

Resistance of Cementitious Binders to Chloride Induced Corrosion of Embedded Steel by Electrochemical and Microstructural Studies

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The high alkaline property in the concrete pore solution protects the embedded steel in concrete from corrosion due to aggressive ions attack. However, a continuous supply of those ions, in particular, chlorides altogether with a pH fall in electrochemical reaction on the steel surface eventually depassivate the steel to corrode. To mitigate chloride-induced corrosion in concrete structures, finely grained mineral admixtures, for example, pulverized fuel ash (PFA), ground granulated blast furnace slag (GGBS) and silica fume (SF) have been often advised to replace ordinary Portland cement (OPC) partially as binder. A consistent assessment of those partial replacements has been rarely performed with respect to the resistance of each binder to corrosion, although the studies for each binder were extensively looked into in a way of measuring the corrosion rate, influence of microstructure or chemistry of chlorides ions with cement hydrations. The paper studies the behavior of steel corrosion, chloride transport, pore structure and buffering capacity of those cementitious binders. The corrosion rate of steel in mortars of OPC, 30% PFA, 60% GGBS and 10% SF respectively, with chloride in cast ranging from 0.0 to 3.0% by weight of binder was measured at 7, 28 and 150 days to determine the chloride threshold level and the rate of corrosion propagation, using the anodic polarization technique. Mercury intrusion porosimetry was also applied to cement pastes of each binder at 7 and 28 days to ensure the development of pore structure. Finally, the release rate of bound chlorides (i.e. buffering capacity) was measured at 150 days. The chloride threshold level was determined assuming that the corrosion rate is beyond 1-2 mA/m² at corrosion and the order of the level was OPC > 10% SF > 60% GGBS > 30% PFA. Mercury intrusion porosimetry showed that 10% SF paste produced the most dense pore structure, followed by 60% GGBS, 30% PFA and OPC pastes, respectively. It was found that OPC itself is beneficial in resisting to corrosion initiation, but use of pozzolanic materials as binders shows more resistance to chloride transport into concrete, thus delay the onset of corrosion.

Keywords : concrete structures; chloride induced corrosion; pore-structure; buffering capacity

1. Introduction

Reinforced concrete is usually durable and cost effective, which has resulted in its extensive use for construction of maintenance-free infrastructures. However, it has become increasingly apparent that attack by aggressive ions such as chlorides and chemical reactions with atmospheric carbon dioxide may cause reinforced concrete structures to deteriorate and thus reduce its service life very much. Past experience has shown that the most important deterioration process is the corrosion of reinforcing steel inside concrete.

Possible approaches to enhancing the resistance to corrosion include enhancing the concrete properties by using high cement content or by replacing OPC with pozzolanic

materials. Literature reviews show that the addition of PFA or GGBS produces fewer capillary pores or/and results in a reduction in the electrical conductivity of concrete, which has the effect of increasing the corrosion-free life of concrete.¹⁻⁴⁾ Despite long history of the use of pozzolanic materials, the values in concerned with the corrosion behavior of the steel embedment have not been extensively reported. A limited conclusive information about PFA, GGBS or SF concrete on the corrosion resistance was given to date.⁵⁻⁷⁾

The present study concerns the assessment of PFA, GGBS and SF on their resistance to chloride-induced corrosion. The corrosion rate, chloride transport, pore structure and buffering capacity of those binders were evaluated using a polarization technique, exposure test to salt solution, mercury intrusion porosimetry and acid buffering test, respectively.

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2. Experiments

2.1 Testing for corrosion rate

The corrosion rate of steel inside mortar was measured. Mortar specimens were cast with a centrally located steel rebar (diameter: 10.0 mm) in a cylinder mould (diameter: 50.0 mm, height: 90.0 mm). The mix proportion of mortar for cement: water: sand was 1.00: 0.40: 2.45. As binders, ordinary Portland cement (OPC), 30% pulverized fuel ash (PFA), 60% ground granulated blast furnace slag (GGBS), and 10% silica fume (SF) were used. The oxide composition of the binders is given in Table 1. Chlorides were added in mixing water at ten levels ranging from 0.0 to 3.0% by weight of binder. After curing of 7, 28 and 150 days in a polythene film to avoid leaching out of ions from mortars, the rate of corrosion was measured using a polarization technique. Prior to a measurement, the specimens were immersed in a 0.5M NaCl solution for 24 h for the stable conductivity of inner mortar. The potential was set ± 25 mV from the corrosion potential at 0.1 mV/s of a scan rate. Then, the polarization curve consisting of anodic and cathodic layers was obtained. The corrosion rate was calculated by the Tafel's extrapolation method as shown in Eq. (1). The IR drop of mortar was compensated by using the interruption technique.

