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Evolution Of Strength And Durability Of Scoria Concrete In Sea Environment

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***Abstract*—This paper presents the performance of volcanic scoria (VS) based blended cement concrete in marine environment. Variables were finely ground VS powder (VSP) content, curing environment and curing age. VSP content as cement replacement was varied from 0 to 35% and the concrete specimens were cured in the actual sea in two different conditions and in normal water for up to 180 days. Volcanic scoria concrete (VSC) showed better performance in terms of evolution of strength, microstructure (pore size and pore volume) and durability (in terms of seawater/chloride ion diffusivity) compared to control normal concrete (NC) due to pozzolanic action of VSP in marine condition.**

Keywords— Natural pozzolans; volcanic scoria; concrete; marine environment; strength; diffusivity; porosity

I. INTRODUCTION

The search for alternative binders or cement replacement materials had been continued for the last decades. Research had been carried out on the use of volcanic ash (VA), volcanic scoria powder (VSP), fly ash (FA), blast furnace slag, rice husk ash, silica fume etc. as cement replacement material [1-8]. The VA, VSP 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 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. ASTM Standards [9-11] exist for the use of natural pozzolans, fly ash, and silica fume and blast furnace slag in concrete. The optimum use of such supplementary cementing materials can improve the workability of concrete and can provide low cost concrete of satisfactory strength [12-14].

Lightweight volcanic scoria (VS) is abundant in various parts of the world including Turkey, Papua New Guinea (PNG) and Saudi Arabia [8]. VS is pyroclastic ejecta, irregular in form and generally very vesicular and has the basic composition of basalt. VS can be utilized in several industrial applications including the manufacturing of lightweight concrete, as a source of pozzolan to manufacture blended cement, as a heat insulating material, in addition to other uses such as fillers, filter materials, absorbents and other architectural applications. Research suggested the manufacture of blended Portland volcanic scoria cement (PVSPC) with maximum cement replacement of up to 20% [8, 14].

This paper presents the results of investigation on the performance of volcanic scoria concrete (VSC) in marine environment where VSP is used as replacement of cement. Durability of concrete is one of its most important properties and the lack of durability can be caused by external agents arising from the environment or by internal agents within the concrete. It is essential that the VSC should be capable of preserving its durability throughout the life of structures.

Although numerous researches had been conducted on the durability properties of blended cement concrete in the normal and marine environment. Little research has been done on the degradation of VSP subjected to aggressive environment especially in actual marine condition [8, 14]. The corrosive action of seawater has been attributed mainly due to sulphate and chloride attack [15-17]. Concrete incorporating fly ash, blast furnace slag, lime stone filler and silica fume exhibited better chloride penetration resistance than ordinary Portland cement (OPC). In addition, such concretes also showed better performance in sulphate environment with significantly lower expansion and better strength retention than OPC concrete [16-21]. The use of chloride ion diffusivity in combination with compressive strength has been trialed in various projects for specifying concrete in marine environment. Australian Standard AS 3600 suggests compressive strength and corresponding concrete cover as the requirements and key properties as recent methods of specifying concrete for coastal and marine structures [16].

In this paper, the performance of VSC is compared with that of normal concrete (NC) based on compressive strength and durability (in terms of ion permeability and diffusivity) at different curing ages under two different seawater curing conditions in addition to normal water curing. The results of this investigation will be helpful for construction and manufacturing industries involved in the use volcanic material based concrete in structures subjected to extreme marine environment.

II. EXPERIMENTAL INVESTIGATIONS

The concrete mixes cast and tested in this experimental program were divided into VSC mixes and control normal concrete (NC) mixes (with 0% VSP). Table 1 summarizes the details of concrete mixes used in this study. Percentage of volcanic ash used as cement replacement in the mixes was varied from 0 to 35% by weight. The NC mix was designed for a 28-day targeted strength of 30 MPa. Water to cementitious material ratio was kept constant at 0.45 in all the mixes. The air content of the mixes varies from 2.3 to 3.5%.

