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Performance of volcanic ash and pumice based blended cement concrete in mixed sulfate environment

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Abstract

The deterioration of concrete structures due to the presence of mixed sulfate in soils, groundwater and marine environments is a well-known phenomenon. The use of blended cements incorporating supplementary cementing materials and cements with low C_3A content is becoming common in such aggressive environments. This paper presents the results of an investigation on the performance of 12 volcanic ash (VA) and finely ground volcanic pumice (VP) based ASTM Type I and Type V (low C_3A) blended cement concrete mixtures with varying immersion period of up to 48 months in environments characterized by the presence of mixed magnesium–sodium sulfates. The concrete mixtures comprise a combination of two Portland cements (Type I and Type V) and four VA/VP based blended cements with two water-to-binder ratio of 0.35 and 0.45. Background experiments (in addition to strength and fresh properties) including X-ray diffraction (XRD), Differential scanning calorimetry (DSC), mercury intrusion porosimetry (MIP) and rapid chloride permeability (RCP) were conducted on all concrete mixtures to determine phase composition, pozzolanic activity, porosity and chloride ion resistance. Deterioration of concrete due to mixed sulfate attack and corrosion of reinforcing steel were evaluated by assessing concrete weight loss and measuring corrosion potentials and polarization resistance at periodic intervals throughout the immersion period of 48 months. Plain (Type I/V) cement concretes, irrespective of their C_3A content performed better in terms of deterioration and corrosion resistance compared to Type I/V VA/VP based blended cement concrete mixtures in mixed sulfate environment.

Keywords: Volcanic ash/pumice; Sulfate attack; Blended cement concrete; Corrosion/deterioration

1. Introduction

The presence of sulfate ion causes deterioration of concrete structural components exposed to marine environments or placed in soils and groundwater contaminated with sulfate salts. Research on concrete deterioration due to the presence of sulfate ions had been continued for decades. Sulfate attack on concrete is a complex process and many factors such as cement type, sulfate cation type, sulfate concentration and exposure period may affect the sulfate resistance [1,2]. The sulfate ions react with C_3A and Ca $(OH)_2$, to produce expansive and/or softening types of deterioration. The sulfate attack in marine environment gives rise to expansive ettringite, gypsum, and brucite and sometimes is associated with calcite formation [3,4].

The sulfate resistance of concrete structures can be improved by controlling sulfate permeation into concrete and the sulfate attack can be prevented either by changing cement from ASTM Type I to Type II or Type V or by introducing pozzolans such as fly ash, blast furnace slag, volcanic ash (VA) and finely ground volcanic pumice (VP) in concrete [5–10].

ASTM Type V cement, with a low C_3A, is recommended in structures placed in such environment. Typically, ASTM Type I cement contains between 8% and 12% C_3A, whereas Type II cement contains less than 8% C_3A and Type V cement less than 5% C_3A. Significant development in cement chemistry over the past two decades, resulted in cements with a high C_3S/C_2S content [11,12]. This increase in C_3S/C_2S ratio results in increased calcium hydroxide content in the hardened cement concrete, thereby enhancing the susceptibility of such cements to softening type of sulfate attack [12,13]. Irassar et al. [14] reported that a low C_3S/C_2S ratio is a significant positive factor in the choice of cement for good sulfate resistance. The sulfate

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permeation can also be controlled by: increasing compactness, lowering water-to-cement ratio, proper curing, surface treatment, and use of precast concrete in place of cast-in-situ concrete [5,13,16].

It is reported that the limitation on C_3A content is not the ultimate answer to the problem of sulfate attack [6,12,15]. Mehta pointed out that Type V cement addresses only the problem of sulfate expansion associated with the ettringite formation [17]. Therefore, Type V cement can be particularly efficacious when calcium sulfate is the attacking medium, although it could be beneficial with respect to the prevention of the formation of gypsum owing to the action of sodium sulfate. Thus, Type V cement is of no avail in the attack of calcium hydroxide and C–S–H and the subsequent loss of strength [17].

The use of blended cement made with supplementary cementitious materials (such as: fly ash, silica fume, and blast furnace slag) is, therefore recommended in sulfate environments [4,7,8]. The sulfate resistance of such blended cement concretes depends on the composition and physical properties of concrete as well as type and concentration of sulfate ion. The improvement in sulfate resistance for fly ash and silica fume based blended cement concretes is reported. This is attributed to the pore refining and pore refinement effect occurring due to pozzolanic reaction where calcium hydroxide becomes bound by fly ash or silica fume converting it into secondary C–S–H gel. However, with additional cementitious materials, the complexity of sulfate attack becomes even greater. Taylor [18] pointed out that if slag has a low alumina content, it improves the sulfate resistance, but with a high content of alumina, the reverse is the case.

Young et al. [19] report that sulfate attack can be prevented by any one of three factors: a low w/c, a low calcium hydroxide content, or a low C_3A content. If their claim is valid, then adequate protection of concrete should be ensured by the use of a low w/c alone or by the use of Type V cement alone. Neville [1] believed that these solutions are too sweeping and not valid under all circumstances. Al-Amoudi [20] reported that lowering w/c has a deleterious effect on the resistance of concrete exposed to magnesium sulfate, the use of Type V cement being of no avail. A likely explanation is that at low values of w/c, there is limited pore space to accommodate the products of reactions with sulfate, namely, magnesium silicate hydrate (which has no adhesive properties) and gypsum.

Although significant progress has been made on the understanding of the mechanism of sulfate attack in concrete, our knowledge and understanding remains inadequate [1]. Still the role of C_3A, cement content, water to binder ratio, and the role of pozzolanic materials remains controversial.

Comprehensive research had been conducted over the last few years on the use of VA and VP in cement and concrete production [5,21–25]. The meaningful use of such volcanic debris can transform them into natural resources and can, not only provide low cost cement and concrete but can, also help to decrease environmental hazard. Research suggested the manufacture of blended Portland volcanic ash cement and Portland volcanic pumice cement with maximum cement replacement of up to 20% [23].

Durability of concrete is one of its most important properties and it is essential that the concrete made with VA and VP based blended cements should be capable of preserving its durability throughout the life of structures. ACI 318-813-1999 and BS 8110-1985 and other codes of practices provide guidelines on the quality of concrete and the type of cement to be used for varying sulfate concentrations. However, these guidelines do not specifically cover the sulfate resistance of VA/VP based blended cement concrete. Until recently, little research had been conducted on the performance of VA and VP based blended cements subjected to such aggressive environments [5,24,26–28]. Moreover, no data is available on concrete deterioration and corrosion of rebars in VA/VP based blended cement concretes when exposed to sulfate-bearing environments.

