826.5
6	0.8313	3153.6	1950.2

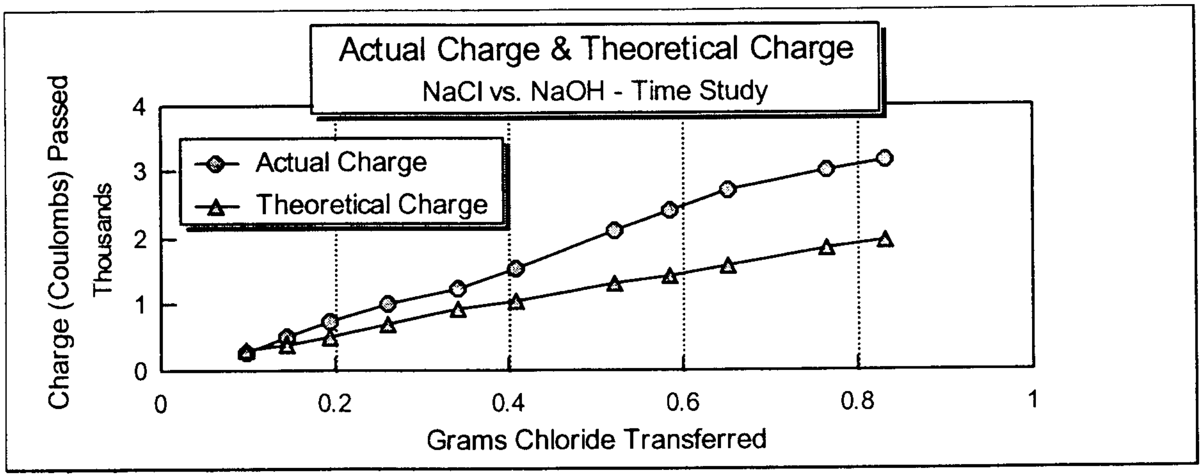

Figure 29. Comparison of actual charge measured in time-study run to theoretical charge calculated by applying Faraday's Law to amounts of chloride ion transferred out of the NaCl cathode compartment

Applying Faraday's Law to the data from Run #5, the sodium chloride versus water system, and plotting theoretical charge and actual charge against chloride ion transferred, results in almost two parallel lines. The plots have almost equal slopes as shown in Figure 30. Actually, the second data point in the actual data plot does not fall in line, but otherwise the overall plot is close to parallel with the theoretical plot. The significance of Run #5 was the replacement of the sodium hydroxide anode solution with water, which greatly reduced the amount of sodium (Na^+) and hydroxyl ions (OH^-) available for carrying charge. The total charge measured in Run #5 was caused predominantly by chloride ion and electrolysis of water.

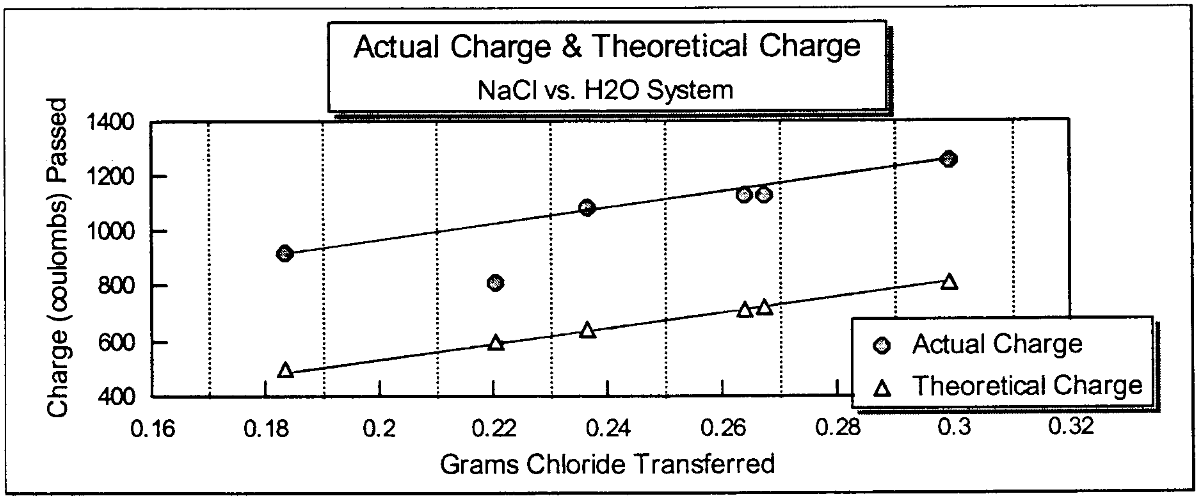

Figure 30. Comparison of actual charge and theoretical charge for sodium chloride vs. water system (Run #5). Theoretical charge calculated by applying Faraday's Law to amounts of chloride ion transferred out of the cathode compartment.