TABLE 1. DETAILS OF CONCRETE MIXES

Mix	Cement kg/m^3	VSP kg/m^3	Aggregate Fine Sand	Aggregate Coarse 20mm kg/m^3	Aggregate Coarse 10mm kg/m^3	Water kg/m^3
0VSP (NC)	320	0	800	270	645	144
5VSP *	16	304				
10VSP	32	288	* numeric represents the percentages of VSP by weight in the VSC mixes			
15VSP	64	256				
20VSP	96	224				
25VSP	128	192				
30VSP	160	160				
35VSP	192	128				

A. *Material and Properties*

Volcanic scoria used in this investigation was collected from a quarry near the town of Goroka in the highland province of Papua New Guinea (PNG). VS samples collected from the source were grounded to fine powder using a ring crusher to obtain a Blaine fineness of about 295 m^2/kg (Table 1). ASTM Type I cement was used as plain cement as well as to manufacture blended cements. Chemical and physical properties of ground scoria powder (VSP) are compared with those of Portland cement (PC) in Table 1.

TABLE 2. CHEMICAL AND PHYSICAL PROPERTIES OF VSP AND CEMENT

	VSP	ASTM Type I Cement (PC)
Chemical properties		
Chemical Compounds	**Mass, %**	**Mass, %**
Calcium oxide (CaO)	5-8	64.1
Silica (SiO_2)	45-50	21.4
Alumina (Al_2O_3)	13-15	5.7
Iron oxide: Fe_2O_3	3-4	3.5
FeO	4-6	
Sulphur trioxide (SO_3)	0.01-0.02	2.1
Magnesia (MgO)	4-6	2.1
Sodium oxide (Na_2O)		0.5
Potassium oxide (K_2O)	4-6	0.5
Loss on ignition	1.25-1.50	1.1
Free lime (CaO)	-	0.7
Physical properties		
Fineness, m^2/kg	290	320
Sp. gravity	2.15	3.15

Chemical analysis indicates that VSP is principally composed of silica (45-50%); while the main oxide component of PC is calcium oxide (60-67%). However, VS also has calcium oxide, alumina and iron oxide (25-33%). The total oxide content of sodium and potassium known as 'alkalis' is found to be higher in scoria (4-6%) that in PC (1% maximum). Ground scoria with a specific gravity of 2.15 was also lighter than PC.

Higher alkali presence in the VSP may have deleterious effects leading to disintegration of concrete due to reaction with some aggregate and affect the rate of gain in strength of cement. Blended cement was produced in the laboratory by thoroughly mixing PC and VSP using a heavy duty paddle mixer. Quantitative XRD analysis of PC and blended cement with 20% VSP (PVSPC) provided valuable information and the phase composition of these materials is presented in Table 3. VSP (fineness of 290 m^2/kg) is found to be coarser than cement (fineness of 320 m^2/kg) which may lead to the increase of setting time. However, the fineness of VSP can be controlled by the user during grinding process.

TABLE 3. POTENTIAL PHASE COMPOSITION OF CEMENTING MATERIALS FROM X-RAY DIFFRACTION

	Plain cement	VSP based blended cement
Phase	**PC**	**PVSPC (20% VSP)**
C_3S	68.1	55.6
C_2S	14.1	9.1
C_3A	8.1	5.3
C_4AF	9.2	6.9
Other	2.4	7.6
Total	99.7	84.5
Glassy fraction*	0.3	15.5

* obtained by difference

The coarse aggregate was 20 mm and 10 mm maximum size crushed stones having a bulk density of 2.5 and absorption of 0.5 percent. River sand having a specific gravity of 2.65 and absorption of 0.6 percent was used as fine aggregate.

B. *Specimen Casting, Curing & Testing Procedure*

Standard concrete cylinders (150 x 300 mm) were cast. The concrete constituents were mixed in a revolving-drum type mixer for ten minutes. The specimens were demoulded after 24 hours of casting and cured in three different curing conditions: normal potable and seawater curing.

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 and situated within the protected area of PNG Halla cement factory in the city of Lae. The authority of the factory helped to ensure the security of the specimens and looked after the specimens. Seawater curing of the specimens was performed in two conditions:

Sea water curing 1: These specimens were submerged alternatively during high tides while during low tide they remain unsubmerged. The period of submergence varied between 10-12 hours.

Sea water curing 2: These specimens were fully submerged for the whole period of curing irrespective of high or low tide condition of the sea.

