Chloride penetration resistance properties of concrete containing mineral admixtures

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ABSTRACT: This paper describes the chloride penetration resistance properties of concrete containing mineral admixtures including fly ash, ground granulated blast-furnace slag powder, silica fume, and meta-kaolin. An electrically accelerated chloride migration test and immersion test were performed for 91 days and 330 days, respectively. Total charge passed and chloride migration coefficient were derived from the accelerated chloride migration test, and chloride penetration depth, water and acid soluble chloride content, and apparent chloride diffusion coefficient were measured from the immersion test. The initial current has a linear relationship with the total charge passed, and it was found that the binding capacity increased as the distance from the concrete surface exposed to chloride solution increased. The effect of types of mineral admixture and their replacement ratios on enhancing the concrete’s resistance against chloride ion penetration could be clarified through the electrically accelerated chloride migration test and immersion test.

1 INTRODUCTION

One of the main causes of premature deterioration of reinforced concrete structures exposed to salt laden environments is chloride ingress and the resulting corrosion of reinforced steel. The chloride permeability of concrete is one of the important properties that need to be assessed in the design of structures to be built in coastal areas. The penetration capacity of chloride ions depends on the micro-structure of hardened concrete, such as the continuity of pore paths and micro cracks. Therefore, durable structures are made from dense concrete by increasing the resistance against chloride invasion and restricting the formation of harmful cracks through proper measures regarding the material and construction processes (Boulfiza et al. 2003).

The BS 8500 (2006), ACI 318 (2008), and KCSS (2003) codes suggest guidelines for mix conditions, including a cementitious material system for concrete exposed to chloride attack environments. Moreover, the ACI 201 committee (2000) reports that the use of several pozzolans positively influences the durability of structures by decreasing the permeability of concrete to as low as 1/10th or 1/100th of that of comparable concrete of equal strength made without pozzolans. It is clear that choosing the optimum composition of cementitious material is a key issue when designing a reinforced concrete structure that is meant to last for a long time in a chloride environment.

Many researchers have also developed test methods to measure the chloride diffusion coefficient under steady state and non-steady state conditions (Page 1981; Dhir et al. 1990; Torii et al. 1997; Tang & Nilsson 1992). The test method under steady state is considerably time consuming, often requiring months or years to obtain results. As such, it is not suitable for a large variety of concrete mixtures. A rapid test method for the chloride permeability of concrete, developed by Whiting (1981), is available and has been adopted as a standard test method of AASHTO T 277 (2005) and ASTM C 1202 (2005). Whereas these methods provide qualitative comparisons such as total charge passed (coulomb), Tang’s method (1996) provides chloride diffusivity based on the theoretical relationship between diffusion and migration in the calculation of the chloride diffusion coefficient from the accelerated measurement.

However, it has been pointed out that the pore solution chemistry may affect the conductivity of concrete containing mineral admixtures in an electrically accelerated chloride migration test (Shi et al. 1998). Also, compared to the natural immersion regime, the binding effect is not taken into account in the electrically accelerated test (Jiang et al. 2004; Tang 1996).

This paper investigates the effects of mineral admixtures on the resistance against chloride ion penetration of concrete containing fly ash, ground
granulated blast-furnace slag powder, silica fume, and meta-kaolin, respectively.

2 EXPERIMENTAL PROGRAM

2.1 Experimental plan

As shown in Table 1, in the experimental plan, the water to cementitious materials ratio (W/Cm) of concrete mixed with and without mineral admixture (plain) ranged from 0.40 to 0.55. The content of fly ash (FA) was 10, 20, and 30% by mass of total cementitious materials as cement replacement. Ground granulated blast-furnace slag powder (GGBS) was replaced with ratios of 30, 50, and 70%. The replacement ratio of silica fume (SF) and meta-kaolin (MK) ranged from 5 to 20% in four steps with equal grade.

Table 2 shows the mix proportions and consistency results of plain concrete.

