

## Resistance of Cementitious Binders against a Fall in the pH at Corrosion Initiation

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At the onset of corrosion of steel in concrete, hydrogen ions usually evolve in the process of electrochemical reaction, thereby decreasing the pH of the pore solution, which can be buffered by cement hydration products, as being representatively illustrated by calcium hydroxide. Hence, a fall in the pH is dependent on properties of cement hydration (i.e. hydration products and degree of hydration). The present study tested acid neutralization capacity (ANC) of cementitious binders of OPC(Ordinary Portland Cement), 30% PFA(Pulverized Fuel Ash), 60% GGBS(Ground Granulated Blast Furnace Slag), 10% SF(Silica Fume) to quantify the resistance of cement matrix to a pH fall. Cement pastes were cast at 0.4 of a free W/C ratio with 1.5% chlorides by weight of binder in cast. Powder samples obtained crushed and ground specimen after 200 days of curing were diluted in still water combined with different levels of 1M nitric acid solution, ranging from 0.5 to 20 mol/kg. Then, the pH of diluted solution was monitored until any further change in the pH did not take place. It was seen that the pH of the diluted solution gradually decreased as the molar amount of nitric acid increased. At some particular values of the pH, however, a decrease in the pH was marginal, which can be expressed in the peak resistances to a pH fall in the ANC curve. The peaks occurred at the variations in the pH, depending on binder type, but commonly at about 12.5 in the pH, indicate a resistance of precipitated calcium hydroxide. The measurement of water soluble chloride at the end of test showed that the amount of free chloride was significantly increased at the pH corresponding to the peaks in the ANC curve, which may reflect the adsorption of hydration products to chlorides.

**Keywords** : acid neutralization capacity; corrosion initiation; hydration products; chloride; cementitious binders

### 1. Introduction

The corrosion of steel in concrete may start by chloride ions and carbonation, accompanying oxygen and sufficient moisture level, although the alkaline pore solution forms the passivation on the steel surface.<sup>1,2)</sup> By electrochemical reaction in the vicinity of steel at pit nucleation, hydrogen ions evolve and thus a pH of the pore solution drops locally. This would destroy the passivity of steel and trigger the corrosion process.<sup>1,3)</sup> However, the corrosiveness can be buffered in the pits by cement hydration products including calcium hydroxide, CSH gel and other alkaline matrixes, which impose important inhibitive properties of concrete, buffering a pH fall of the pore solution and thus causing risk of corrosion.<sup>4,5)</sup> Nevertheless, most studies have not considered the inhibitive nature of cement hydration products in the corrosion process.

The effect of cement hydration products at corrosion

can be determined from acid neutralization capacity (ANC). It has been used to investigate the resistance of cement-based component.<sup>6)</sup> The ANC has been currently improved to measure the acid differential neutralization analysis of cement paste and concrete, to measure the resistance to a pH fall of the suspension.<sup>4,7)</sup> It considered the important inhibitive properties affecting carbonation differently from the early results. The pH data obtained in the ANC test can be represented by an ANC curve, which shows the resistance to a pH fall of hydration products in various binders. In the corrosion process, the representative inhibiting nature affecting the corrosion risk of concrete is cement hydration products. The ANC effect can be estimated only by cement hydration, however, most researches have been done using concrete specimens.<sup>7,8,9)</sup> Thus, this study used cement pastes of cementitious binders to quantify the resistance of cement matrix to a pH fall.

This study investigated the inhibitive property of the binders by the ANC of cementitious pastes with OPC

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(Ordinary Portland Cement), 30% PFA(Pulverized Fuel Ash), 60% GGBS(Ground Granulated Blast Furnace Slag), 10% SF(Silica Fume). The ANC data was obtained by the measurement of the resistance to a pH fall of the suspension, and it was represented as an increment in the amount of acid per unit of a pH reduction. Besides, the concentration of the free chloride contents in the binders measured by a rise of the acid using a potentiometric titration against silver nitrate.