$$I_{corr} = \frac{\beta_a \beta_c}{2.3 R_p (\beta_a + \beta_c)} \quad (1)$$

Where,

I_{corr} = corrosion rate

β_a = anodic curve slop

β_c = cathodic curve slop

R_p = polarization resistance

2.2 Testing for chloride transport

Concrete specimens were cast in a 150 mm cube mould. The mix proportion for the concrete specimens were 350 kg/m³ binder OPC and 10% SF, 519 kg/m³ fine aggregate, and 1355 kg/m³ 10 mm coarse aggregate. The free water/cement ratio was 0.45. The mix proportions for 30% PFA and 60% GGBS concrete were 400 kg/m³ total binder, 680 kg/m³ fine aggregate and 1230 kg/m³ coarse aggregate, and the free water/binder ratio was 0.4. Different concrete mix design was used to meet the target strength development. Specimens were demoulded 24 h after casting then cured in a wet chamber at 95 \pm 1% of the relative humidity. A concrete on one side of the specimen was sawed off so that the concrete cover reached 10.0 mm

for exposure to the chloride solution. An epoxy resin coating was applied to seal the remaining cast surfaces for the one direction penetration of chloride ions. The specimens were initially saturated in a tank containing water for 14 days and were then immersed for 150 days in a 4M sodium chloride solution at 20 °C. The chloride profiles were obtained from samples collected by grinding the concrete surface in 1.0 mm depth increments within 2 hours of removing the concrete specimens from the tank. The total chloride content of samples was determined by potentiometric titration against silver nitrate. The apparent chloride diffusion coefficient was determined for each specimen by fitting the error function solution to the Fick's second law, for non-steady state diffusion in a semi-infinite medium.

2.3 Testing for pore structure

Mercury intrusion porosimetry of cement paste was tested for investigation of the pore structure, ignoring the interfacial zone between cement paste and aggregates. Cement pastes of OPC, 30% PFA, 60% GGBS and 10% SF were cast and cured for 7 and 28 days. Prior to testing, the sample was dried out in an oven at 50 °C for 24 h. The sample was initially evacuated to about 50 μ m Hg (mercury) and the low pressure was generated up to 30 psi by nitrogen gas, and then the pressure was gradually increased to 17000 psi at 1.32 psi/s. The pressure was converted to equivalent pore diameter using the Washburn equation as given in Eq. (2).

$$d = \frac{-4\gamma \cos \theta}{P} \quad (2)$$

Where,

d = Pore diameter

γ = Surface tension: 0.485 N/m

θ = Contact angle: 120°

P = Pressure

2.4 Testing for buffering capacity

A release of bound chloride by acidification of cement matrix was tested. Cementitious binders of OPC, 30% PFA, 60% GGBS and 10% SF were fabricated in paste sample at 0.4 of a free W/C ratio. Chlorides were admixed in mixing water as NaCl at 1.5% by weight of binder. After 150 days of curing, the specimens was crushed and ground to obtain dust sample and then sieved into the 300 μ m fineness sieve. The ground sample was weighed of 3.00 g and 20.0 mol/kg of 1 molar nitric acid together with equivalent still water for a given liquid volume (40 ml)

were added, while the other suspension included only still water as a control. The two suspensions were stirred for 10 min using a magnetic stirrer and kept standing for 20 days. The concentration of chloride ion in the filtered solution (i.e. free chloride) was measured using a potentiometric titration against silver nitrate. Then, the release rate of bound chlorides against a pH fall was calculated.

