cementitious materials in marine and other salt-laden environments is the diffusion coefficient of chloride ions, it is essential to be able to determine the chloride diffusion coefficient of high performance concrete. From this reason, the AASHTO method, developed for the rapid assessment of the chloride permeability of concrete cannot be used because it provides only coulomb data which is not necessarily related to the chloride diffusion coefficient of the concrete tested. Therefore, an alternative accelerated testing technique is required, which makes it possible to determine the chloride diffusion coefficient of concrete of this special concrete.

For the above reason the electrical potential technique was used for rapid determination of chloride diffusion coefficient of the super workable concrete. This technique is based on an electrical potential being applied across a concrete specimen with chloride ions migrating through the concrete so that the flux of chloride ions can be measured in a steady state condition after an initial transition time (1-11). The flux is used to calculate the chloride diffusion coefficient of the concrete using the Nernst-Plank equation (3-5, 7-11). The chloride diffusion coefficient of this high performance concrete was compared with those of normal concretes having W/Cs ranging from 0.4 to 0.65 and with those of concretes containing silica fume.

CONCRETE MATERIALS

Cementitious Materials

The chemical analyses of the normal portland cement, the low heat portland cement and silica fume are summarized in **Table 1**. To reflect industrial practice low heat portland cement was used for the super workable concrete.

Aggregates

The coarse aggregate was river gravel with nominal maximum size of 20 mm, and the fine aggregate was river sand. The gravel was pre-soaked 24 hours prior to mixing and then air dried to saturated surface dry condition. The surface moisture of the sand used for all mixtures was controlled within 2 to 3 % of the saturated surface dry weight. The physical properties of the coarse and fine aggregates are given in **Table 2**.

Superplasticizer

A polycarboxylic acid base superplasticizer was used for concrete with silica fume and with the super workable concrete.

MIXTURE PROPORTIONS

The proportions of the seven concrete mixtures are summarized in **Table 3**.

Normal Concrete (NC)

Four mixture proportions were employed for the normal concretes with normal portland cement being used as the only cementitious material. The W/C were 0.40, 0.45, 0.55, and 0.65, respectively, and are designated as NC40, NC45, NC55, and NC65, respectively. The target slump and air content of these fresh concretes were 100 mm and 2 %, respectively. For NC45, NC55 and NC65 the bulk volume of coarse aggregate per unit volume of concrete was approximately the same. For NC40 the bulk volume of coarse aggregate per unit volume of concrete was similar to that of the super workable concrete. A counter rotating pan mixer of maximum capacity of 100 liter was used.

Concrete with Silica Fume (SF)

For concretes with silica fume the water-to-cementitious materials (normal portland cement + silica fume) ratio was maintained constant at 0.45. Silica fume was incorporated at 5 and 10 % by weight of the total cementitious materials (these mixture proportions are designated as SF5 and SF10, respectively). A superplasticizer was used to give increased slump. A 60 liter double axial mixer with the paddle and blade angles arranged for increased mixing efficiency was used. The mixing time was 120 to 210 seconds. For these two mixtures the bulk volume of coarse aggregate per unit volume of concrete was similar to NC45.

Super workable Concrete (SWC)

The concrete mixture with low heat portland cement alone as the cementitious materials was used for the super workable concrete (designated as SWC). The water-to-cementitious materials ratio was reduced to 0.3 and a relatively large amount of superplasticizer was used. In addition, the bulk volume of coarse aggregate per unit volume of the concrete was 0.50 m^3/m^3 as compared with 0.65 m^3/m^3 of NC45. By using these proportions a highly flowable mixture that was not prone to seggregation was obtained.

SPECIMEN PREPARATION

The fresh concrete was cast into steel cylinders of 100 mm diameter and 200 mm height. Properties of fresh concrete are given in **Table 4**. They were then water curing for 28 days for NC and SWC and for 7 and

28 days for SF. Compressive strength of each concrete mixture is given in **Table 4**. After cured, the cylinder was sliced so as to obtain a disc specimen of the specified thickness. The circumference surface of each disc was coated with an epoxy adhesive and then the specimen was subjected to vacuum saturation according to AASHTO designation T277-83I. They were then tested for chloride diffusion.