## 2. ANC experiment

The present study tested the acid neutralization capacity (ANC) of cementitious binders of OPC, SF 10%, PFA 30% and GGBS 60%, fabricating paste specimens at 0.4 of a free W/C ratio in a cylinder mould of 70 mm in the diameter and 50 mm in the height. Chlorides were admixed in mixing water as NaCl at 1.5% by weight of binder to subsequently measure the release of bound chlorides against a pH fall. The oxide composition of binders is given in Table 1. The specimens were demoulded 24 h after casting, and, were cured for 200 days by wrapping in a polythene film at  $20\pm 1^\circ\text{C}$ , to avoid a leaching out of chloride and hydroxyl ions from the cement matrix, which often takes place in wet curing. Prior to the testing of the ANC of the cement paste, the specimens were dried out for 24 h in an oven at  $105\pm 1^\circ\text{C}$  to minimize the loss of alkaline residue in the pore solution. Then, the specimen was crushed and ground to obtain dust samples and then sieved into the 300  $\mu\text{m}$  fineness sieve. The ground sample was weighted of 3.00 g, and 28 levels of 1 molar nitric acid together with equivalent still water for a given liquid volume (40 ml) was added to produce the different pH levels of suspensions as shown in Table 2. The suspension was stirred for 10min using a magnetic stirrer and then the pH was measured every 3 days until no further change in the pH occurred. The pH meter was always calibrated before each measurement by using a buffer solution of pH 4.01, 7.00 and 10.01.

For measuring the variation in the concentration of free chloride in the cement paste by a pH fall, the suspensions were fabricated in the same way for the measurement of

**Table 2. The concentration of acid solution added to cement paste powder for a suspension**

	Equivalent concentration (mol/kg)	1M Nitric acid (ml)	Still water (ml)
1	0.0	0.00	40.00
2	0.5	0.75	39.25
3	1.0	1.50	38.50
4	1.5	2.25	37.75
5	2.0	3.00	37.00
6	2.5	3.75	36.25
7	3.0	4.50	35.50
8	3.5	5.25	34.75
9	4.0	6.00	34.00
10	4.5	6.75	33.25
11	5.0	7.50	32.50
12	5.5	8.25	31.75
13	6.0	9.00	31.00
14	6.5	9.75	30.25
15	7.0	10.50	29.50
16	7.5	11.25	28.75
17	8.0	12.00	28.00
18	8.5	12.75	27.25
19	9.0	13.50	26.50
20	9.5	14.25	25.75
21	10.0	15.00	25.00
22	11.0	16.50	23.50
23	12.0	18.00	22.00
24	13.0	19.50	20.50
25	14.0	21.00	19.00
26	16.0	24.00	16.00
27	18.0	27.00	13.00
28	20.0	30.00	10.00

the ANC. After 200 days of standing time, the suspension was for 1 min and then filtered with filtering paper. The concentration of chloride ions in the filtered solution (i.e.

**Table 1. Oxide composition of various binders**

	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Mn <sub>2</sub> O <sub>3</sub>	TiO <sub>3</sub>
OPC	64.7	20.7	4.6	1.0	3.0	3.0	0.65	0.13	-	-
PFA	1.7	48.7	18.8	1.0	7.7	0.64	1.9	0.4	-	0.9
GGBS	41.2	34.2	11.7	8.81	1.43	-	0.31	0.29	0.3	0.58
SF	0.31	94.9	0.23	0.04	0.07	0.17	0.56	0.15	-	-

free chloride) was measured using a potentiometric titration against silver nitrate. The concentration of chloride ions measured in ppm was converted into a percentage to weight of the binder to calculate the release rate of bound chlorides and the chloride binding capacity.

### 3. Results

The pH of the suspension was measured at every 3 days, and the data of the steady state pH were obtained at about 20 days. The pH of the suspension gradually decreases as the amount of acid added as shown in Fig. 1. Also, an extent of a pH fall varies according to the type of binders. Cementitious binders with OPC, 30% PFA and 10% SF start at about a pH value of 12.65, but the pH of 60% GGBS initiates below 12.5. The increase of the amount of acid cause the pH reduction of binders, but, at some pH, the pH of binders is unchanged so that the curve has several plateau, even the acid added continuously affecting the resistance to a pH reduction. Until an equivalent concentration increases to 11.0 mol/kg, all binders generally have the gentle slopes, however, after that point, the pH values of 60% GGBS binder and 30% PFA binder drop dramatically. OPC and 10% SF are dropped up to a pH of 10, however, 30% PFA and 60% GGBS are decreased to a pH of 4 with the same amount of acid added. Fig. 1 shows that, at the same environment, the pH fall of the added acid was OPC > 10% SF > 30% PFA > 60% GGBS pastes.

