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Pumice based blended cement concretes exposed to marine environment: Effects of mix composition and curing conditions

Khandaker M. Anwar Hossain *

Department of Civil Engineering, Ryerson University, 350 Victoria Street, Toronto, Ontario, Canada M5B 2K3

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Abstract

Results of an investigation on concrete specimens made with different plain (ASTM Type I, II, and V) and blended cements incorporating different percentages of finely ground pumice up to 30% (as cement replacement) exposed to marine environment for a period of 1 year are presented. Different combinations of mixing water and initial curing conditions simulating cast-in-situ and precast conditions of concreting in marine environment are studied. Blending of Type I and Type II cements with pumice (between 10% and 20%) has shown better resistance against seawater attack than Type V cement with low C_3A. The performance of pumice based concrete mixtures is assessed based on the strength reduction criteria and is supported by data from rapid chloride permeability, porosity and differential scanning calorimetry tests. It is recommended that Type I cement with pumice content between 10% and 20% would be a better choice in marine environment. Results also show that the use of precasting instead of casting-in-situ could considerably mitigate the deleterious effect of marine environment on concrete specimens.

Keywords: Blended pumice cement concrete; Marine environment; Compressive strength; Permeability; Porosity

1. Introduction

The search for alternative binders or cement replacement materials has been continued for the last several decades. Research has been carried out on the use of volcanic ash, pumice, fly ash (FA), blast furnace slag, rice husk ash, silica fume etc. as cement replacement material [1–6]. Volcanic ash, pumice and FA are pozzolanic materials, because of their reaction with lime (calcium hydroxide) liberated during the hydration of cement. Amorphous silica present in the pozzolanic materials combines with lime and forms cementitious materials. These materials can improve the durability of concrete and can also reduce the rate of liberation of heat due to hydration, which is beneficial for mass concrete.

Comprehensive research has been conducted over the last few years on the use of volcanic ash and pumice in cement and concrete production [1,7–9]. The meaningful use of such volcanic materials can transform them into natural resources and can provide low cost cement and concrete. Research suggested the manufacture of blended cements incorporating up to 20% volcanic ash and pumice as replacements of Portland cement [1].

It is essential that the concretes made with volcanic ash and pumice based blended cements should preserve their durability throughout the intended service life of structures. Until recently little research had been conducted on the degradation of such concretes subjected to aggressive marine environment [2,10–13].

The concomitant presence of sulfate and chloride ions in marine environments causes deterioration of reinforced concrete structures and reinforcement corrosion. The effect of the conjoint presence of chlorides and sulfates on the sulfate resistance of hydrated Portland cements is inconclusive and highly debated [14,15]. The sulfate ions react with the hydration products of cement, namely C_3A and $Ca(OH)_2$, to produce expansive and/or softening types of

* Tel.: +1 (416) 979 5000x7867; fax: +1 416 979 5122.
E-mail address: ahossain@ryerson.ca

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deterioration. The sulfate attack in marine environment gives rise to expansive ettringite, gypsum, and brucite and sometimes is associated with calcite formation [16–20].

The sulfate resistance of concrete structures in marine environment can be improved by controlling sulfate permeation into concrete. The sulfate attack can be prevented either by changing cement from ASTM Type I to Type II or Type V or by introducing pozzolana such as fly ash, blast furnace slag, volcanic ash and pumice in concrete [10,14,20–26].

ASTM C 150 Type V cement, with a low C_3A, is recommended in structures placed in such environment. Typically, Type I cement contains between 8% and 12% C_3A, as defined by ASTM C 150, 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 [20,27–29]. This increase in C_3S/C_2S ratio results in an increased calcium hydroxide content in the hardened cement concrete. Thereby, enhancing the susceptibility of such cements to softening type of sulfate attack [20,27–29].

The sulfate permeation can also be controlled by increasing compactness, lowering water/cement ratio, proper curing, surface treatment, and use of precast concrete in place of cast-in-situ concrete [28–30].

It is reported that the limitation on C_3A content is not the ultimate answer to the problem of sulfate attack [21,27,29]. The use of blended cement made with fly ash, silica fume, and blast furnace slag is therefore recommended in sulfate environments [14,17,20,23]. In addition, studies have shown that blended cement concrete has an increased resistance to chloride penetration in structures exposed to seawater [14,20,27].

The evaluation of pumice based blended cement concrete performance in seawater environments will provide useful information for its use in such environments. Also, the type of cement, Type I, II, or V, to be used in pumice based blended cement concrete exposed to sea environments has not been clearly established yet. Often, there is a concern as to the type of cement to be used with supplementary cementing materials for structures exposed to marine environments.

To assess the preceding concerns, plain and blended cement concrete specimens made with different proportions of pumice were exposed to seawater attack in different simulated conditions. Incorporation of Type I, Type II, and Type V cements blended with finely ground pumice has significant practical interest as pumice can be found in many places around the world.

