Effect of magnesium sulphate solution on compressive strength and sorptivity of blended concrete

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Abstract. This paper reports on the result of an experimental investigation carried out to study the compressive strength and sorptivity properties of blended cement concrete exposed to 5% and 10% MgSO₄ solution using fly ash (FA) and silpozz. Usually in sulphate environment the minimum grade of concrete is M30 and the mix design is done for target mean strength of 39 MPa. Silpozz is manufactured by burning of agro-waste rice husk in designed furnace in between 600° to 700°C which is one of the main agricultural residues obtained from the outer covering of rice grains during the milling process. There are four mix series taken with control mix. The control mix made 0% replacement of FA and silpozz with Ordinary Portland Cement (OPC). The first mix series made 0% FA and 10-30% replacement of silpozz with OPC. The second mix series made with 10% FA and 10-40% replacement of silpozz with OPC. The third mix series made 20% FA and 10-30% replacement of silpozz with OPC and the fourth mix series made 30% FA and 10-20% silpozz replaced with OPC. The samples (cubes) are prepared and cured in normal water and 5% and 10% MgSO₄ solution for 7, 28 and 90 days. The studied parameters are compressive strength and strength deterioration factor (SDF) for 7, 28 and 90 days. The water absorption and sorptivity tests have been done after 28 days of normal water and magnesium sulphate solution curing. The investigation reflects that the blended cement concrete incorporating FA and silpozz showing better resistance against MgSO₄ solution when compared to normal water curing (NWC) samples.

Keywords: blended cement concrete; compressive strength; SDF; sorptivity; water absorption

1. Introduction

Durability of concrete has been a major apprehension of civil engineering experts. In addition, over the last few decades it has been under significant scientific and hightech attention. Durable concrete is possible to produce, by part replacement of cement with micro-silica (MS). The use of MS in conjunction with super plasticizers has become the back bone of high strength and high-performance concrete. One of the factors accountable for impairment to concrete is the destructive attack of sulphate and chloride ions. The corrosive action of chlorides is owed to the creation of chloroaluminate hydrate, C3A.CaCl2.10H2O, commonly known as Friedel's salt which makes the concrete softer. Also, a sulphate ion enters into chemical reactions with certain elements of concrete, creating sulphoaluminate hydrates, Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O (ettringite), gypsum with little binding assets. All these reactions result in decrease in strength of concrete. Numerous structures affected by sulphate degradation frequently need to be fixed and repaired or, in maximum cases, they need to be rebuilt. The factors affecting concrete durability are the grades of concrete, depth of cover to reinforcement, site supervision and practice as well as severity of exposure conditions. Durability of concrete may be improved by utilizing industrial by-products which are possessing hydraulic and pozzolanic properties when replacing with OPC. Nowadays, the emerging area is the waste utilization of environmental by product materials such as FA and silpozz to improve concrete durability in marine environment. In construction sectors there is an increasing trend for sustainable development and utilization of FA and silpozz as a supplementary cementitious material (SCM). FA is generated during the combustion of coal for energy production and recognized as an environmental pollutant. Silpozz is manufactured by burning of agro-waste rice husk in designed furnace in between 600° to 700°C. Rice husk is one of the main agricultural residues obtained from the outer covering of rice grains during the milling process which creates environmental problems after disposal. Silpozz is a very good super pozzolan and it is used in place of SF or micro silica at lower cost without compromising the quality aspect. The utilization of FA and silpozz is very important in the active area of research. Silpozz is a very good super pozzolan and it is used in place of SF or micro silica (Panda and Prusty 2015). SF is very costly material and locally unavailable but silpozz is locally and cheaply available material. Silpozz which is a by-product of rice husk can be utilized with SP as a partial replacement of OPC in cement concrete especially in marine site to improve strength and durability as well as it provides economical, technical and environmental advantages which

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are very much essential for sustainability in construction sectors.