Fig. 2 shows the resistance of a pH reduction by the OPC, the 30% PFA, the 60% GGBS, and 10% SF, respectively, which is obtained from each the titration curve of Fig. 1. The point values on each graph express the extent of resistance to a pH drop, and can be obtained by an increment in the amount of acid per unit of a pH reduction from the consecutive two points each the titration curve. The area under the curve between any two points signifies the quantity of acid required to reduce the pH level. Several peaks occur at several pH levels for each binder type, respectively. At a particular pH level, a strong peak occurs to show higher resistance to pH reduction. All binders except the 30% PFA binder show a peak at about pH 12.5 due to the buffering of calcium hydroxide. It is also shown that, OPC has an extensive range of the peaks at pH levels between 12.0 and 12.5. Also, the OPC shows the strong resistance at a pH value of about 11.5 and the OPC shows the smallest pH reduction against the same amount of acid added. The 30% PFA binder has strong peaks at pH values of 11.5 and 10.9, respectively and shows the resistance to a pH value of between pH 11.4 and 11.1. Below the pH of 10.5, the 30% PFA and

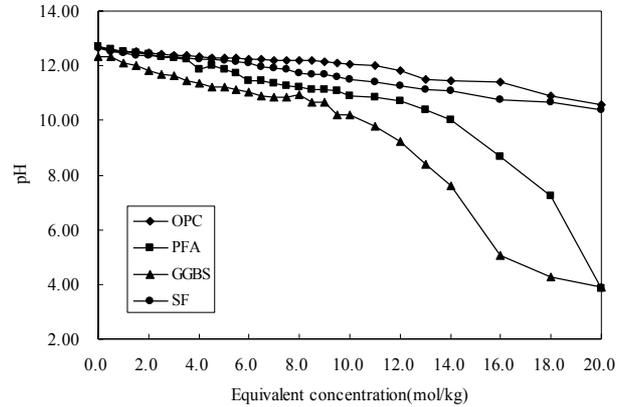


Fig. 1. Titration curves as a function of the quantity of acid added

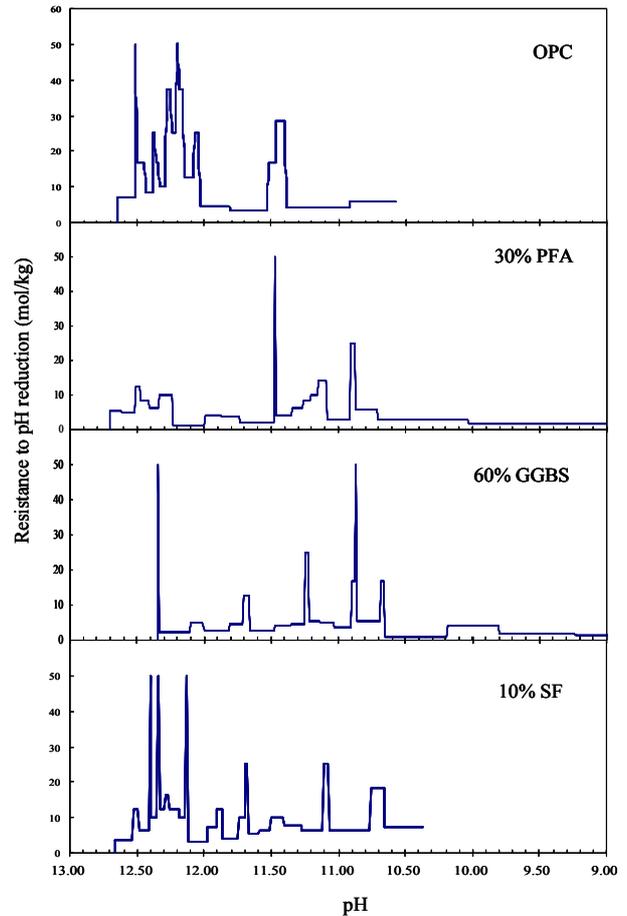


Fig. 2. ANC curve of the resistance to pH reduction each binder

the 60% GGBS binders show the lowest resistance among the binders. Two strong peaks occur at pH level of 12.3 and 10.9 for the 60% GGBS binder and strong resistance to a pH value of 11.2 and 10.7. The 10% SF binder shows

the strongest resistance at a pH of between 12.5 and 12 and also several peaks at pHs 11.7, 11.1 and 10.7. The 10% SF binder in overall shows greater resistance in total than the other binders. These results are due to the properties of the cement hydration products, the degree of hydration for the type of binders.