2. Experimental program

2.1. Materials

Pumice used in this investigation was collected from the Rabaul area of the East New Britain province of Papua New Guinea (PNG) and the source was a volcano called Mount Tavurvur. ASTM C 150 Type I, Type II, and Type V cements were used in preparing the concrete specimens. Blended cements were prepared by replacing 10%, 20%, and 30% of these cements with finely ground pumice. The chemical composition of cements and pumice used in this investigation is provided in Table 1. It was noted that the properties of pumice from the specific PNG source did not vary significantly from time to time.

The coarse aggregate was 20-mm maximum size crushed stones having a bulk density of 2.5 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 (OW) from the water supply and seawater (SW) were used for making concrete.

2.2. Mix proportions, specimen preparation and curing

Concrete mix proportions used for plain and blended cement concrete are presented in Table 2. Usually in marine environments, relatively richer mixes with low water to binder ratio (W/B) are used. This aspect was kept in mind in planning the experimental program. Concrete cubes of 150-mm and cylinders (100-mm dia and 50-mm height) were cast. Depending upon the ingredients used in mixing

Table 1
Comparative study of chemical and physical properties

Oxide compounds (Mass %)	Pumice	Portland cement		
		Type I	Type II	Type V
Calcium oxide (CaO)	6.1	64.1	64.7	65.0
Silica (SiO_2)	59.3	21.4	21.7	21.9
Alumina (Al_2O_3)	17.5	5.7	4.2	3.2
Iron oxide (Fe_2O_3)	7.0	3.5	3.3	3.9
Sulphur trioxide (SO_3)	0.7	2.1	2.3	2.5
Magnesia (MgO)	2.6	2.1	1.9	2.2
Sodium oxide (Na_2O)	3.8	0.5	0.2	0.3
Loss on ignition	1.0	1.1	0.9	0.8
Fineness, m^2/kg	285	320	377	373
Specific gravity	2.04	3.14	3.14	3.14
Tricalcium silicate (C_3S)	–	53.4	58.7	63.8
Dicalcium silicate (C_2S)	–	19.2	17.8	14.6
Tricalcium aluminate (C_3A)	–	9.5	5.6	1.8
Tetracalcium aluminoferrite (C_4AF)	–	10.5	10.0	11.8

Table 2
Details of concrete mixes

Mix	Binder (B) (kg/m^3)		Aggregates (kg/m^3)		Fresh properties
	Cement (C)	Pumice (P)	Fine	Coarse	Slump (mm)*
0%P	415	0	620	1240	75–80
10%P	375	40	606	1240	70–75
20%P	330	85	596	1240	68–72
30%P	290	125	585	1240	66–70

W/B = 0.40 (B = C + P): W = Water; B = Binder.
* For various mixing compositions and varying type of cement.

compositions and curing conditions, the concrete cubes were divided into three simulated groups denoted by OWOW (control concrete), SWSW (cast-in-situ) and OWSW (precast), as presented in Table 3. In this study, seawater (SW) was used as mixing water for making cast-in-situ concrete specimens while ordinary drinking water (OW) was used for the rest. The slump values of concrete mixes are presented in Table 2. All concrete mixtures showed satisfactory workability with no segregation. The air content of fresh concrete mixtures ranged between 2.5% and 3.0%. The normal water curing of the specimens was performed in laboratory curing tanks. For seawater curing, the specimens were subjected to actual sea conditions. The selected site was the shoreline of the Solomon Sea situated within the protected area of Papua New Guinea Halla cement factory in the city of Lae. The concrete cubes and cylinders cured in seawater were kept completely submerged in seawater. However, in the splashing zone, due to wetting and dry effects, the concentrations of salts can be higher than in the bulk seawater.

2.3. Test procedures

The criterion selected for the comparative evaluation of resistance of concrete under marine conditions, was the extent of strength reduction (SR) as a result of seawater exposure supported by data from permeability, porosity and differential scanning calorimetry (DSC) measurements. The compressive strengths of specimens in all the cases were determined as per standard procedure after 28, 91, 180, 270, and 360 days of casting. The compressive strength reduction (SR_t) of concrete was defined as

$$SR_t = (1 - S'_t/S_t) \times 100 \tag{1}$$

where S'_t is the average compressive strength (MPa) of concrete specimens after exposure to marine environment for a period of t days and S_t is the average compressive strength (MPa) of concrete specimens in the absence of marine environment after time t, where t is the curing period in days.

Rapid chloride permeability (RCP) test was conducted as per ASTM C 1202–97 [31] on 100 (diameter) × 50-mm concrete cylinders at 28-day and at 365-day of immersion in various curing conditions to determine resistance to chloride ion penetration. The porosity and pore size distribution were measured using Mercury Intrusion Porosimetry (MIP), which had a measuring pressure ranging from 0.01 to 200 MPa [2]. The differential scanning calorimetry (DSC) test was performed on the hardened mortar samples taken from the crushed concrete cubes (OWSW sample only) after 1 year curing (in seawater) to determine the quantity of Friedel's salt formed due to chloride binding and also quantity of $Ca(OH)_2$ formed in the mortars.

