Rev. Téc. Ing., Univ. Zulia
Vol. 10, No.1, Edición Especial, 1987

STUDY OF THE EFFECTS OF CATIONS ON CHLORIDE CAUSED CORROSION OF STEEL IN CONCRETE

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ABSTRACT

There have been differences observed in chloride ion behavior in concrete depending on the type of associated cation. This paper, which combines an electrochemical study with a pore solution analysis study, is concerned with determining the effects of cations on chloride caused corrosion of steel in concrete.

The effect of $CaCl_2$ and NaCl (mixed in Type I Portland cement concret) on corrosion of steel in concrete was investigated using electrochemical techniques such as anodic potentiodynamic polarization and linear polarization. The results indicated that the corrosion of steel in calcium chloride contaminated concrete was more severe than in sodium chloride contaminated concrete. This observation was made at equal chloride ion concentrations which were in the range of 0 to 2.1 percent based on weight of concrete.

In the pore solution analysis study the effects of $CaCl_2$ and NaCl (mixed in Type I Portland cement paste) on composition of the pore solution was investigated. Samples of pore solution, associated with hardened cement pastes with chloride ion concentration ranging from 0.036 to 1 percent, based on the weight of the cement, were expressed at times ranging from 28 days to 84 days after casting and analyzed to determine chloride, sodium, calcium and hydroxyl ion concentrations.

The pH of the pore solution increased with increased amounts of NaCl. The addition of $CaCl_2$ had the opposite effect. The chloride ion concentrations in the pore solutions associated with pastes containing NaCl were higher than in the ones associated with $CaCl_2$ contaminated pastes.The chloride ion to hydroxyl ion ratios for pastes containing $CaCl_2$ were higher than the pastes containing NaCl.

Other investigators have postulated that the chloride to hydroxyl ionic ratio is important in the corrosion steel in chloride contaminated concrete. The results of this combined electrochemical and pore solution work agrees with the results suggested by these earlier investigators, that increasing Cl^- to OH^- ratios results in increased corrosivity. Thus, the pore solution analysis gives insight to the different corrosion behavior found with NaCl and $CaCl_2$ containing concretes.

Key Words : Corrosion of Steel, Concrete, Chloride Ions, Corrosion Rate, Pore Solution Composition.

RESUMEN

Se han observado diferencias en el comportamiento del ión cloruro en el concreto, dependiendo del tipo de catión asociado. Este trabajo, el cual combina un estudio electroquímico con un estado del análisis de la solución de poro, trata de la determinación de los efectos que los cationes asociados con el ión cloruro, tienen sobre la corrosión del acero en el concreto.

El efecto, del Cl_2Ca y el ClNa (mezclados con el concreto de cemento tipo Portland I), sobre la corrosión del acero en concreto, fue investigado utilizando técnicas electroquímicas tales como polarización potenciodinámica anódica y polarización lineal. Los resultados indican que la corrosión del acero en concreto contaminado con cloruro de calcio era más severa que en concreto contaminado con cloruro de socio. Esta observación fue realizada a iguales concentraciones del ión cloruro el cual estaba en el rango de.0 a 2 o 1 por ciento basada en el peso del concreto.

En el estudio del análisis de la solución de poro, se investigó los efectos de Cl_2Ca y ClNa(mezclados con la pasta de cemento tipo Portland I),sobre la composición de la solución de poro. Muestras de ésta, asociadas con pastas de cemento endurecido con concentraciones del ión cloruro en el rango de 0.036 a 1 por ciento, basada en el peso del cemento, fueron extraídas en tiempos que oscilaban en el rango de 28 a 84 días luego del vaciado y fueron analizadas para determinar las concentraciones de cloruros, sodio, calcio y del ión hidróxilo.

El pH de la solución incrementaba con el incremento en las cantidades de ClNa. El agregado de Cl_2Ca tenía el efecto opuesto. Las concentraciones de cloruros en las soluciones de poro asociadas con pastas conteniendo ClNa eran más altas que en aquellas asociadas con pastas contaminadas con Cl_2Ca. La relación ión cloruro a ión hidróxilo, para las pastas conteniendo Cl_2Ca, eran más altas que para aquellas conteniendo ClNa.