Some of the researchers have reported the utilization of supplementary cementitious materials (SCM) to improve concrete properties in marine and sulphate environment. Jena and Panda (2018) studied the development of compressive strength in blended concrete made with silpozz and fly ash which is used as a partial replacement of cement to improve the durability of marine structures. Mirvalad and Nokken (2016) used slag and fly ash as a supplementary cementing materials (SCM) and found very effective against sulfate attack. Portland limestone cement (PLC) on mixing with cement gets its mass changed and avoids formation of ettringite and thaumasite by increasing the amount of SCM, desired result is obtained as PLC alone cannot do it. Hossack and Thomas (2016) found the external sulfate attack tri-calcium aluminate is mixed with Portland cement. Normally external sulfate attack enters through the hardened surface of cement paste and interacts with hydrated cement compound inside the cement sample and makes it soft with small crack which leads to formation of thaumasite, ettringite and gypsum. The results were such that high C₃A content cement failed much faster than moderate C₃A cement. Sulfate attack was not affected by limestone content in cement. Jena and Panda (2015) studied the development of compressive strength in blended concrete made with silpozz which is used as a substitute material of silica fume (SF) to improve the durability of marine structures. Panda and Prusty (2015) enhanced the strength properties using silpozz as a partial replacement of OPC. Aghabaglou et al. (2015) studied the effects of sulphate attack on strength and penetrability properties of cement soothed kaolin inside an experimental back ground. The results uncovered that the use of ordinary Portland cement is not more feasible than the use of sulphate resistant cement, when cement soothed clay is exposed to succeeding effect of sulphate attack. Experimental relationships among unconfined compressive strength, freeze-thaw cycles, curing period and cement content were also provided. Anwar and Roushdi (2014) showed the properties of concrete containing PC, FA and SF as blended cements for improvements in concrete to resist environmental causes of deterioration. Anwar et al. (2013) concluded that the combinations of 15 to 25% of FA with 5 to 10% SF show satisfactory performance in both fresh and hardened concrete. The SF improves early age performance of concrete with FA continuously refining the properties of hardened concrete as it matures and the replacement of 35% of cement quantity with 25% FA and 10% SF increased the compressive strength by 20% at 180 days. Wegian (2010) investigated on the effects of mixing and curing concrete with seawater on the compressive, tensile, flexural and bond strengths of concrete and the reduction in strength increases with an increase in exposure time, which may be due to salt crystallization formation affecting the strength gain. Sunil (2009) investigated the effects of the quality of mixing water and initial curing on plain and blended cement concrete made with FA were exposed to seawater attack for a period of one year and the performance of these concrete specimens were evaluated by reduction in compressive strength. The results of this study showed that the use of pre casting in place of casting-in-situ mitigates the effect of marine environments on concrete specimens considerably. Oh et al. (2002) developed high-performance concrete using SF to enhance the durability of concrete structures in severe environments such as nuclear power plants, waterretaining structures and other off shore structures. Bouzoubaa et al. (2000) produced laboratory Portland cements blended with high volume fly ash (HVFA) from Canada and U.S.A developed higher compressive strength at all ages and resistance to the chloride - ion penetration. Aburawi and Swamy (2008) reported the effects of salt weathering and curing conditions on the properties of high durability concretes containing chlorides. Thomas et al. (1999) reported that the combination of PC, SF and FA in a ternary cement system should result in a number of obvious synergistic effects. Lane and Ozyildirim (1999) indicated that the ternary system of concrete incorporating small amount of SF showed early compressive strength gain. Berry (1980) found that the strength development of the ternary cement system is relatively slower at early age. Antiohos et al. (2005) mentioned the sustainability of the construction sector and factors affecting the greenhouse gas emissions that are implicated in global warming and climate change. Mehta (2004) noted the utilization of high-volume FA concrete system and its application will enable the concrete industry to become more sustainable. Nehdi (2001) incorporated SF in slag cement and FA cement, the ternary PC, blast-furnace slag and SF and PC, FA and SF blended cements developed and commercially manufactured in Canada. More details about the properties of ternary concrete containing PC, FA and SF as blended cements were studied by Anwar et al. Anwar and Khalil (2015) observed the carbonation phenomenon as a durability reducer of ternary cementitious systems containing Portland Cement (PC), FA and SF and how it develops with time. Popovics (1993) reported the addition of 25% FA and upto 5% SF could only slightly increase the early strength of concrete. Uchikawa and Okamura (1993) reported that the performance of ternary blended cements is better as compared with conventional concrete. This paper focuses the mechanical and durability properties of concrete with FA and silpozz cured in normal water and 5-10% MgSO₄ solution for 90 days and the utilization of waste by-product such as FA and silpozz which creates environmental problems after disposal.

2. Experimental program

2.1 Properties of materials used

OPC 43 grade, FA, Silpozz, fine aggregate, coarse aggregate, normal water, magnesium sulphate solution and super plasticizer are used in this study. The experimental physical properties of OPC such as initial setting time 160 min, final setting time 360 min, standard consistency 32%, fineness 333 m²/kg and specific gravity 3.15 are determined confirming to IS 8112:1989. The physical properties of coarse aggregates obtained as per IS: 383-1970 such as fineness modulus 7.0, specific gravity 2.86, water

Table 1 Chemical and physical properties of cementitius materials

Oxides (%)	Cement (OPC)	Silpozz	FA
SiO ₂	20.99	88.18	58.13
Al ₂ O ₃	6.05	1.61	31.00
Fe ₂ O ₃	6.01	0.56	4.10
Carbon	-	2.67	-
CaO	62.74	1.59	0.60
MgO	1.33	1.63	0.10
K ₂ O	0.40	1.67	0.90
Na ₂ O	0.04	-	0.05
SO ₃	1.82	-	0.12
TiO ₂	.025	-	1.63
Others	-	2.09	0.011
Moisture content (%)	-	0.79	3.0
Loss on ignition (%)	1.14	0.04	0.29
Pł	ysical properties		
Bulk Density (gm/cc)	1.43	0.23	1.2
Specific gravity	3.15	2.3	2.12
Particle size (Micron)	35	25	34
Specific surface, m ² /g	0.33	17	33
Color	Gray	Gray black	Gray

absorption 0.2% and crushing value 24% as well as the properties of fine aggregates such as fineness modulus 3.03 (Zone-III), water absorption 0.6% and specific gravity 2.68. CERA HYPERPLAST XR-W40 high end super plasticizers are used. FA is a fine material and possesses good pozzolanic activity. When FA is used as partial replacement with OPC in blended concrete, low heat is produced and staggers through pozzolanic reactions and ultimately reduces micro-cracking thus improves soundness of concrete. Silpozz can be used as an effective mineral admixture to make special concrete mixes and also improves the durability of marine concrete. The heat of hydration is lowered by as much as 30% when Silpozz is added to concrete, as well as prevents formation of cracks during casting. The chemical and physical properties of FA and silpozz given by the supplier are shown in Table 1.