3. Results and discussion

3.1 Chloride threshold level (CTL)

Fig. 1 depicts the corrosion rate of steel rebar in (a) OPC, (b) 30% PFA, (c) 60% GGBS and (d) 10% SF mortar specimens at 7, 28 and 150 days, respectively. It is

seen that the corrosion rate at 7 days was always the greatest for each binder, while the corrosion rate at 28 and 150 days was in a similar range for all chloride levels in cast. Before depassivation, of which the corrosion rate exceeds 1-2 mA/m²,⁸⁾ it seems that the curing age is beneficial to mitigate the corrosion risk, lowering the corrosion rate, except for 10% SF mortars. It is evident that the curing beyond 7 days does not guarantee the protection of steel or reduce the rate of the corrosion propagation after the onset of corrosion.

The development of the corrosion rate with chlorides in cast gives the information for determining the chloride threshold level for corrosion of steel. Fig. 2 gives the chloride threshold level depending on the curing age. The

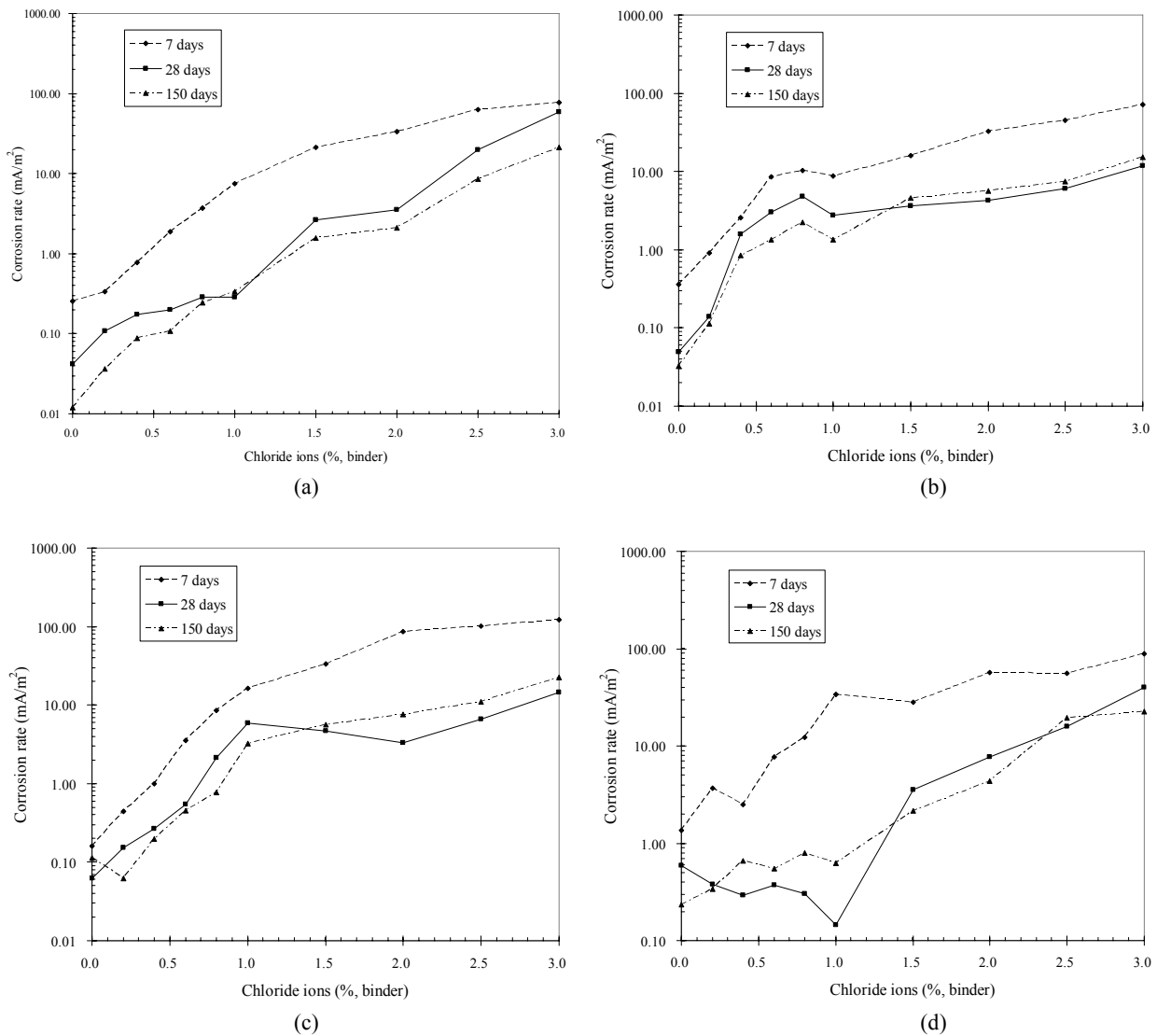


Fig. 1. Corrosion rate of (a) OPC, (b) 30% PFA, (c) 60% GGBS and (d) 10% SF mortars at 7, 28 and 150 days with chlorides in cast ranging from 0.0 to 3.0% by weight of binder

corrosion rate for 10% SF mortars at 7 days always exceeded the critical limit for corrosion initiation accounting for 1-2 mA/m² so that it was not possible to calculate the threshold value. Fig. 2 shows that the chloride threshold level became higher with the curing age, irrespective of binder. This may reflect the inhibitive nature of cement hydration products, which buffers chloride attack and thus a local fall in the pH, in particular, in the vicinity of the steel embedment, leading to acidification of the pore solution.