Otros investigadores han postulado que la relación iónica cloruro a hidróxilo es importante en la corrosión del acero en concreto contaminado con cloruros. Los resultados de este trabajo combinado están de acuerdo con los resultados sugeridos por estos primeros investigadores, quienes indican que incrementando la relación Cl^- a OH^-, resulta en un aumento en corrosividad. Así, el análisis de la solución de poro da un conocimiento profundo sobre el diferente comportamiento corrosivo encontrado con concretos conteniendo ClNa y Cl_2Ca

INTRODUCTION

It is generally accepted that the reinforcing steel is in a passive state in concrete due to the high alkalinity of the pore solution (pH in excess of 13) surrounding the steel. The passive state results from a thin protective film of an iron oxide formed on the surface of the steel. This protective film in most cases provides adequate corrosion resistance. However, presence of chloride ions in concrete results in deterioration of the protective film formed on the surface of the steel, causing the steel to corrode. The corrosion product formed has a larger volume than the metal itself. The volume increase gives rise to tensile stresses in concrete with cracking as the final result [1].

Chloride ions are usually introduced into concrete structures in various ways :

1) Chloride ions can be in the original constituents of the mix such as in water or in the aggregate;
2) Sea water exposure introduces chloride ions in marine structures;
3) Calcium chloride is used as an admixture to accelerate hydration of the cement in some locations;
4) Deicing salts (NaCl) are heavily used on highways and bridges.

It has been known for many years that tricalcium aluminate of portland cement reacts with a chloride solution and removes a portion of the chloride from the solution by forming Friedel's salt, which is an isoluble compound, as follows :

$$C_3A + CaCl_2 + 10\ H_2O \rightarrow C_3A.CaCl_2.10\ H_2O \qquad (1)$$

and may therefore provide protection against steel corrosion [2]. It has been observed [3] that the corrosion rate of steel in concrete when chloride is mixed with fresh concrete is less than corrosion rate when chloride diffuses into hardened concrete. In addition, there seems to be a difference in the behavior of chloride ion depending on the associated cation. The results obtained by Brodersen [4], as shown in Table 1, indicate significant differences between the chloride ion diffusivity coefficients for different chloride compounds in hardened cement pastes.

Table 1. Cloride Ion Diffusivity Coefficients [4]

Compund	$Dx10^8$ cm/sec^2
NaCl	6.21
KCl	6.52
LiCl	6.42
$CaCl_2$	9.43

From these results, it may be inferred that the embedded steel would behave differently in the presence of each one of these salts. Hence the extent of chloride corrosion of steel in concrete may depend on the type of cation associated with chloride ion in the solution.

A knowledge of the chemistry of the pore solution, as mentioned in the literature [5], could be applied both to studies of cement hydration and to studies of reaction involved in alkali-aggregate attack, steel corrosion, and similar problems. Most of the researchers have been primarily concerned with chemical durability problems and little work has been done in relating the changes in pore solution composition to studies such as corrosion of steel in concrete. However, the problem of steel corrosion in concrete has received more attention in recent years because of its impact on bridge deck deterioration. More and more investigators in the corrosion field are becoming interested in obtaining information on changes in pore solution composition, and applying such information to reactions involved in steel corrosion.

This paper, which is the combination of two separate studies, investigates the effects of calcium chloride and sodium chloride on corrosion behavior of steel in concrete and on composition of the pore solution. The effects were evaluated by electrochemical techniques such as anodic potentiodynamic polarization and linear polarization.In addition, the effects were evaluated by analyzing the pore solution expressed from hardened cement paste specimens and determining chloride, soldium,calcium and hydroxyl ions concentrations. This was done so as to find whether or not there is a correlation between the corrosion behavior and the composition of the pore solution.

Experimental

1) Electrochemical Study

Concrete cylinders 7.5 cm dia. x 5 cm height were prepared using Type I Portland cement and a water to cement ratio of 0.45. A steel rebar of 1.05 cm dia. x 5 cm height was embedded in each concrete block as a working electrode. The steel rebar was machined prior to the placement in concrete. The steel concrete air interface was coated with epoxy to prevent the activation of the steel surface at the air-steel-concrete interface.Another steel rebar was embedded in concrete as a counter electrode. A molybdenum/molybdenum oxide (Mo/MoO_3) electrode [6,7] was also embedded near the working electrode surface to reduce the IR drop.

NaCl or $CaCl_2$ was added to some of the concrete sample with the Cl^- concentrations ranging from 0 to 2.1 percent based on weight of concrete. These samples were soaked in distilled water after five days of curing in water cabinet (100 percent humidity).