2.2 Materials

The physical properties and chemical compositions of normal Portland cement (NPC) and mineral admixtures used in this study are listed in Table 3. NPC corresponds to the standard composition requirements of ASTM C 150 as Type I cement. The FA was ASTM Class F type with a SiO₂ + Al₂O₃ + Fe₂O₃ content of 89.1%; the specific gravity was 2.15.

The GGBS corresponds to the physical requirements of ASTM C 989. The SO₃ content was 0.98% and specific gravity was 2.85.

The SF, dried and un-densified product, corresponds to the ASTM C 1240. It contained 91.2% SiO₂, and had a specific gravity of 2.20.

The chemical component of the MK was similar to that of the FA, except the Al₂O₃ contents, and the specific gravity was 2.59.

The specific surface (Blaine) of NPC, FA, and GGBS ranged from 300~400m²/kg, and that of SF

### Table 1. Experimental plan.

<table>
<thead>
<tr>
<th>W/Cm</th>
<th>Remark</th>
<th>Mineral admixture and replacement ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>NPC</td>
<td>-</td>
</tr>
<tr>
<td>0.45</td>
<td>FA</td>
<td>Fly ash</td>
</tr>
<tr>
<td>0.50</td>
<td>GGBS</td>
<td>Ground granulated blast-furnace slag powder</td>
</tr>
<tr>
<td>0.55</td>
<td>SF</td>
<td>Silica fume</td>
</tr>
<tr>
<td></td>
<td>MK</td>
<td>Meta-kaolin</td>
</tr>
</tbody>
</table>

Table 2. Mix proportions of plain mixture.

<table>
<thead>
<tr>
<th>W/Cm</th>
<th>S/a (%)</th>
<th>Unit weight (kg/m³)</th>
<th>Slump (mm)</th>
<th>Air content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water</td>
<td>Cement</td>
<td>Sand</td>
</tr>
<tr>
<td>0.40</td>
<td>45.6</td>
<td>158</td>
<td>395</td>
<td>793</td>
</tr>
<tr>
<td>0.45</td>
<td>46.7</td>
<td>158</td>
<td>351</td>
<td>829</td>
</tr>
<tr>
<td>0.50</td>
<td>47.7</td>
<td>158</td>
<td>316</td>
<td>861</td>
</tr>
<tr>
<td>0.55</td>
<td>47.8</td>
<td>164</td>
<td>298</td>
<td>863</td>
</tr>
</tbody>
</table>

*) SP: super-plasticizer

### Table 3. Physical properties and chemical compositions of cementitious materials.

<table>
<thead>
<tr>
<th>Mark</th>
<th>Specific gravity</th>
<th>Blaine (m²/kg)</th>
<th>Ig. loss (%)</th>
<th>Chemical composition (%)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPC</td>
<td>3.14</td>
<td>329</td>
<td>0.99</td>
<td></td>
<td>22.0</td>
<td>4.6</td>
<td>3.2</td>
<td>63.1</td>
<td>2.1</td>
</tr>
<tr>
<td>FA</td>
<td>2.15</td>
<td>316</td>
<td>3.57</td>
<td></td>
<td>56.4</td>
<td>23.7</td>
<td>9.0</td>
<td>2.5</td>
<td>1.3</td>
</tr>
<tr>
<td>GGBS</td>
<td>2.85</td>
<td>386</td>
<td>0.27</td>
<td></td>
<td>33.7</td>
<td>14.4</td>
<td>0.4</td>
<td>41.7</td>
<td>6.4</td>
</tr>
<tr>
<td>SF</td>
<td>2.20</td>
<td>22,800</td>
<td>2.10</td>
<td></td>
<td>91.2</td>
<td>1.3</td>
<td>0.8</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>MK</td>
<td>2.59</td>
<td>1085</td>
<td>2.13</td>
<td></td>
<td>52.0</td>
<td>40.0</td>
<td>3.0</td>
<td>1.2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### Table 4. Physical properties of fine and coarse aggregate.

