

A study on super-sulfated cement using Dinh Vu phosphogypsum

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Abstract. Super-sulfated cement (SSC) is a newly developed unburnt cementitious material. It is a kind of environmental-friendly cementitious material due to its energy-saving, carbon emission reducing, and waste-utilization. It mainly composes of phosphogypsum (PG) and ground granulated blast furnace slag (GFS), with a small amount of cement. In Vietnam, the Diammonium Phosphate DAP – Dinh Vu fertilizer plant in Dinh Vu industrial zone in the northern port city of Hai Phong – has discharged millions of tons of solid waste containing gypsum after 9 years of operation. The waste has changed the color of the water, eroded metal and destroyed fauna and floral systems in the surrounding area. Notably, according to the environmental impact assessment, the gypsum landfill area is supposed to be 13 hectares and the storage time reaches up to five years. This paper presents the experimental results on SSC using a high amount of Dinh Vu phosphogypsum and GFS in comparison with those of ordinary Portland cement (PC). The results show that the setting time of SSC is much longer than that of Portland cement but the compressive strength of SSC can be obtained 45-50 MPa at the age of 28 days, similar to that of the control sample using 100% PC40, and 69MPa at the age of 90 days. This value even exceeds the compressive strength of the PC40 cement.

1. Introduction

In Vietnam today, the demand of construction materials due to the population growth and to the periodic need of infrastructure renovation is increasing. Considering Portland cement (PC) as the most widely used binder in the construction industry, the PC production, as a result, will be required intensively. This leads to a high CO₂ emission and energy demand, thus, in this aspect, searching for alternative cementitious systems is the most important issue to adapt to these demands in terms of sustainable development and lower energy consumption.

One of the most promising alternative cementing systems is super-sulfated slag cement (SSC), which is mainly composed of ground granulated blast furnace slag (GFS) and sulfate activator (such as gypsum), with a little amount of alkali activator (such as clinker cement or cement) [1, 2]. This cement can consume a large amount of gypsum in general, and an phosphogypsum (PG) in particular. Compared with ordinary Portland cement, super-sulfated cement has many advantages such as low hydration heat evolution, excellent sulfate resistance, using less clinker and more gypsum, and thus more solid waste can be consumed [3-6]. For example, Weiguo et al. [7] studied a type of lime-fly ash-phosphogypsum binder to improve the performances of lime-fly ash binder that was a typical semi-rigid road base material binder. The optimum composition of this binder was 8–12% modified lime, 18–23% phosphogypsum, and 65–74% fly ash (by weight). Moreover, Ding Sha et al. [3] investigated the concrete prepared with super-sulfated phosphogypsum-slag cement, which is made by 45% phosphogypsum, 48% GFS, 2% steel slag, and 5% clinker. The results show that the compressive



strength of super-sulfated slag cement concrete can be obtained 38.6 MPa at the age of 28 days, similar to that of Ordinary Portland cement concrete.

The use of PG in producing cements has been being received much attention, because it is obtained in large amounts and is a readily available source of gypsum. For example, PG was studied to regulate the setting of ordinary Portland cement. It was shown that the impurities present in PG retarded the hydration of OPC to a large extent [8-10]. Only 15% of total PG is used for cement industry as a setting moderator, and for making gypsum plaster... The remaining 85% of PG is not used, causing an environmental trouble and requiring a large area for disposal. Therefore, attempts were made to use PG in applications such as the filler material of road and rail works, the stabilization material in base course, and building constructions [11].

In Vietnam, the Diammonium phosphate (DAP) - Dinh Vu fertilizer plant in Dinh Vu industrial zone in the northern port city of Hai Phong - has discharged about 10 millions of tons of waste after 9 years of operation [12]. According to the complex DAP fertilizer production process, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is a solid waste discharged from nutrient extraction (phosphorus) found in apatite ores. This is a common solid waste, free of hazardous substances. The waste has changed the color of the water, eroded metal and destroyed fauna and floral systems in the surrounding area. Notably, according to the environmental impact assessment, the PG landfill area is supposed to be 10 hectares and the licensed storage time is three years only. However, in reality, the landfill has an area of 13 hectares and the storage time reaches up to five years [12]. Therefore, the large-scale utilization of PG is an urgent environmental problem to be solved in Vietnam.