The corrosion rate of steel in concrete was determined using linear polarization. The linear polarization curves were obtained by scanning the potential from -30 mv of the open circuit potential up to the +30 mv beyond the open circuit potential.

In addition, anodic potentiodynamic polarization curves were also obtained to check the corrosion behavior of steel in concrete. In this experiment, the steel potential was kept at -1300 mv vs Mo/MoO_3 electrode for ten minutes, then the potential was scanned toward positive direction up to +2000 mv vs Mo/MoO_3. In the tests mentioned above, the concrete samples were removed from the distilled water containers prior to the polarization tests, and they were placed back into the containers after the tests.

All of the polarization experiments were accomplished by a PAR potentiostat, manufactured by Princeton Applied Research, Model 173 with universal programmer Model 175 and logarithmic current converter Model 376.

2) Pore Solution Analysis Study

A cylindrical pressure vessel, of similar construction to the one described by Barneyback and Diamond [5,8] was designed and constructed to express pore solution from hardened cement pastes. The design equations and the detailed fabrication procedure of the pore press can be found in [9].

Type I (ordinary) Portland cement and deionized water were used for all cement paste specimens. A water to cement ratio of 0.45 was chosen for this study also.

Sodium chloride or calcium chloride was added to some of the samples with chloride ion concentration ranging from 0.036 to 1 percent based on weight of the cement. Chloride ions were introduced by dissolving either sodium chloride or calcium chloride in the mix water to ensure a uniform distribution of chloride ions throughout the mix. Twelve series of paste samples were prepared, with mix proportions as detailed in Table 2.

The pastes were stirred with a plastic spatula until mixed uniformly. Specimens were then cast in cylindrical plastic bottles of 44 mm dia. x 82 mm height. The bottles were sealed with their caps and stored in a cabinet.

Samples of pore solution were expressed at different stages of curing using a modified pressing procedure described in [9]. These samples were analyzed to determine concentrations of ionic constituents (Cl^-, Na^+, Ca^{++} and OH^- ions). Details of the analytical procedures employed in this study can be found in [9]. Briefly, however, the analytical procedures employed are as follows ·

To determine chloride ion concentration, a modified potentiometric titration employing the Gran end point determination method [10] was used. This method simplifies titrations and improves the overall precision of the procedure.
To determine hydroxyl ion concentration of the pore solution, the samples were titrated using 0.05 N HCl as titrant. The end points of titration were detected using phenolphthalein and bromocresol green-methyl red visual indicators. To determine sodium and calcium ion concentrations, atomic absorption spectrometry was used.

Table 2. Composition of Paste Specimens

Chloride Compound	% Wt. $\frac{\text{Chloride}}{\text{Cement + Chloride}}$	W/C Ratio	No. of Samples Made
NaCl	0.036	0.45	8
NaCl	0.18	0.45	8
NaCl	0.4	0.45	8
NaCl	0.6	0.45	8
NaCl	1.0	0.45	8
$CaCl_2$	0.036	0.45	8
$CaCl_2$	0.18	0.45	8
$CaCl_2$	0.4	0.45	8
$CaCl_2$	0.6	0.45	8
$CaCl_2$	1.0	0.45	8
Blank Sample (1)	-	0.45	8
Blank Sample (2)	-	0.45	16

* (1) The curing period was 28 days.

(2) The curing period was 84 days.

Results

1) Electrochemical Study

Figure 1 is a plot of an anodic potentiodynamic polarization curves for steel in salt (NaCl and $CaCl_2$) contaminated Type I Portland cement concrete. The results show that steel remained in a passive state for samples with no added salt (curve 1) and samples with 0.06 percent Cl^- (curves 2 and 3). However, the corrosion potential of steel in concrete containing 0.06 percent Cl^- as NaCl was more negative than in concrete containing 0.06 percent Cl^- as $CaCl_2$. The region of passivity was reduced or disappeared for samples with 0.3 percent Cl^- (curves 4 and 5). The corrosion potentical of steel was more negative for concrete with 0.3 percent Cl^- as $CaCl_2$ compared to that with 0.3 percent Cl^- as NaCl. In addition, the corrosion potential for steel in concrete with no and low chloride content was more positive than those with higher salt content. The increase in chloride content of concrete also increased the polarization currents as shown. These results indicate that at very low chloride concentrations. reinforcing steel behaves almost the same in the presence of either $CaCl_2$ or NaCl. However, as the chloride concentration in concrete increases, the difference in corrosion behavior of steel in presence of $CaCl_2$ or NaCl becomes more pronounced.