2.2 Mix proportions and identifications

Usually in marine concrete silpozz can be used as an effective material to make a relatively richer concrete mix. Considering this point the minimum grade of concrete is M30 which is suitable for marine environment and designed as per Indian Standard code 10262-2009. The obtained material ratio was (1: 1.44: 2.91), w/b 0.43. The controlled specimen is prepared with 100% OPC without SP and there is no change of quantity of materials. As SP is used in blended concrete mixes, the amount of water was reduced by 20% based upon the several trial mixes in order to maintain the slump in between 25-50 mm. The first blended concrete samples were made 0% FA and the silpozz replacement varied from 10-30% with OPC. The second blended concrete samples were made 10% FA and the replacement of silpozz varied from 10-40% with OPC. The third blended concrete samples were made 20% FA and

Table 2 Details of cementitious materials with SP

Proportions of cementitious materials	Mix Identity
Cement 100% + FA 0% + Silpozz 0% + SP 0%	MC100F0S0
Cement 90% + FA 0% + Silpozz 10% + SP 0.20%	M1C90F0S10
Cement 80% + FA 0% + Silpozz 20% + SP 0.29%	M1C80F0S20
Cement 70% + FA 0% + Silpozz 30% + SP 0.40%	M1C70F0S30
Cement 80% + FA 10% + Silpozz 10% + SP 0.22%	M1C80F10S10
Cement 70% + FA 10% + Silpozz 20% + SP 0.33%	M1C70F10S20
Cement 60% + FA 10% + Silpozz 30% + SP 0.47%	M1C60F10S30
Cement 50% + FA 10% + Silpozz 40% + SP 0.72%	M1C50F10S40
Cement 70% + FA 20% + Silpozz 10% + SP 0.25%	M1C70F20S10
Cement 60% + FA 20% + Silpozz 20% + SP 0.38%	M1C60F20S20
Cement 50% + FA 20% + Silpozz 30% + SP 0.56%	M1C50F20S30
Cement 60% + FA 30% + Silpozz 10% + SP 0.30%	M1C60F30S10
Cement 50% + FA 30% + Silpozz 20% + SP 0.46%	M1C50F30S20

replacement of silpozz varied from 10-30% with OPC. The fourth blended concrete samples were made 30% FA and silpozz varied from 10-20% with OPC. The details of mix identity along with doses of SP are given in Table 2. The materials were batched into the mixer according to the following sequence: coarse aggregate followed by sand, and then cementitious materials (OPC, FA, and Silpozz were well mixed outside the mixer). The total mixing time was three minutes divided into two stages, starting with 60 s dry mixing, followed by the addition of the required water within 30s, then the mixer continued for the next 1.5 min of wet mixing and after adding SP the mixture continued for extra 1.5 to 2 min for wet mixing. The doses of SP were added to the silpozz based samples of 10-40% replaced with OPC. After casting, he concrete moulds were compacted by a vibrator. The samples were finished, stripped from their moulds the day after casting. The specimens were cured in water until testing. Workability of fresh concrete was measured by slump test and compaction factor test just after mixing. It was observed that the slump value varied between 34 to 42 mm and the compaction factor varied between 86.20 to 96.20%. The details of concrete mix quantities in kg/m³ along with slump value and compaction factor are shown in Table 3.

2.3 Specimen preparation and curing condition

Standard concrete cubes of size 150 mm×150 mm×150 mm were used for measuring the compressive strength. The concrete cylinders of size 100 mm diameter and 50 mm height were taken for measuring water absorption and sorptivity. The compressive strength was determined for cube samples after 7, 28 and 90 days of NWC and 5-10% MgSO₄ solution curing. The water absorption and sorptivity was tested at the age of 28 days of NWC and 5-10% MgSO₄ solution curing for the samples of cylinder.

2.4 Preparation of MgSO₄ solution

Magnesium sulfate is a complex chemical compound simply containing magnesium, sulphur and oxygen (MgSO₄). It is of two types: heptahydrate and monohydrate.

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Mix Identity	Cement	Fine Aggregate	Coarse Aggregate	FA	Silpozz	Water	SP	Slump	Compaction
WIX Identity	(Kg/m^3)	(Kg/m^3)	(Kg/m^3)	(Kg/m^3) (Kg/m^3)		water	(Kg/m^3)	(mm)	Factor (%)
MC100F0S0	434.32	624.77	1264.97	0	0	186.76	-	35	82.60
M1C90F0S10	390.88	624.77	1264.97	0	43.44	149.40	0.781	34	85.50
M1C80F0S20	347.45	624.77	1264.97	0	86.86	149.40	1.005	38	90.00
M1C70F0S30	304.00	624.77	1264.97	0	130.33	149.40	1.229	40	92.00
M1C80F10S10	347.45	624.77	1264.97	43.44	43.44	149.40	0.781	37	86.20
M1C70F10S20	304.00	624.77	1264.97	43.44	86.86	149.40	1.005	42	96.20
M1C60F10S30	260.60	624.77	1264.97	43.43	130.33	149.40	1.229	40	92.20
M1C50F10S40	217.16	624.77	1264.97	43.44	173.72	149.40	1.564	41	94.20
M1C70F20S10	304.00	624.77	1264.97	86.86	43.44	149.40	0.781	37	86.00
M1C60F20S20	260.60	624.77	1264.97	86.86	86.86	149.40	1.005	38	90.40
M1C50F20S30	217.16	624.77	1264.97	86.86	130.33	149.40	1.229	41	92.20
M1C60F30S10	260.60	624.77	1264.97	130.33	43.44	149.40	0.800	34	86.50
M1C50F30S20	217.16	624.77	1264.97	130.33	86.86	149.40	1.005	38	92.40

