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Effect of mineral admixtures and repeated loading on chloride migration through concrete*

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Abstract: The effect of fly ash (FA) and ground granulated blast furnace slag (GGBFS) on chloride migration through concrete subjected to repeated loading was examined. Portland cement was replaced by three percentages (20%, 30%, and 40%) of mineral admixtures. Five repeated loadings were applied to concrete specimens using a WHY series fully automatic testing machine. The maximum loadings were 40% and 80% of the axial cylinder compressive strength (f'_c). Chloride migration through concretes was evaluated using the rapid chloride migration test and the chloride concentration in the anode chamber was measured. The results showed that the replacement percentages of mineral admixtures, the curing time and repeated loading had a significant effect on chloride migration through concrete. The transport number of chloride through concrete cured for 28 d increased with increasing FA replacement and markedly decreased with extension of the curing time. 20% and 30% GGBFS replacement decreased the transport number of chloride through concrete, but 40% GGBFS replacement increased the transport number. Five repeated loadings at 40% or 80% f'_c increased the transport number of chloride for all mixes.

Key words: Concrete, Fly ash (FA), Ground granulated blast furnace slag (GGBFS), Chloride migration, Repeated loading
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1 Introduction

Chloride from the external environment may penetrate a concrete surface and induce corrosion of reinforcing steel, which is of great concern in relation to the degradation and durability of concrete structures (Buenfeld *et al*., 1998; Glass and Buenfeld, 2001; Poupard *et al*., 2004; Jaffer and Hansson, 2009). Many mineral admixtures, such as fly ash (FA) and ground granulated blast furnace slag (GGBFS), are used to improve the mechanical properties and the durability of concrete (Chindaprasirt *et al*., 2007). Cyr *et al*. (2006) reported that pozzolanic admixtures combined a physical effect and a chemical effect which contributed to compressive strength. Gonen and Yazicioglu (2007) concluded that FA slightly increased compressive strength, but contributed more to the transport properties of concretes over a longer timeframe. Lawrence *et al*. (2005) reported that the pozzolanic activity of FA led to a maximum excess of compressive strength when the replacement rate was near 35% to 40%. Tongaroonsri and Tangtermsirikul (2009) examined the cracking of FA concrete and reported that FA significantly increased the cracking age of concrete and that the cracking age increased with the increase in proportion of FA replacement (up to 50%). Moon and Shin (2007) found that GGBFS and FA insignificantly improved frost resistance of underwater concrete, but were effective in increasing the corrosion resistance of reinforcing steel-bars in underwater concrete. Türkmen *et al*. (2003) and Sun *et al*. (2004) also reported that mineral admixtures increased the corrosion resistance of reinforcing steel

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bars in concrete. Monteiro *et al*. (1997) found that higher replacements of FA and slag produced a significant reduction in expansion caused by alkali-aggregate reaction. Park *et al*. (2005) and Laskar and Talukdar (2008) concluded that GGBFS and FA could contribute to an increase in the flowability of concrete in the fresh state. Irassar *et al*. (1996) observed that FA and GGBFS could improve the sulfate resistance of concrete buried in soil. Hassan *et al*. (2000) investigated the properties of chloride migration through concrete containing FA and found that FA concrete had poorer characteristics in the short term (Shi *et al*., 2009), but achieved similar or better characteristics in the long term. Hisada *et al*. (1999) found that the transport number of chloride ions slightly increased when FA was used.

Saito and Ishimori (1995) found that the application of static loading up to 90% of the ultimate strength had little effect on chloride permeability. However, a repeated loading at the maximum stress levels of 60% or more caused the chloride permeability to increase significantly. Samaha and Hover (1992) reported that the chloride permeability of concrete was generally not affected after one cycle of uniaxial compressive loading up to below 75% of the maximum load capacity of the concrete. However, at higher load levels, chloride permeability could be increased by as much as 20%. Cao *et al*. (2008) concluded that a moderate compressive load reduced the coefficient of chloride penetration, but it was increased by higher mechanical loads because of the greater development of micro-cracks.

Concrete structures usually are subjected to different environmental conditions and external loadings at the same time (Sun *et al*., 2002; Parant *et al*., 2007). However, there is limited information on the properties of chloride migration through concrete with mineral admixtures and under repeated loading. The objective of this study was to evaluate the effects of FA and GGBFS on chloride migration through concrete subjected to repeated loading.