Previous studies on sulfate attack are conducted mainly by using sodium, magnesium and calcium sulfate solutions [1,15]. However, due to limited solubility of calcium sulfate in water at normal temperatures (about 1400 mg/L SO_4), higher concentrations of sulfate ions in ground waters are generally due to the presence of magnesium and sodium sulfates. Both of these salts are abundant in many parts of the world including Arabian Gulf coast (known as saline sabkha soils) and coastal areas of Papua New Guinea. It is important to study the performance of concretes in such mixed sulfate environment. Extensive research has been conducted by the authors to study the durability of VA and VP based blended cement mortar and concrete exposed to sulfate and mixed sulfate bearing environments [29].

This paper presents the results of the research conducted to assess deterioration and corrosion resistance of 12 concrete mixtures, which comprised a combination of two Portland cements (Type I and Type V) and four VA/VP based blended cements with Type I/V cements having two water-to-binder ratios, exposed to mixed sulfate solution for a period of 48 months. Such a study is of significant practical interest and can be helpful in the selection of VA and VP based blended cements for structures subjected to mixed sulfate environments characterized by the presence of magnesium as exists in many parts of the world.

2. Experimental program

2.1. Materials

Volcanic ash and pumice used in this investigation were collected from the Rabaul area of the East New Britain province of Papua New Guinea and the source was a volcano called Mount Tavurvur. Natural VA collected from the source was dried and sieved to obtain a Blain fineness of 285 m^2/kg (Table 1). Pumice samples collected from the source (consisting of lumps of various sizes ranging from 2 to 64 mm) were grounded to fine powder using a ring crusher to obtain a Blaine fineness of about 295 m^2/kg (Table 1). ASTM C 150 Type I and Type V cements were used as plain cements as well as to manufacture blended cements. Blended cements were produced in the laboratory by thoroughly mixing cement and VA or VP using a heavy duty paddle mixer.

Chemical and physical properties of VA and VP are compared with those of cements in Table 1. Chemical analysis

Table 1
Comparative study of chemical and physical properties of VA, VP and cement

Chemical compounds	VA (mass, %)	VP (mass, %)	ASTM Type I cement (mass, %)	ASTM Type V cement (mass, %)
Calcium oxide (CaO)	6.1	4.44	64.1	65.0
Silica (SiO_2)	59.3	60.82	21.4	21.9
Alumina (Al_2O_3)	17.5	16.71	5.7	3.2
Iron oxide (Fe_2O_3)	7.0	7.04	3.5	3.9
Sulfur trioxide (SO_3)	0.7	0.14	2.1	2.5
Magnesia (MgO)	2.6	1.94	2.1	2.2
Sodium oxide (Na_2O)	3.8	5.42	0.5	0.2
Potassium oxide (K_2O)	3.8	2.25	0.5	0.3
Loss on ignition	1.0	1.5	1.1	0.8
Free lime (CaO)	–	–	0.7	0.6
Physical properties				
Fineness (m^2/kg)	285	295	320	373
Unit mass (kg/m^3)	–	–	3150	3150
Bulk density (kg/m^3)	2450[a]	1870[a]		

[a] Oven dry basis.

indicated that VA and VP 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 VP have calcium oxide, alumina and iron oxide (total about 31%). The contents of oxides of sodium and potassium known as 'alkalis' are found to be higher in VA (5.83%) and VP (7.69%) than that in cement (2.6% maximum).

Table 2
Potential phase composition of the cementing materials from X-ray diffraction

Phase	Plain cements		VA and VP based blended cements			
	Type V	Type I	PVAC (20% VA) Type I	PVPC (20% VP) Type I	PVAC (20% VA) Type V	PVPC (20% VP) Type V
C_3S	71.2	68.1	46.3	46.8	49.1	49.6
C_2S	10.5	14.1	9.5	9.6	7.1	7.2
C_3A	3.5	8.1	5.1	5.3	2.1	1.9
C_4AF	11.1	9.2	6.4	6.4	6.9	6.7
Other	2.9	2.4	5.2	5.1	6.1	5.5
Total	99.2	99.7	72.5	73.2	71.3	70.9
Glassy fraction[a]	0.8	0.3	27.5	26.8	28.7	29.1

[a] Obtained by difference.

Table 3
Grain size distribution and properties of aggregates

Grain size distribution of aggregates			Physical properties aggregates			
Sieve size (mm)	Fine % passing	Coarse % passing		Bulk density (kg/m^3)		Water absorption (%)
				Oven dry	SSD	
20	100	100	Coarse	2570	2640	2.49
12.7	100	71	Fine	2610	2660	0.60
9.5	100	28				
4.75	93	0				
2.36	70.5					
1.18	51.5					
0.6	35					
0.3	20.5					
0.15	8.5					

The oxide contents provided in the chemical analyses (Table 1) 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 1) CaO (free lime); the compounds actually present are C_3S, C_2S, C_3A, etc. Similarly, VA and VP do not have the oxide contents listed in Table 1 as most likely both are primarily glass. Blended cements were prepared by replacing 20% of Type I and Type V cements with VA or VP. Quantitative XRD analysis of Type I, Type V cements as well as blended cements with 20% VA (PVAC) and 20% VP (PVPC) as cement replacement, provided valuable information on the phase composition of these materials (Table 2).

2.2. Concrete mix proportions

ASTM Type I and Type V plain as well as VA and VP based blended (with 20% VA or VP) cements were used in the preparation of concrete mixes. The fine and coarse aggregates were local natural river sand and 20-mm maximum size crushed limestone, respectively. The particle size distributions as per ASTM C 136-01 for aggregates are presented in Table 3. The bulk density and water absorption of aggregates are also presented in Table 3. Table 4 shows the details of mix proportions of 12 different concrete mixtures classified into series A and B. First letter in mix designation represents the series, numeric before VA or VP represents % of VA or VP and roman letter at the end represents type of cement. Two different water-to-binder ratios (W/B) of 0.35 (for series B) and 0.45 (for Series A) were used while the total binder content was kept constant at 400 kg/m^3. A naphthalene sulfonate-based superplasticizer was used at a dosage of 1% (solid mass) by weight of binder in concrete mixtures made with a W/B of 0.35.

