

Comparison of different methods for activation of ordinary Portland cement-slag mortars

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ABSTRACT

This paper compares three methods for activation of OPC-slag mortars (OSM): (1) prolonged grinding of binders (mechanical method), (2) elevated temperature curing of mortars (thermal method), and (3) use of chemical activators such as NaOH, KOH, and Na₂SiO₃·9.35H₂O (chemical method). The proper reactivity of OSM was evaluated using a mixture of 50% OPC and 50% slag. Early and ultimate strengths were compared. All three activation methods accelerated both the slag reaction and strength development rates. However, the chemical method did not show a significant effect on the ultimate strength, while thermal activation increased the early strength by 3 days. Mechanical activation increased the early strengths of the mortar significantly, but about 6% strength loss occurred in the ultimate strength. Although, the application of mechanical and thermal activation methods needs extra equipment and energy, due to more significant of strength improvement; based on current test results, it can be said that mechanical activation is the most efficient and feasible method for the activation of OSMs.

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1. Introduction

In this experimental work, mechanical, thermal, and chemical methods have been used to improve the compressive strength of OSMs. All three methods can be used to activate the potential reactivity of cement constituents.

The mechanical activation is used to increase the specific surface area of the constituents and thus accelerates the hydration rate. Many results indicate that the early strength of a hardened cement paste is directly proportional to the fineness of the cement, but fineness cannot contribute to later-age strength. In contrast, excessively high fineness may increase the water requirement and cause a reduction in later strength gain. In general, increased fineness results in better strength development, but in practice, fineness is limited by economic and performance considerations and factors such as setting time and shrinkage [1]. For better performance, the fineness of GGBFS must be greater than that of cement [2]. At the same time, the requirement to increase fineness reduces productivity and consumes more energy. Prolonged grinding not only increases the surface area of a material, but also the number of imperfections or active centers which exist at the edges, corners, projections and places where the inter-atomic distances are abnormal or are embedded with foreign atoms. These centers are in a higher energy state than in the normal structure. The more of these centers, the faster the rate of reactivity. Millers and Oulton

(1970) observed that percussive dry grinding can cause obvious crystal distortion of kaolinite. It was also recently found that impaction and friction milling of high alumina cement alters its crystallinity and notably modifies its hydraulic behavior.

A strength test on 22 pozzolans (Chatterjee and Lahiri, 1967) indicated no general correlation between the compressive strength of different materials (at 28 or 60 days) and surface area (either by Blain or BET method). However, it was stated that strength increases as fineness increases, for a single material. Different pozzolans have different quantities and nature of reactive components. It cannot be expected that a unique relationship exists between reactivity and surface area for all pozzolans. Prolonged grinding of natural pozzolan also consumes extra energy and reduces grinding productivity [3]. It has been reported [4] that for each 10 m²/kg increasing in Blain fineness, cost of grinding will be increased by about 10%. Elevated temperature curing needs additional equipment and is usually suitable for precast products. It also consumes a great amount of energy. Hydrated mortars and concretes can reach their maximum strength within several hours through elevated temperature curing. However, the ultimate strength of hardened mortars and concretes has been shown to decrease with curing temperature. Variations of mortar and concrete under high temperature are mainly the result of two different mechanisms. One is the variation of material properties of the constituent phases under high temperatures, and the other is the transformation of constituent phases under different temperatures. Therefore, the property of mortar and concrete under high temperatures must be studied from both a mechanical and chemical point of view [5].

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The chemical activation refers to the use of some chemicals to activate the potential reactivity of cementitious components. Alkali-GGBFS is a typical, successful example of chemical activation. GGBFS shows little cementitious properties; nevertheless, it gives very high strengths in the presence of chemical activators such as Na_2SiO_3 , NaOH , and Na_2CO_3 . The activator(s) can be added during the milling of cement, or can be dissolved in the mixing water and added during mixing of mortars and concretes. The technology is very simple and does not need extra equipment. However, in chemical activation method there is an important reality that it cannot be used every activator to activate every type of slag, and then for better performance by chemical activators it needs to have many tests and materials for determination of the best activator. This is an improper point in chemical activation method.

The objective of the current paper is to compare the efficacy of three activation methods, as measured by strength development and initial and ultimate compressive strengths.

2. Research significance

It is known that a lot of slag is produced in the steel-iron industry every year, throughout the entire world. If some means of consumption for these by-product materials can be found, it would help in terms of being environment friendly and also provide significant economic benefits. Moreover, the results of several researches have shown the use of the replacement materials in mortars and concretes has improved durability, which has vital significance for the structures built in aggressive environments, such as those in marine structures, such as big tunnels and bridges with long life spans. However, there is a problem in the use of the materials with initial hydration being lower than OPC and mortars and concretes having low early strengths. There are several ways of resolving this problem; including using mechanical, thermal, and chemical methods of activation, which is precisely the main purpose of this study.

3. Experimental procedure

3.1. Properties of materials

The properties of the materials have been used in the study are as follows.

3.1.1. Cement

The cement used in all mixes was OPC. ASTM C-109-99 was used for determination of the compressive strength of hydraulic cement mortars, by use of 50 mm sided cube specimens. The specific gravity of cement used is by about 3.14. Based on particle size analysis (PSA) tests, the specific surface area (SSA) for OPC was determined to be $1893.9 \text{ m}^2/\text{kg}$. The chemical compositions of OPC used in this research have been determined by the testing method "X-ray fluorescence spectrometry (XRF)". The compositions of OPC are given in Table 1.

3.1.2. Slag

The specific gravity of the slag is approximately 2.87, with its bulk density varying in the range of $1180\text{--}1250 \text{ kg/m}^3$. The color of ground granulated blast furnace slag (GGBFS) is normally whitish (off-white). Based on PSA tests, the SSA for GGBFS has been determined at $3597.2 \text{ m}^2/\text{kg}$. It can be seen that $\text{SSA}_{\text{slag}} = 1.90 * \text{SSA}_{\text{OPC}}$, which means that particles of slag are 90% finer than that of OPC. The compositions of slag are given in Tables 4a and 4b. As with all cementing materials, the reactivity of the slag is determined by its SSA. Based on the definition of slag activity index (SAI) in ASTM C989 [5], it can be seen that $\text{SAI} = (\text{SP}/\text{P}) * 100$, where; SP = average compressive strength of slag-reference cement mortar cubes; P = average compressive strength of reference cement mortar cubes. Both compressive strengths are in MPa. Based on this definition, the slag used in the tests is classified into Grade 120. A result calculation is shown in the bottom of Table 1.