Table 3 Details of mix quantity with slump value and compaction factor (%)



Fig. 1 Curing samples in MgSO₄ solution



Fig. 2 SEM of FA

Heptahydrate (MgSO₄.7H₂O) is commonly known as Epsom salt or sulfate mineral epos mite which usually comes in crystal form. The monohydrate (MgSO₄.H₂O) is normally found in mineral kieserite. It comes in powder form. In this work, heptahydrate is being used to form magnesium sulfate solution. We have taken 5 gm and 10 gm MgSO₄ in 100 ml of water to prepare 5% and 10% MgSO₄ solution respectively. The following equation represents how to prepare the MgSO₄ solution. The samples such as cubes, cylinders and prisms are cured in sulphate solution which is shown in Fig. 1.

 $[MgSO_4(5gm) + H_2O(100 ml) = 5\% MgSO_4 solution]$ $[MgSO_4(10gm) + H_2O(100 ml) = 10\% MgSO_4 solution]$

2.5 SEM of FA and silpozz

The micro structural properties of FA and silpozz

powder samples are shown in Figs. 2-3 by SEM techniques respectively. The studies are based on different micrographs at various magnifications. The FA particles are spherical in shape with a very smooth surface texture which is shown in Fig. 2. The silpozz particles are in angular shape with a very rugous surface texture which is shown in Fig. 3. The better spatial distribution of the hydrates and the consumption of portlandite by the pozzoianic reactions of angular particles of silpozz yield a denser matrix. As a result of which strength increases when silpozz is replaced with OPC. Angular particles act as a fine filler which fills the pores of the cement concrete produces dense microstructure. Angular particles play an active role than the spherical particles in cement concrete matrix. The internal architecture and binding property develops the strength due to active participation of angular size and shape of silpozz particles.

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Fig. 3 SEM of Silpozz

3. Durability properties

Durability tests such as water absorption and sorptivity are done confirming to ASTM C 1585-04. The samples are tested for water absorption and sorptivity after curing 28 days in normal water and 10% MgSO₄ solution. The test procedures are described below for both water absorption and sorptivity test.

3.1 Water absorption test

The 100 mm diameter and 50 mm height cylinder were immersed in water and 10% MgSO₄ solution for 28 days after casting. Then the specimens were oven dried for 24 hours at 110°C temperature. The weights were noted as the dry weight of cylinder. Then the specimen was kept in hot water at 85°C for 3.5 hours. Water absorption in percentage $=\frac{W^2-W1}{W1} \times 100$ where, w_1 =oven dry weight of cylinder in kilograms. w_2 = wet weight after 3.5 hours in kilograms. The average absorption of test samples shall not be greater than 5% with no individual unit greater than 7%.

3.2 Sorptivity test

Sorptivity can be determined by the measurement of the capillary rise absorption rate on reasonably homogeneous material. After casting, the cylinders were immersed in water and 10% MgSO₄ solution for 28 days. The size of the specimen is 100 mm diameter and 50 mm height. Then the specimens were dried in oven at 110°C. Water level was less than 5 mm of the base specimen. The flow from peripheral surface was prevented by sealing properly with non-absorbent coating. Surface water on the specimen was wiped off with a dampened tissue and each weighting operation was completed within 30 sec.

 $S = \frac{I}{\sqrt{t}}$ whereas S = Sorptivity in mm, t = time in minute I $= \frac{w^2 - w_1}{Ad}$, $w_2 =$ weight of specimen after 30-minute capillary suction of water in kg. $w_1 =$ oven dry weight in kg.

A = surface area of specimen through which water penetrated. d = density of water.

4. Results and discussions

4.1 Properties of fresh concrete



Fig. 4 Compressive strength at 7 days vs Types of mixes

Workability was measured in terms of slump and compaction factors which were listed in Table 3 and they fall within the designed range. The slump ranged from 34 to 42 mm. According to the results, most of the concrete mixes were observed moderate slump value and compaction factor. No wide variations in the slump value for the mixes containing increased amounts of silpozz were observed. Only the mix with 10% FA and 40% silpozz was relatively stiff. As the rate of percentage of silpozz increased, the slump value decreased along with the compaction factor. The higher replacement of SF is often accompanied by the use of super plasticizer reported by Shannag. There is no sign of bleeding and segregation of concrete. The compaction factor ranges from 86.20 to 96.20% which shows moderate workable concrete. At the level of 20% replacement of silpozz and 10% FA showed optimal workability and maximum slump value. The slump value is 42 mm and compaction factor 96.20% in the ternary system of concrete with 10% FA and upto 20% silpozz. It is observed that the slump value and compaction factor slightly decreases as the silpozz replacement ratio is high.