2.3. Investigation on fresh, mechanical and durability characteristics

Tests were conducted to evaluate fresh and hardened properties such as slump, air content, compressive strength and density of 12 concrete mixtures with Type I/Type V plain

Table 4
Mix proportions and fresh and strength properties of VA/VP concrete mixtures

Mix ID	VA or VP (%)	W/B	Materials (kg/m^3)				Slump mm	Air content (%)
			W	C	Aggregates			
					Fine	Coarse		
Series A: W/B = 0.45								
AType I	0	0.45	180	400	760	1020	80	2.5
AType V	0	0.45	180	400	760	1020	82	2.5
A20VA-I	20	0.45	180	320	743	1019	110	2.8
A20VA-V	20	0.45	180	320	743	1019	108	2.7
A20VP-I	20	0.45	180	320	720	1019	80	3.0
A20VP-V	20	0.45	180	320	720	1019	78	3.1
Series B: W/B = 0.35								
BType I	0	0.35	140	400	805	1080	80	2.2
BType V	0	0.35	140	400	805	1080	81	2.3
B20VA-I	20	0.35	140	320	786	1019	106	2.6
B20VA-V	20	0.35	140	320	786	1019	107	2.6
B20VP-I	20	0.35	140	320	765	1019	80	2.8
B20VP-V	20	0.35	140	320	765	1019	80	2.7

C: cement, W: water, B: binder.

and VA/VP based blended cements. In addition, durability and micro-structural characteristics of concrete mixtures were evaluated through rapid chloride permeability (RCP), mercury intrusion porosimetry (MIP) and differential scanning calorimetry (DSC).

The slump of fresh concrete mixtures was determined as per ASTM C 143-00 while the air content was determined by pressure meter as per ASTM C 231-97.

150 × 300-mm (for compressive strength) and 100 × 200-mm cylinder (for RCP, MIP and DSC) specimens were cast. Specimens were removed from the moulds (wrapped in wet jute bags) after 24 h of casting and then placed in a water tank at 23 ± 2 °C. After 28 days of water curing, compressive strength test was performed on 150 × 300-mm cylinders as per ASTM C-39.

100 × 200-mm cylinders were transferred to a relative humidity room maintained at 23 ± 2 °C and 50 ± 5% relative humidity and kept there for further 4 weeks until testing at 56 days. At 56 day, RCP test was conducted as per ASTM C 1202-97 on 100 × 50-mm concrete slices to determine resistance to chloride ion penetration. This test determines the electrical conductance of concrete to provide a rapid indication of its resistance to the penetration of chloride ions. The chloride ion resistance of concrete gives an indirect measure of its permeability and internal pore structure, as more current passes through a more permeable concrete.

The porosity and pore size distribution were measured using MIP, which had a measuring pressure ranging from 0.01 to 200 MPa [24]. The contact angle selected was 140° and the measurable pore size ranged from 0.004 to 144 μm. The Washburn equation was used to calculate the pore radii [30]. The samples in the form of pellets of about 5 mm in size, consisted of hardened cement mortar, were collected from the crushed concrete cylinders at 56 day and immediately soaked in acetone to stop the further hydration. The samples were dried in an oven at 60 °C for 48 h before testing.

The DSC test was performed on the hardened mortar samples taken from the crushed concrete cylinders after 56 days of curing to determine the quantity of $Ca(OH)_2$ formed in the mortars. The samples used weighted around 60 mg. The samples were heated at a constant heating rate of 10 °C per minute to 1100–1200 °C, in a dynamic helium atmosphere. The DSC data analysis gave graphs of heat flow between the sample and reference crucibles vs. temperature. DSC thermograms showed peaks due to endothermic (heat absorbing) and exothermic (heat releasing) reactions. The $Ca(OH)_2$ content was equivalent to the area (enthalpy) under the respective endothermic peaks. The endothermic peak for $Ca(OH)_2$ was observed at around 450 °C. The size of the area under the curve was related to the quantity of the material in the sample. At least two DSC analyses were performed for each concrete.

2.4. Investigation on concrete exposed to sulfate bearing environment

2.4.1. Details of specimens

75 mm in diameter and 150 mm in height concrete cylinders with a centrally placed 10 mm diameter reinforcing bar (Fig. 1) were used to study the effect of the sulfate environment on the electro-chemical behaviour of embedded reinforcements in Type I/V plain and Type I/V VA/VP based concrete mixtures. The steel bars embedded in concrete were coated with an epoxy paint at the concrete–air interface and at their ends to prevent crevice corrosion. The reinforcing bars were cleaned thoroughly using silicon carbide paper and degreased before casting in concrete. The steel bar had an effective cover of 25 mm at the bottom.

100 × 100-mm concrete cubes were used to study the effect of the sulfate environment on the physico-chemical characteristics of Type I/V plain and Type I/V VA/VP based concrete mixtures.

2.4.2. Casting and curing of specimens

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,

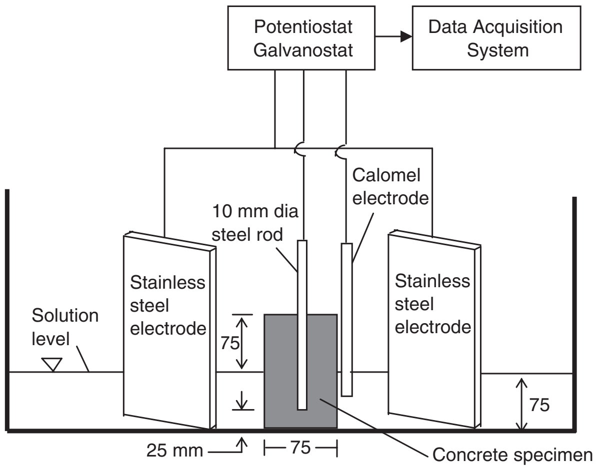

Fig. 1. Experimental set-up for polarization resistance measurements showing a specimen.

specimens were cured for 28 days in potable water in a tank where the ratio of the volume of curing water to the volume of specimens was kept low (around 0.48). A higher ratio would allow much of the cement alkali and perhaps some of the VA and VP alkali to leach out of the concrete. This would seriously influence the subsequent corrosion measurement as loss of the alkali would reduce the margin of the hydroxide ion concentration needed for passivation especially in the presence of chloride [28]. After 28 days of water curing, the cube specimens were air-dried for 1 day in the laboratory (23 ± 2 °C) and their initial weight (W_i) were recorded.