3.1.3. Aggregates

The fine aggregates used in the mixes are graded silica sands with specific gravity, fineness modulus (FM) and water absorption (BS812: clause 21) 2.68%, 3.88% and 0.93%, respectively. The maximum size of aggregate is 4.75 mm. The PSA of the fine aggregates is given in Table 2, and the grain size distribution diagram is drawn in Fig. 1.

3.1.4. Super plasticizer

In order to have appropriate consistency with low a W/B ratio, super plasticizer (SP) is required to be used. The SP used in this investigation is Rheobuild 1100. The specific gravity of SP is approximately 1.195, is dark brown in color, with a pH in the range of 6.0–9.0. The consumed content of SP in the mortar depends on the replacement level of slag. Rheobuild 1100 is a chloride-free product. Meets ASTM C-494. The basic components are synthetic polymers which allow mixing water to be reduced considered. The dosage of R1100 generally varies from 0.8 to 1.2 l/(100 kg)

Table 1
Composition of cementitious materials (% by mass).

For OPC												
P205	SiO_2	Al_2O_3	MgO	Fe_2O_3	CaO	MnO	K_2O	TiO_2	SO_3	CO_2	Cl	
0.07	18.47	4.27	2.08	2.06	64.09	0.04	0.28	0.10	4.25	4.20	0.01	
For slag												
SrO	SiO_2	Al_2O_3	MgO	Fe_2O_3	CaO	MnO	K_2O	TiO_2	SO_3	CO_2	Na_2O	
0.05	31.21	12.96	4.27	0.87	41.47	0.21	0.31	0.49	2.04	6.00	0.11	

For 7 days; $\text{SAI} = 47.57/47.76 = 1.00 > 0.95$; For 28 days; $\text{SAI} = 62.83/50.26 = 1.25 > 1.15$;
 K_b (basicity index) for slag = $(41.47 + 4.27)/(31.21 + 12.96) = 1.03 > 1.00$.
 $1.30 \leq \text{CaO}/\text{SiO}_2 = \text{C}/\text{S} = 1.33$ for slag ≤ 1.40 [5].

Table 2
PSA for silica sand (SS) based on BS 822: Clause 11.

Sieve size (μm)	Sieve no.	WSS + WS (g)	WS (g)	WSS (g)	Ret. %	Cum. Ret. %	Pass. %
4750	3/16 in	409.9	408.3	1.6	0.32	0.32	99.68
2360	No. 7	462.3	375.7	86.6	17.33	17.65	82.35
1180	No. 14	437.2	343.0	94.2	18.85	36.5	63.50
600	No. 25	450.7	316.2	134.5	26.93	63.42	36.58
300	No. 52	379.1	288.7	90.4	18.09	81.51	18.49
150	No. 100	322.1	274.8	47.3	9.47	90.99	9.02
75	No. 200	309.9	275.2	34.7	6.94	97.92	2.08
Pan	–	250.8	240.4	10.4	2.08	–	0.00
Total				499.7	–	388.31	

FM = $388.31/100 = 3.88$ [6,7].

PSA for silica sand used in the mixes is as: 12% mesh 50/100, 18% mesh 30/60, 30% mesh 16/30, 20% mesh 8/16, and 20% mesh 4/6.

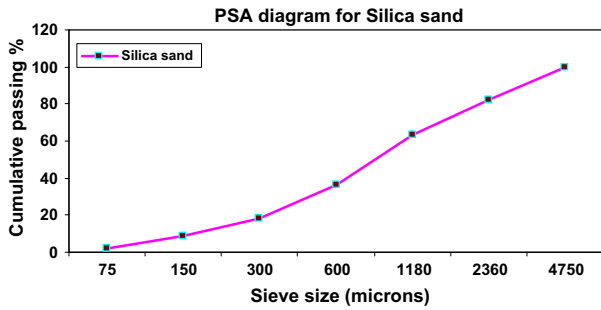


Fig. 1. PSA diagram for silica sand.

of cement. Other dosages may be recommended in special cases according to specific job conditions. It is compatible with all cements and admixtures meeting ASTM and UNI standards.

3.1.5. Water

The water used in all mixes was potable water in pipeline of the lab. It was assumed that the specific gravity of the used water is about 1 g/cm³.

3.1.6. Activators

Chemical reagents NaOH, KOH, and Na₂SiO₃, nH₂O were used as alkaline activators. The dosage of alkaline activators were 2%, 4%, and 6% Na₂O, K₂O, and Na₂O (% by mass), respectively. Based on the mass of slag, these activators were dissolved into mixing water first and then added to the mixing. Some physical and chemical properties of the activators are shown in Table 3.

3.2. Mix proportions and curing

Tables 4a, 5, and 6a and 6b represent the mix proportions for different activation methods. In all mixes, water-binder and sand-binder ratios are 0.33 and 2.25, respectively. Silica sands were used in the mixes. At first, based on PSA, five groups of silica sand were mixed. Two min following that, cement and replacement slag were put into the mixture, followed by 3–4 min of mixing. Mixing water was then added to the mix and mixing was continued for 5 min, following which the required amount SP was added. Mixing was continued for 2 min before the moulds were filled with fresh mortar in two layers. Each layer was compacted with ten impacts by a rod with 16 mm diameter. 24 h after casting, the specimens were demoulded and cured proportionally in water with 23 ± 3 °C or in the room temperature 27 ± 3 °C and 65 ± 18% relative humidity (RH) until the test day.

3.3. Test and mixing procedures

3.3.1. Test for fresh mortar

In order to have appropriate consistency for each mortar mix after casting, a flow table test has been done. The range of flow amounts were between 220 and 235 mm. The test procedure is that following casting, some mortar is put in the truncated brass cone in two layers. Each layer is compacted 10 times by a steel rod with a 16 mm diameter, before the cone is lifted and the mortar collapsed on the flow table. Following that, both the table and mortar are jolted 15 times in a period of 60 s. Jolting the table enables the mortar to consequently spread out and the maximum spread, to the two edges of the table, was then recorded. The average of both records is calculated as flow (mm). The photograph for mixture and flow table test is shown in Fig. 2.

Table 3

Some properties of activators used in the study.

No.	Activator name	Type	Formula/abbreviation	Na ₂ O or K ₂ O (%)	SiO ₂ (%)	H ₂ O (%)	M _s	M (g/mol)
1	Sodium silicate	Solution	Na ₂ SiO ₃ , 1.11H ₂ O/SSS	43.64	42.23	14.13	0.97	142.07
2	Sodium silicate	Solution	Na ₂ SiO ₃ , 9.35H ₂ O/SSS	12	30	58	2.5	290.48
3	Sodium silicate – extra pure	Solution	Na ₂ SiO ₃ , 12.58H ₂ O/SSEP	8	27	65	3.375	348.45
4	Sodium silicate	Granular	Na ₂ SiO ₃ , 9.0H ₂ O/GSS	21.81	21.11	57.08	0.97	284.22
5	Sodium hydroxide	Pellet	NaOH/SH	99	–	–	–	40
6	Potassium hydroxide	Pellet	KOH/PH	85	–	–	–	56

M_s = Molar ratio = SiO₂/Na₂O.

