DETERMINATION OF CHLORIDE DIFFUSION CONSTANTS FOR CONCRETES

OF DIFFERING WATER TO CEMENT RATIOS AND ADMIXTURES

by

David Gilman Smith

Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Civil Engineering

APPROVED:

_____
R.E. Weyers, Chairman

_____   _____
R.D. Walker   S.A. Ardekani

August, 1988

Blacksburg, Virginia

DETERMINATION OF CHLORIDE DIFFUSION CONSTANTS FOR CONCRETES OF DIFFERING WATER TO CEMENT RATIOS AND ADMIXTURES

by

David Gilman Smith

Committee Chairman: Richard E. Weyers
Civil Engineering

(ABSTRACT)

Reinforced concrete exposed to chlorides is subject to rapid deterioration once the concentration of the chloride ion in the concrete reaches a critical level to cause corrosion of the reinforcing steel. The chloride ion diffuses through concrete according to Fick's Law, which is a function of time, a driving concentration, and a diffusion constant. The diffusion constant varies with temperature and the variety of concrete.

The research included determination of diffusion constants for six types of concretes after 8 weeks and 16 weeks of ponding with an NaCl solution. In addition, one set of these samples was subjected to the outside environment while the other was indoors under controlled conditions. The mixes included water to cement ratios of 0.35, 0.40, 0.45, and 0.50, and two water to cement ratios of 0.45 with 15% cement replacement with pozzolan admixtures (silica fume and type F flyash). Thus, the effects of temperature, water to

cement ratio, and pozzolanic admixtures in regard to the diffusion constant for concrete were found.

The method by which a diffusion constant was found is as follows: 1) A 3% solution of NaCl is ponded on top of a four inch thick specimen of concrete. 2) Powder samples of the paste are taken at a specified time at depths of 0.5, 1.0, 1.5, and 2.5 inches. 3) These samples are analyzed for chloride content by potentiometric titration. 4) The data is fit to Fick's Law by nonlinear regression and an effective diffusion constant is determined.

Acknowledgements

Great appreciation is expressed to Dr. Richard E. Weyers for his help and advice in making this thesis possible.

Appreciation is also expressed to   and Dr. Sia A. Ardekani for their statistical assistance.

and   are thanked for all their assistance and tolerance in the laboratory.

Table of Contents

List of Tables

List of Figures

I. <u>INTRODUCTION</u>

<u>Chlorides and Diffusion</u>:

Chloride induced corrosion of reinforcing steel in concrete structures is of serious concern to the owners of any reinforced concrete structure exposed to chlorides. Chlorides, upon reaching a critical concentration in the concrete, reacts with the steel reinforcement and causes corrosion to begin. Since the oxidized form of steel is six times the volume of unoxidized steel, expansion occurs. This expansion then causes deterioration of the surrounding concrete and reults in an unsound structure.

Chlorides may be present in concrete from three major sources. They may have been present in the original mix constituents; chloride bearing water or aggregate and chloride based accelerators. Chlorides may also ingress from external sources (such as seawater or deicing salts) through cracks in the concrete. The third process by which chlorides may ingress into concrete is by diffusion. Diffusion takes place even through the most sound concrete. Whereas the first two processes can be avoided to a great degree by good construction practices, diffusion cannot. Sealers reduce chloride diffusion to some degree but they are short lived.

The diffusion of chlorides into concrete cannot be

entirely stopped. Therefore, in order to predict how long it
will take for the chloride ion concentration to reach the
critical depassivation level, a model was needed. Browne
suggests that the diffusion of chlorides into concrete from
external sources is well represented by Fick's Law of
Diffusion, which relates the ion concentration at a certain
depth and time to a driving concentration and a diffusion
constant (1):

$$\frac{\delta C(x,t)}{\delta t} = Dc \frac{\delta^2 C(x,t)}{\delta x^2} \qquad \text{eqn. 1}$$

where: $C(x,t)$ = the chloride ion concentration at a depth x
at time t

Dc = the chloride diffusion constant for the
concrete in question

A standard solution to equation one is:

$$C(x,t) = Co \ erfc \ (x/(2\sqrt{Dc \cdot t})) \qquad \text{eqn. 2}$$

where: Co = the apparent equilibrium chloride
concentration at the surface of the
concrete

erfc = the complimentary error function

An example plot of equation 2 is given in figure 1. The
power of equation 2 is clear; if the constants (Dc and Co)
are known and the depth of the reinforcing steel is known,
the engineer in charge of construction is able to predict
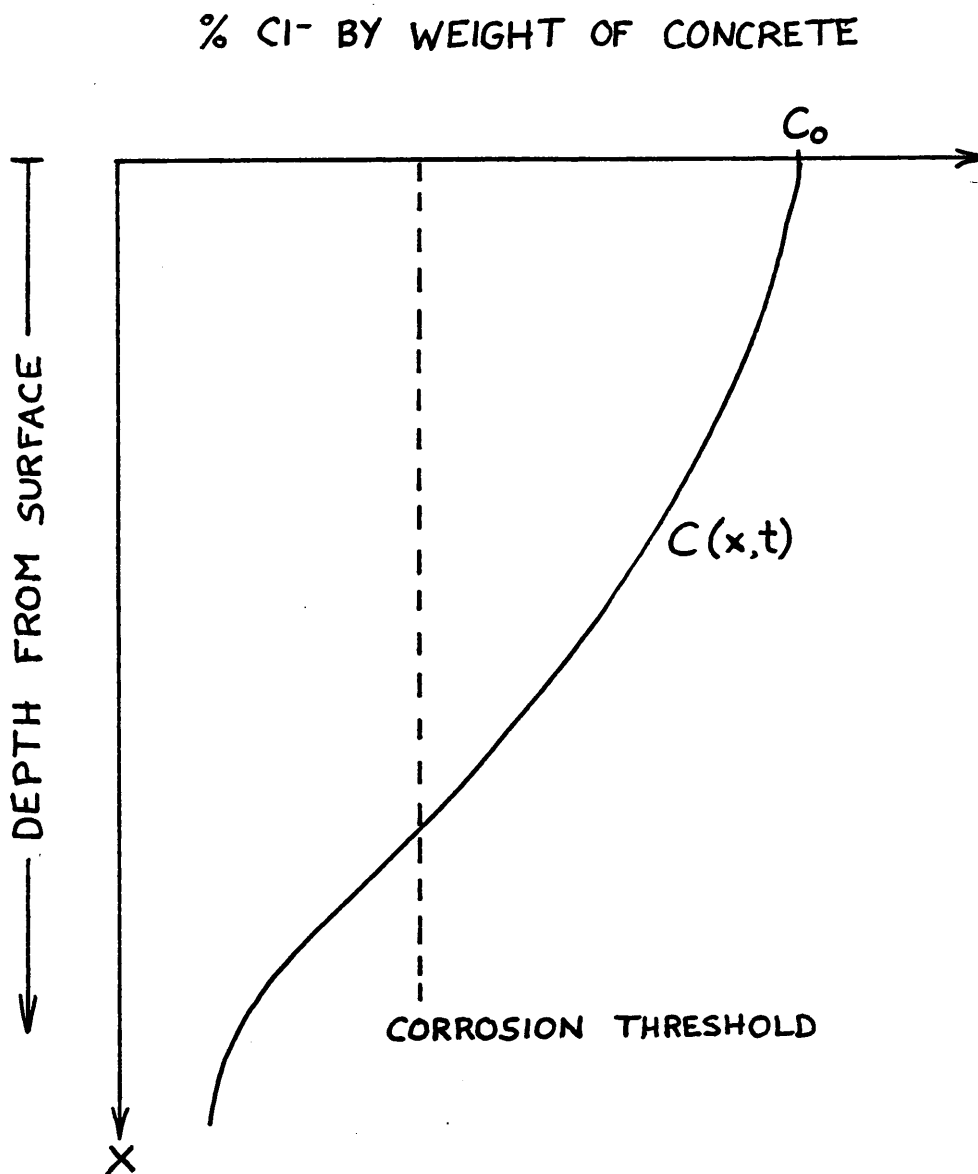
% CI⁻ BY WEIGHT OF CONCRETE