For each mix, 60 cylinders had been cast to provide four cylinders for different curing ages. It was planned to cure the specimens for 7, 14, 28, 91 and 180 days under seawater water curing conditions 1 and 2.

The specimens were examined for any physical changes after the specific curing period and then tested for compressive strength.

After curing period of 180 days in seawater, powder XRD (X-ray diffraction) analysis was conducted on samples taken from the fully submerged (seawater curing 2) cylinder specimens. Samples were also collected from the 180-day cured cylinders (under seawater curing 2) at various depths from the surface using electrical drills. These samples were then ground into fine powder passing the 150μm sieve. The total chloride contents were then measured as per JCI [22]. A 2-M HNO_3 solution was added to the powder, and the mixture was titrated with 0.005M $AgNO_3$ solution to determine the total chloride content of the mortar powder. The results were used to plot graphs of the chloride content versus depth from the surface of the specimen.

The mercury intrusion porosimetry (MIP) was used to measure the total pore volume (TPV) and pore radius of concrete at 7, 14, 21, 56, 91 and 180 days of seawater curing 2 of the specimens.

III. RESULTS

A. Influence of Volcanic Scoria and Seawater Curing Conditions on the Compressive Strength

The typical variation of compressive strength (7, 28 and 180 day) for different curing condition with different VSP content is presented in Fig. 1. Generally the strength is found to decrease with the increase of VSP content for different curing conditions with some interesting exception reflecting the benefit of VSP in marine environment.

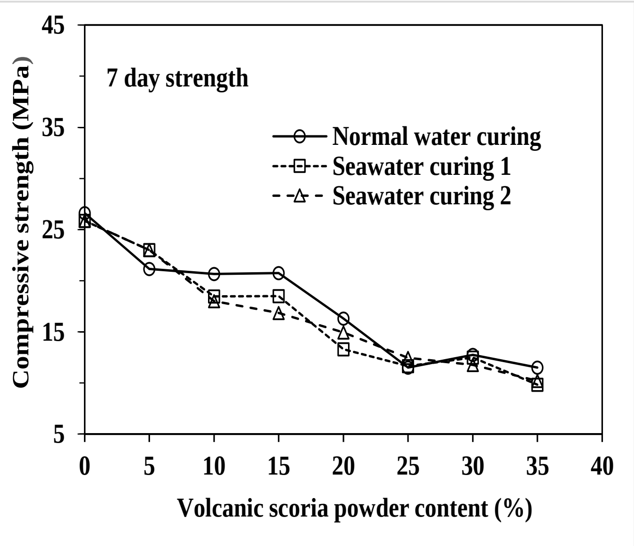
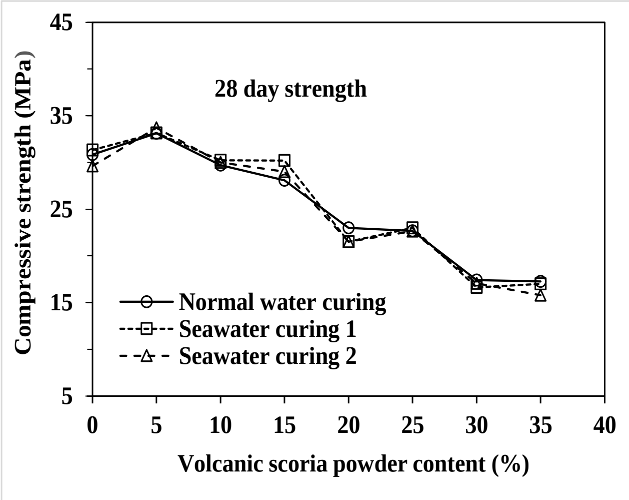