Another logical application of Faraday's Law would be to use experimentally measured total charge data and back calculate the amount of chloride ion transferred from the sodium chloride cathode compartment. This would enable a very easy way to determine chloride ion transferred without actually carrying out chemical titration analyses of cell solutions.

However, this is not possible because, as shown herein, total charge is the sum of several charge contributors other than chloride ion. A back calculation would result in chloride ion amounts that would be too great. This is illustrated in Table 12 in which the measured total charge data from Run #5 (NaCl vs. H_2O) was used to back calculate the amounts of chloride ion transferred. As shown in Table 12, the amounts of chloride ion transfer determined by back calculation are much greater than those actually measured. Figure 31 is a plot of the data given in Table 12 and compares back calculated chloride data to measured chloride data for the six cells in Run #5.

In every cell the back calculated chloride data is significantly greater than the measured data. Table 12 lists the average difference between the two sets of data as 0.1435 grams of chloride ion, while the back calculated data has an average 0.3886 grams. This means that for Run #5, the back calculated data is on average almost 37% higher than the actual measured chloride ion transferred data. Failure of the back calculation to agree with the measured chloride data is further proof that total charge cannot be due only to chloride ion per se.

Table 12. Theoretical Back Calculation of Grams Chloride Ion Transferred

Run #5 NaCl vs. H_2O

Test Cell#	Back Calculation Gram Cl Transf.	Actual Measure Gram Cl Transf.	Difference Grams
1	0.4617	0.2992	0.1625
2	0.4003	0.2367	0.1636
3	0.3201	0.2205	0.0996
4	0.4150	0.2639	0.1511
5	0.4165	0.2672	0.1493
6	0.3377	0.1835	0.1542
Max	0.4617	0.2992	0.1636
Min	0.3201	0.1835	0.0996
Avg	0.3886	0.2452	0.1435

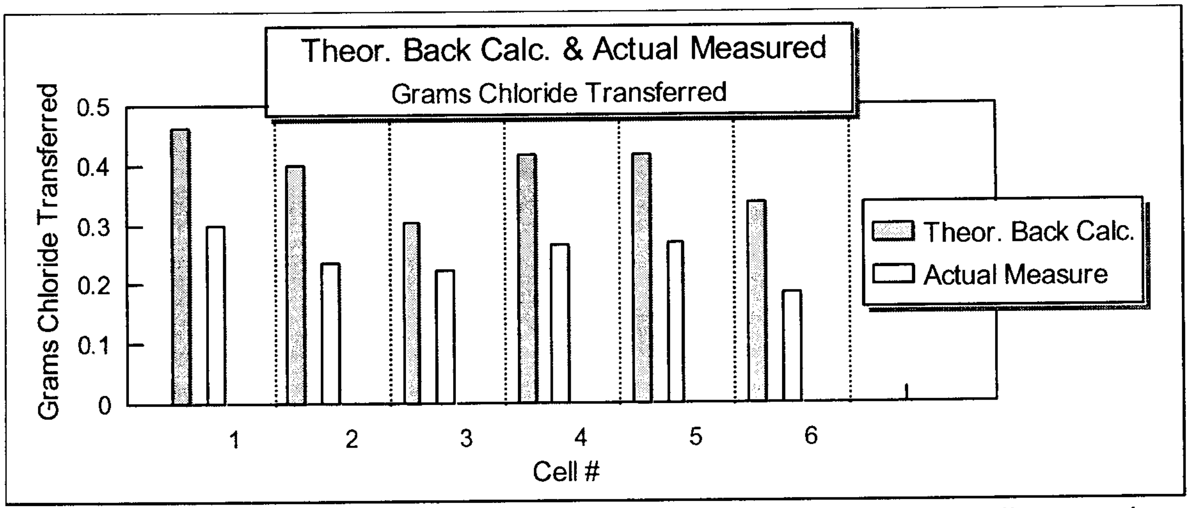

Figure 31. Comparison of theoretical back calculation of chloride ion transferred to the actually measured chloride ion transferred. Theoretical was always higher due to excessive total charge not related to chloride ion.