4.2 Properties of hardened concrete

The strength properties are compressive strength, split tensile strength and flexural strength was determined as per IS 516-1959. The compressive strength, split tensile strength and flexural strength was tested at 7, 28 and 90 days of NWC and magnesium sulphate solution curing.



Fig. 5 Compressive strength at 28 days vs types of mixes

4.2.1 Compressive strength

In this study, the compressive strength test was performed on 150 mm cube specimens at the age of 7, 28 and 90 days for NWC, 5% and 10% MgSO₄ solution curing samples. Three specimens were tested at each testing age and the average compressive strength was reported. The specimens were tested for compressive strength using a 3000 kN capacity concrete compression testing machine. The 7 days compressive strength verses types of mix is presented in Fig. 4. It is observed from the Fig. 4 that the concrete containing 0% FA and 20% silpozz replacing with OPC contributes higher strength after 7 days curing as compared to control specimen. The 28 days compressive strength verses types of mix is shown in Fig. 5.

It observed from Fig. 5 that sample having 10% FA and 20% silpozz improved a little bit more than 7 days curing. The 90 days compressive strength verses types of mix is shown in Fig. 6 from which it is studied that M1C80F0S20 and M1C70F10S20 identity attained higher strength. Silpozz improves the early age strength whereas FA gives the later age strength at 90 days. The strength properties decrease as the time of exposure in sulphate solution curing increases as compared to NWC. The compressive strength (MPa) between NWC and MgSO₄ solution curing samples are presented in Table 4. Addition of silpozz to the cement replacement, due to pozzolanic reactions showed enhanced strength development in NWC samples as compared to MgSO₄ solution curing samples. It may be studied that Silpozz is having average particles size of 25 microns and below, so that it fills the interstices in between the cement in the aggregate as fine filler with the help of SP which gives better strength and resistance to sulphate attack. The addition of SCM such as FA and silpozz with SP enhances the homogeneity of cement paste and densifies the microstructure of the cement considerably as well as improves the strength in NWC samples. On the other hand the sulphate anion that reacts with cement components of concrete forming highly soluble-alkali or alkali earth-salts originates from oxidation of pyrites in the aggregates which deteriorates the strength in MgSO₄ solution.



Fig. 6 Compressive strength at 90 days vs Types of mixes



Fig. 7 SDF obtained from 5% MgSO₄ solution verses Concrete Mix

5. SDF (%) obtained from compressive strength in 5% and 10% MgSO₄ solution curing

The compressive strength test was performed on 150 mm cube specimens at the age of 7, 28 and 90 days for NWC, 5% and 10% MgSO₄ solution curing samples. The SDF presented from compressive strength in 5% and 10% MgSO₄ solution is given in Table 5. The SDF obtained from compressive strength of 5% and 10% $MgSO_4$ solution curing samples are shown in Figs. 7-8 respectively. It is observed from Fig. 7 that the minimum SDF from 5% MgSO₄ solution is 0.18%, 0.35% and 0.74% at the age of 7, 28 and 90 days for the sample M1C80F10S10 respectively. The maximum SDF from 5% MgSO₄ solution is 1.15%, 1.56% and 1.98% at the age of 7, 28 and 90 days for the sample M1C50F30S20 respectively. The maximum SDF from 10% MgSO₄ solution is 2.18%, 2.30% and 2.37% at the age of 7, 28 and 90 days for the sample M1C50F30S20 respectively. The 7, 28 and 90 days SDF in 5% and 10% MgSO₄ solution verses concrete mix is shown in Figs. 9-11 respectively.



Fig. 8 SDF obtained from 10% MgSO₄ solution verses concrete mix



Fig. 9 7 Days SDF in MgSO₄ solution verses Concrete mix

It observed from Fig. 9 that the SDF obtained from 10% MgSO₄ solution curing samples are more compared to 5% MgSO₄ solution curing samples including control mix. Similar trend is found from Figs. 10 and 11 for 28 and 90 days respectively. The rate of SDF is studied more in between 7 to 28 days, but 28 to 90 days, the rate of SDF is slowly processed as compared to first 28 days. For each case, the silpozz based specimens are giving low SDF as compared to FA based samples. The combined replacement of 10% FA and upto 20% silpozz with OPC showed optimal resistance against sulphate attack. Even without FA and upto 40% silpozz replaced with OPC also performed better in sulphate solution.

6. XRD of specimen M1C70F10S20

The mineralogical characterizations of the specimen M1C70F10S20was carried out by X-Ray Diffraction (XRD) study by using a Cu target X-Ray diffractometer after 28 days of SWC. The different mineral phases were identified by comparing the d-spacing which is given in ASTM data cards and shown in Fig. 12 which indicate peaks of