<table>
<thead>
<tr>
<th>Kind</th>
<th>Specific gravity</th>
<th>Absorption (%)</th>
<th>Fineness modulus</th>
<th>Maximum size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine aggregate</td>
<td>2.60</td>
<td>1.20</td>
<td>2.60</td>
<td>5</td>
</tr>
<tr>
<td>Coarse aggregate</td>
<td>2.63</td>
<td>0.53</td>
<td>6.96</td>
<td>25</td>
</tr>
</tbody>
</table>

### Table 5. Physical properties of super-plasticizer.

<table>
<thead>
<tr>
<th>Kind</th>
<th>Specific gravity</th>
<th>Solid contents (%)</th>
<th>Base material</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Super-plasticizer</td>
<td>1.20±0.02</td>
<td>40±2.0</td>
<td>Naphthalene</td>
<td>Dark brown</td>
</tr>
</tbody>
</table>
and MK was 22,800m²/kg and 1085m²/kg as determined by the nitrogen adsorption method.

Table 4 shows the physical properties of washed sand and crushed gravel, and Table 5 shows the physical properties of a naphthalene based superplasticizer used in this study.

2.3 Measurements

The specimens for a compressive strength test and an electrically accelerated chloride migration test were cast in a cylinder of ø100×200mm. Prism shaped specimens (100×100×400mm) were also cast for an immersion test (non steady-state diffusion test). After casting, the specimens were sealed with a poly-ethylene sheet and cured in a constant temperature room with 23±2°C. The specimens were demolded after 1 day at RH 95% and cured on saturated lime water of 23±2°C.

The test set-up for the migration test corresponds to ASTM C 1202. A potential of 30 volts DC was applied for the test to minimize changes in the test regime such as the temperature of the test solutions and current. Because the applied potential was different from that of the ASTM method (60V), the total charge passed derived from this study does not correspond to the ASTM reference. The non-steady-state chloride migration coefficient was calculated from the average temperature of the anolyte solution, the penetration depth of the chloride ion (shown by spraying a 0.1M silver nitrate acid solution), and the test duration (Equation 1, Tang 1996).

\[
D = \frac{RTL}{zFU} \cdot \frac{x_d - a \sqrt{x_d}}{t}
\]

where,

\[
a = 2 \frac{RTL}{zFU} \cdot \text{erf}^{-1}(1 - \frac{2C_d}{C_0})
\]

D : Diffusion coefficient (m²/sec)
Z : Absolute value of ion valence (for Cl, z =1)
F : Faraday constant (96,481.04 J/Vmol)
U : Potential difference (V)
R : Gas constant (8.3143/Kmol)
T : Solution temperature (K)
L : Specimen thickness (m)
x_d : Penetration depth of chloride ion (m)
t : Diffusion duration
erf : Error function
C_d : Chloride ion concentration of color changed area
C_0 : Chloride ion concentration of cathode cell

After curing for 28 days, epoxy was coated on all of the surfaces except two sides (100×400mm) at a right angle to the surface concrete poured. The specimens were then immersed in 3.6% NaCl solution for 330 days. After a specified amount of elapsed time, the chloride penetration front was measured by the colorimetric method and powdered samples were extracted from the concrete at regular 5mm intervals from the end exposed to the chloride solution. Water soluble and acid soluble chloride content was measured in accordance with ASTM C 1218 and 1152, respectively. Based on the chloride profile (total chloride content), the apparent chloride diffusion coefficient was calculated by Fick’s Second Law.

The test flow is shown in Figure 1.

3 RESULTS AND DISCUSSION

3.1 Initial current and total charge passed

Figure 2 shows the total charge passed through the concrete according to the mineral admixture type and the replacement ratio.