2 Experimental

2.1 Materials

For making concrete specimens, ordinary Portland cement (OPC 42.5), Class I FA and GGBFS complying with Chinese Standard GB/T 1596-2005 were used. Their chemical composition and physical properties are shown in Table 1.

River sand with a fineness modulus of 2.82 and apparent density of 2610 kg/m^3 was prepared. Saturated surface crushed diabase with the maximum size of 20 mm and apparent density of 2690 kg/m^3 was used as the coarse aggregate. M-100 naphthalene based with a Na_2SO_4 content lower than 0.1% (w/w) was prepared as a superplasticizer.

2.2 Mix proportions and sample preparation

The concrete mixes were produced with a constant water to binder ratio (W/B) of 0.35, a sand to aggregates ratio of 0.40, and a binder content of 450 kg/m^3. FA and GGBFS were used at a cement replacement level of 20%, 30% and 40% (by total mass of binder). The superplasticizer dosage was adjusted to maintain a slump value of (200±20) mm for all the investigated mixtures, and the superplasticizer used in its powder form was systematically mixed with the solid materials in preparing the mixtures. The mix proportions of the concrete are shown in Table 2.

Up to about 10% (w/w) of the mixing water was placed in the drum before the solid materials were added. Water was then added uniformly with the solid materials. After mixing, a number of cylindrical specimens (Φ95 mm×300 mm) were cast for each mix. A vibrating table was used to ensure good compaction. The specimens' surfaces were then smoothed, and wet burlap was used to cover the concrete. After demoulding (24 h after casting), the specimens were cured at a constant temperature ((20±2) °C) for 28 d in an alkaline solution to ensure the saturation of specimens and to avoid leaching phenomena (Friedmann *et al*., 2004). Three cylinders

Table 1 Chemical composition and physical properties of cement and mineral admixtures

	CaO (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	SO_3 (%)	R_2O^* (%)	Loss (%)	Density (kg/m^3)	Specific area surface (m^2/kg)
OPC	62.28	21.08	5.47	3.96	1.73	2.63	0.80	1.61	3170	335
FA	2.93	65.50	20.60	4.61	2.23	0.26	0.60	3.03	2430	655
GGBFS	42.49	38.61	6.72	0.40	6.71	0.80	0.70	2.53	2860	501

* $R_2O=Na_2O+K_2O$; OPC: ordinary Portland cement; FA: fly ash; GGBFS: ground granulated blast furnace slag

Table 2 Mix proportions of concrete with FA and GGBFS

	Cement (kg/m^3)	FA (kg/m^3)	GGBFS (kg/m^3)	Fine aggregate (kg/m^3)	Coarse aggregate (kg/m^3)	Superplasticizer (kg/m^3)	Water (kg/m^3)	W/B*
C	450	–	–	737	1105.5	2.7	157.5	0.35
FA20	360	90	–			2.7		
FA30	315	135	–			3.3		
FA40	270	180	–			3.3		
S20	360	–	90			2.6		
S30	315	–	135			2.5		
S40	270	–	180			3.0		

* W/B is the ratio of water to binder; C is the control concrete; FA20, FA30 and FA40 is the concrete mixed with 20%, 30% and 40% FA, respectively; S20, S30 and S40 is the concrete mixed with 20%, 30% and 40% GGBFS, respectively

for each mix were used to determine the compressive strength at 28 d. Another two cylinders were subjected to five cycles of repeated loading by a 200-kN fully automatic testing machine (WHY series). The testing machine was fitted out with a system to record the load, and two displacement meters were used to measure the deformation. Five repeated cycles were used in this study because that is the maximum number of setting cycles of the WHY testing machine. Although there is a difference between five repeated cycles and actual conditions, the results obtained in this study can still be referenced for further research.

Kermani (1991) investigated the permeability of stressed concrete after unloading specimens. He found that water permeability was related to the applied stress and identified a threshold stress of about 40% of the ultimate strength. Choinska *et al*. (2007) observed a significant increase in gas permeability only beyond 80% of the ultimate stress. Hearn (1999) obtained a significantly higher threshold (80% of peak stress) than others for water permeability. It was shown that bond cracks began to increase in length, width, and number at about 30%–50% of the ultimate strength. Mortar cracks began to increase noticeably and to form continuous crack patterns at about 70%–90% of the ultimate strength, when concrete was subjected to an increasing compressive load (Saito and Ishimori, 1995). Therefore, 40% f'_c and 80% f'_c were selected as the maximum repeated loadings in this study.