⁹⁾ However, it is notable that an increase in the CTL by curing from 7 to 28 days was significant, compare to an increase in the curing from 28 to 150 days. It suggests that the inhibitive characteristics of hydration may reach the maximized level about at 28 days only, at which about 85-90% of hydration is completed.¹⁰⁾ The variation in the CTL was much affected by binder. It is seen that OPC mortars produced the greatest chloride threshold, compared to pozzolanic materials (i.e. PFA and GGBS). The effect of cement replacement on the CTL has not been clearly known in the literature, despite the widely reported assessment of its effect on chloride transport, thereby being required to further investigation.¹¹⁾

The importance of the polarization resistance, in terms of degree of passivity of the steel surface is shown in Fig. 3. An increase in the corrosion rate by increased chlorides in cast resulted in a marked decrease in the polarization resistance, as the passive film on the steel surface was destroyed or weakened. It is also seen that the polarization resistance was significantly reduced immediately after the onset of corrosion, although it was varied with the corrosion rate of each binder. OPC mortars produced the highest level of the polarization resistance, as the stability of passive film is susceptible to the pH of the pore solution. However, once corrosion initiates, the polarization resistance is rapidly reduced, irrespective of the alkalinity.

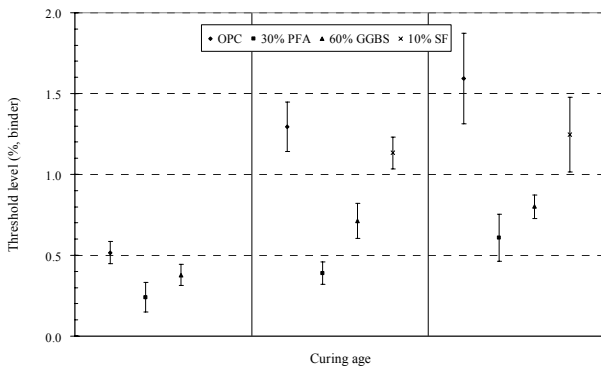


Fig. 2. The chloride threshold level for corrosion for OPC, 30% PFA, 60% GGBS and 10% SF mortars depending on the curing age

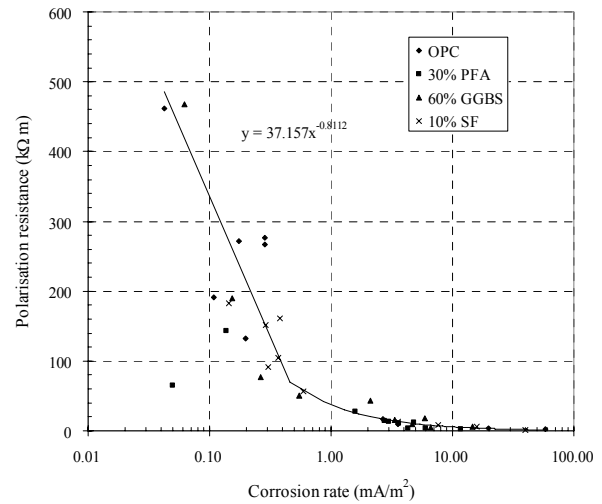


Fig. 3. The relation between the corrosion rate and polarization resistance measured at 28 days for OPC, 30% PFA, 60% GGBS and 10% SF mortars