(f) - *Statistical Analysis of Data:*

To examine the linear relation between total charge and grams of chloride ion transferred, the data from the four NaCl vs. NaOH runs were combined. Each run consisted of six test cells and produced six total charge and six chloride ion transfer measurements. Combining the data resulted in 24 total charge and 24 chloride ion transferred values, that is, 24 data points. Total charge values were plotted against grams of chloride ion values and a linear regression analysis performed. The linear regression plot is shown in Figure 32. By applying Faraday's Law to the grams of chloride transferred data, the fraction of the total charge caused by chloride ions alone was calculated. Plotting the calculated fractional charge due to chloride versus grams of chloride transferred results in a straight line as shown in Figure 33. Analysis data are shown in Table 13.

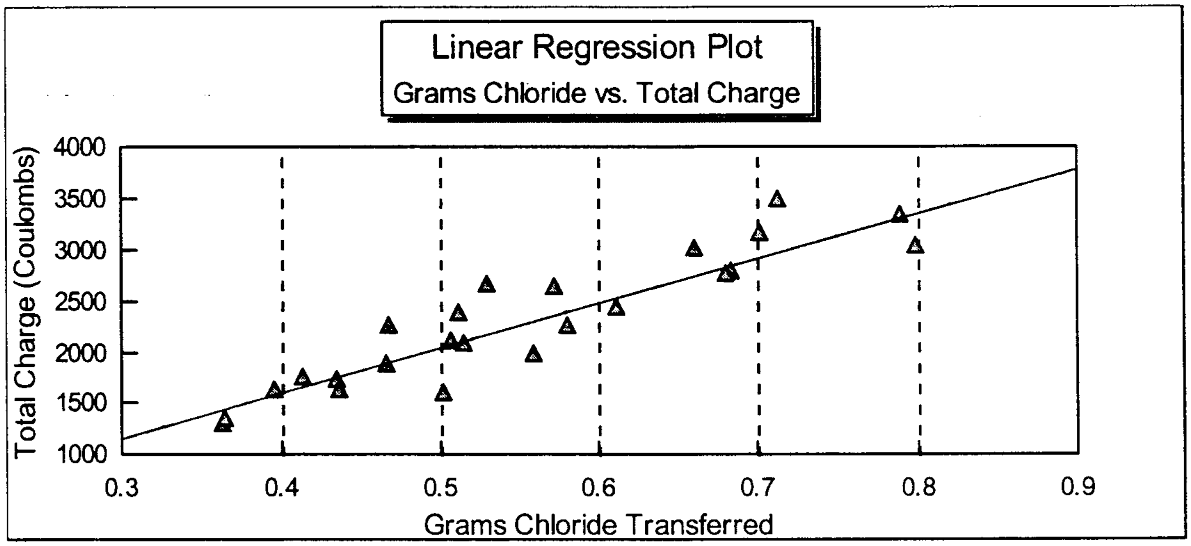

Figure 32. Linear regression plot of charge vs. chloride ion transferred data acquired from sodium chloride vs. sodium hydroxide runs 1 through 4.