Fig. 10 28 Days SDF in MgSO₄ Solution verses Concrete mix



Fig. 11 90 Days SDF in $MgSO_4$ solution verses Concrete mix

Table 4 Compressive strength (MPa) between NWC and MgSO₄ solution curing samples

	NWC			5% MgSO4			10% MgSO4			
NC 11				solut	solution curing			solution curing		
Mix identity		Days			Days			Days		
	7	28	90	7	28	90	7	28	90	
MC100F0S0	36.95	51.15	62.5	36.8	50.8	61.5	36.4	50.2	61.1	
M1C90F0S10	44.5	56.85	66.5	44.35	56.5	65.8	43.90	55.8	65.2	
M1C80F0S20	47.2	58.75	67.8	47.1	58.5	67.2	46.6	57.7	66.54	
M1C70F0S30	41.5	55.4	66.1	41.4	55	65.5	41	54.6	64.9	
M1C80F10S10	43	55	65	42.9	54.7	64.5	42.5	54.3	63.9	
M1C70F10S20	44	56	66.8	43.92	55.8	66.3	43.72	55.54	65.8	
M1C60F10S30	41	54	64.5	40.9	53.5	63.8	40.5	53.2	63.4	
M1C50F10S40	38.5	51	61.5	38	50.2	60.5	37.8	49.7	60.1	
M1C70F20S10	41.15	52.2	63.1	40.95	51.9	62.5	40.49	51.3	61.9	
M1C60F20S20	38.5	48.6	58.25	38.1	48	57.2	37.8	47.6	56.9	
M1C50F20S30	35.6	48.7	55.2	35.2	48	54.2	34.8	47.	53.7	
M1C60F30S10	36.6	43.5	54.7	36.2	43	53.85	35.8	42.5	53.4	
M1C50F30S20	34.8	42.82	50.5	34.4	42.15	49.5	34	41.85	49	

mineralogical characteristics of A: Albite, P: portlandite, Q: Quartz, CS: Calcium Silica and C₃S: Tricalcium Silicate.

Table 5 SDF (%) presented from compressive strength in MgSO₄ solution

	SDF (%) obtained from 5% and									
	10% MgSO ₄ solution curing samples									
Mix Identity	5% N	IgSO4 so	olution	10% N	10% MgSO ₄ solution					
	7 days	28 days	90 days	7 days	28 days	90 days				
MC100F0S0	0.40	0.68	1.60	1.50	1.85	2.24				
M1C90F0S10	0.33	0.61	1.05	1.34	1.84	1.95				
M1C80F0S20	0.21	0.42	0.88	1.27	1.78	1.85				
M1C70F0S30	0.24	0.72	0.90	1.20	1.44	1.81				
M1C60F0S40	0.23	0.54	0.77	1.16	1.27	1.70				
M1C80F10S10	0.18	0.35	0.74	0.63	0.82	1.50				
M1C70F10S20	0.24	0.92	1.08	1.22	1.48	1.70				
M1C60F10S30	1.30	1.56	1.62	1.81	2.55	2.27				
M1C70F20S10	0.48	0.57	0.95	1.60	1.72	1.90				
M1C60F20S20	1.03	1.23	1.80	1.81	2.05	2.31				
M1C50F20S30	1.12	1.43	1.81	2.47	3.49	2.71				
M1C60F30S10	1.09	1.15	1.55	2.18	2.30	2.37				
M1C50F30S20	1.15	1.56	1.98	2.30	2.26	2.97				



Fig.12 XRD of specimen M1C70F10S20 (MgSO₄)

The silpozz is assumed to be as the reactant to produce secondary C-S-H by consuming calcium hydroxide. The formation of pozzolanic gel begins with hydration of elite and blite during hardening process. Decreased calcium hydroxide content of the cement matrix and increased amount of C-S-H gel together with filler effect of silpozz contribute to safe guarding of the matrix against external ingressive ions. Magnesium hydroxide, which is relatively insoluble in water, is known to encompass and block the pores, and protects the C-S-H gel from further attack. Its absence in Portland cement plus silpozz specimens, therefore, makes the C-S-H gel more prone to magnesium sulphate attack.



Fig. 13 SEM of sample M1C70F10S20 (NWC)



Fig. 14 SEM of sample M1C70F10S20 (5% MgSO₄ solution curing)



Fig. 15 SEM of sample M1C70F10S20 (10% MgSO₄ solution curing)

7. Microscopic studies

Since for many years, Scanning electron microscopy (SEM) is acting as a basic tool for the researchers in the field of investigation for internal complexity of structural concretes and hydrated cement pastes. Various techniques such as transmission electron microscopy and petro graphic microscopy can be adopted to investigate the internal architecture. The factors affecting microstructure are the age of concrete, types of cement, water to binder ratio, heat treatment, replacement of chemical and mineral admixtures and many other variables. Furthermore deterioration takes place by various chemical and physical attacks in marine environment which can change their inner structures as well as their characteristics. Internal construction of cement concretes and properties within concretes are essential elements for a structural designer who deals with concrete properties and behaviour in service.