A rich layer of cement paste at the top and a rich layer of aggregate at the bottom of concrete specimens will occur during vibration, caused by the settlement of solid particles and the simultaneous upward migration of water (Kosmatka *et al.*, 2003). In addition, both ends of the specimen are not in a uniform uniaxial compression because of the constraints of the testing machine's up and down platens. Therefore, concrete disks cut off from either end of the specimen will have a wall effect on the test results. In this study, for chloride migration tests, three concrete disks (Φ95 mm×10 mm) were cut from the middle part of the cylindrical specimens using a diamond blade saw. This process does not introduce any excessive cracking (JSCE-G571, 2003). The lateral surface of the samples was covered with epoxy resin.

2.3 Setup of chloride migration through concrete

A migration cell was used to evaluate chloride migration through the concrete. The equipment used is shown in Fig. 1.

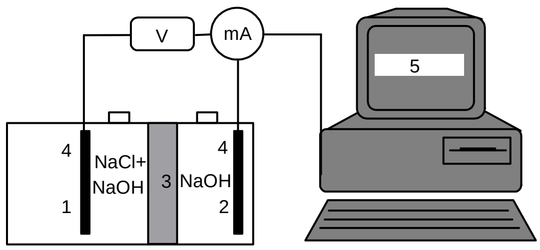


Fig. 1 Equipment of chloride migration test
1: cathode chamber; 2: anode chamber; 3: sample; 4: electrode; 5: pick devices

A mixture of 0.3 mol/L NaOH and 0.5 mol/L NaCl was used in the cathode side. 0.3 mol/L NaOH solution was prepared as the solution for the anode side of the cell. This solution was included to prevent the production of chlorine gas due to the decrease in pH (Hisada *et al.*, 1999). Graphite electrodes were selected to reduce the risk of oxidation and corrosion. A 12-V voltage was controlled between the two sides of the sample during testing, such that the solutions did not reach high temperatures (McGrath and Hooton, 1996). A PClS-10 chlorine meter with a measuring range of 5.0×10^{-5}–1.0 mol/L was used to measure the chloride concentration.

3 Results and discussion

3.1 Strength and deformation of concrete

Three specimens are used to determine the compressive strength for mixtures investigated in this study, as shown in Table 3.

Table 3 Compressive strength values of concrete cured for 28 d

	Compressive strength (MPa)			Mean value (MPa)	Standard deviation
	1	2	3		
C	45.1	44.6	42.9	44.2	1.15
FA20	38.8	38.2	36.4	37.8	1.25
FA30	29.8	30.9	32.0	30.9	1.10
FA40	27.3	26.3	25.3	26.3	1.00
S20	47.6	48.4	50.1	48.7	1.28
S30	52.1	49.3	48.6	50.0	1.85
S40	25.8	26.5	26.9	26.4	0.56

C is the control concrete; FA20, FA30 and FA40 is the concrete mixed with 20%, 30% and 40% FA, respectively; S20, S30 and S40 is the concrete mixed with 20%, 30% and 40% GGBFS, respectively

Compared with the control concrete, FA contributed little to strength at 28 d. The cylinder compressive strength at 28 d was reduced by 14.5%, 30.1% and 44.5% on average for a 20%, 30% and 40% FA replacement, respectively. The strength of the 20% and 30% GGBFS mixes was greater than that of the control concrete at 28 d, whereas 40% GGBFS replacement resulted in a 40.3% strength reduction. This indicates that a certain amount of mineral admixture replacement may have a positive effect on the cylinder compressive strength.

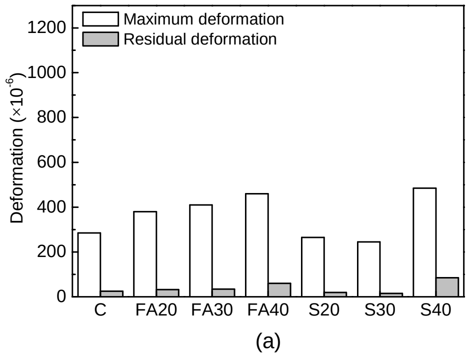
The maximum and the residual deformations are

$$D_{max}=(L_0-L_{min})\times10^{-6}/L_0, \quad (1)$$
$$D_r=(L_0-L_{unloading})\times10^{-6}/L_0, \quad (2)$$

where D_{max} is the maximum deformation, D_r is the residual deformation, L_0 is the initial length of a specimen, L_{min} is the min length of a specimen subjected to cycle loading, and $L_{unloading}$ is the length of a specimen after the repeated test.