Fig. 1: Variation of compressive strength with % of VSP



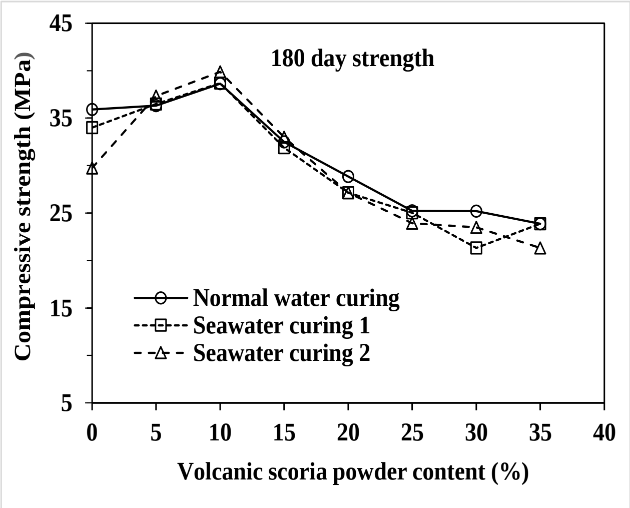


Fig. 1: Variation of compressive strength with % of VSP (contd.)

With the increase in age of concrete (as can be seen from 180 day strength; Fig. 1), the addition of VSP as cement replacement is found to increase the strength of VSC compared to NC for all three curing conditions especially for 5 and 10% VSP. Between 28 and 180 day, the strength of 10% VSC exceeds the strength of 5% VSC as can be seen from the ascending branch of the curves within this range.

At 180 day, the strength of 10% VSP in seawater curing 2 (Fig. 1) exceeds the strength from other two curing conditions which suggests the better performance of VSC with long exposure in the marine environment.

On the other hand, the 91-day strength (Fig.1) of NC in both seawater curing conditions is found to be less than that of normal water curing. This indicates the long-term poor performance of NC in marine environment compared to VSC and hence justifies the use of VSP in marine structures.

B. Influence of curing age and curing condition on the compressive strength of VSC

The performance of NC and VSC with different dosages (up to 35%) of VSP is compared in Fig. 2.

NC shows poor performance in seawater curing. The strength from both seawater curing is less than normal water curing.