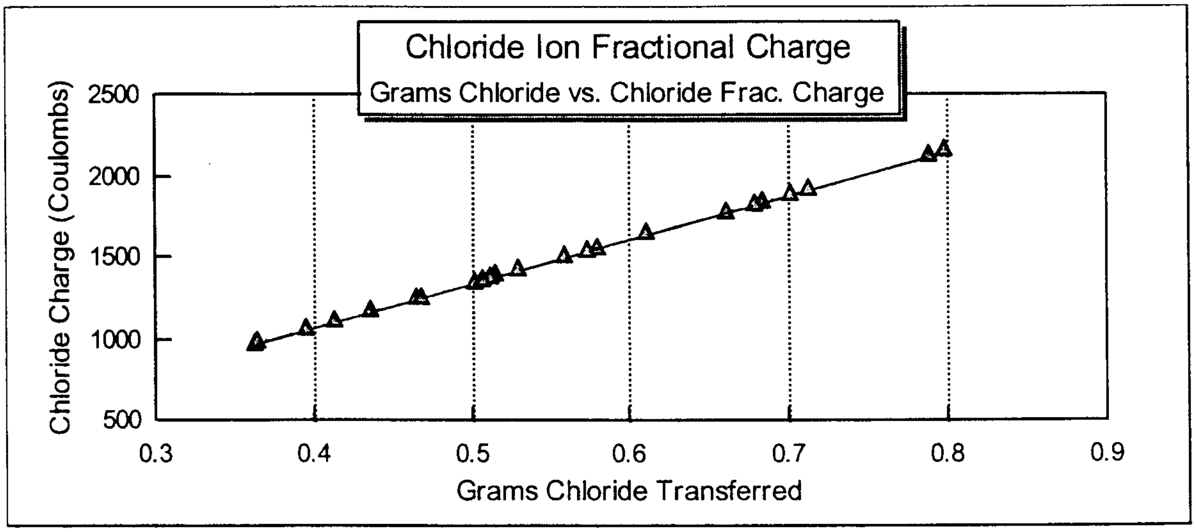

Figure 33. Plot of fractional charge due to chloride ion alone versus grams chloride transferred.

Table 13. Linear Regression Analysis Test Data
(From NaCl vs. NaOH Systems)

	Test Cell #	Data Point #	Gm Chloride Transferred	Total Charge Passed (clbs)	Chloride Ion Charge (clbs)
Run #1					
	1	1	0.4655	1878	1265
	2	2	0.5301	2660	1441
	3	3	0.3624	1315	985
	4	4	0.3640	1373	989
	5	5	0.7121	3488	1935
	6	6	0.4131	1756	1123
Run #2	1	7	0.5023	1610	1365
	2	8	0.6107	2431	1660
	3	9	0.5157	2101	1402
	4	10	0.4352	1736	1183
	5	11	0.5594	1999	1520
	6	12	0.5797	2266	1576
Run #3	1	13	0.3952	1625	1074
	2	14	0.5727	2650	1557
	3	15	0.5118	2397	1391
	4	16	0.4359	1633	1185
	5	17	0.4674	2276	1270
	6	18	0.5071	2105	1378
Run #4	1	19	0.6830	2790	1856
	2	20	0.7985	3049	2170
	3	21	0.7886	3361	2143
	4	22	0.6790	2759	1845
	5	23	0.7015	3183	1907
	6	24	0.6609	3032	1796
	Max		0.7985	3488	2170
	Min		0.3624	1315	985
	Avg		0.5522	2311	1501

While the plot in Figure 32 is not as thoroughly linear as that in Figure 33, it does signify a degree of linearity between *total charge* and grams of chloride transferred. The reliability of regression value (R^2) for Figure 32 is 0.85 at a confidence level of 95%. Regression values (R^2) closer to 1 indicate stronger correlation. The plot in Figure 32 represents total charge contributed by chloride and also by other inherent sources. In comparison, the linear plot in Figure 33 is the result of removing all excess charge and retains charge due only to chloride ions. It represents *chloride charge* instead of total charge. As shown, *two charge relationships exist.* Total charge which is an indicator of *total ionic permeability, and chloride* charge which is an indicator of *chloride ion permeability.* Chloride charge cannot be measured directly via the T-277 method, that is, it cannot be separated or distinguished from the measured total charge experimentally, but it can be determined by way of the Faraday Law calculation. Since it has been shown that grams of chloride transferred is linear with both test run time, and also with the amount of charge generated by chloride ions, then a measure of chloride transferred into the concrete specimen is a direct measure of chloride permeability of concrete. Chloride ion transfer measurement is also a determination of *concrete absorbance of chloride ion* which is another physical property for evaluation of concretes.

(3) - <u>*Concrete Disk & Slab Studies*</u> --

a) <u>*Concrete Disks*</u>:

Studies of concrete disk samples confirmed several facts: 1) chloride ion is not uniformly distributed throughout the disk, 2) chloride ion is concentrated on the face-side of the disk which is in contact with the sodium chloride cathode solution, and 3) the chloride ion does not penetrate very deep into the disk. Due to this non-uniform distribution, a material balance accountability of chloride ion in a permeability cell system requires an analysis for total chloride ion in the disk, whereby the entire disk must be pulverized and uniformly mixed to obtain a representative sample.