The aim of this paper is to present some experimental results of SSC using a high volume Dinh Vu phosphogypsum, slag, Portland cement and quicklime. These results are compared with those of ordinary Portland cement to evaluate the feasibility of SSC application in construction in Vietnam.

2. Materials and Experimental methods

2.1 Materials

Ordinary Portland Cement PC40 But Son, Phosphogypsum, Ground-granulated blast-furnace slag (GFS), and quicklime (QL) were used in making super-sulfated cements. The chemical composition of these materials is represented in Table 1.

Table 1. Chemical composition of raw materials

Raw material	Chemical composition, % by weight									
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	L.O.I
PC	20.3	5.05	3.51	62.81	3.02	-	-	2.0	-	1.83
GFS	34.52	0.66	12.38	41.54	7.25	0.43	0.24	-	-	0.96
PG	8.07	0.87	2.99	30.52	0.69	0.03	0.56	38.5	0.56	21.92
QL	2.21	1.12	0.32	85.04	1.89	-	-	-	0.87	5.19

2.1.1 Phosphogypsum (PG)

In this study, PG gathered from DAP Dinh Vu fertilizer plant, has particle size finer than $11\mu\text{m}$. The specific gravity of PG is 2.34 g/cm^3 .

2.1.2 Ground-granulated blast-furnace slag (GFS)

The samples of blast-furnace slag were ground for 90 minutes in a laboratory ball mill. Physical properties and chemical composition of finely GFS used in this study are shown in Table 2.

Table 2. Properties of ground-granulated blast-furnace slag used in this study

N°	Physical properties	Unit	Value
1	Specific gravity	g/cm^3	2.94

2	Strength activity index	%	104.3
3	The mean particle size	μm	10.2
4	L.O.I	%	0.96

2.1.3 Portland cement (PC)

Ordinary Portland cement PC40 But Son was used in this study with the physical properties shown in the Table 3.

Table 3. Properties of the PC40 cement used in this study

Blaine fineness cm^2/g	Mean particle size, μm	Consistency, %	Specific gravity, g/cm^3	Compressive strength at 3 days, MPa	Compressive strength at 28 days, MPa
3890	11.0	29.5	3.15	29.8	52.2

2.1.4 Quicklime

The quicklime sieved through 0.14mm sieve was added into the mixture of binder containing GFS to combine with SiO_2 in the slag for the formation of the C-S-H product.

2.1.5 Standard sand

An ISO standard sand comply with Vietnamese standard TCVN 6227:1996 [13] was used for determining compressive strength of binder.

2.2 Experimental methods

All mixtures of the super-sulfated cement used in this study are given in Table 4.

Table 4. SSC mixtures used in the study

N°	Mixture notation	Proportion of raw materials in SSC, % by weight			
		PG	GFS	PC	QL
1	CP1	60	30	10	0
2	CP2	50	40	10	0
3	CP3	40	50	10	0
4	CP4	30	60	10	0
5	CP5	60	30	0	10
6	CP6	50	40	0	10
7	CP7	40	50	0	10
8	CP8	30	60	0	10
9	CP9	60	30	5	5
10	CP10	50	40	5	5
11	CP11	40	50	5	5
12	CP12	30	60	5	5
13	CP13	0	0	100	0

The water demand (or standard consistency), setting time, and compressive strength of SSC were determined according to Vietnamese standard TCVN 6017:2015 [14] and TCVN 6016:2011 [15].

The three SSC pastes (CP4, CP8, CP12) after mixing will be allowed to hydrate in a sealed plastic, then the hydrations were stopped at the age of 3 days by a consecutive soaking in acetone during 48 h. Afterwards, the sample were dried and powdered by using agate mortar for FTIR study. The Fourier

transform infrared measurements were recorded with a IR Affinity-1S - SHIMADZU model FTIR spectrometer using the KBr pellets technique.