Table 3
Mixing and curing conditions

Designation[a]	Water used for mixing	Water used for curing	Remarks on specimens
OWOW	Ordinary water	Ordinary water	Control concrete cubes
SWSW	Seawater	Seawater	Concrete cubes (considered in this study as cast-in-situ situation)
OWSW	Ordinary water	Initially cured in ordinary water for 28 days, and subsequently cured in seawater	Concrete cubes reflecting precast situation[b]

[a] First two letters (either OW or SW) represent mixing water and the last two letters (either OW or SW) represent curing water; SWSW: cast-in-situ specimens; OWSW: precast specimens.

[b] Mimicked precasting operation in this study did not consider the achievement of high early strength and the reduction of curing period by elevating temperature (accelerated curing) as normally desired by the precast industry.

3. Results

3.1. Compressive strength reduction

The reduction in compressive strength (SR) in plain and pumice blended cement concrete specimens exposed to marine environments is shown in Figs. 1–6. It is noted that the SR value increases with the increase in age of concrete.

Concretes made with Type II and Type V plain cements are more resistant to seawater attack compared to those made with Type I plain cement (Figs. 1–3). Fig. 1 shows that 10% and 20% blending of pumice in Type I cement have increased concrete durability (in terms of strength) against seawater attack considerably. However, the blending of 30% pumice in cement has not shown any change in the SR value of concrete as compared to plain cement concrete specimens. The data on SRs for concrete with Type II cement specimens indicate a qualitative trend similar to that observed in Type I cement specimens (Fig. 2).

In general, concrete containing lower C_3A Portland cements (Type V cement) showed greater resistance to seawater attack. However, the blending of pumice in Type V cement concrete decreased the overall resistance of these concretes below that of a standard blended Type I Portland cement concrete. After 360-days of exposure to marine environment (as can be noted from Figs. 1 and 3), concrete made with Type I cement with 20% pumice replacement performs similar to Type V sulfate resisting cement in terms of improvement in concrete strength.

SR values for all concretes exposed to marine environments in OWSW are found to be relatively low compared with SWSW situations as per Figs. 1–6. In some cases, the losses have been reduced to even more than 30%. The reduction of strength associated with the use of SW (as mixing water) may be attributed to efflorescence (excessive leaching of salts) with subsequent increase in porosity as well as increased crystallization of ettringite (caused by the presence of dissolved salts especially high amounts of sulfate). The beneficial effect of pumice blending under OWSW conditions was observed more in concrete made

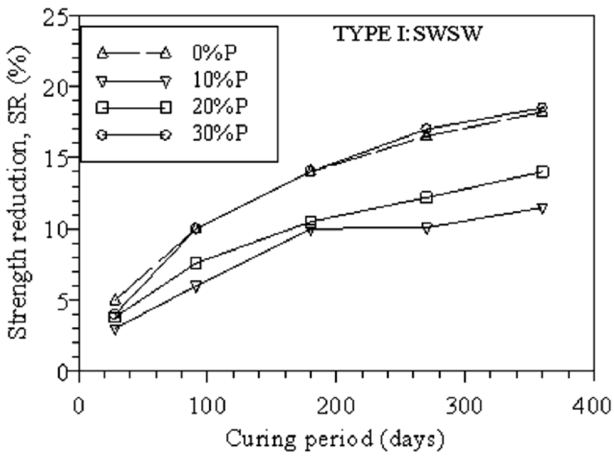

Fig. 1. Strength reduction in Type I concrete under SWSW.

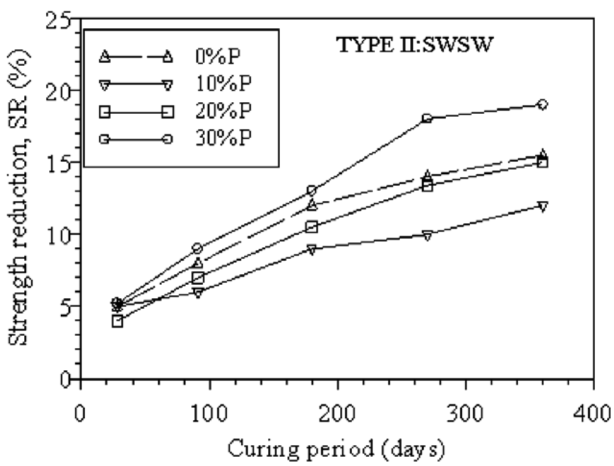

Fig. 2. Strength reduction in Type II concrete under SWSW.