Table 4a

Mix proportions of OSMs for mechanical activation method.

No.	Mix name	OPC (g)	Slag (g)	Water (g)	Flow (mm)	SP (g)
1	OM	1800	0	631.7	230	60
2	OSM/50	900	900	631.7	235	40
3	GS3C0	900	900	631.7	230	26
4	GS0C3	900	900	631.7	220	24
5	GS3C3	900	900	631.7	225	24
6	GS6C0	900	900	631.7	230	28
7	GS0C6	900	900	631.7	225	28
8	GS6C6	900	900	631.7	235	28
9	GS9.5C0	900	900	631.7	220	20
10	GS0C9.5	900	900	631.7	220	24
11	GS9.5C9.5	900	900	631.7	220	22
12	GS13C0	900	900	631.7	225	22
13	GS0C13	900	900	631.7	220	27
14	GS13C13	900	900	631.7	220	26

GSiCi = Mixes made by using the binders grounded in a period of *i* h.

For all mixes: W/B = 0.33, S/B = 2.25.

Table 4b

SSA values (m²/kg) of OPC and slag.

Duration of grinding (h)	0.0	3.0	6.0	9.5	13.0
OPC	1893.9	2390.1	3098.7	2130.1	344.1
Slag	3597.2	3873.2	4180.6	4374.1	2065.1
$r = SSA_{slag}/SSA_{OPC}$	1.90	1.62	1.35	2.05	6.00

A ball mill grinder machine was used to grind the binders' particles.

Table 5

Mix proportions of OMs, OSMs/40, and OSMs/50 for thermal activation method.

No.	Mix name	OPC (g)	Slag (g)	Water (g)	SP (g)	Flow (mm)
<i>For OMs, air and water cured</i>						
1	OM-air cure	1800	–	631.66	28	230
2	OM-water cure	1800	–	631.66	30	230
<i>For OSMs/40, air and water cured</i>						
3	H0/0	720	480	421.11	28	225
4	H60/2	1440	960	842.22	82	230
5	H60/4, 6	1440	960	842.22	90	230
6	H60/8, 10	1440	960	842.22	79	230
7	H60/12, 14	1440	960	842.22	79	230
8	H60/16	1440	960	842.22	82	230
9	H60/18, 20	1440	960	842.22	73	230
10	H60/22–26	2160	1440	1263.33	70	220
<i>For OSMs/50, air and water cured</i>						
11	H0/0	600	600	421.11	35	230
12	H60/2	1200	1200	842.22	76	235
13	H60/4, 6	1200	1200	842.22	91	225
14	H60/8, 10	1200	1200	842.22	90	235
15	H60/12, 14	1200	1200	842.22	73	235
16	H60/16	1200	1200	842.22	76	235
17	H60/18, 20	1200	1200	842.22	62	225
18	H60/22–26	1800	1800	1263.33	60	220
<i>For optimum OSM/50 at 6 ages, only air cured</i>						
19	H60/20	900	900	631.66	43	230

H60/*i, j* means 60 °C temperature with heating time *i* and *j* h.

PSA for silica sand used in the mixes is as: 12% mesh 50/100, 18% mesh 30/60, 30% mesh 16/30, 20% mesh 8/16, and 20% mesh 4/6.

Table 6a

Mix proportions of control mixes and Abbreviations.

No.	Mix name	Curing regime	OPC (g)	Slag (g)	Water (g)	SP (g)	Flow (mm) (g)
1	OM	Water	1800	0	631.7	60	230
2	OSM/40	Water	1080	720	631.7	28	225
3	OSM/50	Water	900	900	631.7	28	220
4	OSM/60	Water	720	1080	631.7	35	225

List of abbreviations

No.	Original statement	Abbr.
1	Ordinary Portland cement (OPC) mortar	OM
2	Slag mortar	SM
3	OPC-slag mortar with <i>i</i> % level of slag	OSM _{<i>i</i>}
4	Potassium hydroxide with <i>i</i> % content (based on mass of slag)	PH _{<i>i</i>}
5	Sodium hydroxide with <i>i</i> % content (based on mass of slag)	SH _{<i>i</i>}
6	Solution sodium silicate with <i>i</i> % content (based on mass of slag)	SSS _{<i>i</i>}
7	Granular sodium silicate with <i>i</i> % content (based on mass of slag)	GSS _{<i>i</i>}
8	Sodium silicate extra pure with <i>i</i> % content (based on mass of slag)	SSEP _{<i>i</i>}

Table 6b

Mix proportions of OSMs for chemical activation method.

No.	Slag level	Mix name	Curing regime	OPC (g)	Slag (g)	Water (g)	SP (g)	Flow (mm)
1	60	PH1	Air	480	720	421.1	45	220
2	60	PH2	Air	480	720	421.1	50	220
3	60	PH4	Air	480	720	421.1	180	220
4	60	PH6	Air	480	720	421.1	230	220
5	60	SH2	Air	480	720	421.1	60	225
6	60	SH4	Air	480	720	421.1	40	220
7	60	SH6	Air	480	720	421.1	65	220
8	60	SSS2	Air	480	720	421.1	128	225
9	60	SSS4	Air	480	720	421.1	255	225
10	60	SSS6	Air	480	720	421.1	310	220
11	50	GSS2	Air	600	600	421.1	70	220
12	60	GSS2	Air	480	720	421.1	70	220
13	50	SSEP2	Air	600	600	421.1	75	225
14	40	SSS2	Water	720	480	421.1	52	230
15	40	SSS3	Water	720	480	421.1	82	230
16	40	SSS5	Water	720	480	421.1	114	225
17	50	PH1.5	Air	600	600	421.1	51	230
18	40	PH2	Air	720	480	421.1	38	230
19	40	PH4	Air	720	480	421.1	60	220
20	40	GSS1.17 + SH3.35	Air	720	480	421.1	110	225
21	40	GSS2.5 + SH2.33	Air	720	480	421.1	147	220
22	40	SSS2 + SH0.6	Air	720	480	421.1	185	220
23	40	SSS3 + SH4.5	Air	720	480	421.1	145	220
24	50	PH2 + SH3	Air	600	600	421.1	80	225
25	50	PH2 + SH5	Air	600	600	421.1	120	225
26	50	PH1 + SH1.5	Air	600	600	421.1	60	220
27	50	PH0.75 + SH1	Air	600	600	421.1	45	230
28	30	PH0.5 + SH0.5	Air	840	360	421.1	27	230
29	40	PH0.5 + SH0.5	Air	720	480	421.1	60	230
30	50	PH0.5 + SH0.5	Air	600	600	421.1	23	235
31	60	PH0.5 + SH0.5	Air	480	720	421.1	26	230
32	50	PH1.5 + SH0.75	Air	600	600	421.1	41	220
For optimum OSM/50 at 6 ages								
33	50	PH0.5 + SH0.5	Air	900	900	631.7	33	230

For all mixes: W/B = 0.33 and S/B = 2.25.