2.4.3. Test solutions and specimen immersion schemes

The cube and cylinder specimens were exposed to mixed sulfate environment by immersing in test solutions in two separate tanks. Two separate exposure tanks were needed to submerge cylinder specimens at a specific height and to fully submerge cube specimens. In this study, the concentration of the test solution was 2.1% SO_4^{2-} (21,000 mg/L) where sodium sulfate and magnesium sulfate (proportioned to provide 50% of the sulfate concentration from each of the two salts) were used to provide sulfate ions. The above exposure condition represents very severe sulfate exposure condition according to ACI 318-99. However, this concentration is prevalent in many parts of the world especially saline soils in Arabian Gulf coast and coastal areas of Papua New Guinea [31]. The level of the solution was adjusted so that half the depth of the cylinder specimens with embedded steel was in the solution at all times (Fig. 1). Cube specimens were exposed to test solution in fully submerged condition for assessing physical deterioration. The solutions in both tanks were periodically agitated and their concentrations were monitored and adjusted each month.

2.4.4. Assessments of physico-chemical deterioration

The physical deterioration due to sulfate attack was evaluated in terms of the reduction /increase in weight of the specimens after 6, 12, 18, 24, 30, 36 and 48 months of immersion. The specimens were retrieved, air-dried for 1 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 Eq. (1):

$$L = \frac{W_i - W_t}{W_i} \times 100 \qquad (1)$$

where W_i = average initial weight of three specimens (g) and W_t = average weight of three specimens after an exposure of t months (g).

The DSC test was performed on mortar samples taken from cubes exposed to sulfate environment for 48 months to determine the quantity of $Ca(OH)_2$ following the procedure as described before.

2.4.5. Assessments of electro-chemical behaviour of embedded steel

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 [32]. Its use and interpretation are described in the ASTM Standard Test Method for Half-Cell Potential of Reinforcing Steel in Concrete (ASTM C 876-1999). Measurement of d.c. polarization resistance with ohmic drop compensation has been applied since the 1970s and provides information about the corrosion rate [33].

Corrosion activity in this study was monitored up to an immersion period of 48 months by measuring the corrosion potentials and polarization resistance at regular intervals. The corrosion potentials were measured 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 (ASTM C 876). The half-cell potential data collected using this technique gives a qualitative indication of the corrosion of reinforcing bars.

The linear polarization resistance technique was used to obtain quantitative information on the performance of concrete specimens in inhibiting reinforcing bar corrosion. The linear polarization resistance (Rp) was determined by running a polarization-resistance scan in the range of ±10 mV of the corrosion potential using a potentiostat/galvanostat with IR compensation. A stainless steel frame placed outside the specimen was used as a counter-electrode, while a saturated calomel electrode was used as a reference electrode. Fig. 1 shows the experimental set-up for the polarization resistance measurements. 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.

2.4.6. Failure criterion due to sulfate attack

Concrete deterioration due to mixed magnesium–sodium sulfate environment is typically manifested by a progressive degradation leading to deterioration and weight loss and is also associated with increased softening and disintegration of the hardened cement matrix, characterized by non-cohesiveness and spalling of the surfaces. These features of binder decomposition akin to eating away of the hydrated cement paste leaving the aggregates exposed are best assessed by the weight loss of concrete materials as illustrated in this study. The strength reduction criterion is not applicable for the specimens used in this investigation while the length change criterion is not suitable for this type of sulfate attack.

With regard to establishing a failure criterion based on weight loss, Cohen and Mather [2] have reported that a loss of 5% (for beams) and 2.5% (for cubes) is to be adopted.

2.4.7. Failure criterion due to steel corrosion

ASTM C 876 criterion can be used to indicate whether the rebars were in an active state of corrosion or not, based on half-cell polarization resistance values. A threshold value of −270 mV SCE (based on saturated calomel electrode) can be used as per ASTM C 876.

Table 5
Strength, durability and micro-structural properties of concrete

Mix ID	28-day density kg/m^3	28-day compressive strength (MPa)	RCP (C)	Porosity (% v/v)	Avg. pore diameter (μm)	Ca(OH)$_2$ Endothermic peak area (J/g)	
						56 days[a]	48 months[b]
Series A: W/B=0.45							
AType I	2401	38	2850	16.46	0.0464	105	75
AType V	2403	37	2805	16.39	0.0461	99	70
A20VA-I	2384	32	2210	14.95	0.0435	72	[c]
A20VA-V	2380	31	2186	14.89	0.0428	67	23
A20VP-I	2365	31	2321	15.40	0.0444	77	29
A20VP-V	2360	30	2316	15.35	0.0438	69	25
Series B: W/B=0.35							
BType I	2410	49	2350	15.10	0.0432	102	74
BType V	2408	48	2306	15.03	0.0427	95	72
B20VA-I	2401	41	1920	13.20	0.0402	71	25
B20VA-V	2398	40	1905	13.11	0.0395	65	21
B20VP-I	2372	42	1985	13.60	0.0413	73	31
B20VP-V	2370	41	1966	13.51	0.0403	67	[c]

[a] Exposed to normal water curing.
[b] Exposed to sulfate solution.
[c] Not tested.

The polarization resistance (PR) values can also be used to predict the time for initiation steel reinforcement corrosion for the embedded rebars in the various concrete mixtures via the use of Eq. (2).

$$C = A/\mathrm{PR} \tag{2}$$

where C=density of corrosion current in μA cm^2; $A=(\alpha_a * \alpha_c)/[2.3(\alpha_a+\alpha_c)]$; α_a and α_c=anodic and cathodic Tafel constants, respectively.

In absence of sufficient data on α_a and α_c for steel in concrete, a value of A equal to 26 in the active state of corrosion is frequently used [34]. Further, if current density (C) is greater than 0.3 μA cm^2 (corresponding to a PR value of 87 kΩ cm^2), the reinforcing steel will certainly be in an active state, and if C is less than 0.1 μA cm^2 (corresponding to a PR value of 260 kΩ cm^2), it is certainly passive [34]. It is therefore, logical to set the PR value of 87 kΩ cm^2 as a threshold value for corrosion activation.

