Sixth International Conference on the Durability of Concrete Structures **Paper Number PSE25**
18 - 20 July 2018
University of Leeds, Leeds, West Yorkshire, LS2 9JT, United Kingdom

Performance of High-volume Fly Ash Self-compacting Concrete Exposed to External Sulfate Attack

T. S. al-Attar
University of Technology, Iraq
A. A. Taha
Ministry of Health and Environment, Iraq

ABSTRACT

The high-volume fly ash concrete, HVFAC, could be defined as any concrete mix having fly ash content larger than 50 percent of the total cementitious materials content. Due to the availability of fly ash in large quantities globally with low cost, HVFAC could be considered as a solution for the environmental impact of Portland cements. In this study the durability of two high-volume fly ash self-compacting concrete, HVFASCC, mixes exposed to the effects of two sulfate aggressive solutions was investigated. The fly ash, class F, contents for these mixes were 50 and 60 percent by weight of Portland cement. The external sulfate attack was simulated by submerging the concrete specimens in 5 percent sodium and magnesium sulfate solutions separately for 240 days. Six mixes were produced for this purpose, they were: 2 reference mixes cured in water, 2 mixes submerged in Na_2SO_4 solution and 2 mixes submerged in $MgSO_4$ solution. The testing program includes: slump flow, V-funnel, L-box, weight change, XRD and the strength tests: compressive, splitting and flexural strengths. The fly ash content has a positive effect on the rheology (workability) of all tested mixtures. In other words, increasing the cement replacement level from 50 to 60 percent has enhanced the filling ability, passing ability, and segregation resistance of the investigated SCC mixes. The test results show that the magnesium solution has the higher harmful effect on all mixes than the sodium solution. The replacements of Portland cement by the assigned percentages of fly ash have significantly increased the resistance of SCC to the external sulfate attack due to lime consuming reaction.

Keywords: Compressive strength, Fly ash, Self-compacting concrete, Sulfate attack, XRD.

1.0 INTRODUCTION

Self-compacting concrete, SCC, is characterized by its high flowability, passing ability (flows through tight spaces and congested reinforcement), and stability (resistance against segregation and bleeding) (Corr and Shah, 2011). In 1987, the Brundtland Commission (UN-mandated World Commission on Environment and Development) defined sustainable development as the measures that meet the needs of the present without affecting the ability of future generations to meet their own needs" (UNWCED, 1987).The term of sustainability and sustainable development is not so difficult to understand, they are simply about finding a good balance between economic well-being, the positive effect to society and the concern for the environment and its resources (Jowitt, 2004). For concrete sustainability, durability is considered as a crucial part where durable concrete has longer life cycle and needs less maintenance and rehabilitation. Incorporation of supplementary cementitious materials, SCM, such as blast-furnace slag, fly ash, and silica fume as partial replacement of Portland cement had been found a very supportive to durability of concrete. Incooperating SCM with Portland cement in concrete would enhance the concrete impacts on environment through several ways. Firstly, by reducing the use of Portland cement and therefore reducing the CO_2 emissions (global warming). Second, most of the SCM are by-products; therefore, consuming these materials will help in solving the landfill problems (waste management). Finally, SCM will improve the performance of concrete in many harsh environments (service life) (Meyer, 2013). In general, SCM, and fly ash in particular, possess Pozzolanic activity which means their reaction with calcium hydroxide to produce calcium silicate hydrate. This process leads to later strength improvement, reduction in heat of hydration, and reduces the rate of concrete free shrinkage, resulting in a decrease in thermal shrinkage cracking (Jowitt, 2004). In the 1980's Canada Center for Mineral and Energy Technology, CANMET, pointed out to a new term high-volume fly ash, HVFA, concrete (Malhotra, 1998). In this concrete, Portland cement was replaced by class F fly ash in 50 - 60 by weight percentages. CANMET reported excellent mechanical and durability properties for this concrete. Madhavi *et al.* (2014) reported that to attain early age strength; low water/cement ratio is essential where w/cm ratio was less for mixture with HVFA comparable with convention concrete.