To determine compressive strength, tested samples were made with a binder combination of (PG, GFS, PC, QL) to standard sand of 1:3 by weight, and the water to binder ratio was fixed at 0.5, by weight. The mortar was cast into 40 mm × 40 mm × 160 mm mold by the vibration method as per TCVN 6016:2011. All samples were demolded after 48 h instead of 24 h specified in the standards due to the long setting time of SSC mortars. Afterwards, these samples were divided into 2 groups:

- Group 1: samples were cured in a sealed plastic bag until testing ages of 3, 7, 28, 90 days
- Group 2: samples were immersed in water until testing ages of 3, 7, 28, 90 days

3. Results and discussion

In this section, the setting time and the compressive strength of SSC using a high volume of PG were studied over through 12 mixtures then compared with the control sample containing 100% Portland cement to demonstrate the effectiveness and feasibility of the SSC application in construction.

3.1 Consistency and setting time

The results of standard consistency tests for SSC containing PG-GFS-PC-QL at different proportions are shown in Figure 1 and Table 5.

Table 5. Standard consistency and setting time of SSC mortars

N°	Mix notation	Standard Consistency, %	Setting time	
			Initial, minute	Final, minute
1	CP1	30.0	2340	2532
2	CP2	30.0	2346	2568
3	CP3	30.5	2352	2598
4	CP4	31.0	2340	2640
5	CP5	30.0	912	1152
6	CP6	30.5	918	1158
7	CP7	30.5	930	1170
8	CP8	31.0	906	1182
9	CP9	30.5	1818	2166
10	CP10	30.5	1824	2190
11	CP11	31.0	1806	2178
12	CP12	31.0	1800	2172
13	CP13	29.5	150	250

From the above results, the overall standard consistency for super-sulfated slag cement pastes are higher than that of the control paste containing 100% cement. This can be caused by the fact that the fineness of binder powder used in 12 mixtures was higher than that of cement in the control sample (CP13).

It is also observed that at the same amount of Portland cement PC or QL, the water requirement does not change significantly among these 12 SSC mixtures from CP1 – CP12 due to the surface area of GFS, which is almost similar to that of PG.