FIGURE 1. DIFFUSION CURVE FOR CHLORIDE IONS IN CONCRETE

how long it will take before the steel begins to corrode due to chlorides. He is also able to estimate the times to maintenance, repair, and eventually replacement (assuming corrosion of the steel reinforcement due to external salts is a problem). Values for the equilibrium chloride concentration and depth of reinforcement are readily found. However, the diffusion constant varies with the type of concrete and temperature (1). Therefore, test methods were developed to evaluate the chloride diffusion resistance of concretes.

Three tests have been devised to test for the diffusion resistance of concrete. The first, AASHTO T 259 ("Standard Method of Test for Resistance of Concrete to Chloride Ion Penetration"), gives a qualitative indication of the resistance of a specimen of concrete to chloride penetration in comparison to a control. The test consists of fabrication of 12x12x3 inch slabs (these are minimum dimensions; larger slabs may be fabricated), moist curing 2 weeks, dry storing (73 degrees Fahrenheit and 50% humidity) for two weeks, then ponding for 90 days with a 3% NaCl solution. Cores are drilled and powder samples are taken at two depths, 1/16 to 0.5 inch and 0.5 to 1.0 inch. The samples are analyzed for chloride ion concentration by AASHTO T 260 ("Standard Method of Test for Sampling and Testing for Total Chloride Ion in

Concrete") and are then compared to a control. However, this
test does not yield a diffusion constant that can be used to
predict length of service. Yet, it does simulate the actual
mechanism by which chloride penetrates into concrete.

The second test is AASHTO T 277, "Standard Method of
Test for Rapid Determination of the Chloride Permeability of
Concrete." In this test cylinders four inches in diameter
are fabricated and moist cured 2 weeks. Then the top two
inches are cut off, sealed around the circumference, and
tested for electrical conductivity. The number of coulombs
that pass through the sample in six hours is then compared
to specified ranges and determined to be 'high', 'low', etc.
The test, like AASHTO T 259, only gives a qualitative
measure of the permeability of concrete. However, unlike
AASHTO T 259, the method does not approximate the mechanism.

The third test method, used by Page, Short and El Tarras
in a similar diffusion study, uses a diffusion cell (figure
2) (2). A 3 millimeter thick disc is sealed between two
compartments; one of which contains a solution saturated
with calcium hydroxide and the other containing the same
except with one mole of NaCl added. The solutions are
analyzed by spectrophotometry at specific times for chloride
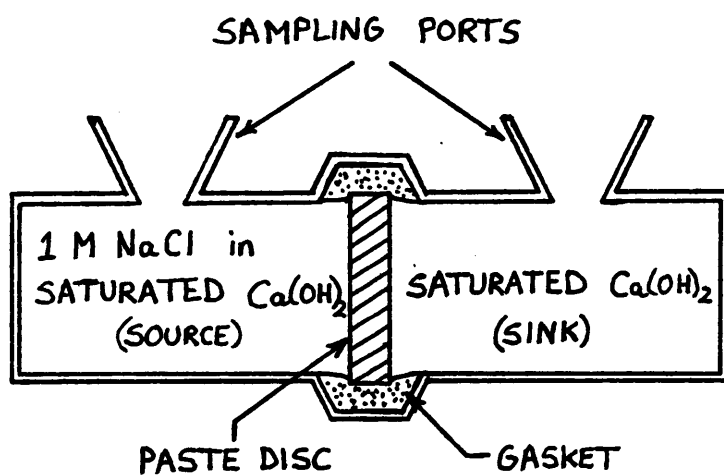content. The results are plotted and Dc is found by the
equation:

FIGURE 2. DIFFUSION CELL

$$J = Dc \ [C(1) - C(2)] \ / \ L \qquad \text{eqn. } 3$$

where J is the flux in moles per cm squared per second, L is the thickness of the disc in cm, C(1) and C(2) are the number of moles of chloride in the source and sink compartments, and Dc is the diffusion constant in cm squared per second (2). This diffusion cell is the more realistic of the rapid tests since it closely approximates the actual mechanism. However, there may be some problem with scaling. For example, in the case of fluid flow around a model aircraft, a scaling factor must be used to obtain the actual flow around the full size aircraft. Thus, a comparison must be done between the results acquired by the diffusion cell and actual full size slabs.

Factors Affecting Chloride Diffusion Rate:

There are several factors that affect the chloride diffusion rate of concrete. Water to cement ratio, time of curing, cement type and pozzolanic admixtures, and temperature all have been reported to affect the chloride diffusion constant. Water to cement ratio has a significant effect. All three types of tests have shown that the lower the water to cement ratio, the lower the chloride permeability. Page, et. al., using the diffusion cell method, found that there is a definite increase in chloride

permeability with increasing water to cement ratio in cement
pastes (2). Ozyildirim and Halstead obtained similar results
using AASHTO T 277 (3) and studies using methods similar to
AASHTO T 259 show this to be true for concrete (4). A
logical explanation would be that the decreased pore sizes
inhibit ion flow. This is evident by the comparative pore
size distributions of different water to cement ratios (2).
Chloride ions may also tend to clog smaller pores when they
progress through the concrete and thus reduce their own
permeability (5).