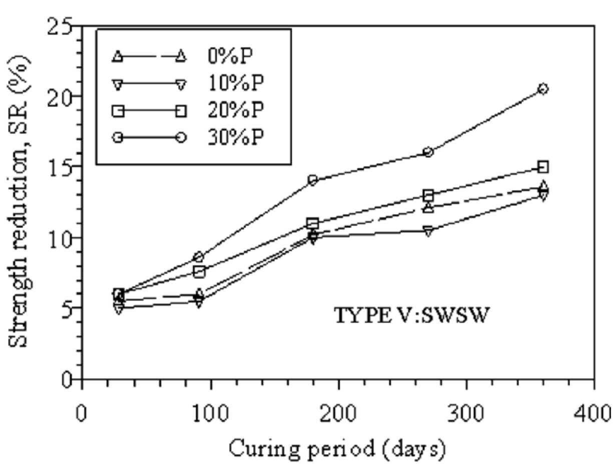

Fig. 3. Strength reduction in Type V concrete under SWSW.

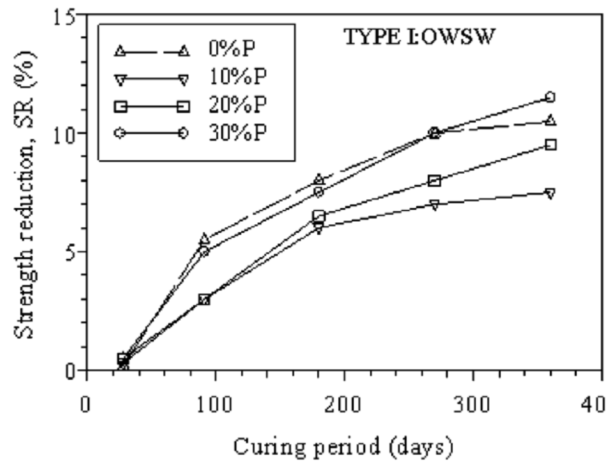

Fig. 4. Strength reduction in Type I concrete under OWSW.

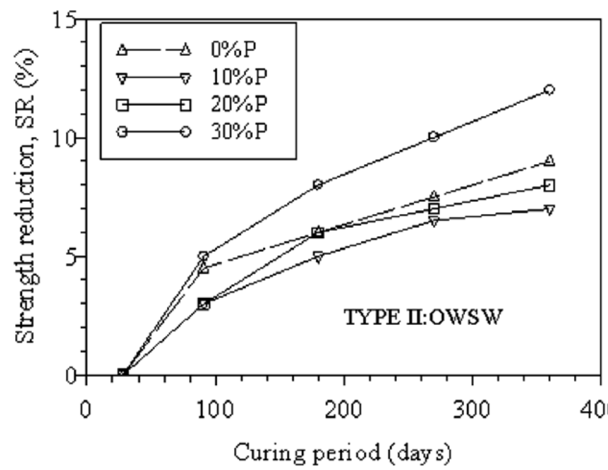

Fig. 5. Strength reduction in Type II concrete under OWSW.

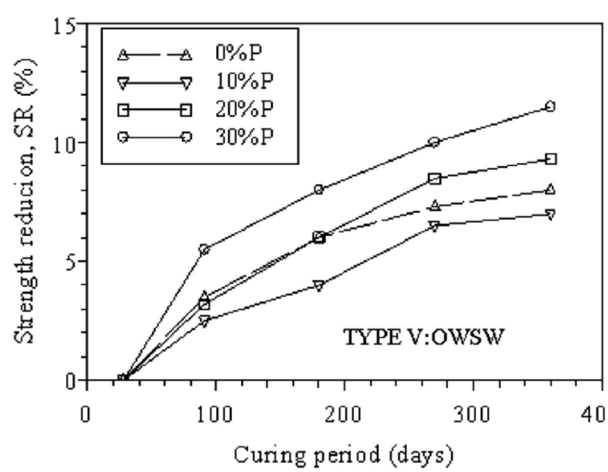

Fig. 6. Strength reduction in Type V concrete under OWSW.

with low pumice replacement of Type I, Type II, and Type V cements. Similar to concrete subjected to SWSW conditions, the blending of pumice in Type I and Type II cements was observed to be more beneficial than the blending in Type V cement under OWSW conditions (Figs. 4–6).

3.2. Development of compressive strength

The variation of compressive strength in Type I, II, and V cement concretes having varying % of pumice with different conditions of curing and mixing as well as curing period (28 and 360 day) is presented in Figs. 7–9. Strength development in all types of cement and curing conditions reveals that:

- strength increases with the increase of pumice content up to about 20% for Type I and Type II cements as can be seen from the 360-day strength (Figs. 7 and 8). The suitable range of pumice for blending is found to be between 10% and 20%. The strength enhancement with the increase of pumice is not evident at an early age (28-day) rather trend shows a decrease.
- strength decreases with the increase of pumice in Type V cement throughout the curing period of 360 days, which suggests that the blending is not beneficial in Type V cement (Fig. 9).