Concrete with fly ash content of more than 40% shows lesser 28 days strength but gains better strength at 90 days. Arivalagan (2013) studied the effect of different proportions of fly ash on SCC in fresh and hardened states. In that study, it was observed that by using more than 40% fly ash the demand for water was reduced. Nehdi *et al*. (2004) investigated the durability of self-consolidating concrete incorporating high-volume fly ash as a replacement of cement. The SCC mixture was produced with w/cm ratio of 0.38 and 50% fly ash. There were enhancements in workability tests. Slump flow ranged between 635-650 mm, and L-Box test ratio ranged between 0.84-0.86 while the segregation index was 14% for SCC reference mixture and 8% for HVFA- SCC mixture. The compressive strength values for HVFA-SCC at later ages, more than 90 days, were higher than reference SCC mix (made with cement only). The resistance to sulfate attack (immersion in 5% sodium sulfate solution for 9 months) recorded better results for HVFA-SCC than SCC reference. Siad *et al.* (2013) investigated the behavior of four types of concrete after immersion in 5% sodium sulfate for 2 years. The four types of concrete were: vibrated concrete, SCC with Limestone filler admixture, SCC-LF, SCC with natural Pozzolan, SCC-PZ, and SCC with fly ash, SCC-FA. The results showed that using SCC-PZ and SCC-FA had recorded the highest values in compressive strength, the lowest weight change and dimensional variation after immersion in 5 percent Na_2SO_4 solution at the age of 720 days.
The aim of this investigation is to evaluate the performance of HVFASCC when exposed to very severe aggressive magnesium and sodium sulfate environments.

2.0 EXPERIMENTAL WORK

2.1 Materials

Cementitious Materials
Iraqi ordinary Portland cement was used in this study with specific surface area of 376m^2/kg. The chemical properties conformed to ASTM C150 (2015). The used fly ash has a specific surface area of773 m^2/kg and it meets the requirements of the ASTM C 618 (2015). The chemical properties of those materials are presented in Table 1.

Aggregate
Two types of aggregate were used in this study. Al Ukhaidher sand was used as fine aggregate. This sand has a specific gravity, SSD, of 2.65 and fineness modulus of 3.07. It was conforming to the ASTM C33 (2013). Crushed gravel from Nibaae region was used in the SCC mixes. This coarse aggregate has a MSA of 20 mm and specific gravity, SSD, of 2.7.

Limestone Powder
Fine Limestone Powder was from the western region of Iraq. It was sieved by 0.125mm sieve to achieve its most benefits according to the EFNARC (2002) requirements. The overall fineness of the material before sieving was 239m^2/kg.

Table 1. Properties of cementitious materials

No.	Property		OPC	FA
1	Oxide Content %.	CaO	66.11	0.96
		SiO_2	21.93	65.65
		Al_2O_3	4.98	17.69
		Fe_2O_3	3.1	5.98
		MgO	2	0.72
		SO_3	2.25	0.4
		Na_2O	---	1.39
		K_2O	---	2.99
2	Loss on ignition LOI		2.39	3.10
3	Lime saturation factor, IR		0.93	---
4	Insoluble residue, LSF		1.29	---
5	Fineness (Blaine), m^2/kg		367	773

2.2 External Sulfate Exposures

According to the ACI Committee 318 (2014), the very severe external sulfate exposure, S3, was adopted in this study. This category assumes that the soluble sulfate concentration in water is more than 10000 ppm. This concentration is similar to most of the groundwater of southern part of Iraq. Two salts were chosen to initiate the external exposure; they were sodium sulfate, Na_2SO_4, and magnesium sulfate, $MgSO_4$. Table 2 illustrates the type and concentration of salts used in curing solutions. The resistance against sodium or magnesium sulfate attack was evaluated by measuring the mass change and compressive strength of concrete specimens submerged in 5% sodium or magnesium sulfate solution as compared to those of specimens cured in tap water for the same age. For this exposure, the method that recommended by Mehta (1983) was adopted. This method recommends controlling the pH of the solution within the range of 6.0–8.0 by adding a suitable amount of sulfuric acid solution (0.1 N H_2SO_4). The correction was performed daily during the first week of submersion, and then it became weekly for the rest of the test period (240 days). In addition to that, the aggressive solutions were totally renewed each 8 weeks with check concentration of salt weekly.