SEM studies are essential for developing mathematical models and durability of concrete. SEM for the sample M1C70F10S20 is given in Figs. 13-15 in NWC, 5% MgSO₄ solution curing and 10% MgSO₄ solution curing respectively. It is studied from Fig. 13 that the black and white matter assumes C-S-H gel which spreads over the aggregates thus acts as a binder for the paste. The isolated black spot stands for voids/ pore spaces. In Fig. 14, the C-S-

Mix identity	Oven dry weight (<i>w</i> ₁) in kg		Wet weight in hot w	t after 3.5 hours immersed vater at 85°C (<i>w</i> ₂) in kg	Water absorption $(\%) = \frac{W2 - W1}{W1} \times 100$		
	NWC	10% MgSO ₄ solution	NWC	10% MgSO ₄ solution	NWC	10% MgSO ₄ solution	
MC100F0S0	0.961	0.939	0.986	0.965	2.60	2.76	
M1C90F0S10	0.935	0.965	0.959	0.991	2.56	2.70	
M1C80F0S20	0.955	0.980	0.979	1.006	2.51	2.65	
M1C70F0S30	0.919	0.982	0.941	1.006	2.39	2.44	
M1C80F10S10	0.930	0.883	0.953	0.905	2.47	2.50	
M1C70F10S20	0.925	0.984	0.947	1.008	2.38	2.44	
M1C60F10S30	0.920	0.982	0.941	1.005	2.29	2.34	
M1C50F10S40	0.918	0.980	0.938	1.002	2.18	2.24	
M1C70F20S10	0.923	0.985	0.947	1.013	2.60	2.85	
M1C60F20S20	0.924	0.981	0.948	1.008	2.59	2.76	
M1C50F20S30	0.921	0.980	0.944	1.006	2.50	2.68	
M1C60F30S10	0.916	0.983	0.940	1.010	2.62	2.80	
M1C50F30S20	0.918	0.980	0.942	1.007	2.61	2.75	

Table 7 Water absorption (%) between NWC and 10% MgSO₄ solution curing samples

Table 8 Sorptivity (10⁻⁴ mm/min^{0.5}) between NWC and 10% MgSO₄ solution curing samples

	Oven dr	Oven dry weight (w_1)		Weight of specimen after capillary		Density of	Sorpt	ivity value
Mix identity		ın kg	suction of water (w_2) in kg		of specimen	water (d) in-	10 ⁻⁴ r	nm/min ^{0.5}
with identity	NWC	10% MgSO4	NWC	10% MgSO4	$(A) = (2\pi rh + \pi r^2)$	ka/mm^3	NWC	10% MgSO4
	NWC	solution	NWC	solution	in mm ²	Kg/IIIII	INWC	solution
MC100F0S0	0.948	0.947	0.962	0.960	9424.77	10-6	0.2711	0.2518
M1C90F0S10	0.987	0.873	0.998	0.882	9424.77	10-6	0.2130	0.1743
M1C80F0S20	0.946	0.963	0.954	0.970	9424.77	10-6	0.1549	0.1355
M1C70F0S30	0.925	0.952	0.932	0.958	9424.77	10-6	0.1355	0.1162
M1C80F10S10	0.942	0.954	0.950	0.961	9424.77	10-6	0.1550	0.1355
M1C70F10S20	0.935	0.949	0.941	0.955	9424.77	10-6	0.1162	0.1162
M1C60F10S30	0.930	0.945	0.935	0.951	9424.77	10-6	0.0968	0.1162
M1C50F10S40	0.912	0.930	0.918	0.935	9424.77	10-6	0.1162	0.0968
M1C70F20S10	0.932	0.950	0.939	0.956	9424.77	10-6	0.1356	0.1162
M1C60F20S20	0.928	0.948	0.934	0.954	9424.77	10-6	0.1162	0.1162
M1C50F20S30	0.925	0.932	0.929	0.937	9424.77	10-6	0.0774	0.0968
M1C60F30S10	0.931	0.934	0.938	0.942	9424.77	10-6	0.1356	0.1549
M1C50F30S20	0.926	0.932	0.931	0.939	9424.77	10-6	0.0968	0.1356

H gels are not widely spread as compared to NWC samples. In this image, most of the places covered with voids and some voids are also seems to be very deep in size. From Fig. 15, it is observed that there are hardly C-S-H gels present and very deep voids are visible. The surface looks like rough and as if there is no proper binding between aggregates and paste.

8. Durability study

Durability tests such as water absorption and sorptivity are done confirming to ASTM C 1585-04. The samples are tested for water absorption and sorptivity after curing 28 days in normal water and 10% MgSO₄ solution. The result and discussions for both water absorption and sorptivity are described below.

8.1 Water absorption test

The graphical plot between water absorption and

concrete mixes is shown in Fig. 16. It is observed from Fig. 16 that the water absorption capacity for conventional concrete is 2.6% and 2.75% both in NWC and 10% MgSO₄ solution samples respectively. It is also observed that 10% MgSO₄ solution blended concrete samples have high absorption capacity as compared to NWC samples. When the replacement percentage of silpozz increases, the absorption capacity decreases. When FA is replaced, again absorption capacity increases and after replacing silpozz, it counteracts the absorption capacity and reduces the rate of absorption. The lowest value of water absorption is 2.18% for sample M1C50F10S40 and highest value is 2.85% for sample M1C70F20S10 in NWC and sulphate solution curing respectively. After replacing FA, the absorption capacity increases for both in NWC and 10% MgSO4 solution samples. Silpozz based samples have higher resistivity then the composite samples having FA and silpozz. The absorption capacity depends on the porosity of concrete, particle size of FA and silpozz and their inner structural mechanism of concrete. The dense and compact structured concrete may give less absorption capacity.Water



Fig. 16 Water absorption verses Concrete mix



Fig. 17 Sorptivity verses Concrete mix

absorption (%) between NWC and 10% MgSO₄ solution curing samples are presented in Table 7.