3. Results

3.1. Fresh properties of VA/VP based concrete mixtures

Table 4 presents the slump and air content of concrete mixtures. The slump of Series A concrete mixtures with W/B of 0.45 (without SP) ranges between 78 and 110 mm while slump in Series B with W/B of 0.35 (with SP) ranges between 80 and 107 mm. Addition of VA seems to increase the slump of concrete mixtures. The air content of Series A concrete mixtures ranges between 2.5% and 3.1% while those in Series B ranges between 2.2% and 2.8%. Increase in W/B increases the air content of Series A concrete mixtures compared to Series B. However, use of SP might also have a influence in the reduction of air content in Series B. Type of cements either Type I or Type V seems to have no influence on the fresh properties of concrete mixtures.

3.2. Strength, durability and micro-structural characteristics of concrete mixtures

Table 5 summaries strength and density (at 28 day) of concrete mixtures as well as test results of RCP, MIP and DSC tests conducted at 56 day. 28-day density of concrete mixtures ranges between 2360 and 2410 kg/m^3. In general, findings can be summarized as: (i) Type I/V VA/VP based blended concrete showed lower strength, higher chloride ion resistance and lower porosity/average pore diameter than Type I/V plain concrete: this can be attributed to the fact that the strength gain of VA/VP based pozzolanic concrete is not merely related to lowering of porosity, (ii) concrete mixtures with higher W/B showed lower strength, lower chloride ion resistance and higher porosity/average pore diameter and (iii) use of type V cements showed slightly better chloride ion resistance and lower porosity with no visible strength gain compared to Type I and (iv) VP based concrete showed lower chloride ion resistance and higher porosity compared with VA based concrete with no significant 28-day strength difference.

Upon hydration of cement, VA and VP 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. DSC analysis mortars taken from crushed concrete (Table 5) reveal that the calcium hydroxide content of the VA and VP blended concrete is lower than that of the plain concrete. This indicates that the pozzolanic reactivity of VA and VP consumes calcium hydroxide resulting from hydration of the cement. Such pozzolanic reaction of VA and VP with calcium hydroxide, produces a denser concrete and thus inhibits the ingress of

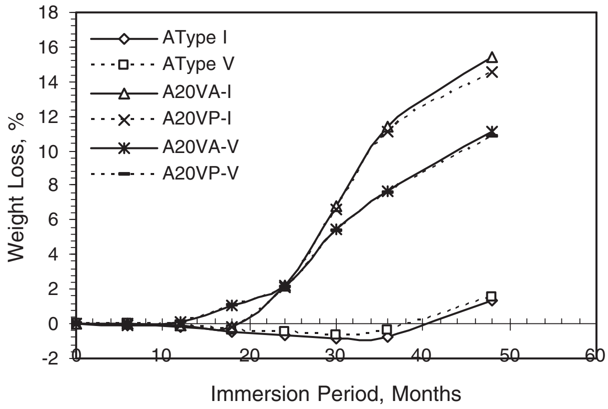

Fig. 2. Variation of weight loss with immersion period (Series A with W/B of 0.45).

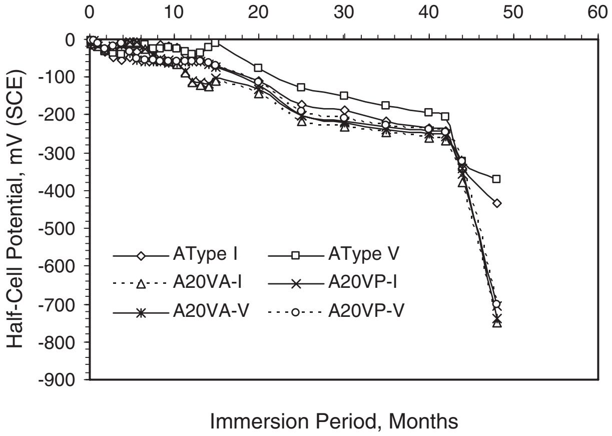

Fig. 4. Variation of half-cell potential with immersion period (Series A).

chloride ions. This can improve the chloride induced corrosion resistance of VA and VP based concrete mixes compared to plain concrete mixes [28]. This is confirmed from lower porosity and higher chloride ion resistance of VA and VP based concrete as observed in this study (Table 5). Previous studies showed that the incorporation of VA and VP as cement replacement in paste and mortar lead to the refinement of pore structure and to the decrease of total pore volume with the increase of curing age [26–28]. Investigation also showed that VA and VP addition improves the concrete resistance against chloride induced corrosion of embedded reinforcement [28]. However, the mechanism of sulfate induced deterioration is different than chloride induced deterioration.

3.3. Deterioration of concrete exposed to mixed sulfate environment based on weight loss

The weight loss of various concrete specimens exposed to sulfate solution with immersion period is presented in Figs. 2 and 3. Results exhibited initially a marginally negative weight loss/gain in weight which is more pronounced in Type I and Type V plain concrete mixtures in Series A with W/B of 0.45 (Fig. 2). This phenomenon is attributable to the filling up of pores by the expansive reaction products, thereby densifying the hardened mortar mix and increasing the weight and strength [33]. Subsequently, the disruption of the hydrated cementitious matrix by these expansive reaction products resulted in a decrease in the weight of specimens, thus increasing the weight loss with immersion period. A decrease in W/B from 0.45 (Series A) to 0.35 (Series B) decreases the negative weight loss phenomenon (Figs. 2 and 3).

Type I VA/VP blended concrete mixes show an increase in weight loss after about 18 months compared with about 10 months for Type V VA/VP blended concrete mixes and 40 months for Type I/V plain concrete mixes (Series A, Fig. 2). The overall weight loss is higher in Type I VA/VP blended concrete mixes compared to Type V VA/VP blended concrete mixes and Type I/V plain concrete mixes. Type I/V plain concrete mixes showed the lowest weight loss compared with Type I/V VA/VP concrete mixes (Fig. 2: Series A). Type I and Type V plain concrete mixes in Series A showed similar weight loss throughout the immersion period of 48 months.