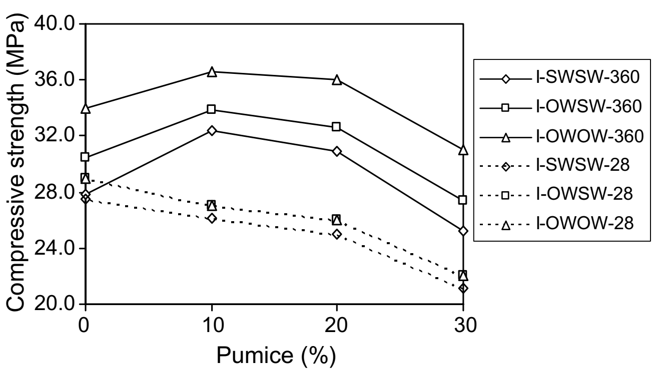

Fig. 7. Effect of various parameters on the compressive strength of Type I concrete.

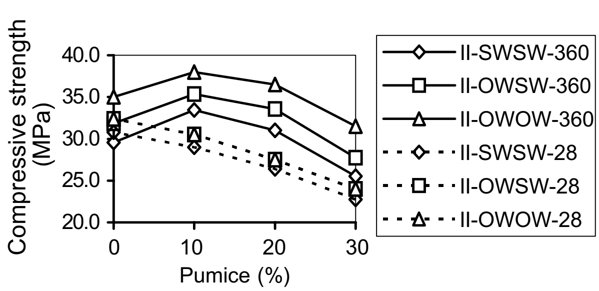

Fig. 8. Effect of various parameters on the compressive strength of Type II concrete.

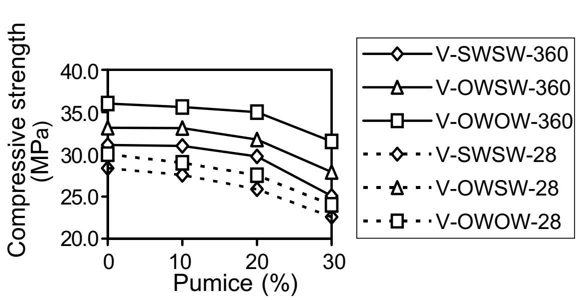

Fig. 9. Effect of various parameters on the compressive strength of Type V concrete.

- strength development is better in OWOW condition -followed by OWSW condition (Figs. 7 and 8). The lowest strength development is found in SWSW condition.
- OWSW concrete shows lower strength reduction compared to SWSW concrete (Fig. 10). The blended cement concrete with 10% pumice exhibits lowest strength reduction even lower than plain cement concrete (0% pumice). This clearly indicates the long-term beneficial effect of pumice in improving the performance of concrete in marine environment.
- Type I cement with appropriate blending of pumice (between 10% and 20%) is the potential choice for the construction of marine structures to improve corrosion resistance of reinforced cement concrete. This is in line with the recommendation of using 20% pumice in blended Portland volcanic pumice cement production using Type I cement [1].
- It is also found that the use of precasting (OWSW condition) in place of casting-in-situ (SWSW condition) increases the resistance of concrete against marine environments appreciably.

3.3. Porosity and rapid chloride permeability

The porosity and rapid chloride permeability (RCP) of plain/blended concrete mixes under OWOW, SWSW, and OWSW situations at 28-day and 365-day is presented in Figs. 11–15. The reduction in porosity with time and with the increase of pumice content is observed under OWOW (control concrete) situation (Fig. 11). The porosity of pumice blended concrete is lower in OWOW, OWSW, and SWSW situations compared with plain concrete (Figs. 11–13). The porosity decreases (Fig. 11) and chloride ion resistance increases (Fig. 14) for plain and blended concretes with age under OWOW situation with blended concrete showing lower porosity and higher chloride ion resistance than plain concrete as pumice content increases. However, types of cements seem to have little influence on porosity and chloride ion resistance under OWOW situation.

On the other hand, porosity increases (Figs. 12 and 13) and chloride ion resistance decreases (Figs. 14 and 15) for plain and blended concretes with age under both SWSW

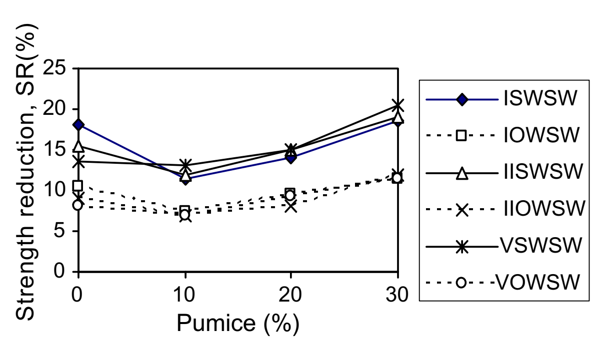

Fig. 10. Strength reduction as a function of pumice content.

