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Chloride induced corrosion of reinforcement in volcanic ash and pumice based blended concrete

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Abstract

This paper reports the results of experiments evaluating the corrosion resistance of plain, volcanic ash (VA) and volcanic pumice powder (VPP) concrete mixes. Variables were VA and VPP additions of 0–20% as cement replacement and cement contents. X-ray diffraction (XRD) analysis, electrochemical and electromechanical measurements and physical tests were used to monitor the corrosive behaviour of embedded steel bars in concretes. Results showed that additions of VA and VPP are effective in inhibiting corrosion of reinforcing bars. The superior performance in inhibiting corrosion in reinforcing steel is attributable to the densification of the cement-paste matrix due to pozzolanic action in the VA and VPP concrete mixes.

Keywords: Volcanic ash; Volcanic pumice; Concrete; Chloride; Corrosion; X-ray diffraction; Electrochemical

1. Introduction

Steel embedded in concrete is protected against corrosion by both a chemical and a physical mechanism. Chemical protection is provided by the high pH (12.5–13.5) of the concrete interstitial solution, which causes passivation of the reinforcing steel. Concrete also provides physical protection, by hindering the access of aggressive agents. Severe corrosion problems, however, occur in many structures. Most frequently, corrosion is induced by the ingress of chloride ions (Cl^-), which leads to a local destruction of the passive film [1]. Addition of supplementary cementitious materials (fly ash, slag, silica fume) as a pozzolanic material to concrete has become common practice in recent years [2]. Research [2–9] had been carried out on the use of volcanic ash (VA), volcanic pumice powder (VPP), fly ash (FA), pulverized-fuel ash (PFA), blast furnace slag, rice husk ash, silica fume etc. as cement replacement material. The VA, VPP, PFA and FA are pozzolanic materials, because of their reaction with calcium hydroxide liberated during the hydration of cement. Amorphous silica present in the pozzolanic materials combines with lime and forms cementitious materials [10]. These materials can also improve the durability of concrete and the rate of gain in strength and can also reduce the rate of liberation of heat, which is beneficial for mass concrete [4,5]. Studies have been published concerning the effect of fly ash on concrete porosity and resistivity [11], pore solution chemistry [12], oxygen and chloride ion diffusivity [11–15], carbonation rates [16], passivation [17] and corrosion resistance [18] especially chloride-induced corrosion.

Volcanic activities are common phenomena in Papua New Guinea. Due to frequent volcanic eruption, volcanic debris such as volcanic ash and pumice are found abundantly. The meaningful use of such volcanic debris can transform them into natural resources, and can not only provide lower cost cement and concrete but can also help to decrease environmental hazard. Comprehensive research had been conducted over the last few years on the use of VA and pumice in cement and concrete production [2,19–22].

Research [2] suggests that the manufacture of blended PVAC (Portland volcanic ash cement) and PVPC (Portland volcanic pumice cement) similar to PFAC (Portland fly ash cement) of type FC is possible with

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maximum replacement of up to 20%. Durability of concrete is one of its most important properties and it is essential that the concrete made with VA and VPP blended cement should be capable of preserving its durability throughout the life of structures. Until recently little research had been conducted on the corrosion resistance of such concrete subjected to aggressive environment [23].

This paper presents the results of investigation on the corrosion resistance of VA and VPP concrete mixes where VA and VPP are used as cement replacement.

2. Experimental investigation

The concrete mixes cast and tested in this experimental program were divided into two series.

2.1. Series I: Constant-water–cement ratio concrete mixes

In this series of concrete mixes, four different cement contents of 275, 300, 350 and 450 kg/m^3 were used. A water cement ratio of 0.45 was kept invariant in all the mixes of this series. Cement content indicates the total cementitious material, i.e., PC alone for plain concrete, PC plus VA for VA mixes and PC plus VPP for VPP mixes. Twenty percent PC was replaced with VA or VPP for the VA and VP concretes. Details of concrete mixes are presented in Table 1.

2.2. Series II: Constant-workability concrete mixes

This series of concrete mixes was designed to have a constant workability of 55–75 mm slump. Total cementitious material contents of 275, 300, 350 kg/m^3 were used. The cement replacement levels with VA or VPP were the same as in series I. Details of concrete mixes are presented in Table 1.

2.3. Materials for concrete mixes

The volcanic ash (VA) and volcanic pumice (VP) used in this investigation were collected from the Rabaul area in the East New Britain province of Papua New Guinea, and the source was a volcano called Mount Tavurvur. The Rabaul area is situated in the worldwide earthquake and volcanic zone known as the 'Belt of Fire'. The cement used was locally manufactured Portland cement (PC) called 'Paradise' conforming to ASTM Type I.