Time of curing can be a factor in chloride permeability
of concrete. Tests of concretes cured for 28, 90, and 365
days showed a definite decrease in permeability as time of
curing increased (3). Densification of the pore structure
seems to be the most plausible explanation.

Cement type and pozzolanic admixtures can also affect
the diffusion constant for concretes. Rasheeduzzafar, et.
al. reported a reduction in chloride permeability with an
increase in the amount of tricalcium aluminate in a cement
(6). However, Gjorv and Vennesland reported that tricalcium
aluminate content had little effect. They also reported that
cements blended with pozzolans resulted in lower chloride
permeabilities. It was suggested that added pozzolans not
only decrease the pore sizes but also reduce the anion

exchange capacity of the system, reducing chloride permeability (7).

The last factor is temperature. Diffusion is a thermodynamic process, therefore the chloride diffusion constant will be affected by temperature. Dc has been shown to vary linearly with absolute temperature (2). Thus, the higher the temperature, the faster the chlorides will diffuse through concrete.

Purpose of Experiment:

The purpose of this experiment was to determine the chloride diffusion constants for concretes with various water to cement ratios and pozzolanic admixtures under laboratory and in-situ conditions. Any relationships between these variables were to be found using statistical methods. This then would enable the prediction of the chloride diffusion constant for a given concrete mix design and environment.

II. <u>EXPERIMENTAL PROCEDURE</u>

In order to find the relationship between water to cement ratio, pozzolanic admixtures, temperature, and the diffusion constant for concrete, the following experiment was devised. To test the effect of water to cement ratio, four batches of differing water to cement ratio were included. To test the effect of pozzolanic admixtures, two batches of the same water to cement ratio as one of the four previous batches were made but included flyash and silica fume, respectively. Temperature was tested by placing two specimens from each batch in a controlled environment and placing two specimens from each batch outside. (During the time frame of this experiment, from February to June, the outside temperature was consistently lower.)

It was desired that the mechanism of diffusion in the test specimens parallel the mechanism in the field. A variation on AASHTO T 259-80 was devised. All the steps in concrete preparation, curing, and ponding were identical to AASHTO T 259-80. However, the sampling procedure differed in order that enough points could be obtained for a viable fit of the diffusion curve. The testing procedure was as follows:

1. A total of six batches of concrete were mixed.

The slump, air content, and unit weight were recorded for each batch. From each batch four 12x12x4 inch specimens and six 3x6 inch cylinders were prepared. Four of the mixes were conventional with the following water to cement ratios: 0.35, 0.40, 0.45, and 0.50. The fifth batch had a water to cementatious ratio of 0.45 with a 15% replacement (by weight) of the cement with silica fume. The sixth batch was the same as the silica fume batch except Type F flyash was used instead of silica fume. The four conventional batches were labeled by their water to cement ratio (35, 40, 45, 50), the silica fume by "SF", and the flyash by "FA". The four specimens from each batch were labeled "A", "B", "C", and "D". There were a total of twenty four specimens fabricated.

2. All specimens were cured under 100% humidity at room temperature for 14 days followed by 14 days of room storage, according to AASHTO T 259-80.

3. An impermeable polymer coating was applied to all of the 12x4 inch sides of the specimens to simulate the condition of being in the body of a slab, preventing lateral ion migration and moisture loss. On the top of each specimen a two inch high wooden dike was placed. These dikes were made from 3/8 inch thick plywood sealed with the same polymer as the concrete. These dikes were then bonded to the

specimens with acrylic latex caulking to prevent leaking of the salt solution (see Figure 3).

4. After the specified curing and storage times, the specimens were placed in their respective environments. The "C" and "D" specimens from each batch were placed outside at the Price's Fork Research Station, where the temperature of the specimens fluctuated with ambient conditions. The specimens were also covered with a large plastic sheet to shield them from precipitation. The "A" and "B" specimens were placed in the Transportation Materials Laboratory at VPI. In this lab the temperature remained 72 degrees Fahrenheit, with it deviating plus or minus 5 degrees. A 3% solution of NaCl and distilled water was then ponded on the top of all twenty four specimens. Plastic sheets were then secured on the tops of the dikes to prevent the solution from evaporating. Every three to four days the solution was recharged in order to maintain a near constant concentration of chloride.

5. For each day an average temperature was recorded for ambient conditions at Price's Fork. Weekly averages were then compiled. Then the grand average was compiled.

6. After eight and sixteen weeks of ponding, concrete powder samples were taken from each specimen. At the eight week point, the samples were taken by using a 7/16 inch
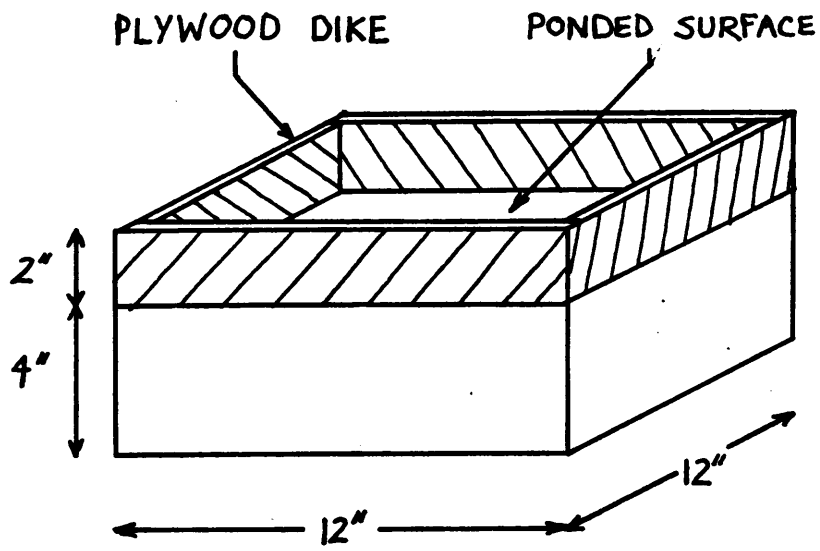
FIGURE 3. CONCRETE TEST SPECIMEN

diameter masonry bit and drilling horizontally into the
sides of the specimens at depths of 0.5, 1.0, and 1.5
inches. When drilling, coarse aggregate were avoided as much
as possible and powder from the first 1/4 inch from the face
of the side was not used. This outer layer of concrete was
not used because of effect that the edge may have had upon
the diffusion behavior. At the sixteen week point, a
different procedure was used due to highly inconsistent
results from the first sampling. The specimens were cut in
half using a slab saw and the inner sides rinsed with
·distilled water to remove any chlorides from the water used
in the cutting process. These inner sides were drilled as
before at 0.5, 1.0, 1.5, and 2.5 inches using a 3/16 inch
diameter bit (figure 4). At both sampling times, care was
taken to obtain samples of the mortar only and not to
include powder secured from the extreme edges. In addition,
powder samples from unponded cylinders were taken by the
corresponding methods at the appropriate times to find the
background chloride content.