The deformations of concrete subjected to repeated loading are shown in Figs. 2a and 2b.

Compared with the control concrete, the maximum deformations at 28 d were increased by 30.8%,



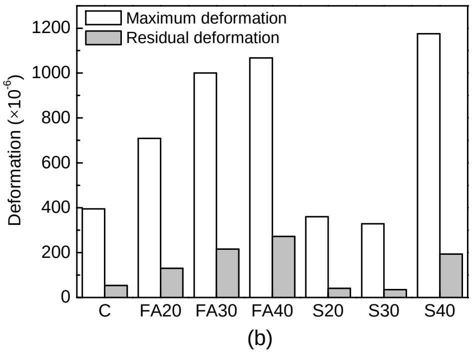


Fig. 2 Deformation of concrete subjected to (a) 40% f'_c and (b) 80% f'_c

41.9% and 56.4%, and the residual deformations by 44%, 52% and 156% on average for a 20%, 30% and 40% FA replacement, respectively, when the repeated loading was 40% f'_c. The deformation of FA concrete showed a significant increase when the repeated loading was raised to 80% f'_c. The maximum deformations were increased by 79.5%, 153.2% and 170.1%, and the residual deformations by 140.7%, 300.0% and 403.7% for a 20%, 30% and 40% FA replacement, respectively, when the repeated loading was 80% f'_c. The starting time of the pozzolanic reaction at the curing temperature of 20 °C was at 28 d or more because the reaction ratio at 28 d was nearly 0%, and the reaction ratio of FA decreases with an increasing FA substitution rate (Hanehara *et al*., 2001). Therefore, the concentration of cement hydration products is lower in high volume FA concrete at 28 d (Lam *et al*., 1998). The lower content of CaO in the FA used in this study was also a factor which increased the deformations.

The maximum deformations of concrete at 28 d decreased by 9.7% and 17.3%, and the residual deformations by 24% and 36% on average for a 20% and 30% GGBFS replacement, respectively, when the repeated loading was 40% f'_c. However, the maximum and residual deformations of concrete subjected to 40% f'_c increased by 66.4% and 240%, respectively, for a 40% GGBFS replacement. There was a similar trend for GGBFS concrete when the repeated loading was raised to 80% f'_c.

For 20% and 30% GGBFS replacement, the unreacted slag particles in the paste may have acted as micro-aggregates with higher modulus of elasticity, increasing the resistance to crack propagation. Also, cracking around the slag particles requires more energy to be dissipated before failure (Douglas *et al*., 1987; Jiang, 2002). However, the micro-aggregate effect of unreacted slag particles is insufficient to compensate for the lower concentration of cement hydration when the replacement of cement by blast furnace slag is 40%. Therefore, the residual and maximum deformations of concrete mixed with 40% GGBFS were significantly greater than those of the control concrete.

3.2 Chloride migration

The effect of mineral admixtures on chloride migration through concrete is shown in Fig. 3. The concentration of chloride migration through concrete shows an approximate linear relationship and increases with the testing time after a different stage. For various FA replacements, the concentration of chloride migration through concrete was greater than that of the control concrete, especially for type FA40 concrete, and increased with the increment of FA replacement. The concentration of chloride migration through concrete slightly decreased when the GGBFS replacement was 20% or 30%. However, a slight increase was observed for 40% GGBFS replacement (Fig. 3).

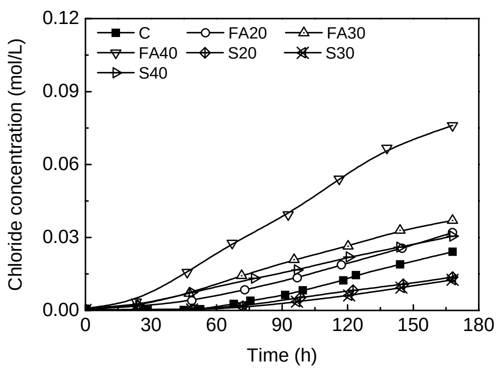


Fig. 3 Effect of mineral admixtures on chloride migration through concrete

Fig. 4 shows the effect of mineral admixtures and 40% f'_c on chloride migration through concrete. Chloride concentration migration through the concretes subjected to 40% f'_c was greater than that of the corresponding nonloaded concretes. A further increment of chloride concentration migration through these concretes was found when the repeated loading was raised from 40% to 80% f'_c (Fig. 5). The effect of mineral admixtures on chloride migration through concrete subjected to 40% f'_c and 80% f'_c was similar to that of no loading.