8.2 Sorptivity test

The comparison results of the sorptivity test between NWC and 10% MgSO₄ samples have shown in Fig. 17.

It is observed from Fig. 17 that the conventional concrete has the highest sorptivity value among all mixes both in NWC and 10% MgSO₄ samples. The samples M1C70F10S20 and M1C60F10S30 have same sorptivity value for both in NWC and 10% MgSO₄. The value of sorptivity decreases by the partial replacement of silpozz and the value increases after partial replacement of FA. The result obtained from the silpozz based 10% MgSO₄ samples is less than the NWC composite samples partially replaced with FA and silpozz. In normal water curing, a significant amount of calcium hydroxide migrates from specimen's pores into surrounding water resulted less dense matrix hence sorptivity is more but in pre-cast samples which have already cured in normal water for 28 days and become hardened stage provides dense matrix. In case of higher water-cement ratio with 20% silpozz replacement, upon



Fig. 18 Replacement of Silpozz verses 28 days compressive strength (FA 0-20 series)



Fig. 19 Replacement of Silpozz verses 90 days compressive strength (FA 0-20 series)

evaporation leaves voids spaces in concrete specimen leads to higher absorption but in lower water-cement ratio, doses of SP enhances the liquidity of silpozz concrete mixes and optimize the compaction results high impermeable concrete and less absorption by Mahmud (2010) which compiles in this study. Sorptivity (10⁻⁴ mm/min^{0.5}) between NWC and 10% MgSO₄ solution curing samples are presented in Table 8.

9. Regression analysis on the basis of test results

The regression analysis was carried out for compressive strength, split tensile strength, flexural strength and bond strength for both NWC and SWC pre-cast specimens in order to establish a strong correlation between the replacements of silpozz in percentage corresponding to respective strength properties. A polynomial relationship in the form of $y=ax^2+bx+c$ seems to the best fit the data with R^2 values. The polynomial relationship is suitable for the present study and the range of limitations are the mix proportion, water to binder ratio, the percentage replacement of silpozz and limitations of SP for FA 0% to 20%. The doses of SP are variable and depend upon the replacement level of FA and silpozz. It is observed that

there is good correlation for strength properties and partial replacement of silpozz with OPC.

9.1 Compressive strength versus partial replacement of silpozz (NWC)

The regression equations and value of correlation coefficient R^2 between compressive strength and partial replacement of silpozz for NWC samples at the age of 28 and 90 are shown in Figs. 18-19. As evident from these results that value of correlation coefficient is varied from 0.9602 to 1. The high values of correlation coefficient indicate that there is strong relationship for compressive strength and replacement of silpozz in percentage. From the study, it is observed that the limitation of SP varies from 0.2 to 0.6% for 0% FA with silpozz 10% to 40%. For 10% FA with 10% to 40% silpozz, the range of SP varies from 0.22 to 0.72% and for 20% FA with 10-30% silpozz, SP range is 0.25 to 0.56%. The correlation factor is very high and it means that, inclusion of silpozz in concrete gives better affect to its strength properties. It makes the matrix dense due to its particle fineness. Due to this, the quality of concrete in term of its density, homogeneity and lack of imperfections improved.

10. Conclusions

A few conclusions may be drawn from the study:

• It may be concluded from this study that the 10% FA and 10-20% silpozz replacement with OPC contributes higher compressive strength as compared to control mix cured in normal water, 5% and 10% MgSO₄ solution.

• When the percentage replacement of FA and silpozz increases more than 40% with OPC the strength properties decreases with respect to control sample for all types of curing specimens.

• It may be recommended that a suitable combination of silpozz and fly ash show satisfactory performance in both fresh and hardened concrete with proper doses of super plasticizer.

• The sulphate solution cured samples have better performance against water absorption. When the replacement percentage of silpozz increases, the absorption capacity decreases. After replacing FA the absorption capacity increases for both in NWC and sulphate solution curing samples.

• The sulphate solution curing samples are showing lower sorptivity value than the NWC samples after 28 days of curing. The conventional concrete has the highest sorptivity value among all mixes both in NWC and sulphate solution curing samples. The samples M1C70F10S20 and M1C60F20S20 have same sorptivity value for both in NWC and sulphate solution curing conditions.

• The ternary systems of concrete mix generally produce good properties especially the resistance to sulfate attack in aggressive environment. It may be recommended that necessary protective work can be done as a surface protection in order to enhance the durability of concrete and decrease the rate of deterioration in industrial aggressive environment.

• In blended concrete with FA and silpozz forms C-S-H gel and C₃S and other helpful compound mineral which develop the dense microstructure and uniform cement concrete matrix. The unhydrated cement occurs due to Silica containing large numbers of aggregate particles in mineral phase known as Quartz. The intensity peaks of Quartz dominating other peaks of C₂S and C₄AF which are not visible in X-RD pattern.

• It is predicted from regression analysis that good correlation obtained for strength properties of concrete and the partial replacements of silpozz varies from 10-40% with 0% FA and 10% FA series and 20% FA with 10-30% silpozz series.

• The addition of SCM such as FA and silpozz with super plasticizer enhances the homogeneity of cement paste and densify the microstructure of the cement considerably as well as improves the strength and durability properties of concrete in sulphate environment.

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