7. Chloride analyses of the powder samples were
performed using a potentiometric titration method. The
procedure is as follows: 1) The sample is weighed and
brought into a slurry by the addition of 10 ml of hot (90 to
100 degrees Centigrade) distilled water; 2) 3 ml of
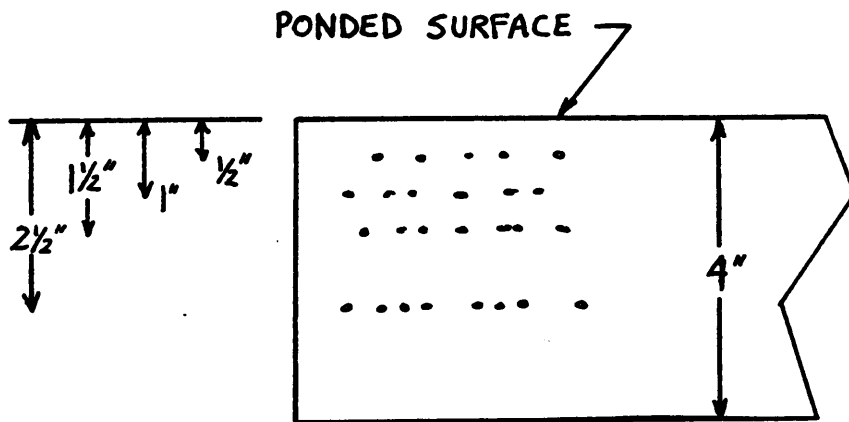
FIGURE 4.   POWDER SAMPLING PATTERN

concentrated nitric acid (reagent grade) is added to digest
the sample and then hot distilled water is added to bring
the solution to 50 ml; 3) The solution is boiled for one
minute then filtered into a beaker; 4) 4 ml of .01 N NaCl
solution is added and then is titrated against using a .01 N
$AgNO_3$ solution and a millivoltmeter equipped with a chloride
ion specific electrode (in this case an Orion Model 94-17B).
A chloride analysis was done for each depth in each
specimen.

8. A diffusion constant for each water to cement ratio,
environment, and time was obtained by using a nonlinear
regression technique. Six data points per diffusion curve
were used at eight weeks and eight points per curve were
used at sixteen weeks. In order to calculate the diffusion
constant at a specific time, for a specific mix and
environmental condition, all the data points complying to
that condition were used. For example, to find the diffusion
constant for the mix "FA" at sixteen weeks under the outside
conditions, the chloride concentrations from the "FA-C" and
"FA-D" at depths of 0.5, 1.0, 1.5, and 2.5 inches would be
used. A computer program, which iterates between specified
values of Co and Dc to find the maximum correlation
coefficient, was written to accomplish this regression. This
program, along with the notes concerning its logic and

operation, is in the appendix.

9. The data was analyzed for the effects of water to cement ratio, environment, and admixtures upon the observed diffusion constants.

III. <u>EXPERIMENTAL RESULTS AND DISCUSSION</u>

The results of the chloride titrations are summarized in table 1. Each value represents the experimentally obtained chloride content in percent by weight of each sample tested. The background chloride was found at eight and sixteen weeks by sampling the unponded cylinders using the appropriate sampling method and then averaging the results together. There was in all concretes a definite pattern of decreasing chloride content with greater depth. The chloride diffusion constants found by the regression technique are presented in detail in table 2. With these constants are the corresponding statistical measures. The temperatures under which the specimens were tested is shown graphically in figure 5. Data concerning the properties and constituents of the concrete mixes are listed in the appendix.

<u>Regression Considerations:</u>

A nonlinear regression technique was used in this study to find the constants used to describe the data points. Therefore, the conventional definitions used for the linear regression procedure to describe the goodness of fit of the derived curves are not applicable. If the standard expression for the total sum of the squares is expanded, the

Table 1

Chloride Analyses

(Percent Chloride by Weight of Sample)

TIME :	8 WEEKS		:	16 WEEKS			:
DEPTH:	0.5"	1.0"	1.5":	0.5"	1.0"	1.5"	2.5":
35-A :	.0236	.019	.0224:	.1197	.0224	.0201	.0225:
35-B :	.0201	.0224	.0247:	.0468	.0178	.0213	.0236:
35-C :	.1475	.0247	.0247:	.0734	.0224	.0213	.0225:
35-D :	.0329	.0201	.0224:	.056	.0224	.0189	.0154:
40-A :	.0259	.0224	.0224:	.2139	.0177	.0178	.0165:
40-B :	.0769	.0213	.0178:	.3155	.0177	.0189	.0142:
40-C :	.0271	.0201	.0155:	.2399	.0165	.0142	.0201:
40-D :	.3664	.0363	.019:	.2309	.0142	.0154	.0154:
45-A :	.024	.017	.0271:	.2423	.0201	.0201	.0177:
45-B :	.0421	.0201	.019:	.3037	.0213	.013	.0201:
45-C :	.0143	.0259	.0201:	.3214	.0201	.0118	.0165:
45-D :	.1892	.0282	.0224:	.2139	.0154	.0165	.0142:
FA-A :	.1081	.0201	.0363:	.1619	.0177	.0177	.0165:
FA-B :	.0436	.0271	.0247:	.2494	.0201	.0201	.013:
FA-C :	.0618	.151	.0247:	.0626	.013	.0165	.013:
FA-D :	.1776	.0247	.0247:	.2813	.0177·	.0142	.013:
SF-A :	.0247	.0247	.0294:	.0224	.0201	.019	.0208:
SF-B :	.0305	.0352	.0271:	.0224	.0231	.0178	.0224:
SF-C :	.0354	.0271	.0294:	.0201	.0165	.0177	.0177:
SF-D :	.0413	.0294	.0305:	.0201	.0165	.0177	.0189:
50-A :	-	.0216	.0236:	.5188	.0272	.0142	.0189:
50-B :	.0794	.0222	.0247:	.4325	.0213	.0201	.0165:
50-C :	.3191	.173	.0201:	.3841	.0284	.0165	.0189:
50-D :	.3884	.1765	.0294:	.3262	.0225	.0142	.0165:
BACKGROUND:	.0178		:	.0144			:

Table 2

Regression Results

MIX, ENVIRN:	:Dc in^2/yr:	Co	:	TIME	:	R SQRD ::
35 INSIDE ::	.075 / :	4.05%	: 8 WEEKS	:		-3.281::
35 OUTSIDE::	.245 / :	1.05%	: 8 WEEKS	:		.47::
40 INSIDE ::	.180 / :	1.00%	: 8 WEEKS	:		.469::
40 OUTSIDE::	.450 / :	1.00%	: 8 WEEKS	:		.412::
45 INSIDE ::	.100 / :	3.50%	: 8 WEEKS	:		.389::
45 OUTSIDE::	.265 / :	1.05%	: 8 WEEKS	:		.338::
FA INSIDE ::	.225 / :	1.00%	: 8 WEEKS	:		.526::
FA OUTSIDE::	.310 / :	1.00%	: 8 WEEKS	:		-.01::
SF INSIDE ::	.115 / :	1.25%	: 8 WEEKS	:		-6.309::
SF OUTSIDE::	.145 / :	1.15%	: 8 WEEKS	:		-2.882::
50 INSIDE ::	.210 / :	1.25%	: 8 WEEKS	:		.956::
50 OUTSIDE::	1.000 / :	1.00%	: 8 WEEKS	:		.828::
**********::	*********	********	:********	:********	:********	***::::
35 INSIDE ::	.120 / :	1.05%	: 16 WEEKS:			.649::
35 OUTSIDE::	.100 / :	1.15%	: 16 WEEKS:			.868::
40 INSIDE ::	.160 / :	2.25%	: 16 WEEKS:			.946::
40 OUTSIDE::	.125 / :	3.10%	: 16 WEEKS:			.999::
45 INSIDE ::	.190 / :	1.80%	: 16 WEEKS:			.98::
45 OUTSIDE::	.155 / :	2.40%	: 16 WEEKS:			.943::
FA INSIDE ::	.175 / :	1.50%	: 16 WEEKS:			.932::
FA OUTSIDE::	.135 / :	1.90%	: 16 WEEKS:			.608::
SF INSIDE ::	.045 / :	3.00%	: 16 WEEKS:			-8.687::
SF OUTSIDE::	.045 / :	2.15%	: 16 WEEKS:			-3.342::
50 INSIDE ::	.190 / :	3.20%	: 16 WEEKS:			.988::
50 OUTSIDE::	.205 / :	2.15%	: 16 WEEKS:			.99::

Figure 5
Temperature Variation of Specimens

TEMPERATURE (F)

TIME (WEEKS)

WEEKLY AVG
OUTSIDE AVG
INSIDE AVG
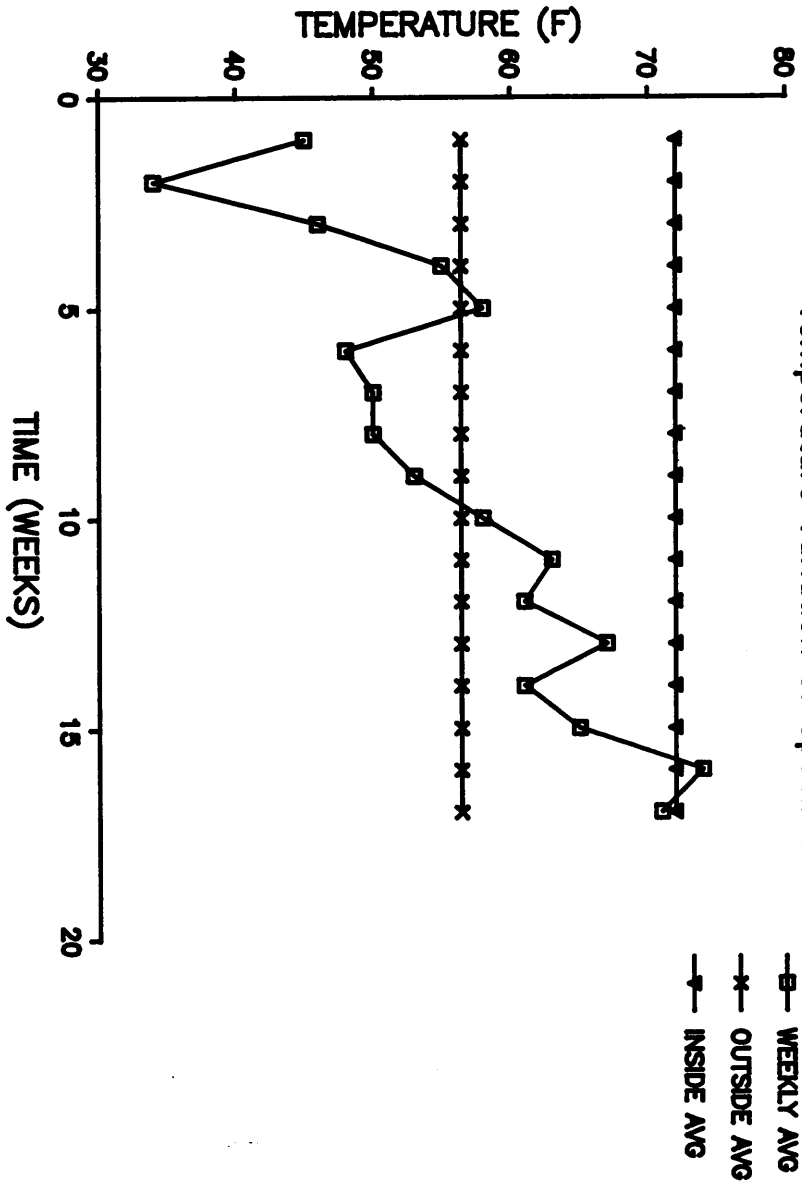
following results (8):

$$\sum (y_i - \bar{y})^2 = \sum (y_i - \hat{y}_i)^2 + \sum \left[(y_i - \hat{y}_i)(\hat{y}_i - \bar{y}) \right] + \sum (\hat{y}_i - \bar{y})^2 \qquad \text{eqn. 4}$$

$$\text{SST} \qquad\qquad \text{SSE} \qquad\qquad\qquad \text{SSZ} \qquad\qquad\qquad \text{SSR}$$

where y_i = observation at x_i

$\bar{y}$ = average of all observations y_i

$\hat{y}_i$ = predicted value at x_i

SST = total sum of the squares

SSE = sum of the squares of the errors

SSR = sum of the squares of the regression

SSZ = a residual term here defined

In a conventional linear regression, the term SSZ is zero and the following familiar relation results:

$$\text{SST = SSR + SSE} \qquad\qquad \text{eqn. 5}$$

However, for nonlinear functions, this is not the case. The usual practice has been to transform the data into a linear function, perform the regression, and define a correlation coefficient (R squared) based upon the transformed data set.