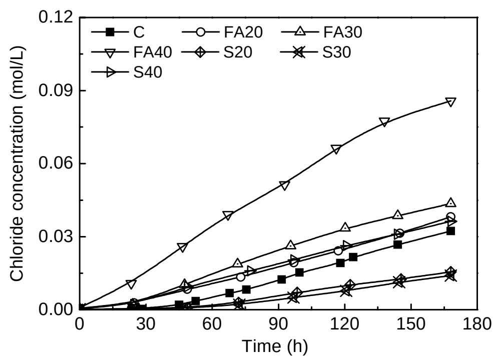


Fig. 4 Effect of mineral admixtures and 40% f'_c on chloride migration through concrete

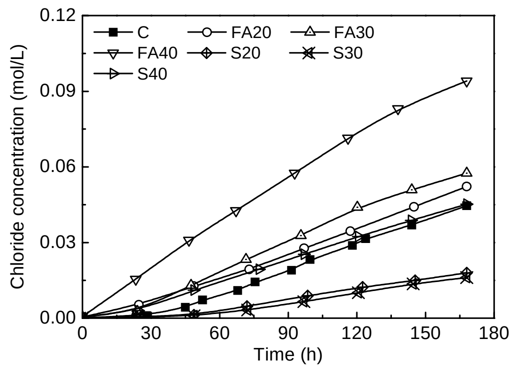


Fig. 5 Effect of mineral admixtures and 80% f'_c on chloride migration through concrete

Chloride migration through concrete with 20%, 30% and 40% FA and cured for 118, 108 and 94 d is shown in Fig. 6. Note that chloride concentration migration through FA40 concrete cured for 94 d was about 0.027 mol/L following the acceleration test. Chloride concentration reduced to 36.2% after 94 d curing time, which is significantly lower than that of FA40 concrete cured for 28 d. Thus, the curing time is an important factor for FA concrete, especially for higher FA replacements.

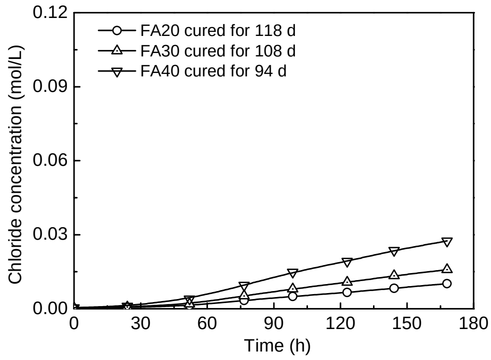


Fig. 6 Chloride migration through FA concretes with different curing times

3.3 Discussion

The steel rebar in concrete is susceptible to corrosion when the concentration of chloride at the steel surface exceeds a critical value (Poupard *et al*., 2004). Therefore, the amount of chloride migration through concrete is an important factor for predicting the service life of concrete structures exposed to chloride in the environment.

The transport number of chloride migration through concretes tested for 168 h is shown in Fig. 7. Note that FA and GGBFS replacement had a significant effect on the transport number of chloride migration through the concretes. Compared with the control concrete, the transport number of chloride migration through concretes cured for 28 d increased by 32.8%, 53.5% and 215.4% for 20%, 30% and 40% FA replacements, respectively. FA can fully react with the hydrates of cement in concrete during longer curing times. The hydrate product can refine the pore structures and adsorb some chloride ions. Therefore, the transport number of chloride reduced to 31.9%, 42.7% and 36.2% for 20%, 30% and 40% FA replacements in concrete cured for 118, 108 and 94 d, respectively. The mean compressive strength of three cylinders with a longer curing time was 60.1, 55.2 and 34.2 MPa for 20%, 30% and 40% FA replacements, respectively, which is significantly greater than that of concretes cured for 28 d.