Chemical and physical properties of the volcanic ash (VA) and the volcanic pumice ground to fine powder form (VPP) are compared with those of PC in Table 2. Chemical analysis indicated that the VA and VPP have similar oxide compositions and are principally composed of silica (about 60%); while the main oxide component of cement is calcium oxide. However, both VA and VPP have calcium oxide, alumina and iron oxide (total about 31%). The contents of oxides of sodium and potassium known as 'alkalis' is found to be higher in VA (5.83%) and VPP (7.69%) than that in cement (2.6% maximum).

The oxide contents provided in the chemical analyses (Table 2) are not indicative of the chemical components present, but are purely analytical summations. Thus the 69% CaO in the cement analysis does not mean that there is 69% of CaO present. Actually there is almost zero (less than 1% as shown in Table 2) CaO (free lime); the compounds actually present are C_3S, C_2S, C_3A etc. Similarly, the VA and VPP do not have the oxide content listed present as oxides—most likely both are primarily glass (Table 2). Quantitative XRD analysis of PC and blended cements with 20% VA (PVAC) and 20% VPP (PVPC) as cement replacement, provided valuable

Table 1
Mix proportion of concrete mixes (Series I and Series II)

Mix ID	W/C series		VA or VPP, kg/m^3	PC, kg/m^3	Aggregates	
	I	(II)			Fine, kg/m^3	Coarse, kg/m^3
0%	0.45	(0.45)	0	275	800	800
20% VA	0.45	(0.47)	55	220	787	800
20% VPP	0.45	(0.48)	55	220	770	800
0%	0.45	(0.45)	0	300	780	800
20% VA	0.45	(0.48)	60	240	765	800
20% VPP	0.45	(0.50)	60	240	746	800
0%	0.45	(0.47)	0	350	760	780
20% VA	0.45	(0.50)	70	280	745	780
20% VPP	0.45	(0.52)	70	280	720	780
0%	0.45		0	450	725	725
20% VA	0.45		90	360	705	725
20% VPP	0.45		90	360	675	725

C: cementitious materials (PC + VA or VPP).
Values in parenthesis represent W/C of Series II.

Table 2
Chemical and physical properties of VA and VPP

Oxide	Chemical Composition (%)			
	VA	VPP	ASTM C618 requirement for fly ash (Class F)	Portland cement (PC) ASTM Type I
Calcium oxide (CaO)	6.10	4.44	–	60–67
Silica (SiO_2)	59.32	60.82	–	17–25
Alumina (Al_2O_3)	17.54	16.71	–	3–8
Iron oxide (Fe_2O_3)	7.06	7.04	–	0.5–6.0
$SiO_2 + Al_2O_3 + Fe_2O_3$	83.9	84.5	Minimum = 70	
Sulphur trioxide (SO_3)	0.71	0.14	Maximum = 5.0	1–3
Magnesia (MgO)	2.55	1.94	Maximum = 5.0	0.1–4.0
Sodium oxide (Na_2O)	3.80	5.42	–	0.5–1.3
Potassium oxide (K_2O)	2.03	2.25	–	0.5–1.3
Free lime (CaO)	–	–		0.5–0.8
Loss on ignition	1.03	1.52	Maximum = 6.0	1.22
Physical properties				
Fineness, m^2/kg	285	295	–	320
Unit mass, kg/m^3		–	–	3150
Bulk density, kg/m^3	2450[a]	1870[a]	–	–

[a] Oven dry basis.

Table 3
Potential phase composition of the cementing materials from X-ray diffraction

Phase	PC, %	PVAC (PC blended with 20% VA), %	PVPC (PC blended with 20% VPP), %
C_3S	68.1	46.3	46.8
C_2S	14.1	9.5	9.6
C_3A	5.9	5.1	5.3
C_4AF	9.2	6.4	6.4
Other	2.4	5.2	5.1
Total	99.7	72.5	73.2
Glassy fraction[a]	0.3	27.5	26.8

[a] Obtained by difference.

information on this aspect. The phase composition of these materials is presented in Table 3.

The fineness of VA and VPP were 285 and 298 m^2/kg, respectively. Both VA and VPP satisfy the requirement of Class F fly ash as per ASTM C618 [24].