2.3 Concrete Mixes

In this study there are two mixes were cast as references to achieve 30MPa as characteristic compressive strength at 28 days for (100*100*100 mm) cubes. The mixture has 500 kg/m^3 of fines content and water to powder ratio of 0.34 by weight. These mixes cured in tap water (Table 3):
- Mix MR50 with 50% fly ash replacement by weight of cement.
- Mix MR60 with 60% fly ash replacement by weight of cement.

The reference mixes were reproduced as mixes M50Mg and M50Na those have the same ingredients but cured in sulfate solutions. The same was done with mix MR60 to produce M60Mg and M60Na. Therefore, the total number of mixes was six.

Table 2. Types and concentrations of salt and ions used in curing solution

Type of salt	Concentration (ppm)	Ions	Concentration (ppm)
$MgSO_4$	50000	Mg^{+2}	19330
		SO_4^{-2}	30670
Na_2SO_4	50000	Na^{+1}	15715
		SO_4^{-2}	34285

Table 3. SCC reference mixes details

Mix	Powder materials content* (kg/m^3)			Aggregate (kg/m^3)		Water (kg/m^3)	S.P$^+$ (l/m^3)
	C	FA	L	Fine	Coarse		
MR50	200	200	100	840	800	170	5.25
MR60	160	240	100	840	800	170	5.4

*: C=cement, FA= Fly ash, L= Limestone Powder
+: SP: Superplasticizer

2.4 Testing Programme

Fresh Concrete Tests
The following tests were carried out according to EFNARC [14]:
- Slump flow and T_{500}.
- V-funnel
- L-box

Hardened Concrete Tests
Table 4 lists the conducted tests, the adopted standards, types and dimensions of tested specimen and age of test for the hardened HVFASCC mixes.

Table 4. Hardened concrete tests

Test	Adopted standard	Specimen type	Dimensions (mm)	Age of test (day)
Compressive Strength	BS EN 12390-3 (2002)	Cube	100*100*100	14, 28, 90, 180, and 240
Splitting Tensile Strength	ASTM C496 (2011)	Cylinder	d=100 h= 200	14, 28, 90,180 and 210
Flexural Strength	ASTM C 78 (2015)	Prism	100*100*400	14, 28, 90 and 180
Weight Change	ASTM C 267 (2012)	Cube	100*100*100	28, 56, 90,180, 210 and 240

3.0 RESULTS AND DISCUSSION

3.1 Results of Fresh HVFASCC

Table 5 lists the result of the conducted tests during the fresh state of mixes. The increase in fly ash content caused a gain in the filling and passing abilities of the investigated SCC mixes. Mix MR60 always showed higher slump flow and (H2/H1) ratio and lower funnel time than mix MR50. The fineness and the uniform spherical shape of fly ash could be the reason for such behavior. All listed test results were conforming to the requirements of the EFNARC (2002).

Table 5. Fresh HVFASCC test results

Type of mixes	Slump flow		V-funnel		L-Box (H2/H1)
	D (mm)	T_{500} (sec)	direct (sec)	after 5minuts (sec)	
MR50	750	3	11	14	0.9
MR60	760	3	8	11	0.95
EFNARC (2002) Requirements	600-800	2-5	6-12	+3	0.8-1

3.2 Results of Strength Development of HVFASCC

Table 6 summarizes the three types of strength development for all mixes with different method of curing and at different ages.