3.2 Chloride transport

After exposure of the concrete specimens to a chloride solution, the apparent diffusion coefficient and surface chloride content were calculated for OPC, 30% PFA, 60% GGBS and 10% SF concrete as shown in Fig. 4. For OPC concrete, the apparent diffusion coefficients ranged from 3.31×10^{-12} to 2.40×10^{-11} m²/s, while 60% GGBS concretes ranked the lowest diffusivity ranging from 0.66×10^{-12} to 2.80×10^{-12} m²/s. 30% PFA and 10% SF concrete produced a similar range of the diffusion coefficient, ranging from 1.11×10^{-12} to 5.87×10^{-12} m²/s. The variations in the apparent diffusion coefficients in a same mix may be attributed to different levels of capillary pore network, which often takes place in the process of compacting concrete specimens. It seems likely that continuous larger air voids, which may be induced by poor compaction in the casting of the concrete, resulted in a more open pore structure which favored the transport of chloride ions. The binder type appeared to have no effect on the surface chloride content. For all mixes of different binders, the surface chloride content ranged from 3.53 to 4.45% by weight of cement. Marginal variation in the surface chloride content may be attributed to the chemistry between concrete surface and chloride solution, where ions repel or/and attract each other and thus form a balance, leading to a constant concentration of chloride ions on the concrete surface. Notwithstanding defects of cement replacement on the chloride threshold level, PFA, GGBS and SF concretes are beneficial in delaying the time to corrosion. An increase in the diffusion coefficient resulted in a significant decrease of the time to corrosion. The benefit of the pozzo-

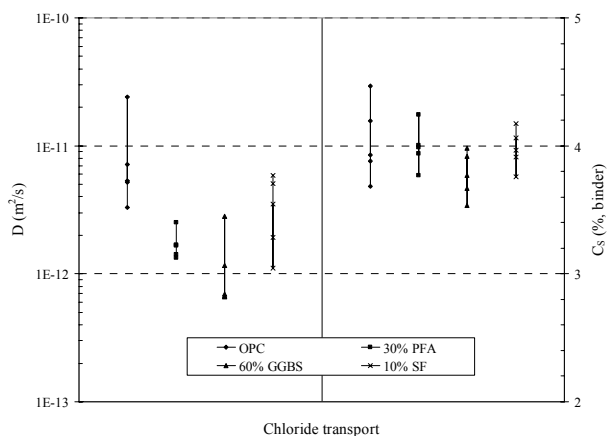


Fig. 4. Chloride transport in terms of apparent diffusion coefficient and surface chloride content for OPC, 30% PFA, 60% GGBS and 10% SF concretes

lanic materials in delaying chloride transport and thus increasing the corrosion free life are supported by a number of previous studies.¹²⁾⁻¹⁴⁾ The increased time to corrosion for PFA or GGBS concrete generally arises from a reduction of chloride transport due to a refinement of pore structure.

3.3 Pore structures

Fig. 5 gives the results of mercury intrusion porosimetry of OPC, 30% PFA, 60% GGBS and 10% SF pastes at 7 and 28 days respectively, including the cumulative volume and the intensity of incremental volume depending on the pore size. The change in the pore volume and the critical pore size depending on the curing is given in Table 1. It is seen that the pore volume was notably decreased by the curing age from 7 to 28 days for all binders, as hydration of binder rapidly occupies the pores in cement matrix at an early age. Unexpectedly, OPC produced the lowest pore volume despite the highest rate of chloride transport in terms of apparent diffusion coefficient. However, the critical pore size for OPC paste was not shifted by curing, whereas the other mixtures shifted the intensified pore size to the lower range. Hence, it seems that the rate of chloride transport may not be governed