The plots of corrosion rate versus percent chloride mixed with concrete as either $CaCl_2$ or NaCl are shown in Figure 2. In both cases the corrosion rate increased as the chloride concentration mixed with concrete was increased. One thing worth noticing is that at very low chloride concentrations (less than 0.15 percent), the corrosion rates of steel in both NaCl and $CaCl_2$ contaminated concrete were fairly close. But at higher chloride concentrations, the corrosion rates of steel in concrete containing $CaCl_2$ were much higher in comparison with the corrosion rates in ooncrete containing NaCl. This finding is compatible with the results of potentiodynamic polarization curves. Therefore, one may infer that the corrosion of steel in calcium chloride contaminated concrete is more severe than in sodium chloride contaminated concrete.

2) Pore Solution Analysis Study

For the sake of comparison between NaCl containing pastes and $CaCl_2$ containing pastes with the some chloride concentration, an attempt was made to keep the curing periods as close as possible.

Results of the hydroxyl ion analysis shown as pH of the pore solutions are presented in Table 3, and a plot of these data is shown in Figure 3. These results show that the addition of sodium chloride to the cement paste causes the pH of the pore solution to increase, whereas the addition of calcium chloride to the cement paste has the opposite effect.

Results of the chloride ion analysis of the pore solutions are listed in Table 4. Figure 4 is a plot of this data which illustrates the chloride ion concentrations of the pore solutions associated with sodium chloride contaminated pastes are higher than the corresponding values for calcium chloride contaminated pastes.

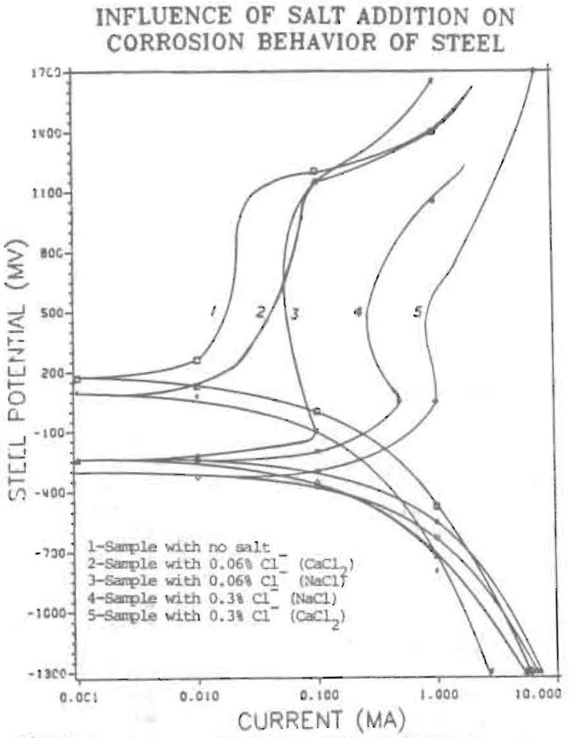

Figure 1. A comparison of anodic potentio-dynamic polarization of steel in salt contaminated Type I Portland cement concrete as a function of salt type (NaCl vs $CaCl_2$)

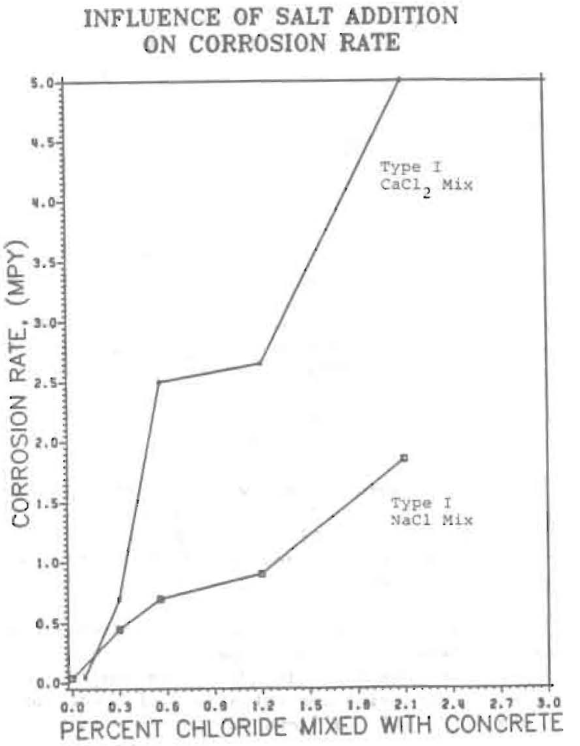

Figure 2. Influence of chloride addition on corrosion rate of steel in salt contaminated Type I Portland cement concrete