Table 6. Strength test results

Mix		MR50	M50Mg	M50Na	MR60	M60Mg	M60Na
Type of Curing		in water	in $MgSO_4$	in Na_2SO_4	in water	in $MgSO_4$	in Na_2SO_4
Strength	Age, (day)						
Comp. (MPa)	14	39.3	39.3	39.3	38.4	38.4	38.4
	28	46.5	43.3	43.2	41.2	40	39.2
	90	56.0	51.5	52	52.1	48	50.7
	180	57.3	48.9	48.8	54.0	47.4	46.5
	240	63.0	48.0	60.0	60.0	45.8	57.3
Splitting Tensile (MPa)	14	3.3	3.3	3.3	3.2	3.2	3.2
	28	3.6	3.6	3.6	3.5	3.4	3.4
	90	4.2	3.8	4	4.1	3.6	3.7
	180	4.5	4.4	4.4	4.3	4.2	4.1
	210	5.2	4.4	4.7	4.9	4.2	4.4
Flexural (MPa)	14	3.5	3.5	3.5	3.5	3.5	3.5
	28	4.0	4.0	3.9	3.8	3.7	3.7
	90	4.7	4.2	4.3	4.5	4.1	4.2
	180	5.4	4.6	4.9	5.2	4.3	4.6

From Table 6 it is observed that mixes M50Mg and M50Na had increasing compressive strength till the age of 90 days (14 days in water plus 76 days in aggressive solutions). After that the compressive strength for mix M50Mg started to decrease with a slow rate and continued decreasing till the age of 240 days. Mix M50Na showed a similar trend till the age of 180 days but later on it came back to gain strength till the age of 240 days. This behavior was also recorded for mixes M60Mg and M60Na as shown in Figures 1 and 2. It is well known that $MgSO_4$ solutions are more aggressive on cement paste because this type of sulfate can attack and disintegrate the calcium silicate hydrates, C-S-H, in addition to the aluminate phases (Neville, 2011).

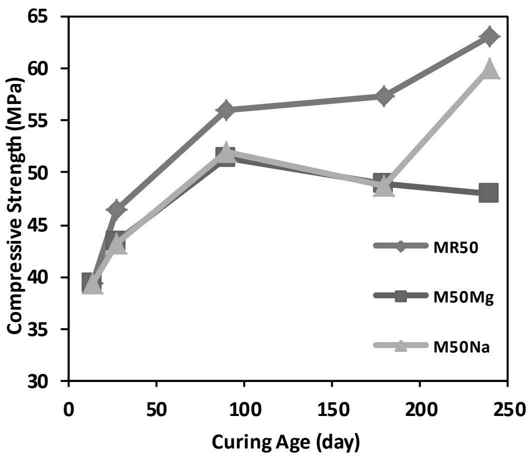

Fig. 1. Compressive strength development with age for mixes contain 50% fly ash

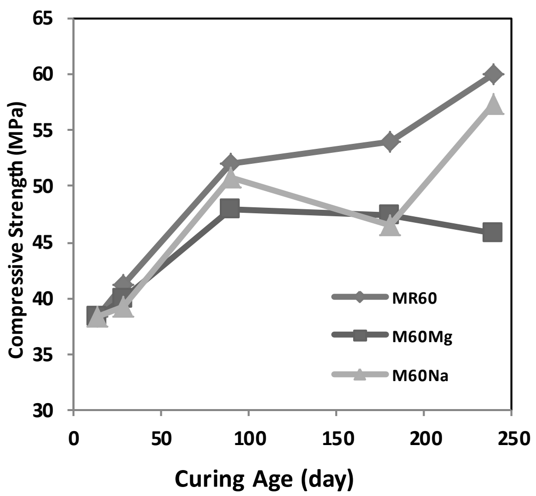

Fig. 2. Compressive strength development with age for mixes contain 60% fly ash

With respect to the behavior of mixes M50Na and M60Na, the following remarks could be considered:

a. the consumption of $Ca(OH)_2$ by Pozzolanic reaction. This reaction prohibited the formation of new gypsum and furthermore reduced the amount of ettringite formed from the reaction between calcium sulfate and alumina.
b. the lower permeability of the concrete due to the existence of fly ash which acts primarily as pore-filler.
c. as a result for the abovementioned reasons and due to the continuous Pozzolanic reaction, new CSH gel was produced and caused the strength gain later, after the age of 180 days.
d. through the hydration of the ternary system, cement, fly ash and Limestone, the production of $Ca(OH)_2$ is slightly less than with cement alone. Moreover, the remaining aluminates will react with calcium carbonate to form a combination of calcium mono- and hemicarbonate instead of sulfoaluminate (Tanesi *et al.*, 2014)