For Series B, weight loss increase seemed to be started earlier (within 10 months for all concrete mixes) than Series A mixes. Unlike in Series A, Type I plain concrete mixes showed higher weight loss compared to Type V plain concrete mixes in Series B (Fig. 3). Similar to Series A, Type I VA/VP blended concrete mixes showed higher weight loss compared to Type V

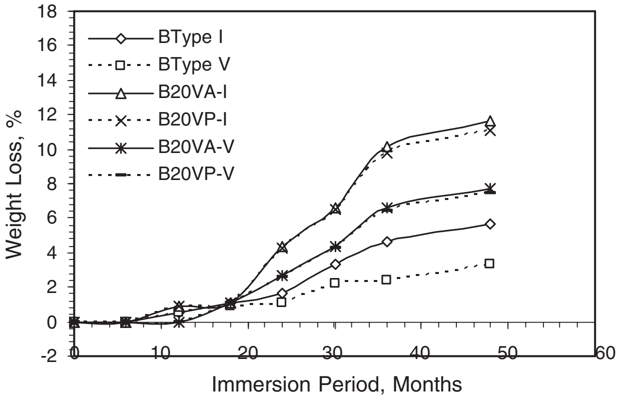

Fig. 3. Variation of weight loss with immersion period (Series B with W/B of 0.35).

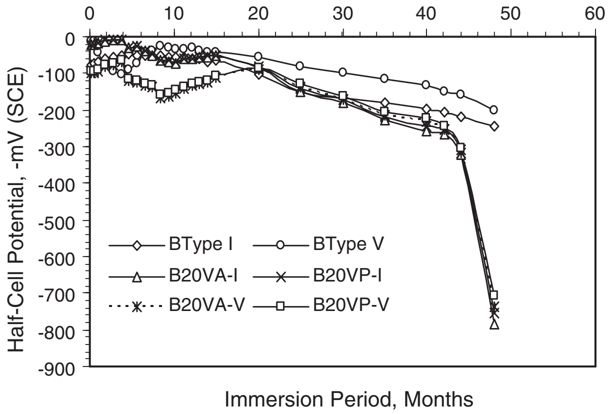

Fig. 5. Variation of half-cell potential with immersion period (Series B).

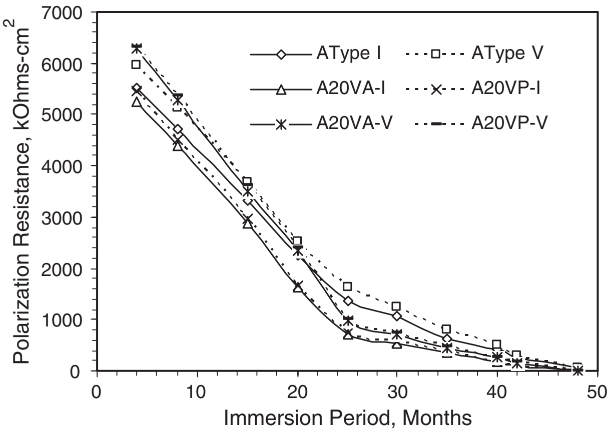

Fig. 6. Variation of polarization resistance with immersion period.

VA/VP based blended concrete mixes with the lowest weight loss observed in Type V plain concrete mixes.

VA and VP based concrete mixtures in Series A and Series B showed similar weight loss throughout the immersion period.

3.4. Corrosion potentials

The corrosion potentials on steel in various concrete specimens are presented in Figs. 4 and 5. These potential time curves were used to evaluate the time to initiation of rebar corrosion based on the ASTM C 876 criterion of −350 mV copper–sulfate electrode (CSE), corresponding to −270 mV saturated calomel electrode (SCE). No significant difference in half-cell potential is observed between Type I VA/VP and Type V VA/VP concrete mixtures as well as between VA and VP based concrete mixtures. Type I/V plain concrete mixtures show less negative half-cell potential than Type I/V VA/VP based concrete mixtures. The rate of increase in negative potential increased significantly (may be due to initiation of active state of corrosion in these mixtures) beyond an immersion period of 42 months for Type I/V VA/VP based concrete mixtures. Figs. 4 and 5 indicate that rebars embedded in all concrete mixtures, except Types I and V with W/B of 0.35 (Series B), exhibited more negative potential than the −270 mV SCE after 48 months of immersion. Therefore, the steel in these concrete specimens was in an active state of corrosion.

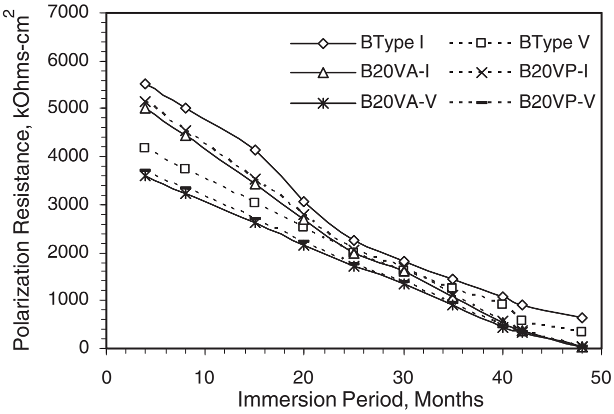

Fig. 7. Variation of polarization resistance with immersion period.

3.5. Polarization resistance

The variation of polarization resistance with immersion period in various concrete mixtures is presented in Figs. 6 and 7. Initial polarization resistance on steel in various concrete mixtures was very high (ranging between 5200 and 6400 kΩ cm^2 for Series A with W/B 0.45; between 3600 and 5600 kΩ cm^2 for Series B with W/B 0.35). The polarization resistance decreased significantly (rate of decrease seems to be higher in Series A with W/B of 0.45 compared to Series B with W/B of 0.35) in an immersion period of 48 months.

4. Discussion

Table 6 shows the variation in the performance of the 12 concrete mixtures in the magnesium–sodium sulfate test solutions after a long-term exposure period of 48 months in terms of weight loss, corrosion potential and polarization resistance. Fig. 8 shows typical deterioration of concrete samples after 48 months of exposure in magnesium–sodium sulfate solutions.

4.1. Effect of type of cement and C_3A content on sulfate attack

The 48-month polarization resistance did not clearly indicate the effect of type of cements (Type I or V) in plain and VA/VP based concrete mixtures. However, based on 48 months corrosion potential data, Type V cements seems to show a slightly better performance in terms of corrosion resistance than Type I cements in both plain and blended cement concretes (Table 6). The 48-month weight loss of Type V plain and VA/VP based concrete mixtures was generally lower compared to those of Type I VA/VP based concrete mixtures with the exception of Type V having a W/B of 0.45 (Table 6).