Table 3 . Influence of Chloride Addition on pH

Treatment	Curing Period (Days)	pH	Std. Dev.
Blank sample (1)	28	13.73	0.01
Blank sample (2)	84	13.69	0.02
0.036% Cl (NaCl)	56	13.71	0.01
0.036% Cl ($CaCl_2$)	51	13.69	0.01
0.18% Cl (NaCl)	61	13.78	0.01
0.18% Cl ($CaCl_2$)	65	13.65	0.01
0.4% Cl (NaCl)	68	13.81	0.01
0.4% Cl ($CaCl_2$)	73	13.59	0.01
0.6% Cl (NaCl)	84	13.84	0.03
0.6% Cl ($CaCl_2$)	84	13.46	0.03
1.0% Cl (NaCl)	28	13.81	0.01
1.0% Cl ($CaCl_2$)	28	13.49	0.01

The chloride ion concentration values from the second column of Table 4 were divided by the corresponding hydroxyl ion concentration values listed in the same table and the results were plotted against percent chloride ions added originally, as shown in Figure 5. These results show that the ratios of chloride ions to hydroxyl ions are higher for calcium chloride-contaminated pastes than sodium chloride-contaminated pastes.

Results of the sodium ion analysis showed that the concentration of sodium ions in the pore solutions associated with pastes containing NaCl increased as the amount of salt in the pastes was increased as expected. The concentration of sodium ions in the pore solutions obtained from $CaCl_2$ contaminated pastes was not affected by Cl^- addition.

Results of the calcium ion analysis of the pore solutions associated with both salt-free and salt-contaminated pastes indicated that the concentration of calcium ions in the pore solutions was basically zero. This finding is in agreement with the data obtained by Diamond [11]. His results showed that the concentration of calcium ions in the pore solution decreases drastically within 24 hours and become nil after 10-15 days of curing.

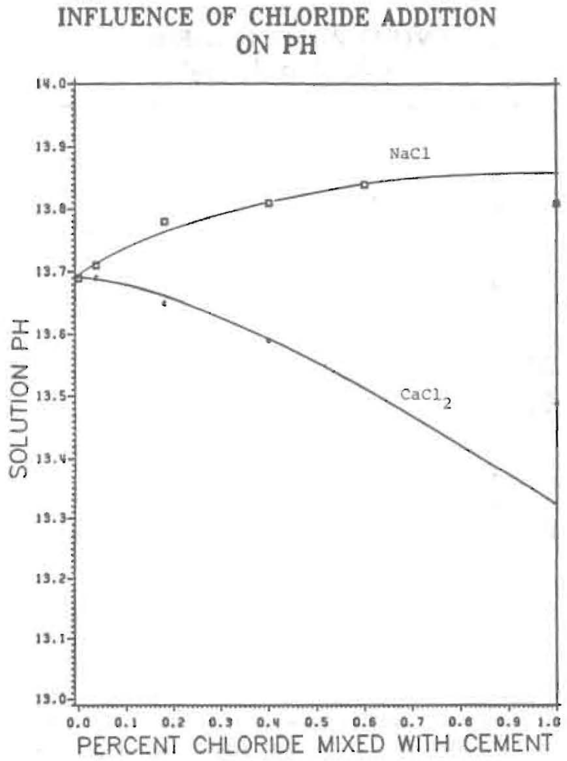

Figure 3 . Influence of chloride additions in the form of NaCl or $CaCl_2$ on pH of the pore solution of hydrated cement pastes.