3.3 Results of Weight Change of HVFASCC

Table 7 shows the results of weight change for mixes exposed to external sulfate attack after being partially submerged in magnesium sulfate and sodium sulfate solutions. In this investigation it was noted that there was always a mass gain for all submerged specimens. This could be justified by the formation of calcium silicate hydrate from hydration of cement or from second hydration of fly ash with $Ca(OH)_2$ and water. Also the formation of gypsum, ettringite and/or calcium monosulfoaluminate could be a reason for this mass increase.

Table 7. Weight change with age for mixtures exposed to external sulfate attack

Mix		M50Mg	M50Na	M60Mg	M60Na
Weight Change, %, at age, days:	28	0.40	0.16	0.37	0.15
	56	0.60	0.24	0.52	0.20
	90	0.80	0.32	0.65	0.30
	180	0.90	0.40	0.77	0.38
	210	0.90	0.45	0.86	0.44
	240	1.05	0.51	0.94	0.50

3.4 Results of XRD Analysis

The XRD pattern for three powder samples were studied and compared. The chosen samples for this study were:

a. Sample from mix MR50 (water-cured) at the age of 28 days.
b. Sample from mix MR50 (water-cured) at the age of 90 days.
c. Sample from mix M50Na (partially submerged in sodium sulfate solution) at the age of 90 days.

Table 8 and Figures 3 - 5 show the details and patterns for the studied powders.

Table 8. Results of the XRD of powder samples taken from mixes MR50 and M50Na

Mix	Age (day)	Ordered Strongest Peaks	Peak No.	2 theta (degree)	d (Aº)	Relative Intensity (%)
MR50	28	1	8	29.48	3.33	100
		2	7	26.69	3.33	40
		3	15	47.59	1.90	17
	90	1	4	29.48	3.02	100
		2	3	26.67	3.33	12
		3	7	39.46	2.28	8
M50Na	90	1	3	29.46	3.02	100
		2	2	26.68	3.33	12
		3	10	48.56	1.87	11

Figure 3 shows that the dominant phases in the tested powder are: calcium silicate hydrates, CSH, quartz, Q, and calcium carbonate, CC*. Small peaks, with relative intensity of less than 5%, were also recorded. These small peaks were: gypsum, CS* and calcium hydroxide, CH. Cement hydration is the source of CSH, quartz is mainly related to the fly ash and the Limestone is the source of calcium carbonate. The low intensity of calcium hydroxide could be considered as an indication to the Pozzolanic reaction of fly ash which consumes $Ca(OH)_2$. If the pattern that is shown in Figure 4 at 90-day age, is compared to the 28-day pattern, the same peaks are recorded but with different intensities. The CSH phase has higher intensity meanwhile quartz and calcium carbonate phases have lower ones. This observation leads to the conclusion that a continuous hydration had taken place, although the mix had high-volume fly ash and low cement content. The calcium hydroxide being in smaller peaks also is evidence that the fly ash has done its role in hydration process. The absence of ettringite, calcium sulfoaluminate, in both patterns gives the rise for the possibility of calcium monosulfoaluminate formation due to the high alumina content, 4.98% in cement plus 17.68% in fly ash (Lea, 2004). The calcium monosulfoaluminate has higher density than ettringite thus causes lower expansion in the microstructure (Balonis and Glasser, 2009).