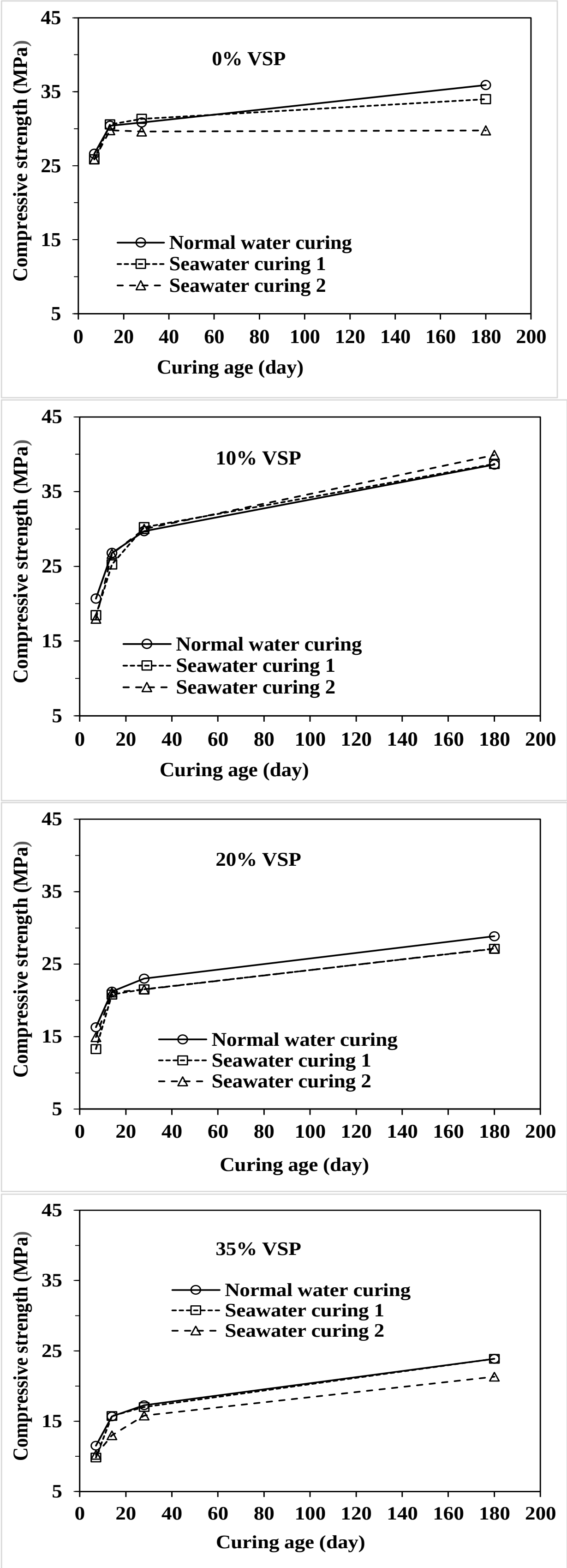


Fig. 2: Performance of VSC with curing age and conditions

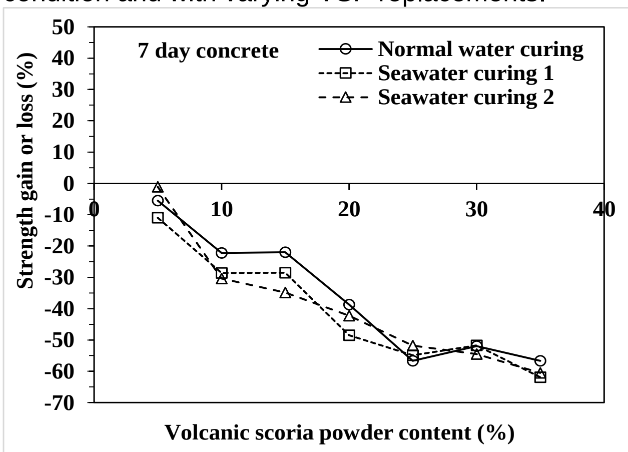
More exposure to the sea condition results in more reduction in strength as can be seen from the lower strength of the specimens in seawater curing condition 2 compared to specimens in seawater curing condition 1. Extension of curing age also leads to more strength reduction in NC and gives an indication of long-term poor performance of NC in marine condition.

The better performance of VSC with curing in marine condition compared to NC for VSP dosages ranging from 5 to 15% is observed. Within the curing age of 180 day, the strength of VSC in seawater curing conditions exceeds the strength of normal water curing. It is interesting to note that more severe seawater curing (condition 2) produces higher strength within 180 day.

The performance of VSC with VSP dosages ranging from 20 to 35% is also examined. Seawater curing seems to produce lower strength compared to that of NC. At VSP dosage of 25%, the 28-day strength in all three curing conditions seems to produce similar strength and on the other hand 91-day strength is reduced in seawater curing. The lower strength development of VSC with VSP dosages ranging from 20 to 35% particularly in the long term, suggests the identification of an optimum dose of VSP. Current results suggest an optimum dose of VSP ranges between 5 and 15%.

C. Effect of Curing Age/Condition and VSP content on Strength Gain or Loss

Fig. 3 shows the strength gain (+ve value) or loss (-ve value) expressed as % in VSC compared to control normal concrete under different curing condition and with varying VSP replacements.



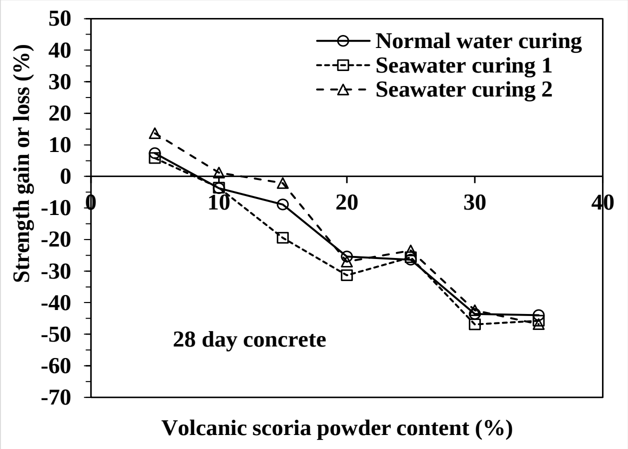


Fig. 3: Comparative study of strength loss or gain

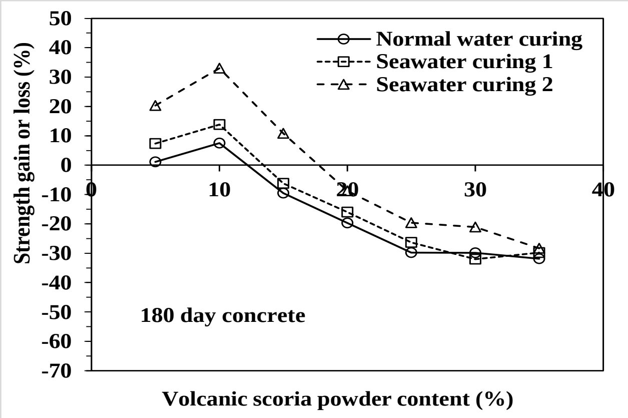


Fig. 3: Comparative study of strength loss or gain (contd.)