PSA for silica sand used in the mixes is as: 12% mesh 50/100, 18% mesh 30/60, 30% mesh 16/30, 20% mesh 8/16, and 20% mesh 4/6.

3.3.2. Test for hardened mortar

Three cubic samples, with lengths of 50 mm, were used for each age. Samples produced from fresh mortar were demoulded after 24 h, and then cured in room temperature with 27 ± 3 °C and $65 \pm 18\%$ RH, and in the water with 23 ± 3 °C before the samples were used for compressive strength tests. Compressive strength measurements were carried out using an ELE testing machine press with a capacity of 2000 KN, and a pacing rate of 0.5 KN/s. Compressive tests have been done according to BS 1881, Part 116, 1983.

3.3.3. Mortar mix method

Initially, five groups of silica sand are put in as a mixture and mixed for 2 min. Following that, the cement and slag are added and mixing is continued for 3–4 min. The activator is then poured into the calculated water and mixed until completely dissolved. The solution is then added into the mixture and mixing is continued for

2 min. Finally, SP is added and mixing continued for 2 min; immediately following the completion of the mixing, the flow table test is done and the specimens are moulded. For each mix, the duration of mixing time takes about 8 to 10 min.

4. Results and discussion

4.1. Mechanical method

In the mechanical method, fourteen mix proportions of OSMs have been used with two mixes as control. For each mix, it is important to have high early strength. In this method, 50% of cement replacement has been selected as the optimum level of slag. The main finding proves that the use of ground slag and OPC,

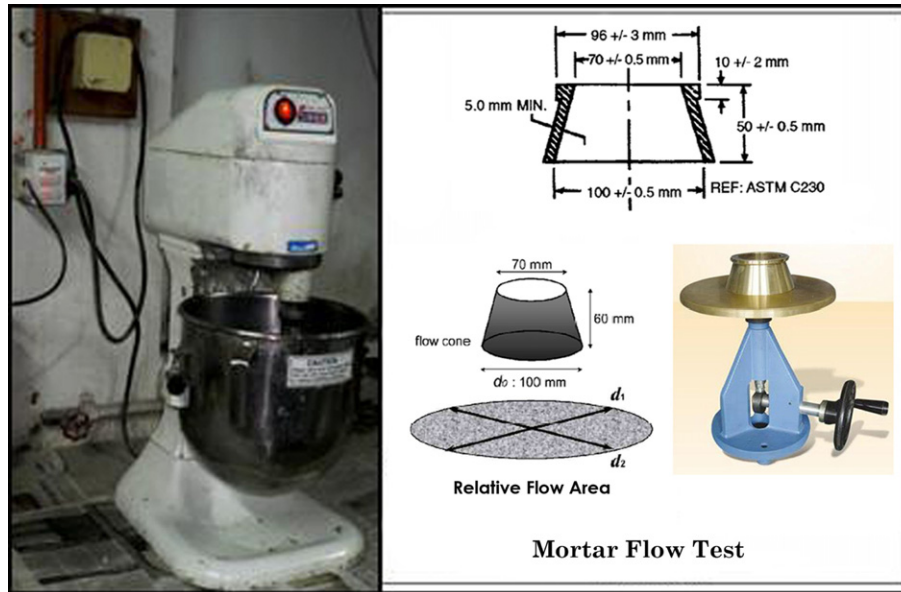


Fig. 2. Photograph for mixer and flow table test.

maximum compressive strength can be achieved for OSMs. It was found that 65 MPa at 7-day and 80.08 MPa at 28-day strength. These strength levels have been obtained for the mortar whenever the slag and OPC were ground for a period of 6 h, by a proper grinder machine. For grinding of OPC and slag particles a ball mill grinder machine was used. At first, OPC and GGBFS are weighed by a balance with ± 0.1 g accuracy, and then put in the cylinders of the grinder machine. The machine used for grinding of the materials has three cylinder boxes; each cylinder has four spherical steel balls, each with a diameter of 50.6 mm and a mass of 533.3 g. 650 g of materials are put in each box; following that, the machine is turned on for periods of 3, 6, 9.5, and 13 h. The pacing rate of the grinder machine is around 110 rpm. In Table 4a this mortar has been named as GS6C6 (optimum mortar).

In this part of study, three groups of OSMs have been used. In the first group, both OPC and ground slag were used. In the second group, only ground slag was used, and in the third group, only ground OPC used.

For first group of mortars, it is seen that the maximum strengths is attributed to $r = 1.35$. It is noted that the strength levels of the first group are more than those of other groups. At $r = 1.35$ the strength at 28 days is 80.08 MPa. The r factor is defined as the ratio of SSA slag to SSA OPC. This factor is dimensionless. For better performance of OSMs, it is generally accepted that r should be more than 1.0. From Table 4b it is clear that the optimum mortar is attributed to minimum $r = 1.35$. In this case both OPC and slag were separately ground in duration of 6 h.

The results of compressive strength vs. age of curing, for all three groups of OSMs used in mechanical method, are shown in Fig. 3, Part A. The best curve fitting of compressive strength vs. age of mortar, for three groups of OSMs, is shown in Fig. 3, Part B.