The coarse aggregate was 20 mm maximum size crushed limestone having a specific gravity of 2.65 and absorption of 0.5%. River sand of fineness modulus 2.40 having a specific gravity of 2.65 and absorption of 0.6% was used as fine aggregate. Ordinary drinking water was used in the concrete mixes.

2.4. Specimen casting and testing

Prismatic concrete specimens measuring 65 × 100 × 300 mm with a centrally placed 12 mm reinforcing bar were cast (Fig. 1). The steel bar had an effective cover of 25 mm at the bottom. The concrete constituents were mixed in a revolving-drum type mixer for 4 min. After casting, the specimens were wrapped in wet jute bags for curing for 24 h prior to demoulding. After demoulding, each sample was cured in potable water for 28 days in a container maintaining 8 mm of water on sides and top. The ratio of the volume of curing water to the volume of sample was kept low (around 0.48). A higher ratio would allow much of the cement alkali and perhaps some of the VA and VPP alkali to leach out of the concrete. This would seriously influence the subsequent corrosion measurement—loss of the alkali would reduce the margin of the hydroxide ion concentration needed for passivation in the presence of chloride.

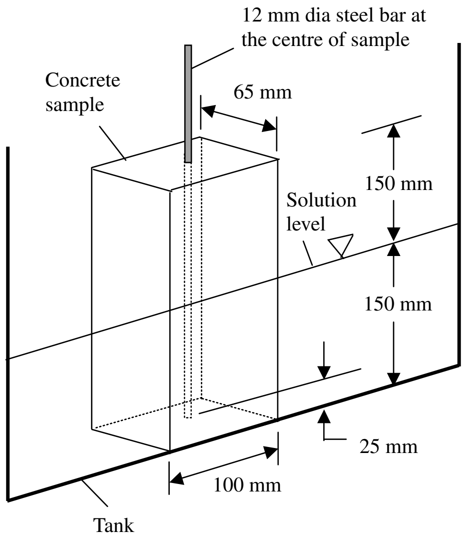

Fig. 1. Schematic diagram of a prismatic concrete specimen (sample) in a tank.

At the end of the curing period, the specimens were placed in a tank containing a 5% sodium chloride solution. The level of the solution was adjusted so that half the depth of the sample was in the solution at all times (Fig. 1). The concentration of the solution was monitored and adjusted each week.

The corrosion process of steel in concrete can be followed using several electrochemical techniques. Monitoring of open circuit potential (OCP) is the most typical procedure to the routine inspection of reinforced concrete structures [25,26]. Its use and interpretation are described in the ASTM Standard Test Method for Half-Cell Potential of Reinforcing Steel in Concrete [27]. Measurement of d.c. polarization resistance with ohmic drop compensation has been applied since the 1970s and provides information about the corrosion rate [18].

Corrosion activity in this study was monitored up to an age of 650 days using a high impedance voltmeter and noting the potentials against a saturated calomel electrode (SCE). Half-cell potentials more positive than −270 mV represent a passive state of corrosion while potentials more negative than −270 mV represent an active state of corrosion [27]. The half-cell potential data collected using this technique gives a qualitative indication of the corrosion of reinforcing bars.

Electromechanical techniques were used to obtain quantitative information on the performance of the plain and VA and VPP concrete specimens in inhibiting reinforcing bar corrosion. The corrosion rates were determined by running a polarisation-resistance scan using a potentiostat/galvanostat with IR compensation and using the Stern–Geary equation [28]. The Tafel constants were determined by running anodic and cathodic polarization scans. Current-interrupt technique was used to compensate for the internal-resistance (IR) drop between the concrete and the reinforcing bar.

The physical deterioration of the specimens was evaluated in terms of the reduction/increase in weight of the specimens at 650 days. The specimens were retrieved, air-dried for one day in the laboratory environment, cleaned gently with a towel to remove loose particles and weighed. The weight loss of the concrete materials (L) was determined using the following relationship:

$$L = \frac{W_i - W_t}{W_i} \times 100$$

where W_i = average initial weight of three specimens and W_t = average weight of three specimens after an exposure of t days.

At the end of corrosion-monitoring test at 650 days, the specimens were split open, and the steel bars were carefully removed from the embedded concrete. The rust on the steel bars was then removed by immersion in 10% di-ammonium hydrogen citrate solution at a temperature of 50 °C for 24 h. After removal, they were cleaned to remove all rust and weighed to determine their weight loss resulting from the corrosion.

After curing time of 650 days immersed in the saturated calcium hydroxide solution, powder X-ray diffraction (XRD) analysis was conducted on samples taken from around the steel bars of the specimens.