A single material balance determination carried out in these studies via pulverizing resulted in an 89% accountability of chloride ion. Although a higher percent accountability was anticipated, the result is supportive of the permeability cell results indicating that more than 99% of the transferred chloride ion remains in the disk and does not reach the sodium hydroxide anode compartment. There is very little, if any, complete migration of chloride ion through the disk from one face side to the opposite side. It may well be that the 60 volts applied in ASTM T-277 method to hasten chloride ion migration serves only to hasten transfer of chloride ion out of the sodium chloride solution in the cathode compartment, but does not actually cause increased migration or transport of the ion through the concrete to reach the sodium hydroxide anode compartment.

b) Concrete Slabs:

While the concrete slabs contained more chloride ion and at deeper profile depths than the disks, the probable cause was that the slabs had far greater contact time (90 days) with the sodium chloride salt solution than the disks (6 hours). It should be noted that it is the comparison of chloride content in the concrete slabs and disks that are being compared, and not chloride permeability expressed as total charge (coulombs) compared to slab profiling (grams chloride). Other investigators have attempted to do the latter, that is, relate total charge to slab profiling. This does not seem feasible for several reasons, but mainly because total charge is not specific to chloride ion per se, and therefore not indicative of grams of chloride, while profiling is specific to grams of chloride.

Summary

These studies were undertaken to develop a quantitative determination of chloride ion permeability in concrete based upon measuring the chloride ion migration in the concrete. It was intended to find a correlation to AASHTO standard method T-277 ("Electrical Indication of Concrete's Ability to Resist Chloride") by measuring the amount of chloride ion which migrated through concrete samples and comparing the chloride values to total charge measurements as determined by the T-277 method. A direct relationship between total charge and chloride ion permeability has never been previously established. While these studies do show a relationship between the two, they also show that total charge is not a measure, per se, of chloride ion permeability. Total charge is a composite of charges from several sources including chloride, but is not unique to chloride ion. A method based upon chloride ion concentration would define permeability as grams of the species of most interest (chloride) instead of electrical units in coulombs. These studies have shown that a measure of the amount of chloride ion transferred into, or absorbed by the concrete is an accurate measure of chloride permeability of concrete. Permeability data expressed as *grams chloride (transferred or absorbed)* is very accurate and more practical for making evaluations and comparisons of concretes. Grams of chloride are readily applicable for subsequent calculations such as % Cl and lbs/yd^3 than are coulombs of electrical total charge.

In summary, the following results regarding the physical and chemical processes within the cell were obtained using the applied voltage test cell technique as described in AASHTO method T 277 - 93.

1) *Most of the chloride ion which is transferred out of the sodium chloride cathode compartment of the cell remains in the concrete disk specimen and never reaches the sodium hydroxide anode compartment.*

On average, approximately 99.8% chloride ion remained in the concrete disk. The amount of chloride ion transferred out of the cathode area is appreciable, about 0.5 grams. The amount on average reaching the sodium hydroxide anode area is only about 0.001 grams (0.2%).

2) *Most of the chloride ion remaining in the disk is concentrated on the face-side in contact with the sodium chloride cathode cell solution.*

The chloride is not uniformly distributed throughout the concrete disk. Most of the chloride is within 0 to 3.81 cm (0 to $1^1/_2$ in.) depth on the side of the disk in contact with the sodium chloride solution.

3) *Theoretically, the total charge measured* *<u>was always greater</u>* *than that possibly caused by the amount of chloride ion transferred out of the cathode compartment. This is another indication that there are contributors to total charge other than chloride ion.*

The amount of charge produced by an anion or cation reacting at an electrode can be calculated by applying Faraday's Law which relates the amount of electrical charge passed and concentration of ions.

4) *There is a background charge present within the measured total charge, caused by the electrolysis of water at the anode and cathode electrodes in the cell system.*

Replacing sodium chloride and sodium hydroxide solutions with water in the respective cell compartments generated a significant total charge of about 1000 coulombs. *This background charge was produced without any migration of ions from salt solutions, but was due to the electrolysis of water*. The background charge was appreciable and represents about one third to one fourth the total charge obtained with the standard NaCl vs. NaOH cell systems which contain an abundance of ions. Another source of background charge would also be possible due to extraction or solubilizing (by the salt solutions) of ions inherent within the concrete sample.