4.2. Thermal method

In the thermal method, 29 mix proportions of OSMs have been used and two mixes as control. For each mix, two points are important. Firstly, a higher percentage of slag is preferable because it has economic and environmental advantages and also helps to improve durability of the mortars. Secondly, it improves early strength. It is apparent that an increase of replacement slag causes early strength to be reduced, since the slag has lower initial hydra-

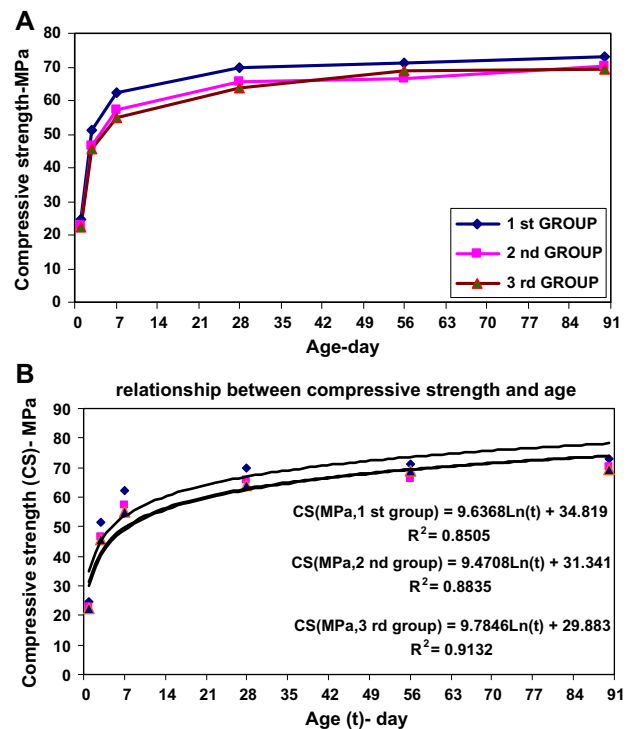


Fig. 3. Compressive strengths vs. age for three groups of mortars. Part A: relationship; Part B: curve fitting.

tion heat than that of OPC. Moreover, for short-term purposes the use of low levels of slag is neither economic nor durable. It is clear that the use of high levels of slag in mortars and concretes has many benefits from standpoint of economic and environmental. By using high levels of slag it can be said that the use of cement will be more reduced. This means that production and emission of carbon dioxide (CO_2) is significantly decreased, in due to it is generally accepted production of one ton of OPC is caused to produce one ton of (CO_2). In addition, with use of higher levels of the slag, more compact structure can be obtained. In this research, it is

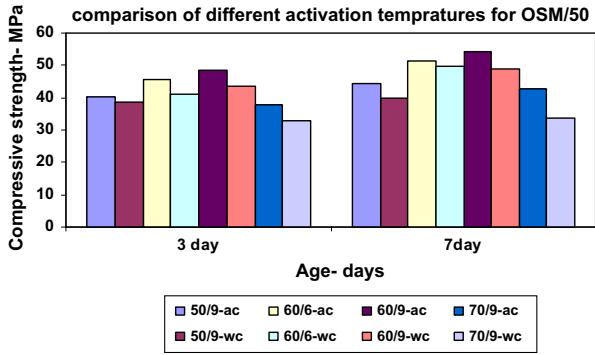


Fig. 4. The effects of different temperatures on early-age strengths of OSM/50.

desirable to know the optimum temperature and the duration that will provide the highest early strength at 3 and 7 days.

In the study, the effects of 50 °C, 60 °C, and 70 °C temperatures were considered on the early strengths at 3 and 7 days of OSM/50. The results are shown in Fig. 4. It is apparent that 60 °C has the most enhancing effects on early-age strengths, so it was selected as the optimum temperature.

The results obtained for compressive strengths based on heating time, are shown in Fig. 5. Based on the results, it can be seen that 3 and 7 days strengths, for specimens cured in the water, both without being heated and with 2 h heating time, are greater than whenever cured in room temperature. This reality has proven for both OSM/50 and OSM/40. However, as soon as the heating time is increased to 4 h and more, the aforementioned statement is reversed. Conversely, whenever heating time is increased to 4 h and more, the strength of specimens cured in room temperature is improved compared to the strength of specimens cured in water. It appears that this is due to; room temperature and a high RH of

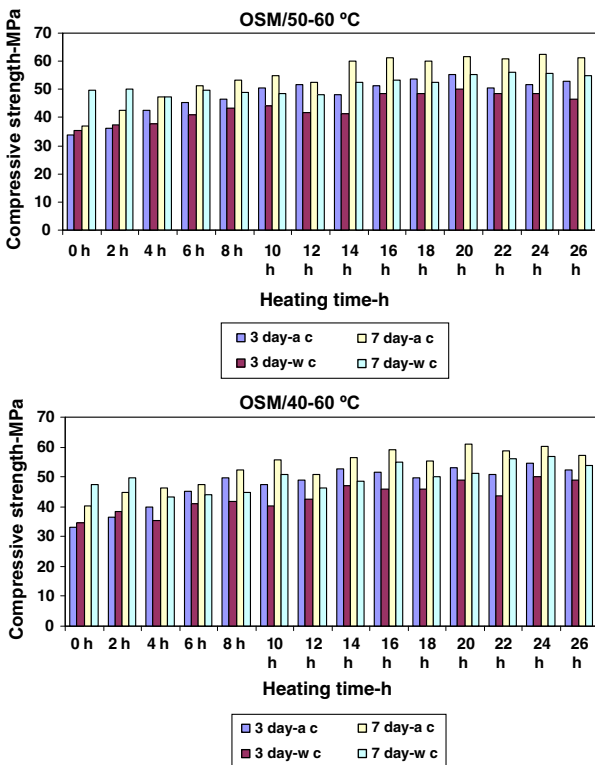


Fig. 5. Compressive strength vs. heating time for OSM/50 and OSM/40 cured in room temperature and water.

the room’s air. Elevated curing temperature accelerates the chemical reactions of hydration, and increase the early-age strength. However, during the initial period of hydration, an open and unfilled pore structure of cement paste forms and therefore negatively affects the properties of hardened mortar and concrete, especially at later ages [6,7]. Hardened mortars and concretes can reach their maximum strength within several hours through elevated temperature curing. However, the ultimate strength of hardened mortars and concretes has been shown to decrease with curing temperature.

It was found that by increasing curing temperature from 20 °C to 60 °C and the heating time up to 48 h a continuous increase in compressive strength occurred [8]. Studies have shown that there is a threshold maximum, heat-curing temperature value in the range of 60–70 °C, beyond which heat treatment is of little or no benefit to the engineering properties of concrete.

It is noted that the maximum 3 and 7 days strengths of OSM/40s and OSM/50s specimens are 21.65%, 18.98% and 21.78%, 20.00% greater than those of OM’s specimens cured in room temperature. It is observed that there is strength loss by about 2.2% whenever 56 days strength is compared to 28 days strength. This has been previously reported by other researchers [9]. Whereas the main objective of elevated temperature curing is to achieve early strength development, it is generally acknowledged that there is also strength loss as a result of heat curing. Another mix of OSM/50 as the optimum mix has been designed for optimum temperature and heating time (H60 °C – 20 h) for six ages; 1, 3, 7, 28, 56, and 90 days. The results of compressive strength vs. age of the specimens cured in room temperature, is a logarithmic relationship as:

$CS - T - ac = 5.2039 * \ln(t) + 50.664$, with $R^2 = 0.9311$; where CS is compressive strength in MPa, t is curing age in days, and ac denotes curing regime in room temperature.