The total charge passed through the plain concrete decreased with age in a range of 2300~3300°C at 7 days and 1600~2400°C at 28 days. Moreover, it decreased to 1200~2000°C and 1000~1600°C at 56 and 91 days, respectively (data not shown in the figure).

At 7 days, the total charge passed through the concrete replaced with 30% of FA was similar to that of plain concrete while that of concrete with FA10 and FA20 was slightly lower than that of plain concrete. As the replacement ratio of FA was increased, the total charge passed was influenced more by the density of hardened concrete, which was measured as a compressive strength. However, the total charge passed decreased with an increased FA replacement ratio at 28 days, and the effect of FA replacement increased as increased age.

The total charge passed through the GGBS concrete significantly decreased as the replacement ratio of GGBS was increased, even at just 3 days. Compared to plain concrete, replacement of 30% GGBS reduced the total charge passed by 30~40% and replacement of 50~70% GGBS reduced the total charge passed by 60~80%. It is clear that the total charge passed through the concrete replaced with GGBS was more influenced by the use of GGBS and accordingly its replacement ratio, than the W/B ratio.

<table>
<thead>
<tr>
<th>Measuring age (days)</th>
<th>28</th>
<th>56</th>
<th>91</th>
</tr>
</thead>
<tbody>
<tr>
<td>Migration test</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Casting 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water curing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Immersion test</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Casting 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water curing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Immersed period</td>
<td>28</td>
<td>91</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>330</td>
</tr>
</tbody>
</table>

Figure 1. Test schedule.
The total charge passed through the SF concrete measured at 7 days gradually decreased as the replacement ratio of SF was increased and the W/B ratio decreased. The concrete with 15% SF showed a similar total charge passed with the concrete having 30% GGBS at 7 days, while the concrete with 5% SF showed lower total charge passed compared to the concrete with 30% GGBS at 28 days. Based on these results, the resistance of concrete replaced with SF against charge passed was significantly improved during 7–28 days compared to other mixtures.

At 7 days, the total charge passed for the concrete replaced with MK decreased gradually within a replacement ratio of 5–10% while that for the concrete replaced with MK exceeding 10% decreased rapidly as the replacement ratio was increased. However, at 28 days, the total charge passed decreased gradually as the replacement ratio was increased.

Figure 3 shows the relationship between the initial current and the total charge passed measured through the accelerated chloride migration test. The initial current showed a linear relationship with the total charge passed in a range from 1.85 to 3500C and the correlation coefficient was found to be 0.9969, indicating a strong regression. These results agree well with the findings of Feldman et al. (1994) and Zhao et al. (1998). However, Jiang et al. (2004) reported that the relationship between initial current and total charge passed was linear up to only approximately 2000C. The discrepancy between the findings in this paper and those of Jiang et al. is attributed to the difference in the applied voltage and test duration. To minimize the changes of the test regime such as the temperature of the test solution and the current, this paper applied 30V for 6 hours and the temperature increases of the test solution were controlled to be below 10°C during the test.

Based on the results of the electrically accelerated migration test, the total charge passed could be determined with high accuracy by measuring the initial current before finishing the accelerated chloride migration test.

3.2 Chloride migration coefficient

Figure 4 shows the chloride migration coefficient of concrete specimens according to the type of mineral admixture and the replacement ratios.
The migration coefficient of plain concrete decreased with age and was 20~36×10^{-12}m^2/s at 7 days and 16~27×10^{-12}m^2/s at 28 days. It decreased to 10~21×10^{-12}m^2/s at 91 days (data not shown in the figure).

The migration coefficient of concrete replaced with FA increased as the replacement ratio was increased at 7 days; these results deviated from those of total charge passed. It is clear that the migration coefficient derived from the chloride penetration depth differs from the total charge passed even though both results were obtained via the same test method. However, the migration coefficient of FA concrete was similar to that of plain concrete at 28 days, and decreased with an increase of the replacement ratio after 28 days.