CHLORIDE DIFFUSION TESTING

Testing Conditions and Measurement

The schematic view of the test is illustrated in **Fig. 1**. The left-hand side and right-hand side of the concrete disc specimen in the diffusion cell were exposed to 3 % sodium chloride solution (compartment I) and 0.3 N sodium hydroxide solution (compartment II), respectively. Electrical potential difference or direct current voltage (Δ E) was applied between the cathode and the anode electrodes, in which the compartment I acted as the cathode and compartment II was the anode. Under a given electrical potential, chloride ions in compartment I migrate through the concrete and accumulate in compartment II after a certain elapsed time (transition time). The solution in compartment II was sampled by taking about 5 mL at 24 to 48 hours interval and then tested for the concentration of chloride ions using an auto titration apparatus. The concentration of chloride ions in compartment I was maintained constant in the course of the test. Also, the alkalinity of the solution in compartment II was maintained at pH ranging 11 to 13 so as to prevent the evolution of chlorine gas from compartment II (1,7). As indicated in **Fig. 2** it was expected that the rate of increase in concentration of chloride ions in compartment II would become constant with respect to elapsed time after an initial transition time. After a steady state flow was achieved a linear regression line with respect to the concentration of chloride ions and elapsed time was determined. Its slope was taken as the flow rate of chloride ions in concrete, which was used to calculate the flux of chloride ions (J_{CL}). The chloride diffusion testing was carried out at a temperature of 25 ℃ and a relative humidity of 50 %.

Calculation of Chloride Diffusion Coefficient (D_{CL})

The effective chloride diffusion coefficient of concrete was calculated from the modified Nernst-Planck equation using the flux obtained from electrical potential tests (4,5,9). When using the equation the assumption that the electrical potential gradient is linear under steady state flow of chloride ions within the concrete specimen must be made. Also, an electrical potential drop due to an interaction between the electrode and solution will occur and should be considered. This was done by acually measuring the real electrical potental difference between left- and right-hand side surfaces of the disc specimen and it was found to be about 83 % of the originally applied electrical potential difference (ΔE) of 15 V (11). Thus, the equation used in this research was given below:

$$D_{CL} = \frac{RT}{z_{CL} F C_{CL} \left(\frac{\alpha \Delta E}{l}\right)} J_{CL} \qquad (1)$$

D_{CL} : the chloride diffusion coefficient of concrete (cm^2/s)
J_{CL} : the flux of chloride ions ($(mol/(s \cdot cm^2))$)
z_{CL} : the valency of chloride ions (-1)
F : the Faraday constant (9.648×10^4 C/mol)
R : the gas constant (8.314 $J/(K \cdot mol)$)
T : the absolute temperature (298 K)
ΔE : the electrical potential difference applied between cathode and anode electrodes (V)
l : the thickness of disc specimen (mm)
α : equal to 0.83 for 15 V and represents the real potential difference after the two surface effects are considered
C_{CL} : the concentration of chloride ions in compartment I, which is maintained equal to 3 % in the course of the electrical diffusion test

Thickness of Specimen and Applied Voltage

In order to determine appropriate thickness of concrete specimen and applied voltage preliminary experiments were carried out. The thickness of disc specimen should be large enough for the maximum size of coarse aggregate (20 mm). Also, a thicker disc specimen would reduce polarization effects. However, it would take a longer time to complete the test as the thickness became larger. To speed up the test the applied voltage could be increased to increase the flux of chloride ions. However, as the voltage becomes larger, the temperature of the solution in each compartment would increase due to the Joule effect (4). For these reasons, optimum thickness and applied voltage needed to be determined. Therefore, preliminary experiments were conducted with the thickness of disc specimen being successively 30, 50 and 70 mm while three different electrical potential differences, i.e., 15, 23 and 30 V were applied.

TEST RESULTS AND DISCUSSION

Preliminary Experiments

Figure 3 shows the increase of concentration of chloride ions in compartment II with elapsed time where the thicknesses of the concrete specimens were 30, 50, and 70 mm and with the applied voltage maintained at 15 V for NC65. As expected, the transition time to reach steady state flow of chloride ions became longer and the slope of the regression line decreased as the thickness of disc specimen increased from 30 to 70 mm. The flux of chloride ions obtained using the slope permitted the calculation of D_{CL} from **Eq. (1)** for each thickness of disc specimen. In **Fig. 4**, the relationship between D_{CL} and the disc thickness is given. Disc specimen with 30 mm in thickness showed a slightly lower D_{CL} than those of specimens of 50 and 70 mm in thickness. However, disc specimens with 50 and 70 mm in thickness had a similar D_{CL}. Therefore, disc specimen with the thickness larger than or equivalent to 50 mm was thought to be appropriate for testing in this research.