3. Results

3.1. Constant water–cement ratio mixes (Series I)

The half-cell potentials of concrete samples of this series of mixes are plotted against the period of immersion in Figs. 2–5. The concrete samples with VA and VPP initially showed higher potentials (more negative) or equal potentials as compared to the plain-cement concrete specimens for a certain period of time.

At latter stages, however, the specimens containing VA and VPP exhibited lower potentials (less negative) than plain-cement concrete specimens. Further, VA and VPP specimens generally took longer time to reach the active potential boundary (−270 mV) [27] than plain-concrete specimens.

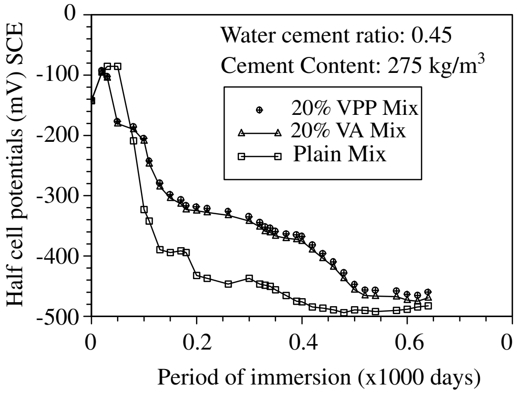

Fig. 2. Half-cell potentials of reinforcing bars in plain, VA and VPP concrete mixes (Series I).

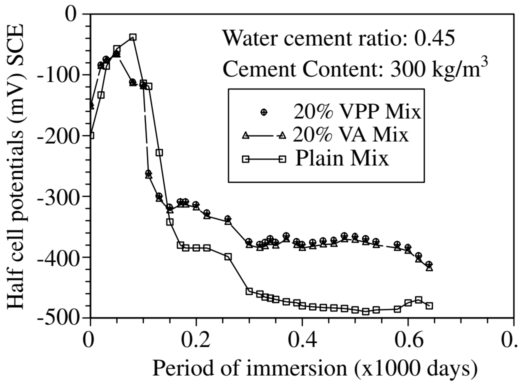

Fig. 3. Half-cell potentials of reinforcing bars in plain, VA and VPP concrete mixes (Series I).

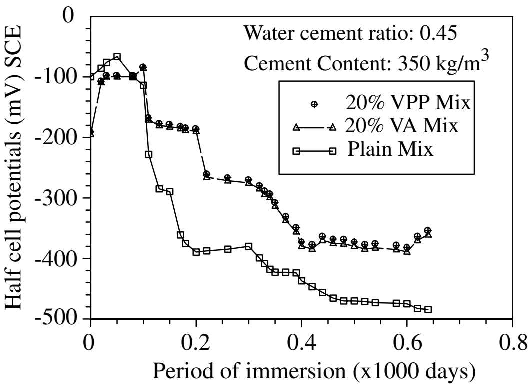

Fig. 4. Half-cell potentials of reinforcing bars in plain, VA and VPP concrete mixes (Series I).

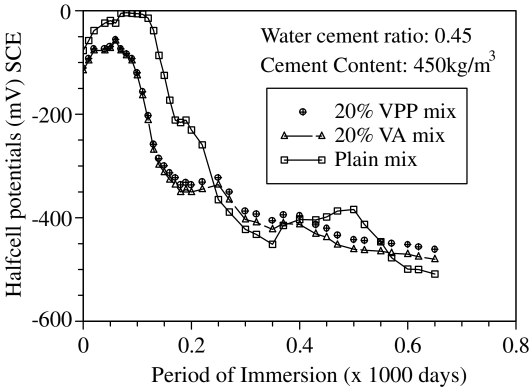

Fig. 5. Half-cell potentials of reinforcing bars in plain, VA and VPP concrete mixes (Series I).

The corrosion rate of reinforcing bars in plain, VA and VPP concrete specimens is plotted against cement content in Fig. 6. These curves show that there were only insignificant differences in the corrosion rates of reinforcing bars in plain-concrete specimens containing cement contents of 275, 300, 350 and 450 kg/m^3. The corrosion rate of reinforcing bars in plain concrete was in the range of 1.85–2.10 mils per year (mpy) compared to 0.7–0.85 in VA and 0.55–0.7 in VP concrete mixes.