At the age of 7 day, all VSC mixes loss their strength compared to normal concrete and the loss of strength is found to be higher in sea water curing conditions 1 and 2 compared to normal water curing. But at the age of 28 day, 5% VSC started to gain strength (+ve values) compared to NC. It records 14 to 15% strength enhancement in seawater curing condition 2 compared to about 4 to 5% in seawater curing condition 1 and normal water curing. Beyond 5%, the loss of strength can be observed but strength loss is found to be less in seawater curing condition 2 compared to other two conditions. It reflects the overall better performance of VSC in seawater curing.

The benefit of marine environment on the performance VSC is clearly revealed at the curing age of 91 day, which can be seen from Fig. 3. The seawater curing condition 2 exhibits better performance with about 20%, 33% and 10% strength gain compared to NC for VSC with 5%, 10% and 15% VSP content, respectively. Even the seawater curing condition 1 exhibits better performance compared to normal water curing with strength gain of about 5% and 12% for VSP content of 5% and 10%, respectively. The range of VSP content for strength gain extends from 5 to 15% in the case of seawater curing 2 compared to 5 to 10% in curing condition 1 and normal water. Extension of curing age beyond 180 day, can show strength gain beyond 20% of VSP.

IV. Mechanism of Marine Resisistance: Evolution of Strength, Durability and Microstructure

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 35000 ppm of dissolved salts - about 78% of the salt is sodium chloride, and 15% is chloride and sulphate 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 [23-24]. The effect of the conjoint presence of chlorides and sulfates on the sulfate resistance of hydrated Portland cements is inconclusive and highly debated [25]. The sulfate attack in marine environment gives rise to expansive ettringite, gypsum, and brucite and sometimes is associated with calcite formation [26].

The corrosive action of seawater has been attributed to the reaction of MgSO4 with Ca $(OH)_2$ liberated, forming gypsum and $Mg(OH)_2$ according to the following equation:

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

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

$$3\ CaSO_4 + C_3A + 3\ H_20 = C_3A.\ 3\ CaSO_4.\ 3\ H_20$$

(ettringite)

When ettringate and partly $CaSO_4$ are liberated, they enlarge the volume, resulting in concrete expansion affecting the durability of concrete. Expansion caused by ettringite formation is the most widely recognized mechanism of sulphate attack. In addition, the chlorides presents in seawater reacts with $Ca(OH)_2$ liberated as well as C_3A to form calcium hydochloroaluminate and possibly thaumastic simultaneously according to:

$$MgCl_2 + Ca(OH)_2 \rightarrow Ca\ Cl_2 + Mg\ (OH)_2$$

$$CaCl_2 + C_3A + 10H_2O \rightarrow C_3A.CaCl_2.10H_2O$$

The formation of calcium hydrochloroaluminate could be one of the factors leading to reduction of concrete strength. The principal methods available to prevent sulfate attack using sulfate-resisting construction materials are changing Type I to Type II or Type V cement and introducing pozzolana such as fly ash, blast furnace slag in concrete [25, 27-33]. Researchers have shown that limitation on C_3A content is not the ultimate answer to the problem of sulfate attack [25, 30, 34, 35]. The use of blended cement made with fly ash, silica fume, and blast furnace slag is therefore recommended in sulfate environments [27].

The long-term improvement of strength of VSC in marine environment is confirmed from the current test results. Despite corrosive action of seawater, the strength of VSC having 5 to 15% VSP is increased compared to NC and normal water curing conditions within a period of 180 day. This is an indication of the development of resistance against corrosive action of seawater due to the presence of VSP in VSC. The presence of VSP improves the strength of VSC 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.