Table 4. Influence of Chloride Addition on the Ratio of Cl^- to OH^-

Treatment	Avg. Cl, N	Avg. OH, N	Cl^-/OH^- Ratio
Blank Sample (1)	0.00233	0.5322	0.0044
Blank Sample (2)	0.00263	0.4944	0.0053
0.036% Cl (NaCl)	0.00394	0.5082	0.0078
0.036% Cl ($CaCl_2$)	0.00308	0.4850	0.0064
0.18% Cl (NaCl)	0.0219	0.6070	0.0361
0.18% Cl ($CaCl_2$)	0.0171	0.4455	0.0383
0.4% Cl (NaCl)	0.0741	0.6484	0.114
0.4% Cl ($CaCl_2$)	0.0411	0.3851	0.107
0.6% Cl (NaCl)	0.183	0.6839	0.267
0.6% Cl ($NaCl_2$)	0.117	0.2891	0.404
1.0% Cl (NaCl)	0.554	0.6525	0.850
1.0% Cl ($CaCl_2$)	0.350	0.3102	1.13

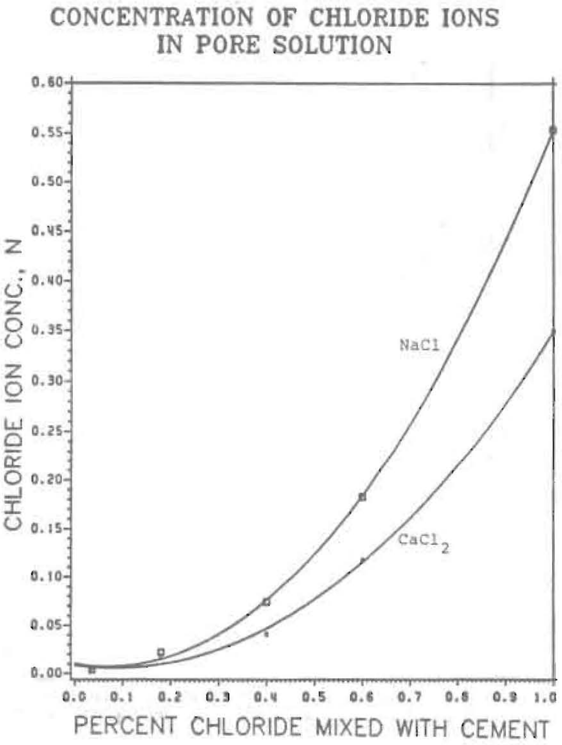

Figure 4 Influence of chloride additions in the form of NaCl or $CaCl_2$ on concentration of chloride ions in pore solution.

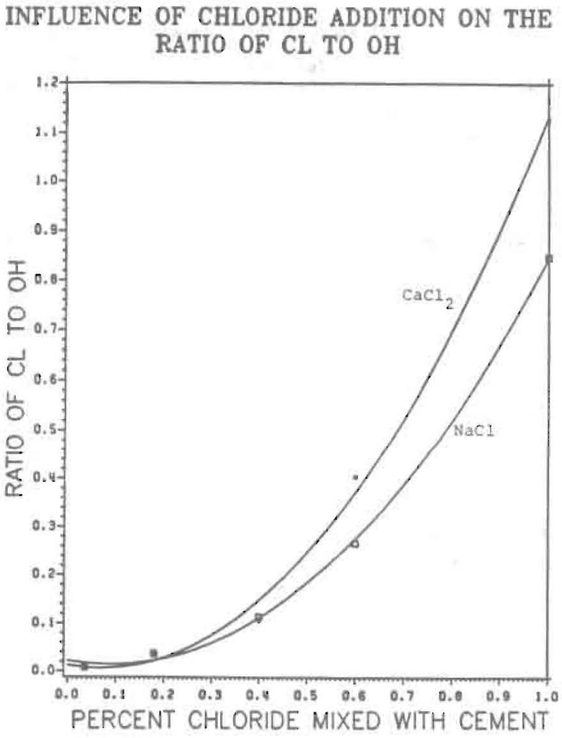

Figure 5 . Influence of chloride additions in the form of NaCl or $CaCl_2$ on the ratio of Cl^- to OH^-.

DISCUSSION

The results from electrochemical tests indicated that the corrosion of steel in concrete/$CaCl_2$ system is more severe than in concrete / NaCl system. Cations associated with chloride may play a role in the corrosion behavior of steel in concrete. The differences in corrosion behavior of steel in concrete in the presence of NaCl or $CaCl_2$ may be due to the different interaction behavior of these salts with the concrete matrix.