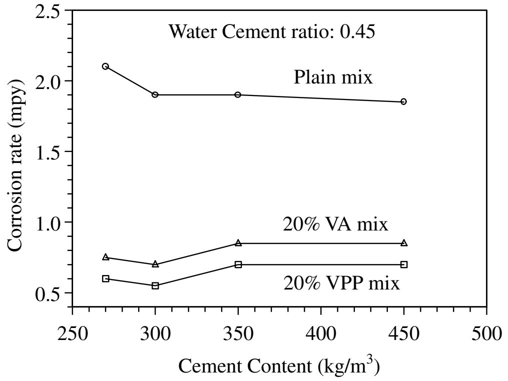

Fig. 6. Corrosion rate of reinforcing bars in plain, VA and VPP concrete mixes (Series I).

The corrosion rate was 2.8 (3.5), 2.71 (3.45), 2.24 (2.71), 2.18 (2.64) times lower in VA and VPP (values in parenthesis) specimens containing 275, 300, 350, 450 kg/m^3 of the cementitious material, respectively, than the corresponding plain-concrete specimens. Surprisingly the corrosion rate of reinforcing bars in VA and VPP concrete specimens containing 275 and 300 kg/m^3 of cement were lower than those containing cement contents of 350 and 450 kg/m^3.

The variation of half-cell potentials in VA and VPP concrete mixes were found similar to each other but corrosion rate seemed to be slightly higher in VA mixes than VPP mixes.

3.2. Constant workability concrete mixes (Series II)

The half-cell potential of reinforcing bars in the concrete specimens designed to have a workability of 55–75 mm slump are plotted against period of immersion in Figs. 7–9.

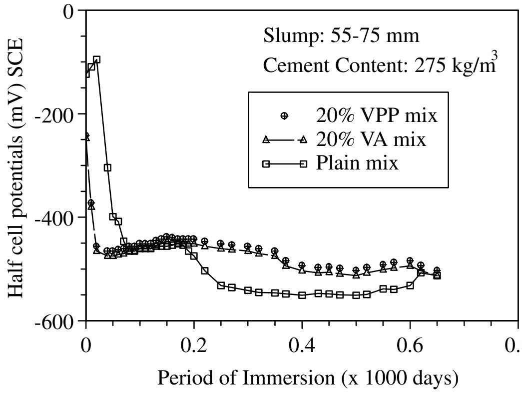

Fig. 7. Half-cell potentials of reinforcing bars in plain, VA and VPP concrete mixes (Series II).

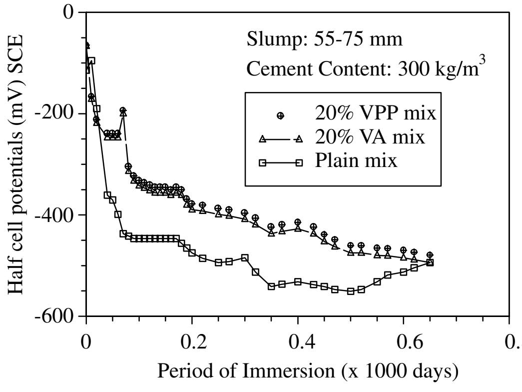

Fig. 8. Half-cell potentials of reinforcing bars in plain, VA and VPP concrete mixes (Series II).

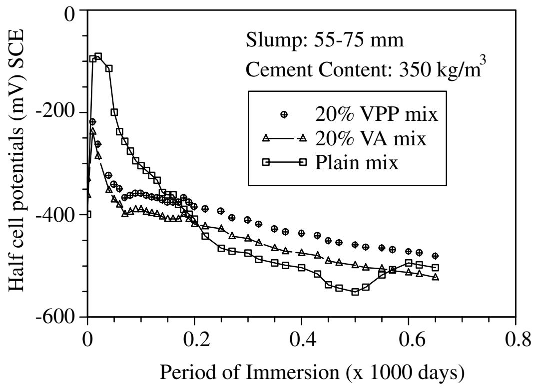

Fig. 9. Half-cell potentials of reinforcing bars in plain, VA and VPP concrete mixes (Series II).

The plain-concrete specimens tested in this series generally showed lower potentials than the VA and VPP concrete specimens at early ages. At later ages, up to 600–650 days of exposure, the VA–VPP concrete specimens exhibited somewhat lower potential than the plain-concrete specimens.