The XRD curves (Fig. 4) of the powder samples taken from the fully submerged specimens (seawater curing 2) reveal that the calcium hydroxide content of the VSP–blended specimens is lower than that of the plain concrete (NC) specimens. This indicates the pozzolanic reactivity of VSP that consumes calcium hydroxide resulting from hydration of the cement.

Comparatively higher Friedel's salt formation in VSC mixes compared to control mix is also confirmed from the XRD spectra in Fig. 4. Similar phenomena were also observed in fly ash concrete [36].

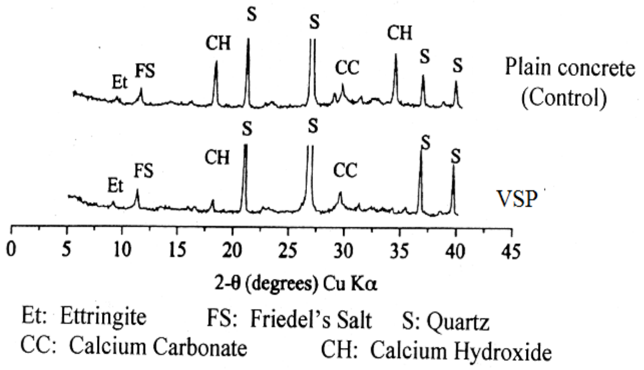
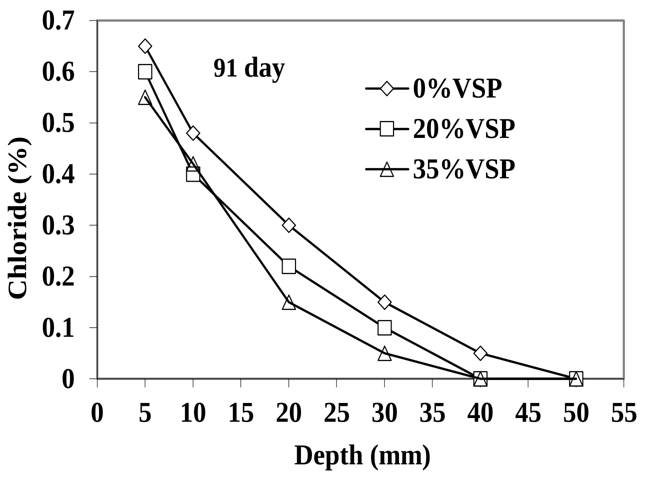


Fig. 4: XRD Spectra of concrete samples (180 day)

The VSP certainly does not have C_3A which can adsorb more chloride ions to form Friedel's salts. The presence of lower C_3A content in PVSPC compared to PC (Table 2) confirms the fact. It is more likely that VSP has aluminium in the glass that is available for the chemical reaction resulting in Friedel's salt production.



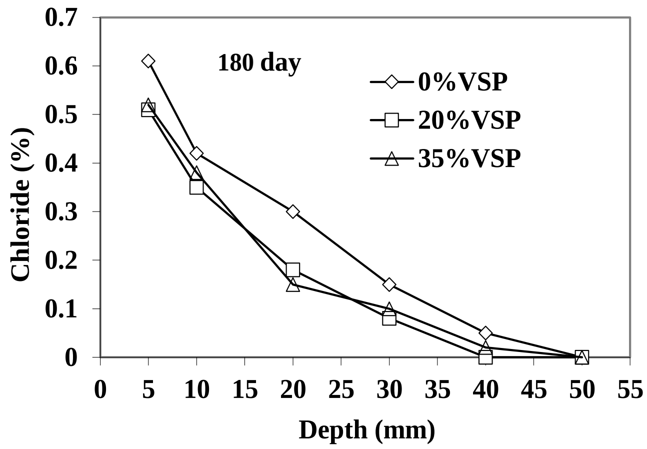


Fig. 5: Chloride concentrations at various depth from the surface for VSC specimens

Friedel's salt formation consequently lowers the levels of free chloride and hence, can reduce the chloride ion diffusivity of concrete. This can be evident from Fig. 5 which shows the chloride concentration profiles of the cylinder specimens fully submerged for 91 and 180 days under seawater curing 2. The chloride content (both 91 and 180 day) at different depths decreased with the increase of VSP content. The partial replacement of cement by VSP results in a reduction in chloride ingress significantly beyond the depth of 25 mm (at 180 day) compared with the control concrete (with 0% VSP). 35% cement replacement by VSP results in the lowest chloride ingress at deeper depths in all sets of specimens. This can also be attributed to the capability of VSP to partially obstruct voids and pores leading to a decrease of pore size with refinement of pore structure and to a smaller effective diffusivity for chloride or other species.