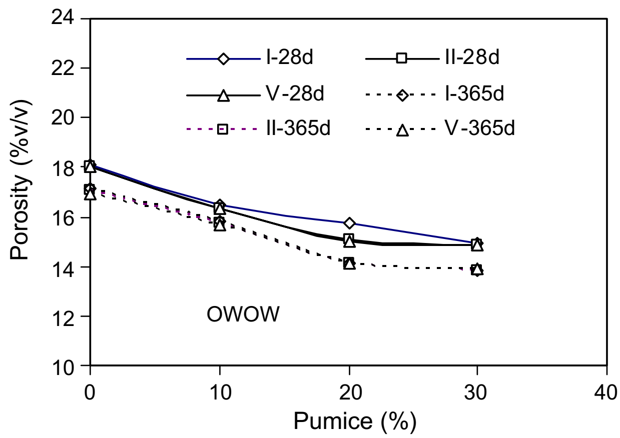

Fig. 11. Influence of pumice content, age and types of cement on porosity.

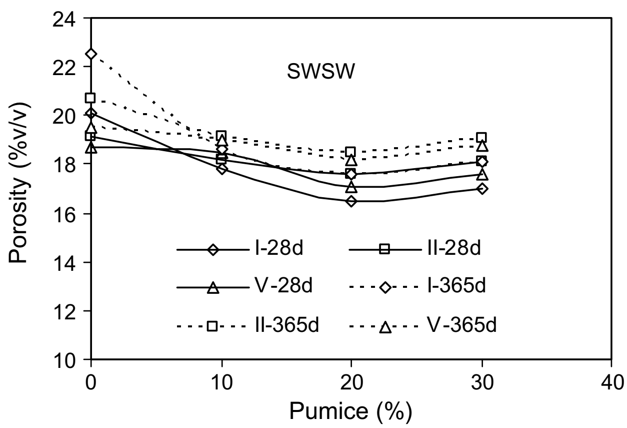

Fig. 12. Influence of pumice content, age and types of cement on porosity.

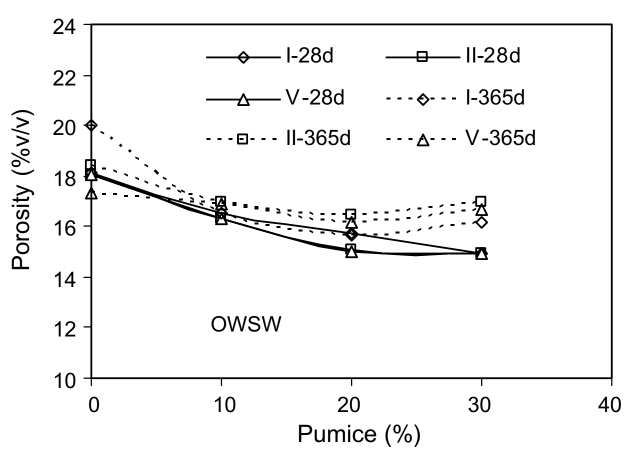

Fig. 13. Influence of pumice content, age and types of cement on porosity.

(cast-in-situ) and OWSW (precast) situations with blended concrete showing lower porosity and higher chloride ion resistance than plain concrete as pumice content increases. In general, Type I plain cement concrete shows higher porosity and lower chloride ion resistance that Type I

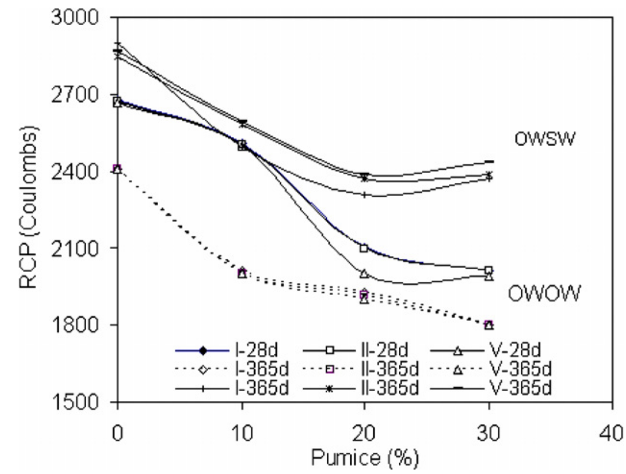

Fig. 14. Influence of pumice content, age and types of cement on chloride permeability.