4.3. Chemical method

In this method, five groups of activators were used as follows.

The first group is a pellet of NaOH. The second activator is a pellet of KOH, and the third a solution of $Na_2SiO_3 \cdot 9.35H_2O$. The fourth group is a combined activator as: $(Na_2SiO_3, nH_2O)_2 + NaOH_{0.583}$ with the last being $NaOH_{0.5} + KOH_{0.5}$ (% by mass of slag). With respect to the activators used, the $NaOH_{0.5} + KOH_{0.5}$ mix leads, in all cases, to the highest strengths values, followed by the $(Na_2SiO_3, 9.35H_2O)_2 + NaOH_{0.583}$ solution and then by KOH_1 . NaOH gives the lowest strength values whenever it is used alone. It was determined that the effect of the combined activators being better than that of an individual one. The activity of GGBFS is determined by the quantities and the properties of amorphous glass, as well as the chemical compositions. Facts have been proven that the higher the proportion of glass, the greater is the activity of slag at the same chemical compositions [10].

The results obtained show that when the aforementioned are considered, they do not have the same significance on the strengths. It seems the most relevant factor is the alkali-activator nature. For compressive strength, the relevant factors may be attributed with age. This order seems be as: activator nature, activator concentration, and specific surface of slag. The last factor is curing temperature and is only significant at 3- and 7-day ages. The significant role of an alkali activator is based on the fact that slag alone reacts with water very slowly, but hydroxyl ions $(OH)^-$ are supplied by alkali activators. They are known to increase the hydration rate by promoting dissolution of aluminate and silicate network in the slag [11].

The efficiency of an activator depends on several factors. Among them, the type, ambient temperature, dosage and water/slag ratio are significant. Another significant factor is the physico-chemical

nature of the material to be activated [11]. In this activation method, three sets of activators have been used. In the first set, the alkali activators, NaOH, KOH, and Na₂SiO₃, 9.35H₂O (solution/granular) were used for 2%, 4%, and 6% by mass of slag. In the second set, the combination of alkali activators NaOH and Na₂SiO₃, 9.35H₂O (solution/granular) used for different molar ratio (*M_s*) 0.25, 0.50, 0.75, and 1.00. In the third set, the alkali activators NaOH and KOH have been used for different combinations. Finally, by comparison of the results of the three sets of activators used, the optimum set was acquired. The optimum selected set of activators is shown in Fig. 6.

It is noted that in the first set of activators, the best activator is KOH with a 1% content of K₂O as mass of slag. Up to 60% slag replacement and use of KOH₁ as activator has yielded the best results. For the second set of activators, the best combination is (Na₂SiO₃, 9.35H₂O)₂ + NaOH_{0.583} with *M_s* = 0.75. Up to 50% slag replacement and use of second set yielded the highest early strengths. In the third set of activators, the best combination was NaOH_{0.5} + KOH_{0.5}. Up to 50% slag substitution and use of a third set of activators yielded the best results. By comparison of the obtained optimum results for the three sets of activators; it was shown that the optimum set is attributed to the third set of activators.

The use of an optimum set of activators enabled the creation of another mix as an optimum mix proportion for specimens cured in room temperature. These were created for six ages 1, 3, 7, 28, 56, and 90 days. The results of compressive strength vs. age for optimum mix, has the best curve fitting as:

$CS - C - ac = 5.6738 * \ln(t) + 25.433$, with $R^2 = 0.8169$; where CS is compressive strength in MPa, *t* is curing age in days, and ac denotes curing regime in room temperature.

4.4. Comparison of different methods

From Fig. 7 it is observed that SMs, OMs, and OSMs cured in the water do not have strength loss, but the OSMs activated by chemical, thermal, and mechanical methods have strength loss at 90, 56, and 56 days, respectively. The results show that strength loss in alkali-activated mortars depends on the level of slag used, the type and dosage of alkali activator, and the regime of curing. The reason for the loss of strength can be due to internal or external reasons. The internal reasons are those linked to the chemical composition of the reacted products. The external reasons are due to the variability of specimens, testing procedures, flatness of testing procedures. One other factor that has an important effect is the temperature. The initial curing temperature has an important effect and can reduce or increase strength at long curing times, i.e. advanced age.

A strength comparison of OMs and OSMs showed that OMs have higher strengths until 7 days ages when compared to OSMs, but

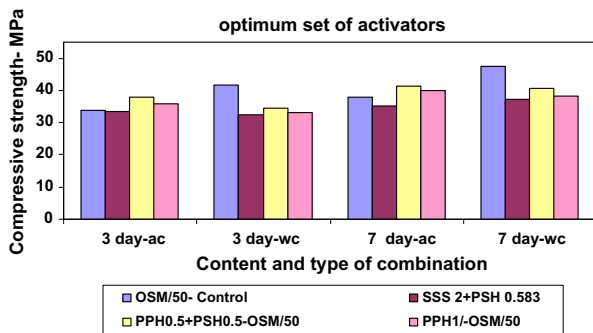


Fig. 6. Selection of optimum set of activators.

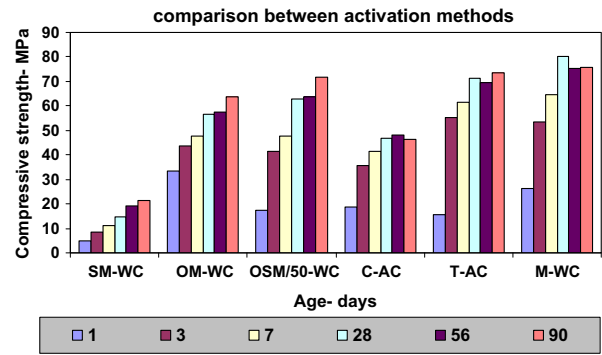


Fig. 7. Compressive strength vs. age for different OSMs and activation methods.

after 7 days this statement is reversed. Additionally, the ultimate strength of OSMs is more than that of OMs.

From Fig. 8 it can be deduced that whenever the chemical method is used for activation of OSM/50 (for all ages except 1 day), not only did the strength improve, but that there was also a strength loss from 3 until 90 days compared to inactivated OSM/50. This is due to the presence of cement in OSM/50. This subject has been previously confirmed by other researchers [12].

The addition of alkalis to Portland cement results in a reduction of strength after 3 or 7 days, because of the hydration chemistry and the morphology of the hydration products are changed due to the presence of alkalis [13].

Strength development, due to the thermal activation method at a 3 days age, is more than that of the mechanical activation method, but for 7 days and more, this statement is reversed. Furthermore, it can be said that use of the thermal method is better than the mechanical method until 3 days. After 3 days, the mechanical method is the optimal method.