$$R^2 = \text{SSR/SST} \qquad\qquad \text{eqn. 6}$$

According to Kvalseth (9), equation six does not give an accurate indication of how good the nonlinear model is since the predicted values used in the calculation of SSR are for the transformed model. He suggests that in the case of a nonlinear model with no intercept (as the regression in this

case), the R squared should be defined as:

$$R^2 = 1 - SSE/SST$$ eqn. 7

This R squared is for the actual nonlinear function. In the calculation of the SSE, the predicted values for the nonlinear function are used. This gives a more appropriate indication of how good the coefficients fit the curve to the data. R squared in this case has the same meaning as in the linear case when comparing fits to the same model. The range from 0 to 1 still has the same significance, with 1.0 being a perfect fit and 0.0 being a very poor fit. However, Kvalseth asserts that if the R squared is negative, as in several cases in this project, the model is then inappropriate in describing the data.

This negative value of R squared is due to the SSZ term in equation 4. In a nonlinear regression where the fit is fair to good, SSZ will be very small, compared to SSR and SSE, and in the positive or negative range. If the model is inappropriate, SSZ will be large and negative, a small SST results, and R squared is negative. Therefore, the interpretation of the correlation coefficient for the nonlinear regression results should be considered carefully.

In addition to the aforementioned statistical anomalies, there is another issue dealing with the regression results. In the technique, Co ranged from 1.00% to 5.00% chloride by

weight of concrete and Dc ranged from 0.005 to 1.000 inches
squared per year. The Co was limited to that range due to
the fact that a 3% NaCl solution was ponded on the
specimens; even if leaching of chloride into the dike and
evaporation caused the chloride concentration to fluctuate,
the solution was recharged frequently enough to keep it well
in the specified range. Previous literature suggests that
the range of Dc for concretes are well within the limits of
iteration here (2). Thus, if the optimum Dc or Co for a
certain water to cement ratio is <u>near</u> the limit for that
variable, the fit might not be the best fit, but the most
realistic. However, if the regression yields a value of Co
or Dc which is <u>at</u> the boundary for that variable, it might
not be a good fit. Also, for concretes from the same batch,
the Co values should approximately correspond (within
1.00%). Therefore, the R squared for this regression data
should not be the sole criterion for judging the regression
good or bad; the values of Co should also be taken into
consideration.

<u>Sampling Considerations:</u>

At eight weeks, a 7/16 inch diameter drill bit was used.
By sampling with such a large drill bit, it is quite
probable that a fair amount of powder samples came from

coarse aggregate and not exclusively from the mortar. Even though this could be accounted for in some degree from a larger value of the background chloride present, there is no way to tell if indeed that was the correct background for each powder sample. Also, at the eight week sampling, the samples were drilled from the outside wall of the specimens. There was no definitive indicator of if the sealer used affected the acid soluble amount of chloride. In addition, the effect of the edge itself could have played a significant role in the behavior of the diffusion model. The cumulative influence of all these factors caused the accuracy of the diffusion constants to be poor compared to the results of the sampling technique used at the sixteen week point. In two cases (non silica fume mixes), the model was inappropriate for the data. Only two regressions obtained an R squared over 0.6 (50 inside and 50 outside) and one occurred at a boundary condition for Co. Therefore, the data was not considered to be conclusive.

To eliminate the sources of error encountered at the eight week sampling, the technique used at sixteen weeks was changed. First, the specimens were cut in half by a slab saw and rinsed with distilled water to eliminate any chlorides resulting from the cutting procedure. A 3/16 inch diameter bit was then used to take powder samples on the cut sides of

the specimens. Sampling on the internal cut sides eliminated any edge effects and the influence of the sealer. Since the aggregate could be seen and the bit was much smaller, the aggregate was avoided and virtually no aggregate powder was taken. As can be seen by the consistency of the data at sixteen weeks, the second sampling technique was more descriptive. Therefore, the diffusion constants derived from data at eight weeks were not included in the statistical analyses and thus the effect of time upon the diffusion constants could not be found.

Effect of Temperature Upon the Diffusion Constant:

The statistical analysis (table 3) performed on the sixteen week data shows that there is a significant difference in the diffusion constants between the samples that were inside and outside at the 75% level of confidence. Despite this low level, temperature does affect the diffusion rate, as the literature shows. From a thermodynamic point of view this is logical. Previous work by others suggest that in the diffusion cell test, the diffusion constant varies inversely with the absolute temperature (2). This may be why the statistical difference between inside and outside diffusion constants are not more acute. The difference in absolute temperature between inside

Table 3

Statistical Inferences

<u>Randomized Block Design Test Results:</u>

Source	Deg. of Freedom	F Value	Level of Significance
Inside/Outside:	1	2.528	75 %
W/C Ratio	3	10.288	95 %
Error	3	-	-
Total	7	-	-

<u>Diffusion Constant - W/C Ratio Relation at 95% L.O.S.:</u>

$$Dc = -0.093 + 0.585 \ (W/C)$$

$$R^2 = 0.85$$

<u>Diffusion Constant - W/C Ratio Relations at 75% L.O.S.:</u>

Inside: $Dc = -0.039 + 0.480 \ (W/C)$

$$R^2 = 0.87$$

Outside: $Dc = -0.147 + 0.690 \ (W/C)$

$$R^2 = 0.97$$

80% Confidence Interval: $-0.267 \leq Dc \leq 0.594$

and average outside conditions is only 3%. A much larger difference in temperature could have yielded better results.