5) *Five different salts,* *<u>all chloride ion free,</u>* *produced total charge which in most cases was equal to, or greater than total charge obtained with NaCl vs. NaOH systems.*

The amount of total charge varied with *the nature and concentration of the salt,* for example, the kind of *<u>anion</u> such as* SO_4^{-2} or NO_3^{-1}, and the kind of *<u>cation</u> such as* Ca^{+2}. This simply illustrates that *any ionic species (anion or cation) present in cell solutions will produce charge in addition to that caused by chloride ion.*

Conclusions

A quantitative determination of chloride ion permeability of concrete measured as grams of chloride can be accomplished utilizing AASHTO standard method T-277. Measurement of the chloride ion which transfers out of the sodium chloride cathode cell reservoir and enters the concrete specimen is a direct measure of chloride migration and permeability. It is also a measure of *concrete absorbance of chloride ion.* Permeability/ absorbance is measured as grams of chloride ion.

While total charge (coulombs) and chloride ion permeability (grams Cl) appeared to have a quantitative and linear relation, this is not the case. Total charge developed in the test cell was found *not to be caused by chloride ion alone. Total charge was found to be a summation of additional charges* due to the electrolysis of water at the electrodes, and to the presence of large amounts of other ions (Na^+ and OH^-) in the cell system.

Total charge is a measure of *the total ionic conductivity or electrical conductivity of the concrete which includes the chloride ions,* but total charge is not specific to chloride ion per se and therefore, is not a measure of chloride ion permeability. The quantitative and linear relation observed was between total charge and total ionic conductivity, and not solely due to chloride ion conductivity. There is of course, a quantitative and linear relation between chloride ion charge and chloride ion permeability, but charge resulting specifically from chloride ion alone cannot be isolated and measured as such via the procedure in method T- 277.

Faraday's Law relates charge (coulombs) and quantities of substances (ions) reacting in electrolytic cell systems. Application of Faraday's Law to measured chloride ion data enabled the calculation of charge (coulombs) specifically due to chloride ion alone. The calculated chloride charge (coulombs) and measured chloride ion concentrations exhibited a quantitative and linear relation as was expected. The law made evident and confirmed that total charge is not a measure of chloride ion nor of chloride ion permeability.

Chloride ion permeability of concrete, or concrete absorbance of chloride ion determined by this procedure would have the advantage of being measured in grams of chloride ion instead of coulombs of charge. With the permeability test cell technique described in AASHTO standard method T-277, *the accuracy and reliability of measuring grams of chloride ion is far greater than measuring electrical charge as coulombs.* This enables a more accurate and reliable evaluation of concrete permeability by chlorides, or concrete absorbance of chlorides.

References

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2. AASHTO T 277-93, Standard Method of Test for Electrical Indication of Concrete's Ability to Resist Chloride.

3. AASHTO T 259-80, Standard Method of Test for Resistance of Concrete to Chloride Ion Penetration.

4. AASHTO T 260-84, Standard Method of Sampling and Testing for Total Chloride Ion in Concrete and Concrete Raw Materials.

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Appendix A

Concrete Mixes For Permeability Studies

Actual Mix

MIX 1 - W/C = 0.40

Component	Weight	Yield (cu.ft.)
Cement	75.5 lb	0.38
Silica Fume	0.7 gal. (4 lb. solids)	0.03
Stone	161.0 lb	0.94
Sand	146.2 lb	0.88
Water	31.6 lb	0.51
Air	48.4 ml	0.19
WRDA 19	133.9 ml	------
Air Content	6.2%	
Slump	3.5 in	
Concrete Temp.	22 C^0	

MIX 2 - W/C = 0.42

Component	Weight	Yield (cu.ft.)
Cement	104.0 lb	0.46
Silica Fume	0.8 gal. (5.2 lb. solids)	0.04
Stone	268.0 lb	1.56
Sand	186.0 lb	1.12
Water	45.7 lb	0.73
Air	40.0 ml	0.22
WRDA 19	159.7 ml	------
Air Content	6.2 %	
Slump	3.75 in	
Concrete Temp.	22 C^0	