The effect of magnitude of applied voltage was studied on NC55 with the thickness of 50 mm and the result is given in **Fig. 5**. Higher applied voltages resulted in shorter transition times and larger slopes of the regression lines. **Figure 6** shows a change of D_{CL} with applied voltages. When tested with the applied voltage of 23 and 30 V, D_{CL} was larger than with 15 V. These larger values for D_{CL} probably resulted from an increased temperature. This was confirmed by observing increased temperature in solutions in the cell tested at 23 and 30 V but not at 15 V. In general, D_{CL} tended to be constant with applied voltages less than or equivalent to 15 V and no heating of the solutions was observed. Therefore, to avoid the Joule effect and hence the heating the applied voltage of 15 V was selected for this research.

Comparison with Diffusion Cell Method

The results of the electrical potential method are compared with those obtained from a conventional diffusion cell test using companion concrete specimens (see **Figure 7**) (7). This result shows comparable chloride diffusion coefficients of concrete between the two testing methods. In fact the electrical potential test took only 5 days to determine the chloride diffusion coefficient of the concrete whereas the other test method took about 17 months. Based on the comparison studies the electrical potential technique was selected as the most appropriate method for determining the chloride diffusion coefficient of concrete after a reasonably short testing period. As can be seen in **Fig. 7**, Dhir et. al. (2) and Andrade et. al. (5) represent values of chloride diffusion coefficients determined by the electrical potential method that are slightly smaller than those by the diffusion cell method.

Effect of W/C

To investigate the effect of W/C on D_{CL} by the electrical potential method developed for this research, NC40, NC45, NC55 and NC65 were tested with the thickness of 50 mm and the applied voltage of 15 V. The results are given in **Fig. 8** and it can be seen that the test method provided an effective method of determining chloride diffusivity of concrete within 3 weeks of the start of the test. The increased W/C resulted in a decreased transition time and an increased slope of the regression line. In **Fig. 9** the relationship between W/C and D_{CL} is given where D_{CL} exponentially increases with increasing W/C. In general a higher W/C results in a higher permeability of concrete when the degree of hydration is similar. This was confirmed for the chloride diffusion in this research using the electrical potential technique. According to The Concrete Society report (12), NC55 and NC65 lie within the range of concretes with high chloride diffusivity since the D_{CL}s are larger than 5×10^{-8} cm²/s while D_{CL}s of NC40 and NC45 are similar to those of concretes with average chloride diffusivity which ranges from 1 to 5×10^{-8} cm²/s.

D_{CL} of High Performance Concrete

The results of studies on SF5 and SF10 after 7-day and 28-day of moist curing period are shown in **Fig. 10**. The increase of concentration of chloride ions for SWC after 28-day of moist curing period is also shown in **Fig. 10**. The slope of the regression line for SF5 is slightly larger than that for SF10 for both curing periods. In addition, the effect of the curing period on the transition time and the slope of the regression line is significant where SF5 and SF10 cured for 28 days have a longer transistion time and a smaller slope of the regression line than those for the curing period of 7 days. This relates primarily to the degree of hydration and of the pozzolanic reaction of these concretes with silica fume. SWC resulted in a shorter transition time and larger slope of the regression line as compared with those for SF5 and SF10 with the same curing period.

Values of D_{CL}s for all concrete types under investigation in this research are given in **Fig. 11** and **Table 4**. Concrete with silica fume is generally believed to perform well in high chloride environments. This was confirmed by this study which showed lower D_{CL}s for SF5 and SF10 than those for corresponding normal concretes and super workable concrete after a 28-day of curing period. As expected, D_{CL} for SF5 is slightly higher than that for SF10 regardless of the curing periods. Thus, the use of silica fume has a beneficial effect on the resistance to chloride ions diffusion and hence can reduce D_{CL}. The D_{CL} of SWC is lower than that of NC40 and this is probably because it has the lowest W/C which is typically employed for super workable concrete. Based on this, SWC should show a significantly greater resistance in the field of the penetration of chloride ions under marine and other chloride-laden environments as compared to conventional concrete. The effect of lower bulk volume of coarse aggregate per unit volume of concrete, which is another typical factor for SWC, does not appear to adversely affect the chloride diffusion.