The migration coefficient of GGBS concrete decreased when the replacement ratio was increased to 50% at 7 days while that of concrete with 70% GGBS increased slightly in comparison. However, there was no difference in the migration coefficient of concrete according to the replacement ratio at 28 days and the migration coefficient of GGBS concrete was 40~56% of that of plain concrete. The total charge passed through the concrete with GGBS decreased as the replacement ratio was increased while the migration coefficient showed no variation with the replacement ratio after 28 days.

The migration coefficient of concrete specimens with SF or MK replacement decreased as the replacement ratio was increased. The migration coefficient of concrete with SF was 2.4~12.5×10^{-12}m^2/s at 28 days, or was 2~7 times lower than that of plain concrete. Also, the migration coefficient of concrete with MK was 4.6~17.9×10^{-12}m^2/s at 28 days, which is roughly 1.4~3.3 times better than that of plain concrete in terms of resistance against chloride invasion.

The chloride migration coefficient of concrete generally decreased with the elapse of time. Thus, the migration or diffusion coefficient is a function of time and this time dependent property can be delineated by Equation 2.

\[ D = D_0 \left( \frac{t_a}{t} \right)^a \]  

where,  
\( D \) : Diffusion coefficient at \( t \) (m^2/sec)  
\( D_0 \) : Diffusion coefficient at \( t_0 \) (m^2/sec)  
\( t \) : Age(day)  
\( t_0 \) : Datum age(day)  
\( a \) : Age factor

Figure 5 shows the age factor of concrete according to the type of mineral admixture and the replacement ratios.

The age factor of plain concrete was 0.18~0.23 and that of concrete replaced with a mineral admixture increased as the replacement ratio was increased.

The age factor of FA concrete increased as the replacement of FA was increased and that of FA30 was 0.39~0.49, which is twofold higher than that of plain concrete. The GGBS concrete showed an age factor in a range of 0.28~0.52. The age factor devi-
ated from the W/B ratios while it was not significantly affected by the replacement ratio of GGBS.

The concrete with SF showed a noticeable increase in age factor with an increase of the replacement ratio. The age factor of the concrete with 5% SF was similar to that of the concrete with 30% FA, and the concrete with W/B 0.40 and 15% SF showed the highest age factor, at 1.1.

The concrete replaced with MK also showed an increasing slope in its age factor curve as the replacement ratio was increased.

The age factor indicates the improvement capacity of concrete in terms of resistance against chloride invasion with the elapse of time. More specifically, the higher the age factor is, the greater the increase in resistance with time. From an analysis of the age factor, it is clear that the resistance of concrete could be improved through replacement with a mineral admixture but the effect varies according to the type of mineral admixture.

3.3 Chloride profile

Figure 6(a) shows the average chloride content according to the distance from the concrete surface exposed to chloride solution. The water soluble chloride was considered as free chloride and the residue of water soluble chloride subtracted from the acid soluble chloride was considered as fixed chloride.

The free and fixed chloride content decreased as the distance from the surface increased. In a range of 0–5mm, in the vicinity of the surface, the total chloride content was 0.48% of the concrete weight and it consisted of 0.33% of free chloride and 0.15% of fixed chloride. The free chloride holds up to 68% of the total chloride and is 2.1 times higher than the fixed chloride content. However, the ratio of free to total chloride content decreased as the distance from the surface increased and approached the fixed chloride content. The high concentration of free chloride in the surface layer of the concrete appears to be attributable to the physical adsorption of concrete hydrates (Sakurata & Maruya 1999).

Figure 6(b) shows the ratio of fixed to total chloride content (binding ratio) for the average of all of the concrete specimens and for the concrete replaced with MK. The average binding ratio was 31% between 0–5mm, and increased with the distance from the surface, converging to 50% beyond 20mm.

The binding ratio of the concrete replaced with MK was slightly higher than the average value. The binding ratio between 0–5mm was 35% (4% higher
than average) and that for 25~30mm was 58% (8% higher than average). The binding capacity of the concrete with MK appears to be attributable to the chemical component, Al₂O₃ which holds up to 40% of MK.