Fig. 3 shows the amount of added acid per unit pH reduction, respectively. The OPC and 10% SF requires more acid to achieve the unit pH reduction of 12, 11, 10 and 9 than the 30% PFA and the 60% GGBS does. Also, the acid demand of each binder in each unit generally decreased as the pH level falls, except the pH level of 12, where the amount of required acid is smaller than that of pH 12-11 for 30% PFA, 60% GGBS and 10% SF. The more the pH level of OPC drops, the less acid are needed for 30% PFA, 60% GGBS and 10% SF the amount of acid to achieve the pH reduction to 11, 10 and 9 also decreases. The total amount of acid to reach the 9 level of pH is OPC > 10% SF > 30% PFA > 60% GGBS. However, for the pH of 12-11 and 11-10, the 10% SF requires the largest amount of acid, and the 30% PFA and 60% GGBS requires almost the same amount of acid, but less than that by the 10% SF. When the pH of each binder drops to 10-9 pH level, the amount of acid added is less than 5 mol/kg and the OPC shows a higher resistance to pH fall than the acid demand by the 10% SF, 60% GGBS and 30% PFA.

Fig. 4 obtained by the measurement of the concentration of free chloride using potentiometric titration against silver nitrate. It shows that the free chloride content increases by pH fall for each binder of OPC, 30% PFA, 60% GGBS and 10% SF. The free chloride content in the suspension with no acid is 67% for OPC, 50% for SF, 46% for PFA and 57% for GGBS, respectively. As the acid increases in the suspension, the bound chlorides release to free chlorides. However, although more acid was added to the

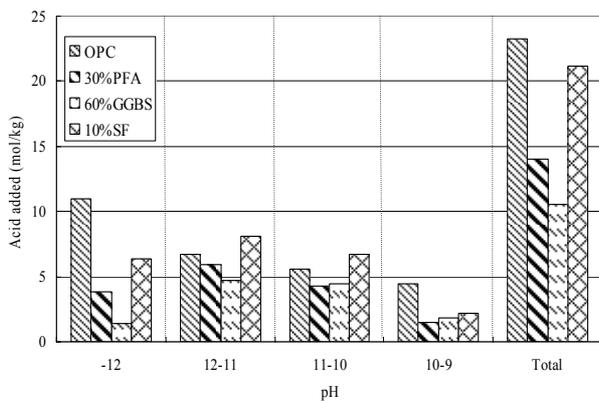


Fig. 3. Amount of added acid per unit pH reduction

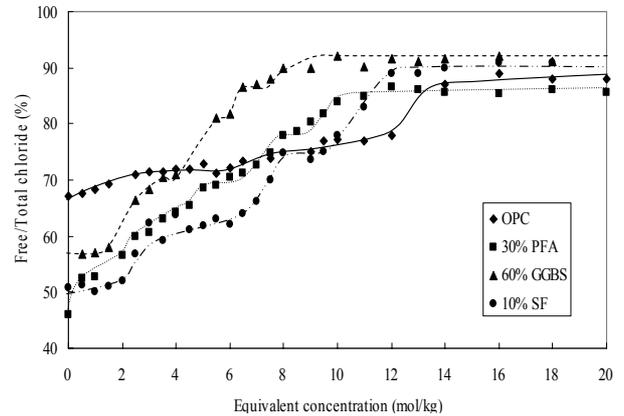


Fig. 4. The free chloride content to a pH fall

suspension, the free chloride content reached to a certain limit. The free chloride content of OPC increased slightly until the amount of the acid added was 11 mol/kg in the suspension, and then increased sharply between the acid 11 and 14 mol/kg. In the mixed acid is more than 14 mol/kg, the free chloride content reaches to a limit value. The 30% PFA starts the smallest initial value of the soluble chloride. The amount of the free chloride content increase until the acid added to 10 mol/kg. After this, the free chlorides are no longer increased. Until the amount of the acid increases to 8 mol/kg, the free chlorides of the 60% GGBS increased as step-wise manner for the phases between the adding acid 0 and 2, between 3.5 and 4, between 6 and 7. The free chlorides content for the 60% GGBS was firstly stabilized among for all binders. The 10% SF increases the acid soluble chloride with similar manner by the 60% GGBS, but the free chloride content was stabilized most slowly. It is notable that bound chlorides are released by about 85-95% of total, when acid is fully supplied to the suspension.