Table 6
Weight loss, corrosion potential and polarization resistance after 48 months of exposure

	Concrete weight loss (%)	Corrosion potential, SCE (mV)	Polarization resistance (kΩ cm^2)	Corrosion initiation (months)
W/B = 0.45				
Type I	1.34	−434	51	44
Type V	1.51	−372	69	44
20VA-I	15.4	−749	22	44
20VP-I	14.6	−704	22	44
20VA-V	11.1	−738	8	44
20VP-V	10.9	−701	8	44
W/B = 0.35				
Type I	5.7	−245	630	No corrosion
Type V	3.3	−203	347	No corrosion
20VA-I	11.6	−784	25	44
20VP-I	11.0	−753	26	44
20VA-V	7.7	−736	40	44
20VP-V	7.5	−707	41	44

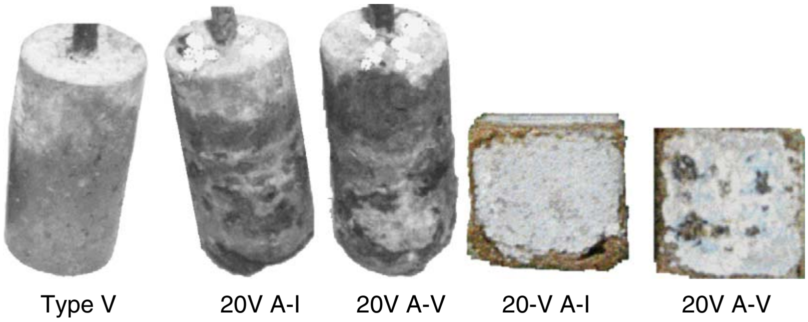

Fig. 8. Typical deterioration of concrete samples after 48 months of exposure (W/B = 0.45).

Neville [35] observed no significant difference between the performance of Type V sulfate resisting and Type I (C_3A content of 9%) cements upon exposure of concrete specimens to both weak and saturated $MgSO_4$ solutions. Previous research also observed no significant difference between the performance of ASTM Type I and Type V cements when both were exposed to a marine environment [36]. About 8% C_3A is typically needed to consume the gypsum that is invariably added to regulate the time of set during the early hydration of cement [37]. Consequently, for the Type I Portland cement used in this study, only 0.1% C_3A would remain to react with sulfates, which is unlikely to cause extensive damage. Kalousek et al. [6] confirms that limitations on C_3A and C_4AF contents are not the ultimate answer to the problem of sulfate attack. This situation may also be explained from the mechanisms of sodium sulfate and magnesium sulfate attack as summarized in the following equations [38]:

$$CH + NS + 2H \rightarrow CSH_2 + NH \tag{3}$$

$$CH + MS + 2H \rightarrow CSH_2 + MH \tag{4}$$

$$C_4AH_{13} + 3CSH_2 + 14H \rightarrow C_6AS_3H_{32} + CH \tag{5}$$

$$C_4ASH_{12} + 2CSH_2 + 16H \rightarrow C_6AS_3H_{32} \tag{6}$$

$$C_3A + 3CSH_2 + 26H \rightarrow C_6AS_3H_{32} \tag{7}$$

$$C_xSi_yH_z + xMS + (3x + 0.5y - z)H \rightarrow xCSH_2 + xMH + 0.5ySi_2H \tag{8}$$

$$4MH + SiH_n \rightarrow M_4SiH_{8.5} + (n - 4.5)H \tag{9}$$

where C = CaO, N = Na_2O, M = MgO, S = SO3, Si = SiO_2, H = H_2O.

In sodium sulfate (NS) environment, NS reacts with calcium hydroxide (CH) to form calcium sulfate (gypsum, CSH_2) as per Eq. (3). This reaction may eventually continue to completion, i.e., leaching of all CH. Calcium sulfate formed can subsequently react with C_3A, usually via the formation of monosulfoaluminate, to form ettringite ($C_6AS_3H_{32}$) as per Eq. (7). It is to minimize the reaction with C_3A that Type V cement was developed. In magnesium sulfate (MS) environment, MS reacts with all products of hydration of cement; the important resulting compounds are calcium sulfate and brucite (MH) as in Eq. (4). Calcium sulfate can proceed to react with C_3A to form ettringite, eventually. Specifically, in the case of sodium sulfate, the use of cement with a low C_3A content minimizes the extent of reaction with sodium sulfate and, therefore, of the formation of ettringite.

In mixed sulfate environment, the mode of sulfate attack is predominantly controlled by MS due to generation of brucite (MH) as in Eq. (4). Brucite being insoluble (its solubility is 0.01 g/l compared to 1.37 g/l for CH) and its saturated solution having a pH of about 10.5, causes the destabilization of both ettringite and calcium silicate hydrate (C–S–H). The formation of secondary ettringite is significantly hindered in such environments. C–S–H decomposes, liberating CH. This CH reacts with MS and forms further brucite and gypsum. This reaction continues until gypsum is crystallized out [39]. Brucite reacts also with silicate hydrate arising from the decomposition of C–S–H, and results in the formation of magnesium silicate hydrate, which lacks cohesive properties. These reactions take place even when the C_3A content in the cement is very low [39]. Accordingly, this type of sulfate attack is typically characterized by a deterioration akin to eating away of hydrated cement mortar/paste and progressively reducing it to a cohesionless granular mass that may expose the aggregate in case of concrete associate with loss of strength. This type of sulfate attack is mainly attributed to the formation of gypsum as in Eqs. (3) and (4). Since ettringite ceases to be a deteriorating parameter in mixed sulfate environments, the role of C_3A content in sulfate attack (Eqs. (5)–(7) will not be effective. Accordingly, sulfate attack in plain cements will be initiated by Eqs. (3) and (4) and will proceed directly to Eqs. (8) and (9). These reactions (Eqs. (3), (4), (8) and (9) do not involve any aluminate phase in the deterioration mechanisms and, therefore, the ettringite formation will practically be inhibited. Consequently, the influence of C_3A content on the sulfate attack in mixed sulfate environments does not appear to be crucial as is the case in Na_2SO_4 environments.

Although two types of Portland cements with a C_3A content varying in the range of 3.5% (Type V) to 8.5% (Type I), the results of weight loss, corrosion potential and polarization resistance show that the sulfate attack is not totally or predominantly controlled by the C_3A content.