The effect of VSP on the pore size distribution within the total pore volume (TPV), for pore sizes less than 20nm (micropores) and pore sizes greater than 20nm (macropores) at different curing ages (for seawater curing 2) is presented in Fig. 6. It is noted that increasing levels of replacement of cement with VSP (up to 35%) produce a refinement of pore structure. Such refinement of pore structure is attributed to the lowering of permeability/diffusivity of VSC and hence, leads to the improved long-term seawater ion resistance and durability.

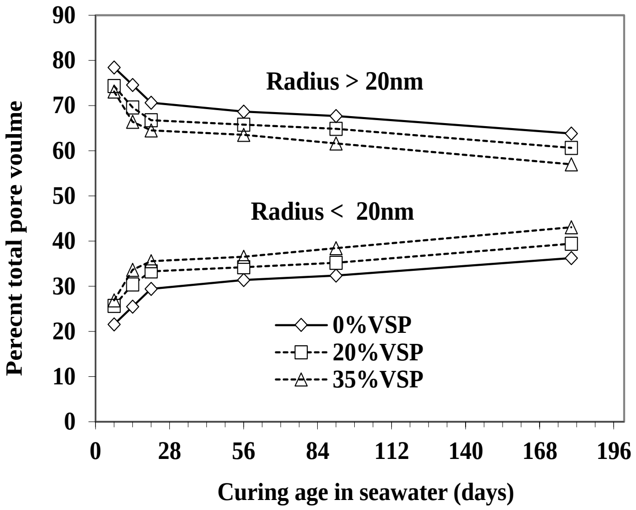


Fig. 6: Pore size distribution with seawater curing time

The consumption of $Ca(OH)_2$ by VSP prevents the formation of ettringite and calcium hydrochloroaluminate, thus alleviating the corrosive attack of seawater. However, the reaction of VSP with $Ca(OH)_2$ could be dependent on the amount of VSP in the mix and curing age. As the pozzolanic action of VSP is a slow process, its benefit will be reflected in the long-term improvement of strength or durability (as confirmed from this research) of VSC compared to normal concrete. Investigations are in progress to study the long term (10-year period) strength and durability performance of VSC under marine environment.

V. Conclusions

The performance of volcanic scoria concrete (VSC) incorporating different dosages of finely ground scoria powder (VSP) as cement replacement (0 to 35% by weight) is presented and compared with that of control normal concrete (NC) in seawater and normal water curing conditions. The following conclusions are drawn from the study:

- The seawater curing showed better performance of VSC (with about 20%, 33% and 10% strength gain for 5%, 10% and 15% VSP content, respectively) compared to NC. The strength gain range may further increase when curing age is further extended beyond 180 day.
- Seawater curing condition 2 (fully submerged for whole duration) exhibits better performance with a maximum strength gain of 33% at 180 day compared to seawater curing condition 1 (10 to 12 hours of submergence per day depending on tidal condition). The better performance of VSC depends on the use of optimum amount of VSP in the mix and curing age. The optimum amount of VSP identified from this study ranges between 5 to 15%. VSP can enhance the long-term strength of VSC compared to NC due to its pozzolanic action. In this study benefit is clearly revealed at the curing age of 180 day.
- X-ray diffraction (XRD) analysis confirms the presence of lower calcium hydroxide content and formation of comparatively higher Friedel's salt (reduces the levels of free chloride) in the VSC specimens compared with the control concrete specimens. In addition, the incorporation of VSP leads to refinement of the pore structure. The proportion of pores with radii smaller than 20nm is increased as the replacement level of cement by VSP increased. These processes reduce the diffusion of seawater ions in the VSC and improve long-term durability.
- VSP blended specimens have shown better resistance to chloride ingress exhibiting the lowest chloride ingress at deeper depths. This study suggests the application of VSP blended concrete in marine structures to provide better durability.

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