Effect of Water to Cement Ratio Upon Dc:

The analysis also showed that the water to cement ratio was significant at the 95% confidence level in affecting the diffusion constant. If the 95% level of confidence is specified and temperature is not considered effective, the following relation between the chloride diffusion constant and water to cement ratio (for W/C in the range from 0.35 to 0.50) was found:

$$Dc = -0.093 + 0.585 \ (W/C) \qquad \text{eqn. 8}$$

where Dc is in inches squared per year and water to cement ratio is the actual value. The R squared for this equation is 0.85. If temperature is considered effective, as stated previously, two equations result:

Inside: $Dc = -0.039 + 0.480 \ (W/C)$ eqn. 9

Outside: $Dc = -0.147 + 0.690 \ (W/C)$ eqn. 10

For equation 9, the average temperature was 72 degrees F. and the R squared was 0.87. For equation 10, the average temperature was 56 degrees and the R squared was 0.97. Therefore, considering the literature, equations 9 and 10 may be a better indication of the relationship between water to cement ratio (between 0.35 and 0.50) and the diffusion

constant for their respective temperatures.

Effect of Flyash Upon D_c:

The statistical study done on the effects of the type F flyash yielded contrasting results. For the inside flyash specimens, the diffusion constant is almost identical to the value predicted for a conventional mix at that temperature. The outside value for the diffusion constant is within the 80% confidence limits for the outside concrete with a water to cement ratio of 0.45. Even though this value is not statistically different, due in part to the low degrees of freedom, flyash seems to have lowered the diffusion constant in this case. This may be due to several reasons. The actual volume of cementing agents increased, which may have lowered the effective water to cement ratio. Other factors such as smaller crystal sizes or reduced tricalcium aluminate content may have contributed also. In addition, it has been suggested that a decrease in the anion exchange capacity of the paste, caused by a decrease in the amount of hydroxyl anions due to the cement replacement, may also have affected the diffusion constant (7).

Effect of Silica Fume Upon Dc:

The effect of silica fume on the diffusion constant is

more profound than flyash, even to the point that the data
in all four cases does not remotely fit the model. Thus, the
diffusion constants for the silica fume mix in this study
cannot be statistically compared to any others. In comparing
the chloride contents of the silica fume mix results to
those of the 45 mix, there is a statistically lower ion
content in the silica fume mix at 0.5 inches but not at
other depths. This is easily noticed from the pattern of
chloride concentrations. Therefore, the silica fume mix was
more effective at resisting chloride penetration in the top
one half inch and prevented further ion migration down into
the concrete. The fact that silica fume densifies the
transition zone between the aggregate and paste may explain
why very few chlorides have penetrated. Other factors
similar to those above concerning flyash may also affect the
diffusion constant. Regardless of why and only having
qualitative proof, silica fume dramatically increased the
resistance to chloride penetration of the concrete mix in
this study.

IV. CONCLUSIONS

Experiment Conclusions:

The following conclusions can be made based on this research:

1. There is a statistically significant relationship at the 95% confidence level between the chloride diffusion constant and the water to cement ratio of those concretes having water to cement ratios from 0.35 to 0.50 and not having pozzolanic admixtures.

2. The temperature under which concretes in the above category are subjected to chlorides significantly affects the diffusion constant at the 75% confidence level. The equations derived to relate the water to cement ratio to the diffusion constant were as follows:

$$Dc = -0.039 + 0.480 \ (W/C) \qquad \text{eqn. 9}$$
$$Dc = -0.147 + 0.690 \ (W/C) \qquad \text{eqn. 10}$$

Equation 9 represents the relation for concrete with an average temperature of 72 degrees Fahrenheit while equation 10 is for an average temperature of 56 degrees F.

3. The addition of type F flyash seems to reduce the diffusion coefficient for concrete. However, in this study only one of two diffusion coefficients for the flyash mix was marginally reduced.

4. The addition of silica fume causes the resulting concrete not to behave according to Fick's Law. The rate of chloride diffusion was significantly decreased in the silica fume mix but the magnitude cannot be assessed.

5. The method of concrete powder sampling had a significant affect upon the accuracy of chloride analyses. Samples should not be contaminated with sealers, should not be near edges, and should be drilled with the smallest practical drill bit in order to obtain a pure mortar sample.

Implications for Industry:

The implications for the concrete industry are clear. In order to increase the time to initiation of chloride induced corrosion of reinforcing steel in concrete, the water to cement ratio of mixes utilized should be reduced. Also, silica fume, when appropriate, should be used. The result will be concretes that have a higher strength and a greater resistance to chloride penetration.

Further Research Recommendations:

The exact relationship between water to cement ratio, pozzolanic admixtures, temperature, and the diffusion constant of concrete is not known. The test method used in this research is very time consuming, but the mechanism of

diffusion is very similar to that in the field. The
diffusion cell test, used by Page, et. al. (2) yields
diffusion constants for similar concretes under similar
conditions that are very close to those obtained in this
experiment. Therefore, if the results of the diffusion cell
test could be correlated to tests similar to the one in this
work, concrete mixes could be evaluated economically and
quickly. The result would be development of chloride
resistant concrete mixes that will benefit the entire
industry.

References

1. Browne, R.D., "Mechanisms of Corrosion of Steel in Concrete in Relation to Design, Inspection, and Repair of Offshore and Coastal Structures," <u>SP 65-11</u>, American Concrete Institute, Detroit, Michigan, 1980.

2. Page, C.L., N.R. Short and A. El Tarras, "Diffusion of Chloride Ions in Hardened Cement Paste," <u>Cement and Concrete Research</u>, Vol. 11, pp. 395-406, 1981.

3. Ozyildirim, C. and W.J. Halstead, "Resistance to Chloride Ion Penetration of Concretes Containing Fly Ash, Silica Fume, or Slag," <u>VTRC 88-R11</u>, Virginia Transportation Research Council, Charlottesville, Virginia, February 1988.

4. Newlon, H. and H.N. Walker, "Relationship Between Properties of Hardened Concrete and Bridge Deck Performance in Virginia," <u>VHTRC 85-R23</u>, Virginia Highway and Transportation Research Council, Charlottesville, Virginia, February, 1985.

5. Midgley, H.G. and J.M. Illston, "The Penetration of Chlorides Into Hardened Cement Pastes," <u>Cement and Concrete Research</u>, Vol. 14, pp. 546-558, 1984.

6. Rasheeduzzafar, H. Dakhil and K. Mukarram, "Influence of Cement Composition and Content on the Corrosion Behavior of Reinforcing Steel in Concrete," <u>SP 100-75</u>, American Concrete Institute, Detroit, Michigan, 1987.