by the pore volume, but the distribution of pore size.¹⁾ This is supported by the fact that ions or molecules move in cement matrix through capillary pore network, but other pores (i.e. gel pores and interlayer pores) does not provide either continuous paths for ions (i.e. entrapped/entrained air) or the size of the pores is not sufficient for ion transport (i.e. gel pores). It is seen that the change in the pore volume for OPC due to the curing was higher than for PFA or GGBS pastes. This may be attributed to the difference of the rate of hydration; PFA and GGBS hydrate at a lower rate, but subsequently produce the denser pore structure by a latent hydration.

3.4 Buffering capacity

Fig. 6 gives the percentage of free and bound chlorides to 1.5% of total, depending on nitric acid is applied to the suspension of paste powder. It is seen that the chloride binding is much influenced by binder; the order of binding capacity was 60% GGBS > 30% PFA > 10% SF > OPC. This order was not changed even after addition of acid to the suspension. Also, it is notable that the portion of free chlorides, when acid is fully applied, accounts for only about 90% to total (i.e. not 100%). It has an important implication in assessing the chloride profile, as the content of acid soluble chlorides does not directly indicate total chlorides, which may explain overestimation of chloride ingresses.

4. Conclusions

In the present study, the characteristics of pozzolanic materials as binders in concrete in terms of resistance to chloride attack were examined by tests on corrosion rate, chloride transport, pore structure and buffering capacity. As the binders for pastes, mortars and concrete, OPC, 30% PFA, 60% GGBS and 10% SF were used. The obtained conclusion from the experimental study is as follows:

1) It was found that the chloride threshold level was much affected by the curing age and binder type. An increase in the curing age resulted in a significant increase in the threshold value, irrespective of binder, from 7 to

Table 1. Change in the pore volume and the critical pore size of OPC, 30% PFA, 60% GGBS and 10% SF pastes

Binder	Pore volume (ml/g)		Critical pore size (nm)		Change (%)
	7 days	28 days	7 days	28 days	
OPC	0.1989	0.1205	942	941	65
30% PFA	0.2337	0.1607	941	493	45
60% GGBS	0.1887	0.1425	941	755	32
10% SF	0.2203	0.1348	942	492	63