From Fig. 9 it can be observed that:

The greatest strength development at 1 day is attributed to mechanical, chemical, and thermal activation methods.

The greatest strength development at 3 days is attributed to thermal, mechanical, and chemical methods of activation.

The highest strength development at 7, 28, 56, and 90 days are attributed to mechanical, thermal, and chemical activation methods.

In summary, it can be said those at all ages except 1 day, the chemical method has the last rank of activation. At 1 day, the chemical method has the second rank of activation. Moreover, the greatest strength development at 3 days is related to the thermal method and for 7 days and more, the first rank of activation is attributed to the mechanical method.

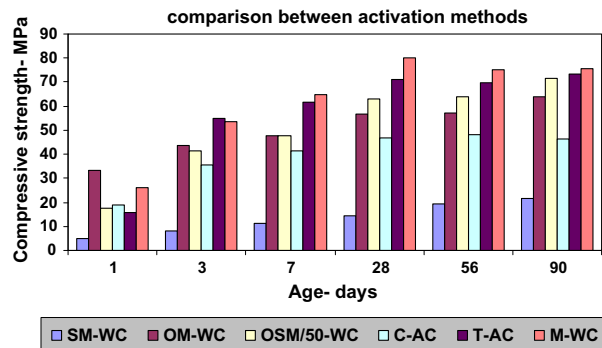


Fig. 8. Compressive strength vs. separate ages for different OSMs and activation methods.

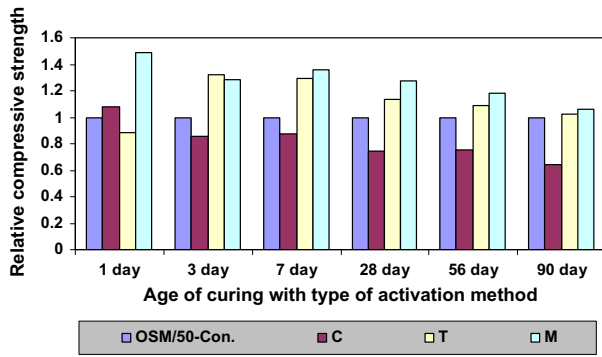


Fig. 9. Relative Compressive strength vs. age and type of activation method.

Regardless of the higher expenses for mechanical and thermal methods, due to both methods having the highest strengths, they can be proposed as simple and feasible first and second rank methods of activation. The chemical method had a positive effect on strength at only 1 day by about 8%. This method also showed strength loss from 3 until 90 days instead of strength development, so it is not proposed as a feasible method of activation.

From Fig. 10 it can be observed that:

The chemical activation method developed strength at only the first day and reduced it at all other ages until 90 days, compared to OSM's strengths for same ages.

The thermal activation method has been developed at all ages, except at 1 day age. It can be remembered that the specimens heated after 1 day. It is noted that strength growth is the highest (32%) at 3 days, and then from 7 until 90 days the increments are reduced. The strength growth at 90 days is 3%.

The mechanical activation method had the highest strength growth at the first day ($\approx 50\%$) and about 30% at 3 days. From 7 days with 36% of strength growth until 90 days, the increment of strength development has been gradually reduced. At 90 days the strength growth was only about 6%. Some diagrams are drawn in Fig. 11. These diagrams are a curve fitting of compressive strength vs. curing age for SMs, OMs, and OSMs and also the activation methods of OSM/50, namely Chemical (C), Thermal (T), and Mechanical (M) methods. From this Figure it can be seen that the best curves fittings are logarithmic relations as, $a * \ln(t) + b$. Comparison of regression relations show that the best curve fitting is related to the thermal activation method. Additionally, it is observed that there is a logarithmic relation for estimation of strength, based on the

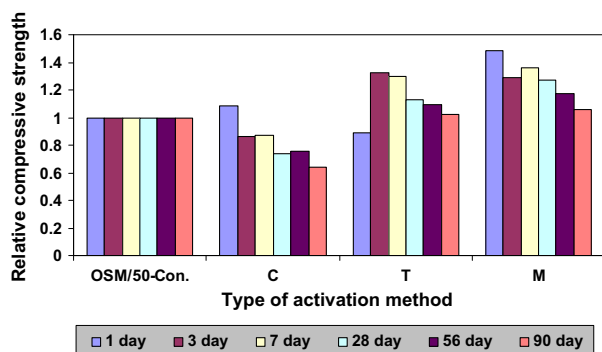


Fig. 10. Relative Compressive strength vs. type of activation method.

curing age for OSM/50. The value of the correlation factor of the relation is $R^2 = 0.9472$.

5. Conclusions

5.1. For mechanical method

- All three groups of mortars have significant effects on strength improvement, especially at early ages, whilst the greatest effect is related to the first group.
- The maximum strengths obtained are attributed to the first group of OSMs. The strength obtained at 28-day of optimum OSM (GS6C6) is 80.08 MPa. It is noted that this strength was obtained only by using 250 kg/m^3 of cement. This shows highly importance of the research, because of the strength is very high and has many benefits from standpoint of economic and environmental. In fact, this is a novelty.
- For all groups of mortars, strength loss has occurred only at long ages.
- Fine grinding leads to the generation of a larger surface area, but due to the agglomeration phenomenon there is limitation on the SSA of OPC and slag.
- The results obtained show that ground slag has a greater effect on strength improvement at early and long ages compared to ground OPC.

5.2. For thermal method

- Based on the experimental results obtained in the study it was specified there is an optimum temperature to obtain high early strength for the materials used in this study. It is determined that 60°C is the optimum temperature. Duration of heating time is also very important to gain high early strength. For the slag used in this study, 20 h is the optimum heating time. Usually, as heating time increases towards the optimum, the compressive strength will increase.
- The maximum strengths obtained of OSM/50 cured in room temperature at 3 and 7 days, are 55.29 and 61.63 MPa, respectively. It can be seen that these strength levels are 21.78% and 20.00% more than those for OPC's specimens cured in room temperature and 26.12% and 29.04% more than those for OPC's specimens cured in the water, respectively.
- If the mortar is heated more than the optimum heating time, it is specified that this will not lead to increasing early strength of mortar.
- According to the results of study and other researches [14,15], it can always be said that thermal activation is one of the applicable methods for the activation of OSMs. It is well known that this method is usually used in precast concrete plants.
- It has been shown that the specimens' strengths at 3- and 7-day of OSM/40 and OSM/50 cured in water without heating and with use of 2 h heating after demoulding, are more than those cured in room temperature. However, as soon as the heating time is increased towards 4 h and above, this statement is reversed. This is a new finding, has much importance in precast industry with many advantages in arid regions to cure concrete structures.