4.2. Effect of W/B

A reduction in the W/B from 0.45 to 0.35 enhanced the weight loss of both Types I and V plain cement concrete mixtures. Type I and Type V plain concrete mixes with W/B of 0.45 had a weight loss of 1.34% and 1.51%, respectively, after an exposure period of 48 months compared with 5.7% and 3.3% for the same concrete mixtures with W/B of 0.35 (Table 6). Such deleterious effect of lower W/B is also reported from other research studies [6,20,37]. A likely explanation is that at low W/B, there is limited pore space to accommodate the products of reaction with sulfate namely, magnesium silicate hydrate (which has no adhesive properties) and gypsum. However, Kalousek et al. [6] stated that actual effect of high W/B on sulfate resistance is not clearly understood.

Despite the higher degree of sulfate deterioration in low W/B concrete mixtures (W/B = 0.35), the low negative corrosion potentials and high polarization resistance values reveal that their embedded reinforcing steel was still in a passive state compared with those of high W/B of 0.45 after 48 months of immersion (Table 6). This can be attributed to the fact that the initiation of corrosion in embedded steel is not only a function of concrete deterioration.

4.3. Effect of VA and VP on sulfate resistance

Concrete specimens with W/B of 0.45 exhibited an increase in weight loss from 1.34% (Type I plain cement) to 15.4% (Type I VA and VP blended cements) within the 48 month of immersion period (Table 6). An increase in weight loss from 5.7% (Type I plain cement) to 11.6% (Type I VA and VP blended cements) was observed in specimens with a W/B of 0.35. Concrete specimens with W/B of 0.45 exhibited an increase in weight loss from 1.5% (Type V plain cement) to 11.1% (Type V VA and VP blended cements). An increase in weight loss from 3.3% (Type V plain cement) to 7.7% (Type V VA and VP blended cements) was observed in specimens with a W/B of 0.35. Type I/V VA/VP based blended cement concrete specimens showed higher and faster rate of deterioration than those of Type I/V plain cement concrete specimens. Similar faster rate of deterioration was observed in specimens with fly ash, silica fume and slag blended cements in magnesium-based sulfate environment [40–42]. The higher deterioration in Type I and Type V VA/VP based blended cement concretes in sulfate environment compared to Type I and Type V plain Portland cement concretes can be attributed to the presence of Mg^{2+} cations associated with $MgSO_4$. The consumption of portlandite ($Ca(OH)_2$) by the pozzolanic reaction in VA and VP blended cements causes Mg^{2+} cations to react directly with the calcium silicate hydrate (C–S–H) gel converting it to cohensionless, porous, reticulated magnesium silicate hydrate (M–S–H) gel as illustrated in Eqs. (8) and (9).

The consumption of $Ca(OH)_2$ by pozzolanic reaction is evidenced by the presence of lower quantity of $Ca(OH)_2$ in Type I/V VA/VP based blended cement concrete compared to Type I and Type V plain cement concrete without exposure to sulfate environment (at 56 days) and after exposure to sulfate environment for 48 months (Table 5 based on DSC analysis).

It is also noted that the Type I/V VA/VP based blended cement concrete specimens exhibited weight loss which were more than the 2.5% failure criterion (Table 6). Use of Type V cements reduced the deterioration of VA/VP based concrete specimens compared with those of Type I possibly due to lower C_3A content.

The type I/V VA/VP based blended cement concretes showed inferior performance compared with Type I/V plain cement concretes in terms of corrosion resistance at 48 month of immersion. This could be attributed to the advance stage of deteriorations (in Type I/V VA/VP based blended concretes) at this period whereby a weight loss that ranged between 7.47% and 15.4% (Table 6) which is higher than 2.5% was observed. High degree of deterioration in blended cement concrete mixtures could not preserve the integrity of the internal structure and enabled the SO_4 ions to diffuse to the steel, leading to corrosion of reinforcing steel. On the contrary, the specimens made with plain Type I/V cements exhibited better resistance to sulfate attack, especially specimens with W/B of 0.35 where reinforcing steels were not found to be in active state of corrosion (polarization resistance $> 87\ \mathrm{k\Omega\ cm^2}$) after 48 months of exposure. This might be attributed to the mechanism of $MgSO_4$ attack as well as to the diffusion of SO_4 ions.

5. Conclusions

The deterioration and corrosion resistance of volcanic ash (VA) and finely ground volcanic pumice (VP) based Type I and Type V blended cement concretes in mixed magnesium–sodium sulfate environment for an immersion period of 48 months are evaluated through physico-chemical deterioration of concrete and electro-chemical behaviour of embedded steel. The influence of type of cement (ASTM Type I or V to be used in VA or VP based blended cements) and water-to-binder ratio on sulfate resistance is also studied. The following conclusions are drawn from the study:

1. Type I/V VA/VP based blended cement concrete mixtures exhibited an advanced stage of deterioration (poor performance) when compared to Type I/Type V plain cement concrete mixtures after 48 months of immersion in mixed sulfate environment. This can be attributed to the consumption of portlandite by the pozzolanic reaction in VA/VP blended cements that causes Mg^{2+} cations to react directly with C–S–H gel converting it to cohensionless, porous, reticulated M–S–H gel.
2. Use of Type V cements reduced the deterioration of VA/VP based blended concrete specimens compared with those of Type I. However, Type I/V VA/VP based blended cement concrete specimens exhibited weight loss which were more than the 2.5% failure criterion.
3. A reduction in the W/B from 0.45 to 0.35 enhanced the weight loss (deterioration) of both Type I and V plain cement concrete mixtures possibly due to the limited pore space to accommodate the products of reaction with sulfate. However, a decrease in W/B from 0.45 to 0.35, decreases the weight loss of Type I/V VA/VP based cement concretes.
4. Type I/V VA/VP based blended cement concrete mixtures showed inferior performance compared with Type I/V plain cements in terms of corrosion resistance after 48 months. Specimens made with plain Type I/V cements exhibited better resistance to sulfate attack, especially specimens with W/B of 0.35 where reinforcing steels were not found to be in active state of corrosion after 48 months of exposure.

The results presented in this study will provide assistance to the readers in understanding the performance of Type I/V VA/VP based blended cement concretes in mixed sulfate environment.

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