In Fig. 5, which displays the XRD pattern of a powder taken from mix M50Na at the age of 90 days, the main three peaks were for: calcium silicate hydrates, CSH, quartz, Q and calcium carbonate, CC*. Gypsum, CS*, was existed in small relative intensities, less than 5%. The peaks for calcium hydroxide were so small that could be neglected. This pattern could point out to that gypsum has been formed in the beginning through the reaction between sodium sulfate and calcium hydroxide and then this formation discontinued due to calcium hydroxide consumption by fly ash. Another source for the detected gypsum may be the used cement itself.

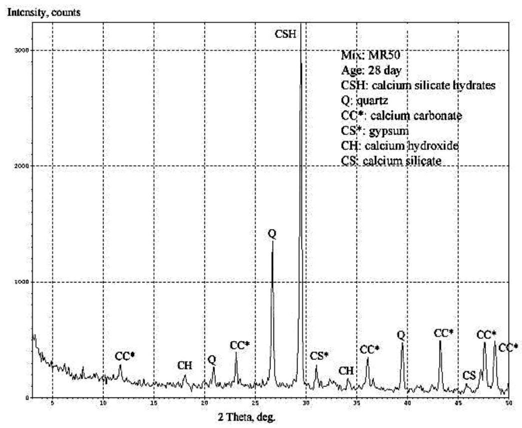

Fig. 3. XRD pattern for mix MR50 at age of 28 days

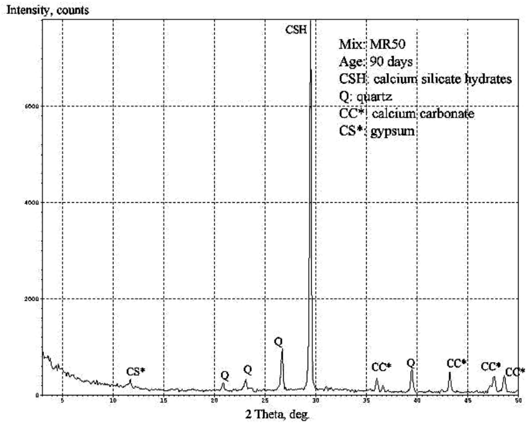

Fig. 4. XRD pattern for mix MR50 at age of 90 days

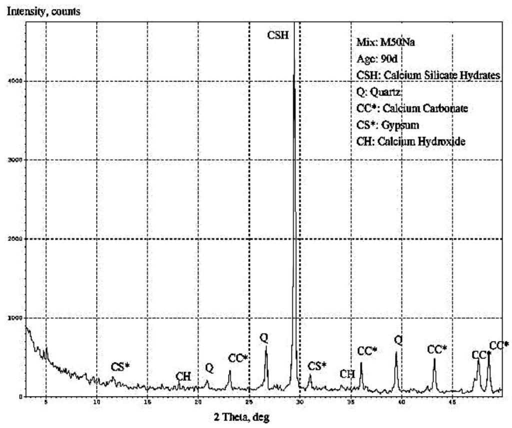

Fig. 5. XRD pattern for mix M50Na at age of 90 days

4.0 CONCLUSIONS

According to the results that were obtained from the experimental program, the following conclusions were extracted:

1. The fly ash content has a positive effect on the rheology (workability) of all tested mixtures. In other words, increasing the cement replacement level from 50 to 60% has enhanced the filling ability, passing ability, and segregation resistance of the investigated SCC mixes.
2. For magnesium sulfate exposure, there was a continuous degradation in strength and that could be attributed to a two-folded reaction; the exchange of cations Ca^{+2} and Mg^{+2} to form $CaSO_4$ and $Mg(OH)_2$ and the attack of magnesium sulfate to the calcium silicate hydrates.
3. When dealing with sodium sulfate exposure, a different development trend for strength was observed. There was degradation in strength till the age of 180 days and then a strength gain occurred till the end of test period, 240 days. This behavior could be resulted from:
   a. The consumption of $Ca(OH)_2$ by Pozzolanic reaction. This reaction prohibited the formation of new gypsum and furthermore reduced the

amount of ettringite formed from the reaction between calcium sulfate and alumina.

b. The lower permeability of the concrete due to the existence of fly ash which acts primarily as pore-filler.

c. As a result for the abovementioned reasons and due to the continuous Pozzolanic reaction, new CSH gel was produced and caused the strength gain later, after the age of 180 days.