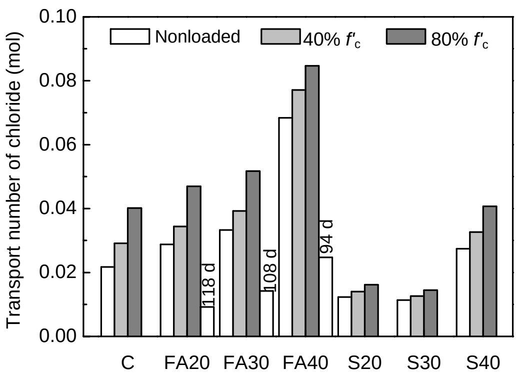


Fig. 7 Transport number of chloride migration through concretes

The transport number of chloride decreased by 43.3% and 47.9% for 20%, 30% GGBFS replacements, respectively. These decreases may have occurred because the pozzolanic reaction of GGBFS in concrete at an early age may form more C-S-H gel and $3CaO{\cdot}Al_2O_3$. C-S-H gel can improve the pore structures, adsorb more chloride ions and block the diffusing path, reducing the permeability of the concrete. C_3A can adsorb more chloride ions to form Friedel's salt, $C_3A{\cdot}CaCl_2{\cdot}10H_2O$. In addition, the number of total ions of Ca^{2+}, Al^{3+}, $AlOH^{2+}$, and Si^{4+} in GGBFS concrete is greater than that in pure Portland cement concrete, and the ion concentration of GGBFS concrete is higher than that of the control concrete. Ions with a lower diffusing ability may restrict the movement of chloride ions (Dhir *et al*., 1996; Hisada *et al*., 1999; Leng *et al*., 2000; Luo *et al*., 2003). However, the transport number of chloride increased by 26.6% for 40% GGBFS replacement compared with the control concrete. The C-S-H gel and C_3A formed by the pozzolanic reaction of GGBFS were insufficient to compensate for the lower concentration of cement hydration when the replacement of cement by GGBFS was 40%.

Compared with nonloaded specimens, repeated loading increased the transport number of chloride for all mixes. For example, the transport number of chloride increased by 34.2% and 85.0% when the control concrete was subjected 40% and 80% f'_c, respectively. The length, width, and number of micro-cracks in concrete subjected to 40% f'_c will increase. Mortar cracks will increase noticeably and form continuous crack patterns when concrete is subjected to 80% f'_c (Saito and Ishimori, 1995). Thus, 40% f'_c and 80% f'_c repeated loading usually increases the permeability of concrete with or without mineral admixtures.

The rate of the pozzolanic reaction requires a prolonged period of moist curing if the full benefits of adding an admixture are to be realized. Without sufficient moist curing, an admixture will act mainly as a noncementitious filler. In addition, the pozzolanic reaction is more sensitive to temperature than regular hydration and can proceed quite rapidly under steam curing (Maltais and Marchand, 1997). The pozzolanic reaction of FA in hardened paste cured at 20 °C begins at the age of 28 d. For FA specimens cured at 40 °C, it will start at the age of 7 d and shows a reaction ratio of 12% (Hanehara *et al*., 2001). There is evidence that at higher early age temperatures, the strength development of GGBS concrete is significantly enhanced because the rate of reaction is greater at higher temperatures (Barnett *et al.*, 2006).

Therefore, the replacement percentages of mineral admixtures, the repeated loading and the curing time have significant effects on chloride migration through concretes. More research is needed on the effects of changes in exposure conditions or curing temperatures on concretes with mineral admixtures so that the results can better be related to actual practical conditions.

4 Conclusions

From the results obtained in this study the following conclusions can be drawn:

A 20% to 40% FA replacement results in a lower cylinder compressive strength at the age of 28 d. A 20% and 30% GGBFS replacement has a significant positive effect on the cylinder compressive strength, but 40% GGBFS replacement reduces the strength at the age of 28 d.

Curing time is an important factor for chloride migration through FA concretes. The transport number of chloride through concretes cured for 28 d increased with the replacement by FA and markedly decreased with the extension of the curing time.

The transport number of chloride through concrete containing 20% and 30% GGBFS was lower than that of the control concrete, but 40% GGBFS replacement increased the transport number of chloride.

Five loadings at 40% f'_c or 80% f'_c increased the transport number of chloride for all mixes investigated in this study.

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