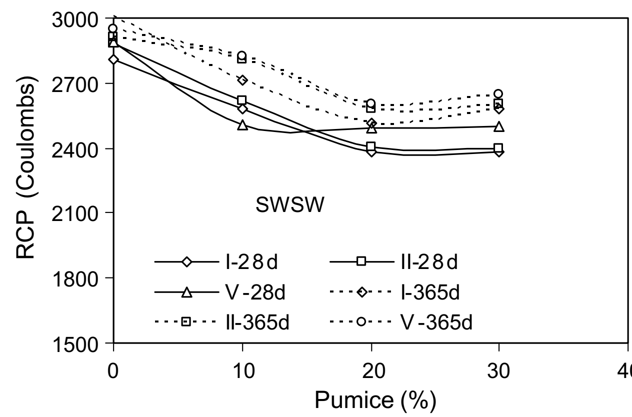

Fig. 15. Influence of pumice content, age and types of cement on chloride permeability.

and Type V (Figs. 12–15). However, blending Type I cements with 20% pumice produces the best performance showing lower porosity and higher chloride ion resistance under both OWSW (precast) and SWSW (cast-in-situ) situations (Figs. 12–15). Both plain and blended concretes under OWSW (precast) situation exhibit lower porosity and higher chloride resistance than SWSW (cast-in-situ) situation possibly due to leaching of salts and crystallization of ettringite, as explained earlier (Figs. 12–15).

4. Discussion

4.1. Mechanism of seawater attack

The chemical deterioration of concrete in marine environments has been a topic of interest to concrete technologists in the last few decades. Seawater contains up to 35,000 ppm of dissolved salts- about 78% of the salt is sodium chloride, and 15% is chloride and sulfate of magnesium. The concomitant presence of sulfate and chloride ions in marine environments causes deterioration of reinforced concrete structures and reinforcement corrosion. The reaction of the concrete with the sulfate ions in marine environments is similar to that of sulfate ions in non-marine environments, but the effects are different due to the presence of chloride ions in the former [12–14,28].

The corrosive action of seawater has been attributed to the reaction of $MgSO_4$ with $Ca(OH)_2$ liberated, forming gypsum and $Mg(OH)_2$, according to:

$$MgSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Mg(OH)_2 \qquad (2)$$

The gypsum formed reacts with calcium hydroxide liberated during hydrolysis of calcium silicates and forms calcium hydrosulphoaluminate.

$$3CaSO_4 + C_3A + 3H_2O = \underset{\text{(ettringite)}}{C_3A \cdot 3CaSO_4 \cdot 3H_2O} \qquad (3)$$

When ettringate and partly $CaSO_4$ are liberated, they enlarge the volume, resulting in concrete expansion affecting the durability. Expansion caused by ettringite formation is the most widely recognized mechanism of sulfate attack. Although no significant expansion of specimens was observed within the one year study period, the strength reduction with age (Figs. 1–6) associated with increase in porosity (Figs. 12 and 13) and decrease in chloride ion resistance (Figs. 14 and 15) of plain and blended cement concrete specimens (as observed in this study) support these facts.

In addition, the chlorides present in seawater reacts with liberated $Ca(OH)_2$ as well as C_3A to form calcium hydochloroaluminate (Friedel's salt) in a process known as "chloride binding" and possibly thaumastic simultaneously, according to:

$$MgCl_2 + Ca(OH)_2 \rightarrow CaCl_2 + Mg(OH)_2 \qquad (4)$$

$$CaCl_2 + C_3A + 10H_2O \rightarrow \underset{\text{(Friedel's salt)}}{C_3A \cdot CaCl_2 \cdot 10H_2O} \qquad (5)$$

The formation of calcium hydrochloroaluminate could be one of the factors leading to reduction of concrete strength. However, "chloride binding" also offers benefit to concrete resistance by indirectly reducing the corrosive action of sulfate ions in marine environments. Higher rate of diffusion of chloride ions (than that of the sulfate ions) in seawater allows the chloride ions to permeate through the concrete surface much faster than the sulfate ions and react with C_3A in the process of chloride binding to form Friedel's salt. As a result, the quantity of C_3A available for the sulfate ions to react and form either gypsum or expansive ettringite is reduced. Further details of the performance of pumice based blended cement concrete in sulfate and mixed sulfate environments can be found from references [13,14].

4.2. Marine resistance of pumice blended cement concrete

The rate of deterioration of concrete in marine environment is dependent on its total porosity. The porosity of concrete decreases with time due to the processes of cement hydration and carbonation [32]. Pumice is 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 can improve the long-term corrosion resistance of concrete structures. The presence of pumice (like fly ash, silica fume, and blast furnace slag) improves strength and durability due to its pozzolanic reaction with $Ca(OH)_2$ to produce a greater solid volume of cementitious calcium silicate gel leading to an additional reduction in capillary porosity during hydration [2,14,23,24]. The consumption of $Ca(OH)_2$ by pumice prevents the formation of ettringite and calcium hydrochloroaluminate, thus alleviating the corrosive attack of seawater. The consumption of $Ca(OH)_2$ by pozzolanic reaction of pumice is evidenced by the presence of lower quantity of $Ca(OH)_2$ in Type I/II/V pumice based blended cement concrete compared to Type I/II/V plain cement concrete (Fig. 16 based on DSC analysis). Lower porosity and higher chloride ion resistance of pumice blended concrete specimens under OWOW (normal water curing), OWSW (cast-in-situ) and SWSW (precast) situations supports these facts (Figs. 11–15). However, the pozzolanic reaction of pumice with $Ca(OH)_2$ depends on the combination of amount of pumice in the mix and curing age. This is evident from the better performance of 20% VP based blended cement concrete compared to that of 30% within the curing period of one year. This can be attributed to the fact that the portion of pumice beyond 20% remained inactive (within the stipulated one year study period) and could not take part in the pozzolanic reaction (as it is normally a slow process) but it can contribute to the improvement of long-term performance.