Appendix A

Concrete Mixes For Permeability Studies

Actual Mix

MIX 3 - W/C = 0.43

Component	Weight	Yield (cu.ft.)
Cement	87.5 lb	0.44
Silica Fume	0.8 gal. (4.6 lb. solids)	0.05
Stone	225.0 lb	1.31
Sand	165.5 lb	1.00
Water	39.6 lb	0.61
Air	33.4 ml	0.19
WRDA 19	133.9 ml	------
Air Content	6.2 %	
Slump	4.0 in	
Concrete Temp.	22 C^0	

Appendix B

Description of Apparatus and Equipment

Chloride permeability tests were carried out according to AASHTO T-277 standard method, "Resistance of Concrete to Chloride Ion Penetration". Modification of the apparatus described in the method was made in order to test six concrete specimens simultaneously instead of one as prescribed, and to also automate the procedure to measure current in coulombs per second and calculate total charge. A computer control system was incorporated into the apparatus. The apparatus consists of four major components. Modification of these components are described as follows

(1) Specimen Cells --

The cells were manufactured according to the specifications in AASHTO T-277, but have some modifications. The NaCl compartment has a 3 ohm, 25 watt shunt resistor epoxied to it. This resistor is wired in series with the cell and serves the purpose stated above. The NaOH compartment has a voltage divider epoxied to it. The voltage divider, which is wired in parallel with the cell, consists of a 25 kilohm, 10 watt resistor in series with a 1 kilohm, 10 watt resistor, with voltage being measured across the 1 kilohm resister. The divider is required because the voltage across the cell must be kept at 60 volts (+/-2volts) and the device monitoring the voltage across the cell can only deal with voltages of 5 volts or less. The divider has a voltage drop of [1/(1+25)] x [total voltage across divider]. When the total voltage is set to 60 volts, the drop is 2.31 volts, which is well below the maximum of 5 volts.

Both the shunt and the divider resistor are connected to the measurement apparatus by an audio-type XLR three conductor plug. This provides positive contact and easy connection. Two of the conductors are used on each plug (looking into the plug with the clip facing down, the right pin is positive and the left pin is negative). The plugs and the corresponding jacks on the box containing the connections to the interface cards are labeled to identify which are to be attached. The brass and copper conductor assembly has been replaced with a conductor plate made of 304 Stainless Steel. The plate has 6 mm holes drilled on center of a series of concentric circles. The connection of the power supplies to the cells are facilitated using high quality banana jacks and plugs. The plugs are labeled to match the corresponding cell halves. A silicone rubber has been molded into the cell over the conductor to provide a watertight seal.

(2) Power Source --

The source consists of two 30 volt DC power supplies, wired in series to provide the required 60 volts. The power switches have been removed and the power supplies have been wired directly to the control system. The positive side of the source has also been wired to the control system to allow switching off the power to any of the six cells independently.

Appendix B

Description of Apparatus and Equipment

(3) Computer System --

The computer provides a base for the control system and its operational program. It uses a standard ISA bus. Any functioning system meeting the following minimum requirements is suitable: 640 KB RAM, 120 MB hard drive, 3.5 inch high density floppy drive, CGA monitor and adapter, 101 keyboard, two open bit slots, MS-DOS v3.1 or higher, QuickBASIC v4.x.

(4) Input/Output Control System --

This consists of two Advantech PCL-711 multifunction I/O expansion cards and two PCLD-786 digital output solid state relay boards. The 711 is a user addressable device that provides sixteen digital inputs (which are not used here), sixteen digital outputs (ten are used from the first card), eight analog inputs (all are used on both cards -- the first four cells are tracked by the first card and the second card tracks the last four) and one analog output (not used).

The 786's are connected to the first 711 card and the relays that control the power to the cells are mounted on it. The digital outputs switch the relays on and off. There are eight opto-electrical relays mounted on the first 786 and two on the second. The first relays on the first 786 are made to switch AC voltage (to control the power supplies) and the remainder of the relays are built to switch DC voltage (to control voltage to the cells). The analog inputs are used to measure voltages as follows: eight are used to measure the voltage across the shunt resistors, the other eight are used to measure the voltage across the voltage dividers. The relays allow the 711 to control voltages above its maximum of 10 volts. The AC relays are rated for 250 VAC at 3 amps. The DC relays are rated for 100 VDC at 1 amp. This is more than sufficient to control the devices connected to them. The 711's are controlled by the operational program, which activates their functions as necessary.