## 4. Discussion

### 4.1 Corrosion process

It is well known that a high alkalinity of the concrete pore solution protects embedded steel against corrosion. However, the corrosion process occurs by chloride ions or carbonation in the environment, accompanying oxygen and moisture for cathodic reaction.<sup>1),2)</sup> At pit nucleation, the corrosion process starts by the electrochemical reaction.<sup>1),3)</sup> By this reaction, a pH of the pore solution in the vicinity of steel is decreased and then bound chlorides releases to free.<sup>10)</sup> This causes the breakdown of the passive film and thus impose the corrosion risk.<sup>1),11)</sup> However, the cement hydration products can buffer a pH fall by the

chloride attacks, being called repassivation, which was quantified experimentally in this study on the ANC. These act as corrosion inhibitors for the steel in concrete, affecting a pH fall of concrete and a corrosion risk.<sup>3,11)</sup> At some particular pH, the pH of the binders of OPC, 30% PFA, 60% GGBS and 10% SF is not decreased due to the cement hydration products though the amount of acid added increases. In particular, all binders appear the marginal reduction of the pH of suspension at a pH of 12.5 by calcium hydroxide.<sup>12)</sup> Beside this, there are the several steady states of pH even with the added acid. The several steady states can be represented with the peak in the ANC curve. Magnitude of the peaks show the resistances to a pH fall which depends on the hydration products, the degree of hydration for each binder. The several peaks at the high pH in each curve exhibit the pH affected by the binder characteristics. Particularly, the peak at the pH of about 12.5 indicates the pH depended on calcium hydroxide. The OPC is greatly affected by the calcium hydroxide than the other binders, it is verified the largest amount of added acid for a pH reduction to 12. The other peaks would also show dependency on the properties of hydration products. PFA, GGBS, SF have the strongest resistance to pH reduction by the hydration products buffering the acidification at between pH 12 and pH 11, it is represent the several peaks at pHs in pH 12-11. However, it is shown that the SF is affected a lot also by calcium hydroxide than PFA and GGBS due to the lower replacement rate in the SF binder. In brief, the location and magnitude of a peak are determined by the cement hydration products.

#### 4.2 Buffering capacity

The chloride binding is a process that chloride ions are removed from the pore solution in the hydrated binder phase.<sup>13)</sup> The chloride binding is an important factor which accounts for corrosion risk and it was reported that binding capacity affecting the corrosion of steel in concrete.<sup>14,15)</sup> Higher binding capacity implies the lower free chlorides content in the pore solution and thus the corrosion risk is mitigated, thus leading to a higher chloride threshold level (CTL).<sup>16)</sup>

However, the influence of the chloride binding capacity on the CTL is subjected to debate to date.<sup>17)</sup> Suryavanshi et al.<sup>18)</sup> show that the CTL of the materials like SRPC produce low binding capacity. OPC with 11.2% of C<sub>3</sub>A produced higher CTL than SRPC with 1.41% of C<sub>3</sub>A. It is supported by Oh et al. the CTL, expressed by total chloride, of SRPC with 0.45 by weight of cement is smaller than the CTL of OPC with ranging from 0.78 to 0.93.<sup>19)</sup> However, Hasson and Sorenson hold a opposite view, say-

ing that the CTL of SRPC can be higher than that of OPC.<sup>20)</sup> The acid neutralization capacity (ANC) is more dominant factor than the chloride buffering capacity. In corrosion process, the bound chlorides are released with decrease of pH. When the pH falls, the buffering capacity decreases and the ANC indicates the resistance to a release of bound chlorides. That is, for the corrosion initiation, the CTL is influenced by the chloride buffering capacity rather than by the binding capacity. However, chloride binding capacity is still suggested as an important factor in corrosion propagation.

### 5. Conclusions

The acid neutralization capacity (ANC) shows the resistance of the cementitious binder made with OPC, 30% PFA, 60% GGBS and 10% SF, respectively, to a fall of pH. The pH reduction of the suspension was measured to obtain the resistance to a predetermined quantity of acid. In addition, the concentration of the free chlorides also was measured using a potentiometric titration against silver nitrate.

1) The pH of the suspension gradually decreased with the amount of acid for each binder. The steady states pH occurred against the quantity of acid added. When the acid is supplied 20 mole/kg in the suspension, the pH reduction was OPC > 10% SF > 30% PFA > 60% GGBS pastes.

2) The peaks to express the resistance of a pH reduction due to different hydration products and rate of hydration were obtained for each binder. All binders show the first peak at about pH 12.5 due to the buffering of calcium hydroxide. The location and intensity of peaks are determined by the cement hydration products. When the ANC was calculated up to a fall in the pH of 10, the ANC of OPC is twice 60% GGBS and the order was OPC > 10% SF > 30% PFA > 60% GGBS.

3) The bound chloride was sharply released to free chloride at lower resistance to pH. The soluble chloride reaches up to about mostly increased to between 85% and 95% before pH value of 11.

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