5.3. For chemical method

- In this study the activators sodium hydroxide, potassium hydroxide, and sodium silicate have been used. It was determined that the highest effect is attributed to sodium silicate and the lowest for sodium hydroxide, whenever the activators were used alone.

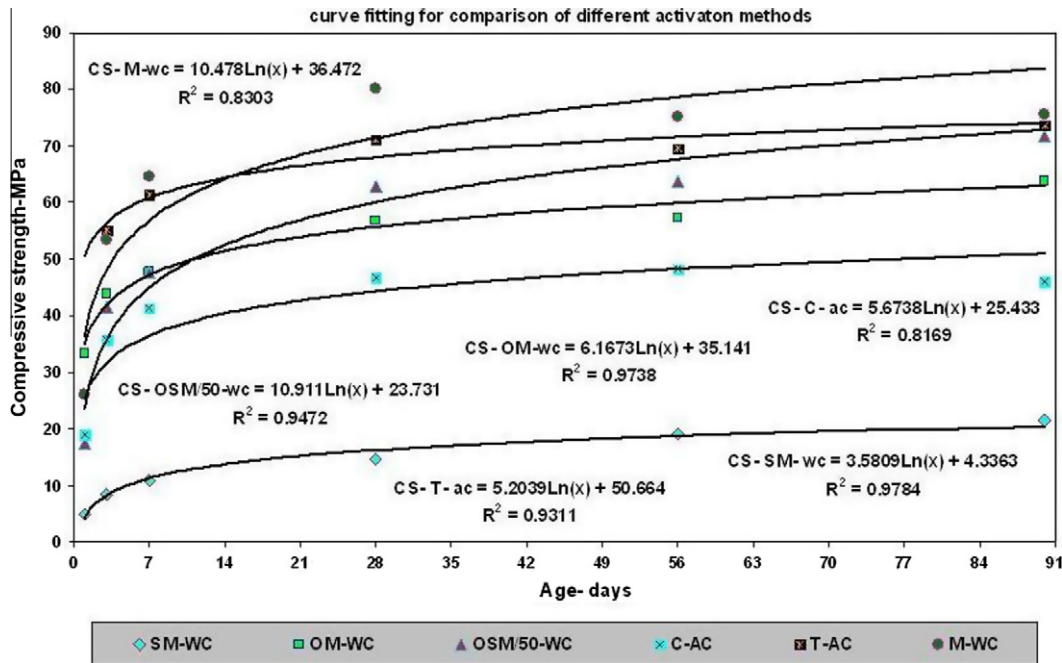


Fig. 11. Curve fittings of Compressive strength vs. age for OSMs and their activation methods.

- It has been considered that the greatest strength improvement is related to combination of sodium hydroxide and potassium hydroxide, followed by combination of sodium silicate and sodium hydroxide.
- The best curve fitting of the strength of optimum combination of activators is a logarithmic relation as: $CS - C - ac = 5.6738 * \ln(t) + 25.433$, with $R^2 = 0.8169$; Where CS is compressive strength in MPa, t is curing age in days, and ac denotes curing regime in room temperature.
- The maximum strength obtained due to chemical activation is 85% of OM's strength at 56 days.
- Due to leaching in the water cured regime, the strength of specimens cured in the water were less than those cured in room temperature.
- In some mixes, strength loss has been observed. The results obtained show that strength loss in alkali-activated mortars depends on the level of slag used, the type and dosage of the alkali activator, and the curing regime.

5.4. Specific results

- The best curve fitting to show the relationship between strength development and age of curing of OSMs and their activation methods, are logarithmic relations in the form $a * \ln(t) + b$; Where a and b are constants for each specific relationship.
- At all ages except 1 day, the chemical method has the last order of activation. At 1 day, it has second order. Additionally, the highest strength development at 3 days is attributed to the thermal method; and at 7 days and more the first order of activation is related to the mechanical method.
- In summary, regardless of the greater expenses of the mechanical and thermal methods; due to both methods having the highest strengths, they can be recommended as simple

and feasible first and second orders methods of activation. The chemical method had a positive effect on strength at only 1 day by about 8%. This method showed strength loss in duration of 3–90 days instead of strength improvement, so it is not proposed as a feasible method of activation.

References

- [1] Caijun Shi, Robert L Day. Comparison of different methods for enhancing reactivity of pozzolans. *Cem Concr Res* 2001;31(5):813–8.
- [2] Nanjing Institute of Chemical Technology, Cement Technology. Beijing: Chinese Construction Press; 1985.
- [3] Lee Jaesung. Experimental studies and theoretical modeling of concrete subjected to high temperatures. Ph.D. Thesis, University of Colorado, USA; 2006.
- [4] Jin-Keun Kim, Sang Hun Han, Seok Kyun Park. Effect of temperature and aging on the mechanical properties of concrete, Part II. Prediction model. *Cem Concr Res* 2002;32(7):1095–100.
- [5] Pal SC, Mukherjee A, Pathak SR. Investigation of hydration activity of ground granulated blast furnace slag in concrete. *Cem Concr Res* 2003;33(9):1481–6.
- [6] Neville AM. Properties of concrete, Fourth and final ed. Malaysia: Prentice Hall; 2008.
- [7] Neville AM, Brooks JJ. Concrete technology. Malaysia: Prentice Hall; 2008.
- [8] Brooks JJ, AL-kaisi AF. Early strength development of Portland and slag cement concretes cured at elevated temperatures. *ACI Mater J* 1990;87(5):503–7.
- [9] Shi C. Strength, pore structure and permeability of alkali-activated slag mortars. *Cem Concr Res* 1996;26(12):1789–99.
- [10] Bougara A, Lynsdale C, Ezziane K. Activation of Algerian slag in mortars. *Constr Build Mater* 2009;23(1):542–7.
- [11] Xinghua Fu, Wenping Hou, Chunxia Yang, Dongux Li, Xuequan Wu. Studies on Portland cement with large amount of slag. *Cem Concr Res* 2000;30(4):645–9.
- [12] Vladimir Zivica. Effectiveness of new silica fumes alkali activator. *Cem Concr Compos* 2006;28(1):21–5.
- [13] Caijun Shi. Activation of natural pozzolanz, fly ashes and blast furnace slag. Ph.D. Thesis, The University of Calgary, Canada; 1992.
- [14] Barnett SJ, Soutsos MN, Millard SG, Bungey JH. Strength development of mortars containing ground granulated blast-furnace slag: effect of curing temperature and determination of apparent activation energies. *Cem Concr Res* 2006;36(3):434–40.
- [15] Zain MFM, Radin SS. Physical Properties of high-performance concrete with admixtures to a medium temperature range 20–50 °C. *Cem Concr Res* 2000;30(8):1283–7.