The corrosion rate of reinforcing bars in plain and VA–VPP concrete specimens of this series are plotted against cement content in Fig. 10. For the plain-concrete mix, corrosion decreased from the leanest mix to the middle one, then did not change. For the VA concrete corrosion increased from the leanest mix to the middle one, then decreased to about the same value as the leanest one—net effect of cement content practically zero. For the VPP concrete mix, there was no change from the leanest to the middle one, then a very slight reduction. The corrosion rate of reinforcing bars in plain-concrete specimens was in the range of 1.9–2.3 mpy compared to 1.3–1.4 mpy in VA, and 0.9–1.0 mpy in VPP specimens. Despite wide differences in cement content, the corrosion rate changed hardly at all in VA and VPP concrete specimens. Even change for the plain concrete was small from the leanest to middle cement content. The corrosion rate of reinforcing bars was 1.77 (2.3), 1.36 (1.9) and 1.46 (2.11) times lower in VA and VPP (values within parenthesis) concrete specimens containing 275, 300 and 350 kg/m^3 of the cementitious material, respectively, than corresponding plain-concrete specimens.

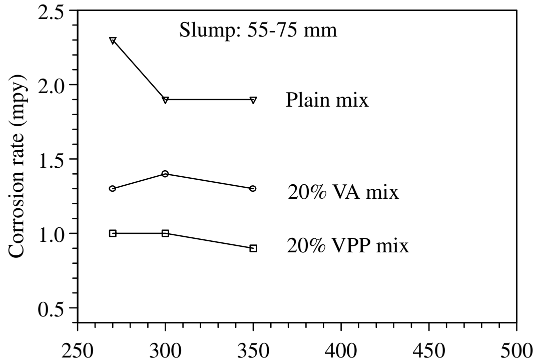

Fig. 10. Corrosion rate of reinforcing bars in plain, VA and VPP concrete mixes (Series II).

4. Discussion

Table 4 summarizes the performance of 18 concrete mixes in terms of corrosion potential, weight loss of steel bars and overall weight loss of specimens. Concrete deterioration due to sodium chloride solutions is typically manifested by a progressive degradation leading to deterioration and weight loss and is also associated with disintegration of hardened cement matrix and spalling of the surfaces. Chloride deterioration and reinforcement corrosion are discussed based on each of these tests as well as XRD analysis.

4.1. Weight loss of concrete specimens

Overall weight loss of concrete specimens ranges between 1.5% and 3.5% (Table 4). A loss of mass of 5% for beam specimen under sulfate attack was reported to be as satisfactory [30]. Losing 1.5–3.5% of the mass of the specimen due to spalling may not be considered satisfactory in reinforced concrete slabs—where the loss is all from the cover. The weight loss in VA and VPP mixes was higher than the plain-concrete mixes. This may be attributed to the higher alkali presence in VA and VPP (Table 2). Alkali, if present in soluble forms may have deleterious effects leading to disintegration of concrete due to reaction with some aggregates.

4.2. Weight loss of steel bars

The weight loss of steel bars embedded in VA and VPP concrete in Series I ranges between 0.39% and 0.53% while between 0.69% and 0.80% is observed in plain concrete (Table 4). In Series II, weight loss of steel bars in VA and VPP concrete ranges between 0.59% and 0.74% while in plain concrete it ranges between 1.01% and 1.10%. No significant differences in weight loss of steel bar are noted between VA and VPP concrete specimens. The increase of cementing materials is found to reduce the weight loss of steel bars in series I but not in series II. It is found that the weight losses of steel bars embedded in the VA and VPP concrete specimens are lower than those of plain-concrete specimens in both series I and series II. This is an indication that VA and VPP concrete have better corrosion resistance than plain concrete. Steel bars embedded in series II mixes shows higher weight loss than those embedded in series I mixes

Table 4
Performance of 18 concrete mixes in terms of corrosion potential and weight loss

Cementing materials (kg/m^3)	Mixes	Half-cell potential (mV); (SCE)		Weight loss (%) (650 day)		Time for corrosion initiation (day)
		0 day	650 day	Specimens	Steel bar	
Series I: Constant W/C = 0.45						
275	0%	−143	−483	1.8	0.80	90
	20% VA	−143	−469	3.2	0.51	130
	20% VPP	−140	−460	3.1	0.53	130
300	0% VA	−200	−480	1.6	0.72	130
	20% VA	−150	−418	3.0	0.49	130
	20% VPP	−150	−412	2.9	0.48	130
350	0%	−100	−485	1.5	0.69	130
	20% VA	−195	−361	2.8	0.41	300
	20% VPP	−191	−354	2.8	0.39	300
Series II: Constant workability Slump: 55–75 mm						
275	0%	−124	−513	2.1	1.01	40
	20% VA	−247	−513	3.5	0.69	10
	20% VPP	−242	−503	3.6	0.67	10
300	0%	−114	−494	2.0	1.05	40
	20% VA	−67	−494	3.4	0.61	70
	20% VPP	−65	−479	3.3	0.59	70
350	0%	−199	−504	1.9	1.10	20
	20% VA	−361	−523	3.0	0.71	0
	20% VPP	−332	−481	3.1	0.74	0

which indicates that constant workability mixes have lower corrosion resistance than constant W/C mixes.