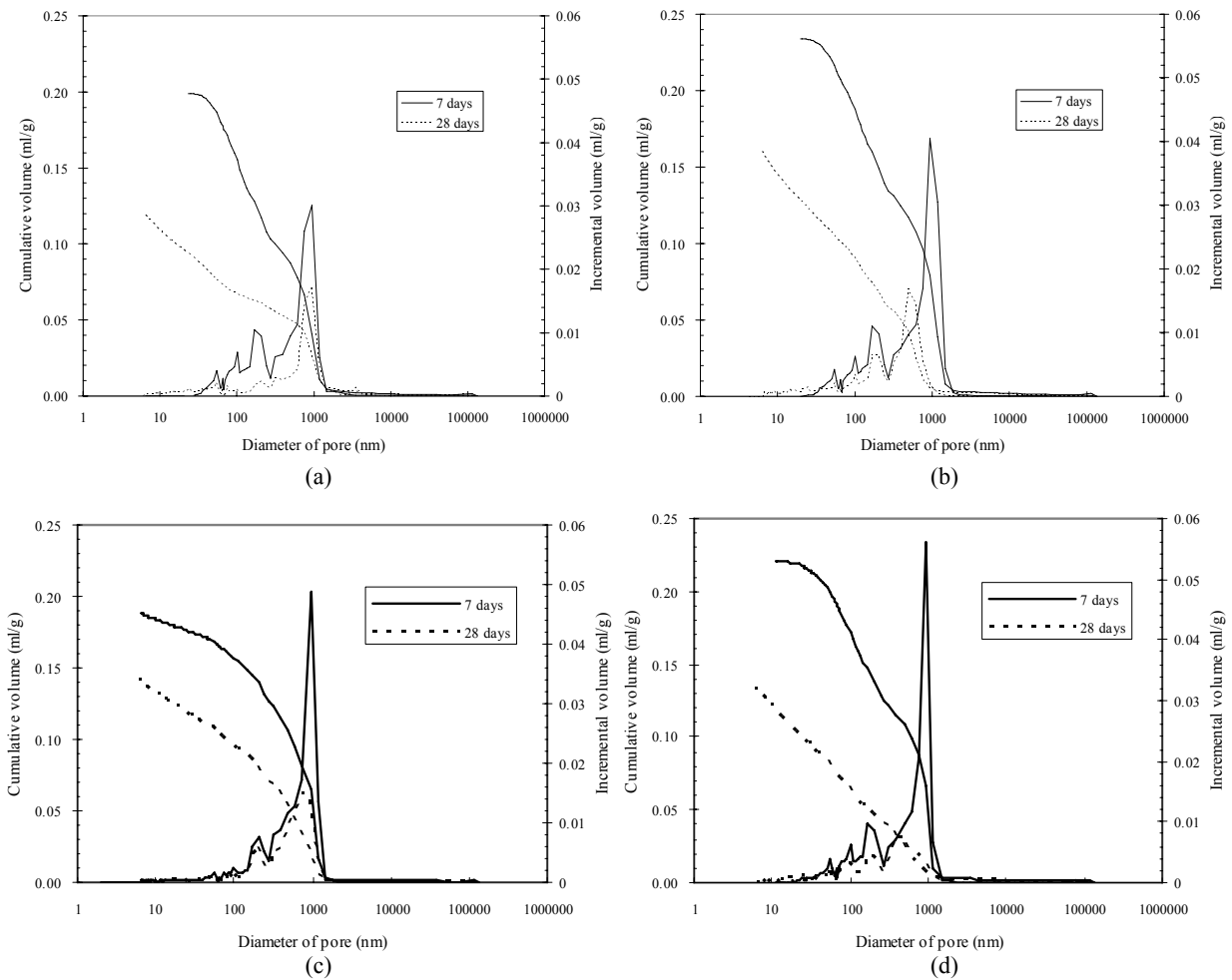


Fig. 5. Pore structure measured using mercury intrusion porosimetry for (a) OPC, (b) 30% PFA, (c) 60% GGBS and (d) 10% SF pastes

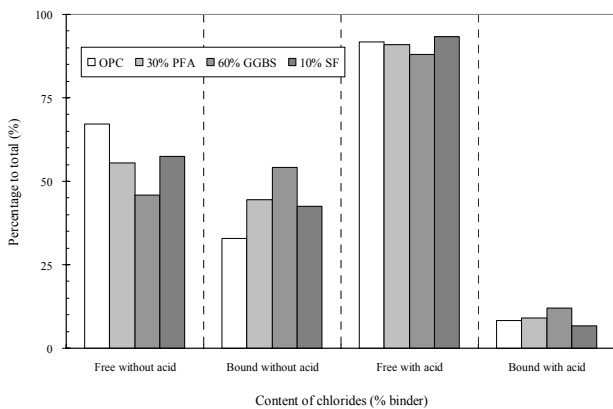


Fig. 6. Rate of release of bound chlorides to free by addition of nitric acid to the suspension of paste in still water

28 days, but only marginal change for the variation in the curing from 28 to 150 days. Also, OPC mortars pro-

duced the greatest level of the polarization resistance, related to the passivity of the steel surface before the onset of corrosion.

2) The rate of chloride transport measured for the 60% GGBS concrete was ranked the lowest level, compared to the other binders. However, there was negligible effect to the surface chloride content by each binder, presumably due to the chemical balance between the concrete surface and chloride ions in a chloride solution.

3) Mercury intrusion porosimetry showed that OPC pastes produced the lowest pore volume at 28 days, but the critical pore volume was the greatest, leading to a highest rate of chloride transport. The change in the pore volume for OPC was significant, compared to PFA or GGBS paste, having a low hydration rate and a latent hydration.

4) The release of bound chlorides to free chlorides against a pH fall by addition of nitric acid to the suspension for the binders accounted for only about 90% to total,

although chloride binding capacity was influenced by the binder. It implies that acid soluble chlorides do not mean total chlorides, with which the chloride profile prediction may be overestimated.

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