The results tabulated in Table 3 indicate that the pH of the pore solutions associated with NaCl contaminated pastes increases as the percent of salt (NaCl) in the mix is increased. However, increasing the amount of calcium chloride in the mix causes the pH of the pore solution to decrease (see Figure 13). These findings are consistent with the results of Diamond [12] and Andrade [13].

The reason why the addition of NaCl causes the pH of the pore solution to increase, whereas the addition of $CaCl_2$ has the opposite effect, is not completely understood. However, the following mechanism is proposed :

According to Taylor [14], after cement is mixed with water, the composition of the liquid phase tends to move toward the equilibrium :

$$CaSO_4.2H_2O(S) + 2\ MOH\ (aq.) \rightleftarrows M_2SO_4(aq.) + 2H_2O\ +$$

$$+\ Ca(OH)_2\ (S) \qquad (2)$$

where M represents the alkalis (Na and K). Because of the common ion effect, the concentration of the calcium hydroxides and calcium sulphate in solution will be depressed. Eventually, the $SO_4^{=}$ is used up in the formation of a calcium aluminate sulphate hydrate and only the hydroxides remain. The results obtained by Diamond [11] and in this study showed that essentially all of the calcium ions are removed from the pore solution. Therefore, the only hydroxides that are left in the solution are basically the hydroxides of potassium and sodium.

In the case where $CaCl_2$ is added to the mix water, additional calcium ions are present in the liquid phase at the beginning. Some of these calcium ions probably react with tricalcium aluminate of the cement to form Friedel's salt shown in equation (1) and the rest of them react with the cement matrix as described by Taylor taking more hydroxyl ions out of the solution. This reaction perhaps continues until the calcium ion concentration in the solution is reduced to zero. Due to this fact, less hydroxyl ions are present in the pore solutions associated with $CaCl_2$ contaminated pastes causing the pH to be lower in comparison with salt-free samples. This explanation is also supported by the solubility product value for $Ca(OH)_2$ [15], which shows that the concentration of calcium ions in highly alkaline pore solution is extremely low (in the order of $1x10^{-5}$ moles / liter).

In the case where NaCl is added to the mix water, a portion of the chloride ions is removed from the solution by C_3A causing a decrease in chloride ion concentration of the liquid phase. However, sodium cations remain in the solution. The presence of these sodium cations in the pore solution requires more hydroxyl ions (anions) in the solution to maintain an equilibrium of electric charges in the pore solution. In addition, it is also obvious that in reaction (2) the sodium ions compete for hydroxyl ions to form sodium hydroxide. Due to these facts, the pH values of the pore solutions associated with NaCl containing pastes are higher in comparison with salt-free pastes.

The results plotted in Figure 4 indicate that the concentrations of chloride ions in pore solutions associated with NaCl containing pastes are higher than the corresponding values for $CaCl_2$ containing pastes. This may be due to the differences in chloride-binding capacity of C_3A in the presence of $CaCl_2$ or NaCl.

Figure 5 shows that the equilibrium ratios of Cl^- to OH^- ions are higher for calcium chloride contaminated pastes than sodium chloride-contaminated ones. These ratios are fairly close at very low concentrations. However, the deviation between $CaCl_2$ pastes and NaCl pastes becomes more pronounced as the salt concentration in the pastes increases. Data presented in Tables 3 and 4 indicate the pH was influenced more by addition of these salts than was the Cl^-. Since the differences in hydroxyl ion concentrations become larger and larger as the salt concentration in the pastes increases, the deviation in Cl^-/OH^- ratios between $CaCl_2$ pastes and NaCl pastes becomes more pronounced at higher salt concentrations.

Arup and others [16] have postulated that the ratio of Cl^- to OH^- is significant in the corrosion behavior of reinforcing steel in concrete. Higher ratios of Cl^- to OH^- may lead to greater breakdown of the passive layer normally presente on the steel surface, rendering the reinforcement more susceptible to corrosion. Since these ratios in $CaCl_2$ containing samples were higher than those containing NaCl, one can conclude that the $CaCl_2$ system is more corrosive than the NaCl system.

The above findings confirm the results of the electrochemical study. Indeed, there is a correlation between the corrosion behavior and the composition of the pore solution.

CONCLUSIONS

The following conclusions may be drawn based on the results found in this study :

1) Corrosion of steel in concrete containing $CaCl_2$ is more severe than steel in concrete containing NaCl.