4.3. Corrosion potentials and corrosion rate

The corrosion potentials at the beginning (0 day) and at the end of exposure period (650 day) are incorporated in Table 4. Hence, the ASTM C 876 criterion [27] can be used to indicate whether the rebars were in active state of corrosion or not. The potential time curves (Figs. 2–5, 7–9) are used to evaluate the time to initiation of rebar corrosion based on the ASTM C 876 [27] criterion of −270 mV SCE (saturated calomel electrode) and included in Table 4.

The steel in series I concretes including both plain and VA–VPP mixes was in a passive state of corrosion (showing less negative potential than threshold −270 mV SCE) while some VA–VPP mixes in series II were in active state of corrosion from the beginning. At the end of the curing period of 650 days, the steel in all the concrete mixes in both series I and series II were in the active state of corrosion. Time for initiation of corrosion increases in VA–VPP mixes compared to plain mixes in series I but such definite trend is absent in series II. Time for corrosion initiation is lower in series II compared with series I. In series I, time of initiation of corrosion in VA–VPP mixes is extended up to 300 days.

The rate of corrosion of reinforcing bars was low in VA and VPP concrete specimens compared to plain-concrete specimens (Figs. 6 and 10). The data showed that the rate of corrosion in the plain-concrete specimens in which water cement ratio was kept constant was nearly the same in all the mixes investigated in this series. This indicates that increasing the cement content of plain-concrete without an attendant change in the water cement ratio is not beneficial in inhibiting the corrosion of reinforcing bars.

The data further showed that the rate of corrosion was lower in VA and VPP concrete specimens containing cementitious contents of 275 and 300 kg/m^3 than those containing cement contents of 350 and 450 kg/m^3. This indicates that VA and VPP addition is more beneficial in leaner mixes.

The VA and VPP concrete specimens cast and tested in the constant workability series also showed higher resistance to corrosion than the plain-concrete specimens. The performance of VPP is found to be slightly better than VA in corrosion prevention at early ages. This may be due to increased fineness of the VPP compared to VA, which leads to better pozzolanic action.

In the literature some criteria relating the corrosion rate obtained from d.c. polarization measurements and the probability of corrosion and/or expectable lifetime were published [31,32]. According to Moosavi et al. [31] the criteria presented in Table 5 can be applied.

Based on the criteria, the concrete performance can be categorized based on the corrosion rate as:

Table 5
Corrosion criteria

Corrosion rate (mpy)	Degree of corrosion
<0.01	Insignificant (passive)
<1.0	Low
1–10	Moderate
10–30	High
>30	Very high

- In the case of series I: corrosion rate (Fig. 6) in plain-concrete falls often moderate degree of corrosion while those in VA and VPP concretes fall after only a low degree of corrosion. This reflects the beneficial effect of VA and VPP in inhibiting the corrosion process.
- In the case of series II: corrosion rate in plain, VA and VPP concrete (Fig. 10) all fall often a moderate degree of corrosion, although corrosion rate is lower in the VA and VPP concretes.
- The beneficial effect of VA and VPP in inhibiting corrosion is less in the constant workability mixes (Series II) than constant W/C mixes (Series I). Presumably this reflects the higher water content need in the VA and VPP concrete mixes in series II compared to series I (Table 1). This higher water content definitely negates some of the pozzolanic effect on corrosion.
- Steel in all concrete mixes was in active stage of corrosion after 650 days as confirmed from the corrosion potential as per ASTM C 876 [27].

4.4. General discussion

The results in this investigation show that VA and VPP addition to concrete mixes appears to improve the long-term corrosion resistance of concrete. The role of VA and VPP is related with both the initiation and the progression of corrosion. VA and VPP are added as fine granulates and upon hydration of cement, they have the capability of partially obstructing voids and pores. This leads to a decrease of pore size and to a smaller effective diffusivity for either chloride or other species. This improves the long-term corrosion resistance of concrete structures. The pozzolanic [23] reaction of VA and VPP with calcium hydroxide, also produces a denser concrete and thus inhibits the ingress of chloride ions. This takes place at a slower rate.