CONCLUSIONS

An electrical potential method was developed and used to determine chloride diffusion coefficients (D_{CL}) of concretes with different W/Cs ranging from 0.4 to 0.65, concretes with silica fume and super workable concrete. On the basis of this research the following conclusions are drawn:

1) The electrical potential method provides a reasonable estimation of the chloride diffusion coefficient of concrete within a relatively short period of time and this test method has the possibility of replacing conventional chloride permeability tests which take a much longer testing time in order to obtain the chloride diffusion coefficient for concrete.

2) An appropriate thickness of concrete specimen for the electrical potential method was found to be at least 50 mm. In addition, an applied voltage less than or equal to 15 V was appropriate.

3) The electrical potential test was used to develop the following relationship between W/C and D_{CL}:
$D_{CL} = \{0.32 \cdot \mathrm{EXP}[5.47 \cdot (W/C)]\} \times 10^{-8}$ cm²/s.
This relationship applies only to concrete not containing silica fume and with a 28-day curing period.

4) Concrete with 5 and 10 % silica fume replacements for normal portland cement had D_{CL} of 3.14 and 2.99 x 10^{-8} cm^2/s, respectively, after a 7-day curing period and 1.14 and 0.82 x 10^{-8} cm^2/s, respectively, after a 28-day curing period. These values were lower than those of coressponding normal concretes and super workable concrete.

5) Super workable concrete having the lowest W/C had a D_{CL} of 1.97 x 10^{-8} cm^2/s which was lower than those of normal concretes without silica fume.

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TABLE 1—CHEMICAL ANALYSES OF CEMENTS AND SILICA FUME

	LOI[#4]	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Na_2Oeq	C
OPC[#1]	1.6	21.3	5.1	2.8	64.6	1.5	2.0	0.37	0.43	0.65	-
LPC[#2]	0.6	26.8	2.6	2.4	64.1	0.6	2.2	0.22	0.32	0.47	-
SF[#3]	2.59	95.1	0.19	0.05	0.20	0.26	0.11	0.20	0.81	-	1.36

#1: Normal portland cement, #2: Low heat portland cement, #3: Silica fume, #4: Loss on ignition (wt. %)

TABLE 2—PHYSICAL PROPERTIES OF AGGREGATES

	Coarse Aggregate[#1]	Fine Aggregate[#2]
Specific Gravity	2.66	2.60
Absorption (%)	1.35	2.22
Fineness Modulus	6.46	2.63
Maximum size (mm)	20	5

#1: River gravel, #2: River sand

TABLE 3—PROPORTIONS OF CONCRETE MIXES

Mix No.	Concrete Type	W/C[#1]	Quantities kg/m^3					
			Water	Cement	Silica fume	Fine Agg.	Coarse Agg.	SP[#2]
NC40	Normal concrete without mineral additives	0.4	223	556	--	845	736	--
NC45		0.45	189	420	--	702	1035	--
NC55		0.55	189	344	--	763	1037	--
NC65		0.65	189	291	--	818	1025	--
SF5	Concrete with silica fume	0.45	178	376	20	708	1037	2.0
SF10		0.45	178	356	40	708	1018	1.5
SWC	Super workable concrete	0.3	165	550	--	903	784	1.6

#1: Water-to-cementitious materials ratio, #2: Superplasticizer (% by wt. of cementitious materials)

TABLE 4—PROPERTIES OF FRESH AND HARDENED CONCRETE

Mix. No.	NC40	NC45	NC55	NC65	SF5	SF10	SWC
Slump (mm)	70	90	80	95	200	190	580[#1]
Air (%)	1.9	1.7	1.7	1.9	2.5	6.0	1.8
Strength[#2] (MPa)	67.7	51.7	48.0	35.3	56.2	59.7	70.5
D_{CL} (x 10^{-8} cm^2/s)	2.61	4.30	6.26	11.2	1.14(3.14)[#3]	0.82(2.99)	1.97

#1: Slump flow, #2: 28-day compressive strength, #3: After a 7-day curing period