2) The pH of the pore solutions associated with salt-contaminated cement pastes is dependent on salt concentration.

3) The pH of the pore solutions associated with NaCl contaminated pastes increases as the NaCl content of the mix is increased.

4) The pH of the pore solutions associated with $CaCl_2$ contaminated pastes decreases as the $CaCl_2$ content of the mix is increased.

5) The concentrations of chloride ions in the pore solutions associated with NaCl contaminated pastes are higher than the ones in the pore solutions associated with $CaCl_2$ contaminated pastes.

6) The Cl^- to OH^- ratios for calcium chloride contamianted pastes are higher than the ones for NaCl-contaminated pastes. This finding may help to explain why the corrosion of steel in concrete/$CaCl_2$ system is more severe than in concrete/NaCl system.

REFERENCES

[1] DEHGHANIAN, C. : *"The Electrochemical Behavior of Steel in Salt Contaminated Concrete"*, Ph.D. Dissertation, School of Chemical Engineering, University of Oklahoma, 1980, p.1.

[2] MEHTA, P.K. : *"Effect of Cement Composition on Corrosion of Reinforcing Steel in Concrete"*, Chloride Corrosion of Steel in Concrete, ASTM, 1977.

[3] DEHGHANIAN, C. and LOCKE, C.E.:*"Electrochemical Behavior of Steel in Concrete as a Result of Chloride Diffusion into Concrete : Part 2,"* Corrosion, Vol. 38, No. 9, Sept. 1982, pp. 494-499.

[4] BRODERSON, H.A. : *"The Dependency of Transport Processes of Different Ions in Concrete From the Structure and Composition of Cement Stone"*, Ph.D. Dissertation, Technical Institute of Rhine, Aachen.

[5] BARNEYBACK, R.S. and DIAMOND, S. : "*Expression and Analysis of Pore Fluids from Hardened Cement Pastes and Mortars*", Cement and Concrete Research, Vol. II, 1981, pp. 279-285.

[6] LOCKE, C.E. and DEHGHANIAN, C. : "*An Embeddable Reference Electrode for Salt Contaminated Concrete*", Materials Performance, Vol. 18, No. 2, Feb. 1979, pp. 70-73.

[7] DEHGHANIAN, C., ROOT, C. and LOCKE, C.E. : "*Review of Embeddable Reference Electrodes for Portland Cement Concrete*", Paper 45, Corrosion/81, NACE, Houston, Texas, 1981.

[8] BARNEYBACK, R.S. : "*Alkali Silica Reactions in Portland Cement Concrete*", Ph.D. Dissertation, School of Civil Engineering, Purdue University, 1983, pp. 40-45.

[9] FARZAMMEHR, H. : "*Pore Solution Analysis of Sodium Chloride and Calcium Chloride Containing Cement Pastes*", M.S. Thesis, School of Chemicla Engineering, University of Oklahoma, 1985, pp. 23-27, 76-101.

[10] CLEMENS, G.G.; REYNOLDS, J.W. and McCORMICK, R. M. : "*Comparative Study of Procedures for the Analysis of Chloride in Hardened Concrete*", Report No. FHWA-RD-77-84.

[11] DIAMOND, S. : Paper Presented at the 64th Annual TRB Meeting, Section 207, Washington, D.C. Jan. 1985.

[12] DIAMOND, S., Personal Communication, School of Civil Engineering, Purdue University.

[13] MOLINA, A.; BLANCO, M.T. and ANDRADE, C.: "*Corrosion Rate of Three Different Types of Galvanized Coatings of Steel Reinforcements in Contact with Mortar*", Proceedings of the 9th International Congress on Metallic Corrosion, Vol. I, National Research Council, Toronto, Canadá, 1984, pp. 412-417.

[14] TAYLON, H.F.W. : "*The Chemistry of Cements*", Vol. I, Academic Press, Inc., New York, NY, 1964, p. 324.

[15] Lange's Handbook of Chemistry, 12th Edition, McGraw-Hill, Inc., New York, NY, 1979, p. 5-8.

[16] ARUP, H. : "*The Mechanisms of the Protection of Steel by Concrete*", Corrosion of Reinforcement in Concrete Construction, Edited by A.P. Crane, Ellis Horwood, Pub., Chichester, for the Society of Chemical Industry, London, 1983.

Recibido el 17 de marzo de 1987