7. Gjorv, O.E. and O. Vennesland, "Diffusion of Chloride Ions From Seawater Into Concrete," <u>Cement and Concrete Research</u>, Vol. 9, pp. 229-238, 1979.

8. Ott, L., <u>An Introduction to Statistical Methods and Data Analysis</u>, <u>Second Edition</u>, PWS Publishers, Boston, MA., 1984.

9. Kvalseth, T.O., "Cautionary Note About R-Squared", <u>The American Statistician</u>, Vol. 39, No. 4, pp. 279-285, November 1985.

Appendix A

Regression Program

The Fortran computer program used to perform the
nonlinear regressions in this thesis has several aspects
that should be covered. There are three main parts to this
program: the data entry section, the computational section,
and the output section.

The input section, from lines two to twenty three, is
for the input of data points. In this version, there is a
maximum of eight data points per regression. This may be
increased to any number of points by inserting the required
number of points in the "DIMENSION" statements in lines two
and three. The rest of the program is entirely interactive
(with the exception of limits to Dc and Co). The "C(M)"
values are _percent_ chloride ion by weight of the sample
tested. The "X(M)" values are the depths below the
equilibrium concentration of chloride (in this thesis the
surface). The background chloride is also in percent by
weight of sample. No specific format is needed for any of
the input.

The computational section consists of an averaging "DO"
loop followed by a nest of three "DO" loops. Lines twenty

four to thirty calculate the average value of the chloride concentration and the total sum of the squares (SST). This is done outside of the nested loops in order to save on computation time. The outer nested loop iterates the diffusion constant from 0.005 to 1.000 inches squared per year in 0.005 intervals. The middle loop iterates the equilibrium concentration between 1.00% and 5.00% by weight of the concrete in steps of 0.05%. Within the middle loop is the inner loop and an optimization sequence. The inner loop (lines thirty six through thirty nine) calculates the sum of the squares of the errors (SSE) for the combination of Dc and Co specified by the outer and middle loops. The R squared is then calculated as per equation seven:

$$R^2 = 1 - SSE/SST \qquad \qquad \text{eqn. 7}$$

Lines forty one through forty seven identify if the R squared for a specified combination of Dc and Co is greater than the previous; if it is greater, those values of Dc, Co, R squared, SSE, and SST become the optimum values. When the loops finish the iterations, these optimums define the best fitting diffusion curve over the ranges of the variables.

The output section simply prints to the screen the optimum values along with appropriate labels. No option for an output file was used; the keyboard "PRINT SCREEN" was used if a hard copy was desired.

The function used to describe the diffusion curve is not included in most statistical packages. This program was developed to iterate an optimum curve to fit the data. The statistical measures used are consistent with suggestions made by Kvalseth for regression of nonlinear functions (9).

```
C THESIS.FOR ITERATES A SOLUTION FOR THE DIFFUSION CONSTANT
        DIMENSION C(8)
        DIMENSION X(8)
        SUM=0.0
        SSTA=0.0
        RSQRD=-20.0
        WRITE (*,8)
8       FORMAT (2X,'ENTER THE NUMBER OF OBSERVATIONS')
        READ (*,*) K
        WRITE (*,11)
11      FORMAT (2X,'ENTER THE NUMBER OF WEEKS OF PONDING')
        READ (*,*) T
        DO 20 M=1,K
        WRITE (*,15) M
15      FORMAT (2X,'ENTER C(',I1,'), THE CONCENTRATION IN %')
        READ (*,*) C(M)
        WRITE (*,18) M
18      FORMAT (2X,'ENTER X(',I1,'), THE DEPTH IN INCHES')
        READ (*,*) X(M)
20      CONTINUE
        WRITE (*,22)
22      FORMAT (2X,'ENTER BACKGROUND CHLORIDE, %')
        READ (*,*) CB
        DO 26 N=1,K
        SUM=SUM+C(N)
26      CONTINUE
        AVG=SUM/FLOAT(K)
        DO 30 N=1,K
        SSTA=SSTA+(C(N)-AVG)**2
30      CONTINUE
        DO 49 I=1,200
        DC=FLOAT(I)*0.005
          DO 48 J=0,80
          CO=FLOAT(J)*0.05+1.0
          SSEA=0.0
            DO 39 N=1,K
            DIFFE=C(N)-CB-CO*ERFC(X(N)/(2.0*SQRT(DC*T/52.0)))
            SSEA=SSEA+DIFFE**2
39          CONTINUE
          RSQ=1-SSEA/SSTA
          IF (RSQ.GT.RSQRD) THEN
            SSE=SSEA
            SST=SSTA
            RSQRD=RSQ
            DCOPT=DC
            COOPT=CO
          ENDIF
```

```
48      CONTINUE
49    CONTINUE
      WRITE (*,51) T
51    FORMAT (2X,'TIME EQUALS ',F4.1,' WEEKS')
      WRITE (*,53)
53    FORMAT(3X,'DCOPT',3X,'COOPT',7X,'SSE',8X,'SST',6X,
     'R**2')
      WRITE (*,56) DCOPT,COOPT,SSE,SST,RSQRD
56    FORMAT (2X,F6.4,3X,F6.4,3X,F8.7,3X,F8.7,3X,F6.3)
      STOP
      END
```

Appendix B

Concrete Mix Data

Mix	35	40	45	SF	FA	50
Dry Weights						
(lb per cyd)						
Coarse Agg.	1845	1845	1845	1845	1845	1845
Fine Agg.	958	950	1148	1121	1129	1198
Type I Cement	828	775	622	541	541	560
Type F Flyash	–	–	–	–	81	–
Silica Fume	–	–	–	81	–	–
Water	290	310	280	280	280	280
Properties						
Slump (inches)	5.0	2.5	1.0	3.0	1.5	2.5
Air (%)	5.5	5.2	5.0	5.2	6.2	6.8
Unit Wt. (pcf)	146	147	140	148	145	144
Strength (psi)						
14 Days	6040	4520	4740	6520	4250	4240
28 Days	6300	5000	5320	7350	5030	4970

Materials Parameters:

Cement: Portland Type I, S.G.= 3.15

Coarse Aggregate: Crushed limestone, 1" maximum size,
                     0.48% adsorption, S.G.(dry)= 2.83

Fine Aggregate: Natural sand, 1.67% adsorption,
                     F.M.= 2.8, S.G.(dry)= 2.53

Flyash: Type F, S.G.= 2.40

Silica Fume: Elkem F-100-T, S.G.= 2.20

The vita has been removed from
the scanned document