The XRD curves of the specimens taken around the steel bars reveals that the calcium hydroxide content of the VA and VPP-blended specimens is lower than that of the plain-concrete specimens (Fig. 11). This indicates that the pozzolanic reactivity of VA and VPP that consumes calcium hydroxide resulting from hydration of the cement. This improves the corrosion resistance of VA and VPP concrete mixes compared to plain-concrete mixes. This is in accord with the lower corrosion rate in VA and VPP concretes.

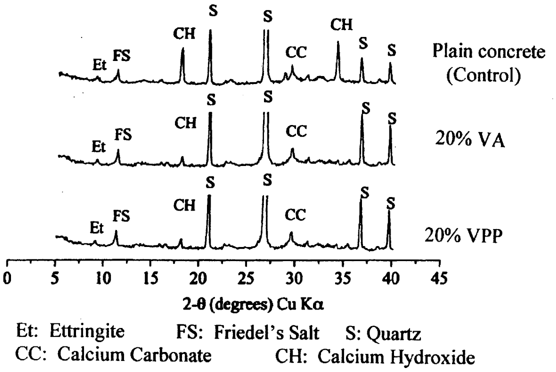

Fig. 11. XRD spectra of specimens.

Comparatively higher Friedel's salt formation in VA and VPP concrete mixes compared to plain-concrete mix is confirmed from the XRD spectra in Fig. 11. Similar phenomena were also observed in fly ash concrete [29]. The VA and VPP certainly do not have C_3A which can adsorb more chloride ions to form Friedel's salts. The presence of lower C_3A content in PVAC and PVPC compared to PC confirms the fact (Table 3). It is more likely that VA and VPP have aluminium in the glass that is available for the chemical reaction resulting in Friedel's salt production. Friedel's salt formation consequently lowers the levels of free chloride and hence reduces the chloride ion diffusivity of concrete. This process reduces the localized corrosion of steel. The reduction in the localised corrosion of embedded steel in VA and VP concretes is confirmed from the lower weight loss of steel bars (Table 4). The presence of VA and VPP also affects the composition and thickness of the passive films. Films formed in paste solutions have revealed a thickening and a higher degree of hydration under the influence of fly ash [17].

Previous study [15] reported that the addition of fly ash leads to a decrease in concrete porosity, which is directly related to its chloride resistivity. A reduction of chloride diffusivity in concrete to half its value was observed as a consequence of a 50% replacement of cement by fly ash [15]. The VA and VPP used in this study conform to the ASTM Specification for Class F fly ash which does not necessarily mean that these materials behave like fly ash. However, it is reported that the incorporation of VA and VPP as cement replacement in mortar leads to the refinement of pore structure and to the decrease of total pore volume with the increase of curing age [33,34]. A lower porosity corresponds to a lower free cross-section and to an increase in path tortuosity, affecting the diffusion of solvated species. The beneficial effects of VA and VPP concerning corrosion initiation and corrosion rate similar to fly ash appear to be justified.

5. Conclusions

Chloride induced corrosion resistance of reinforcement in VA and VPP blended concretes monitored for 650 days was studied. From the results of the various tests performed, the following conclusions could be drawn:

1. Blended concretes with 20% cement-replaced by VA and VPP perform better in resisting reinforcing bar corrosion than does plain concrete.
2. Increasing the cement content of plain concrete without an attendant change in the water–cement ratio is not beneficial in inhibiting the corrosion of reinforcing bars. VA and VPP addition is more beneficial in leaner mixes.
3. The concrete weight loss (after 650 days of exposure) in VA and VPP mixes was higher than the plain-concrete mixes. This is attributed to the higher alkali presence in VA and VPP which may lead to the disintegration of concrete due to reaction with some aggregates. The lower weight loss of embedded steel bars in VA and VPP mixes also showed their better corrosion resistance than plain-concrete mixes.
4. The time for corrosion initiation was lower in constant workability series II compared with constant W/C series I. In series I, time of initiation of corrosion in VA–VPP mixes was as long as up to 300 days. Concretes in both series I and II were found to be in active state of corrosion after 650 days.
5. XRD confirms the presence of lower calcium hydroxide content and formation of comparatively higher Friedel's salt (reduces the levels of free chloride) in the VA and VPP–blended specimens compared with the plain-concrete specimens. These processes reduce the chloride ion diffusivity of concrete and hence reduce the localized corrosion of steel. This is in accord with the lower corrosion rate observed in VA and VPP concretes compared with plain concrete.

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