3.4 Chloride diffusion coefficient

Figure 7 shows the chloride diffusion coefficient at 91 and 330 days for the immersion test.

The diffusion coefficients of plain concrete with W/B ratios ranging from 0.40 to 0.55 was 8.7~14.1×10⁻¹² m²/s at 91 days and 4.7~12.0×10⁻¹² m²/s at 330 days. The diffusion coefficient of FA concrete was 6.8~15.2×10⁻¹² m²/s, similar to that of plain concrete, at 91 days while it decreased to 2.7~6.7×10⁻¹² m²/s at 330 days. Moreover, the diffusion coefficient decreased as the replacement ratio was increased, and that of concrete with 30% FA was less than half that of plain concrete, i.e., 2.73~4.87×10⁻¹² m²/s, at 330 days. The concrete replaced with 30% GGBS showed different diffusion coefficients according to the W/B ratios while the 50% and 70% GGBS specimens versus W/B ratio. The diffusion coefficient of the concrete with 30% GGBS was 40~50% of that of comparable plain concrete at 91 days and 25~35% at 330 days.

The diffusion coefficient of the concrete with SF was lower than that of plain concrete and decreased as the W/B ratio decreased. At 91 days, some of the SF concrete showed chloride penetration depth below 5mm and, consequently, the diffusion coefficient could not calculated due to the lack of a sufficient chloride profile. However, at 330 days, the diffusion coefficient decreased as the W/B ratio decreased and the replacement ratio of SF increased, falling in a range of 0.9~4.4×10⁻¹² m²/s.

The diffusion coefficient of the concrete with MK decreased as the replacement ratio was increased to 15% while that of the concrete with 20% MK was similar to that of the concrete with 15% MK. Based on the results for the diffusion coefficient, it appears that the effective replacement ratio of MK was 15% in terms of increasing the resistance against chloride penetration.

Table 6 shows the regression results between the total charge passed, the migration coefficient derived from the electrically accelerated migration test, and the diffusion coefficient derived from the immersion test. The relationship between the results of the migration test and the diffusion coefficient showed a good correlation at corresponding measuring stages. It appears that both the hydration of cement and the pozzolanic reaction of the mineral admixture complexly influence the concrete’s resistance against chloride penetration according to the elapsed time.

Based on the results of this study, the total charge passed and migration coefficient are useful variables to investigate the resistance of concrete against chloride penetration within a short time. However, it is necessary to consider the effects of the mineral admixture on the resistance of concrete according to the time elapsed when selecting the test time for concrete containing mineral admixtures.
4 CONCLUSION

The main conclusions that can be drawn from this study are as follows:

1. The total charge passed has a linear relationship with the initial current and the total charge passed could be determined with high accuracy by measuring the initial current before finishing the accelerated chloride migration test.

2. The age factor of plain concrete was 0.18–0.23 and that of concrete replaced with a mineral admixture increased as the replacement ratio was increased. It is clear that the resistance of concrete with the elapse of time could be improved through replacement with a mineral admixture.

3. In a range of 0–5 mm, in the vicinity of the surface, the total chloride content was 0.48% of the concrete weight, and it consisted of 0.33% of free chloride and 0.15% of fixed chloride. However, the ratio of free to total chloride content decreased as the distance from the surface increased and approached the value of the fixed chloride content.

4. The binding ratio of the concrete replaced with MK was slightly higher than that of average of all of the concrete specimens. The high binding capacity of the concrete with MK appears to be attributable to the chemical component Al₂O₃, which holds up to 40% of MK.

5. The results of the migration test and diffusion coefficient showed a good correlation at corresponding measuring stages. However, it is necessary to consider the effect of the mineral admixture on the resistance of concrete with the elapse of time when selecting the test time for a concrete specimen containing mineral admixtures.

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