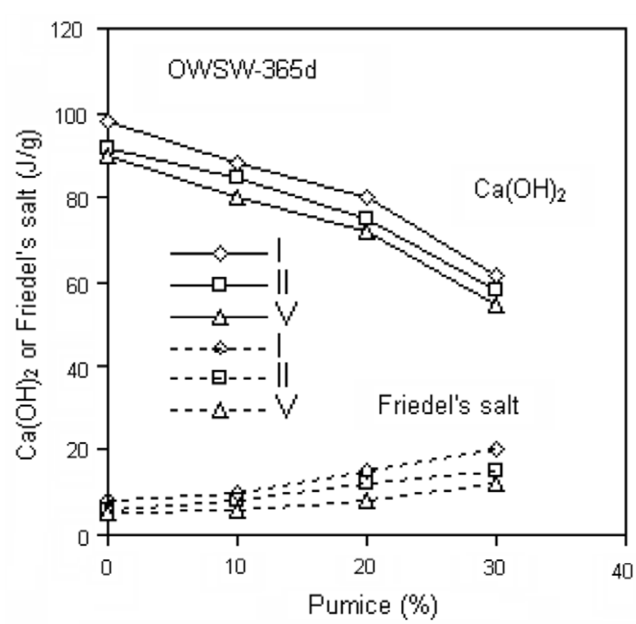

Fig. 16. Differential scanning calorimetry (DSC) results.

The better performance of Type I/II/V blended cements compared to Type I/II/V plain cements in marine environment (associated with concomitant presence of sulfate and chloride) is also attributable to the chloride binding leading to the formation of Friedel's salt (as per Eqs. (4) and (5)) as evidenced by the presence of higher quantity of Freidel's salt in pumice based blended cement concrete (Fig. 16). The formation of Friedel's salt consequently supports the assumption that less ettringite crystallizes from the pore solution when chlorides are present, because of its high solubility in chloride containing solutions, and thus causes lower expansion in pumice based concrete compared to plain concrete. The lower porosity of pumice based concrete compared to plain concrete in marine environment supports the fact (Figs. 12 and 13).

If a marine structure is made of precast elements and is erected at site, then the hardened concrete will be subjected to seawater attack at mature state as compared to a structure made of cast-in-situ elements. Since the porosity of concrete reduces with corresponding hardening of concrete (as confirmed from the increase in porosity of concrete under normal water curing OWOW, Fig. 11), it is expected that the seawater attack will be less in structures made of precast elements. The above fact was found true from the experimental results obtained under simulated precast and cast-in-situ conditions. Both plain and blended concretes under OWSW (precast) situation exhibit lower porosity and higher chloride resistance than SWSW (cast-in-situ) situation (Figs. 12–15).

5. Conclusions

Concrete specimens prepared using plain and finely ground pumice blended Type I, Type II, and Type V cements were exposed to marine environments under two different conditions of mixing water and simulated precast and cast-in-situ concreting. The performance of pumice based concrete mixtures is described based on strength reduction with age as well as results obtained from rapid chloride permeability, porosity and differential scanning calorimetry (DSC) tests. Based upon the experimental study, the following conclusions are drawn:

1. In comparison to OWOW condition (where ordinary water is used for mixing and curing concrete), the compressive strength of concrete decreases in marine environment and the strength loss increases with the age of exposure.
2. The use of Type I and Type II blended cements with pumice (between 10% and 20%) has increased concrete resistance against seawater attack. The use of pumice in combination with Portland cements with very low C_3A content such as ASTM Type V, did not result in a level of resistance equal to or greater than that of Type I or Type II Portland cements in marine environments.
3. The precasting is beneficial in marine environments as observed in all the three types of plain and blended cements. In some cases, the loss in strength has been reduced to even more than 30% in simulated precast situations.
4. The blending of pumice in Type I cement is observed to be more beneficial than the blending in Type II or Type V cements against marine environments in both simulated precast and cast-in-situ situations. Blending Type I cements with 20% pumice produces the best performance showing lower porosity and higher chloride ion resistance under both OWSW (precast) and SWSW (cast-in-situ) situations. This indicates that a Type I blended pumice cement is a potential choice for the construction of marine structures.
5. In view of the high chloride combining capacity of high C_3A Type I cement (as confirmed from the higher Friedel's salt formation in DSC analysis), a potentially useful approach in the marine environment would be to generally specify the use of a Type I cement modified with 10–20% pumice. The use of precasting in place of casting-in-situ will further increase the resistance of concrete against marine environments.

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