4. In the studied ternary system, cement, fly ash and Limestone, through hydration the production of $Ca(OH)_2$ could be slightly less than with cement alone. Moreover, the remaining aluminates may react with calcium carbonate to form a combination of calcium mono- and hemicarbonate instead of sulfoaluminate.
5. There was always a mass gain for all partially submerged specimens in aggressive solutions. This could be justified by the formation of calcium silicate hydrate from hydration of cement or from second hydration of fly ash with $Ca(OH)_2$ and water. Also the formation of the denser calcium monosulfoaluminate, instead of ettringite, and/or or calcium mono- or hemicarbonate could be reasons for this mass increase.

References

ACI Committee 318, 2014. Building code requirements for structural concrete - ACI 318M-14. ACI manual of concrete practice.

Arivalagan, S., 2013. Experimental analysis of self-compacting concrete incorporating different ranges of high-volumes of class F fly ash. Scholars Journal of Engineering and Technology, 1(3): 104-111.

ASTM, 2015. Standard specification for concrete aggregates – ASTM C33M – 13.

ASTM, 2015. Standard test method for flexural strength of concrete (using simple beam with third-point loading - ASTM C78M -15a.

ASTM, 2015. Standard specification for Portland cement – ASTM C150M – 15.

ASTM, 2015. Standard test methods for chemical resistance of mortars, grouts, and monolithic surfacings and polymer concretes – ASTM C267 – 01 (reapproved 2012).

ASTM, 2015. Standard test method for splitting tensile strength of cylindrical concrete specimens- ASTM C496M -11.

ASTM, 2015. Standard specification for coal fly ash and raw or calcined natural Pozzolan for use in concrete – ASTM C618 – 12a.

Balonis M. and Glasser, F. P., 2009. The density of cement phases. Cement and Concrete Research, 39(9):733-739.

BSI, 2002. Method for determination of compressive strength of concrete cubes – BS EN 12390 Part 3.

Corr, D. J. and Shah, S. P., 2011. Design and application of high-volume fly ash self-consolidating concrete with the incorporation of nanoparticles. Final report. Infrastructure Technology Institute.

EFNARC, 2002. Specification and guidelines for self-compacting concrete. Association House.

Jowitt, P.W., 2004. Systems and sustainability: sustainable development, civil engineering and the formation of the civil engineer. ICE, 1-11.

Lea, F. M., 2004. Chemistry of Cement and Concrete. 4th ed. Elsevier.

Madhavi, T. Ch., Swamy Raju, L. and Mathur, D., 2014. Durability and strength properties of high-volume fly ash concrete. Journal of Civil Engineering Research, 4(2A): 7-11.

Malhotra, V. M., 1998. Fly ash, silica fume, slag and natural Pozzolans in concrete. ACI SP-178.

Mehta P. K., 1983. Mechanism of sulfate attack on Portland cement concrete. Cement and Concrete Research, 13: 401-406.

Meyer, C., 2013. The greening of the concrete industry. 2013 World congress on advances in structural engineering and mechanics, ASEM13: 79 – 92.

Nehdi, M., Pardhanb, M. and Koshowski, S., 2004. Durability of self-consolidating concrete incorporating high-volume replacement composite cements" cement and concrete research, 34: 2103-2112.

Neville, A. M., 2011. *Properties of Concrete*. 5th ed. Prentice Hall.

Siad, H., Kamali-Bernard, S., Mesbah, H. A., Escadeillas, G. and Mouli, M., 2013. Characterization of the degradation of self-compacting concretes in sodium sulfate environment: Influence of different mineral admixtures. Construction and Building Materials, 47: 1188-1200.

Tanesi, J., Bentz, D. P. and Ardani, A., 2013. Enhancing high-volume fly ash concrete using fine Limestone Powder. ACI SP-294: Advances in Green Binder Systems. American Concrete Institute.

UNWCED, 1987. Our common future. United Nations report.