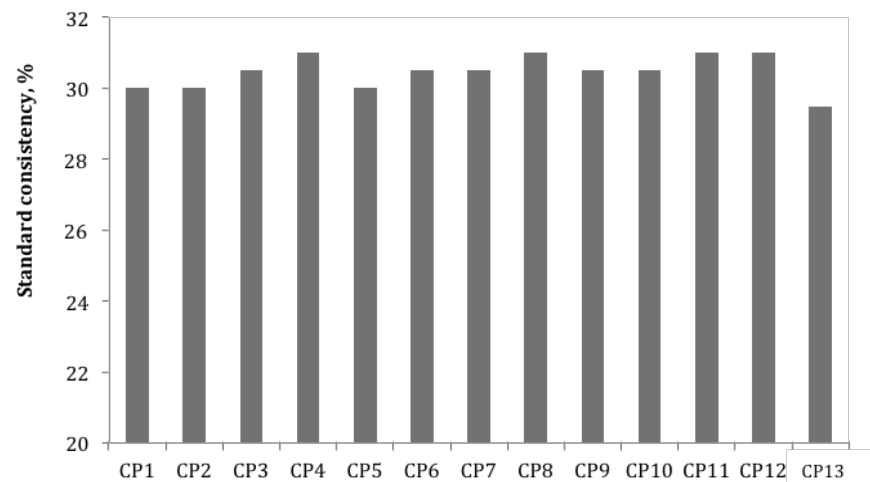


Figure 1 Standard consistency of the SSC pastes using PG

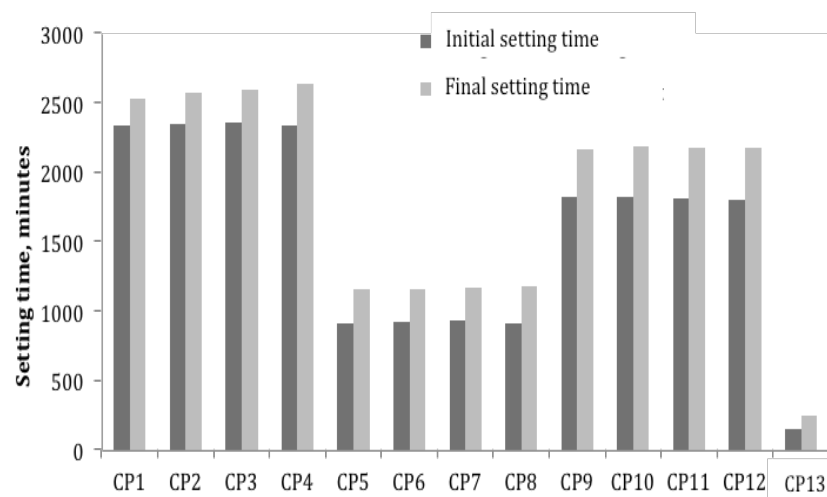


Figure 2. Setting time of the SSC pastes and the control mixture

The results in the Table 5 and Figure 2 show that the setting time of the SSC pastes is much longer than that of the control mixture (CP13 containing 100% cement). The initial and final setting time of the control mixture is 150 minutes and about 250 minutes, respectively, but the setting time of the SSC mixtures lasted longer, even up to 1800-2600 minutes. The observed retardation in setting times can be mainly due to the combined effect of a lower cement content. The results also show that the setting time of mixtures seem not to be influenced by the addition of PG or GFS.

When incorporating quicklime, the setting time of the SSC mixture is significantly decreased. The setting time of SSC mixtures using 10% quicklime is shorter than that of mixtures using 5%QL, 5% PC or 0% QL, 10% PC. This can be explained that the addition of quicklime enhances the hydration process and shortens the setting time. It is possible that the higher amount of Ca(OH)_2 , C-S-H and ettringite formed in the mixture containing 10% quicklime, promoted a denser matrix and shortened the setting time.

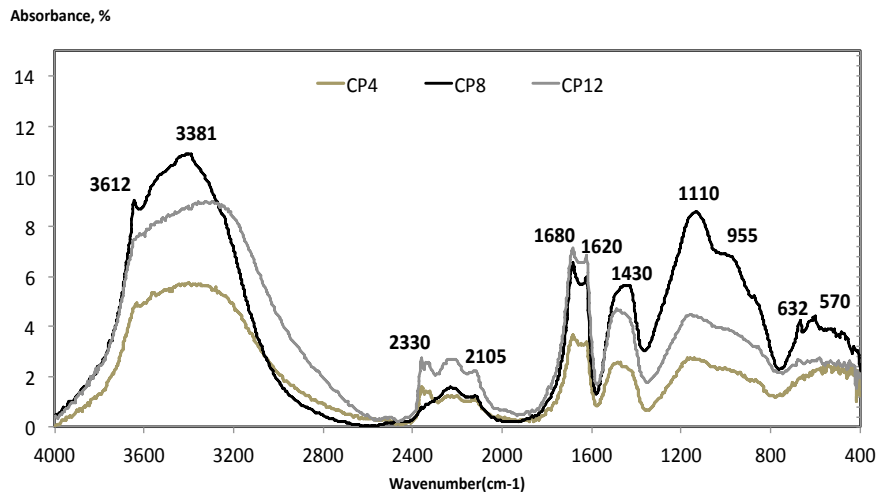


Figure 3. FTIR spectra of SSC pastes CP4, CP8 and CP12 at 3 days after mixing

The FTIR spectrum of the 3 preventative SSC samples on the Figure 3 shows a sharp band at 3630 cm^{-1} associated to O-H stretching vibrations of portlandite ($\text{Ca}(\text{OH})_2$) and the area from 2800 to 4000 cm^{-1} is correspond to the bond water in the 3 compositions. The peak at 1110 cm^{-1} is due to ν_3 modes of SO_4^{2-} and the weak bands at 632 cm^{-1} and is due to ν_4 modes of SO_4^{2-} . The strong asymmetric stretching Si-O band (ν_3) is shifted to high frequencies centered at 955 cm^{-1} indicates that the formation of C-S-H [16]. Up to 3 days of hydration, the intense sulfate band (SO_4^{2-}) in ettringite at 1100-1160 cm^{-1} are observed in the 3 samples but more distinct for the CP8 sample when compared to the CP4 and CP12 samples at early age and it implies that quicklime enhance the Aft formation than Portland cement. This indicates that the initial reactions are faster due to the higher amount of ettringite present in the CP8 sample.

It is also observed that the variation in intensities of the band at 955 cm^{-1} and 570 cm^{-1} of are highest for the CP8 sample and occur from early age onwards; But in the other hand, the intensity of the band observed at 955 cm^{-1} , 1100 cm^{-1} of CP12 are less when compared to the CP4 sample. The above results explain the fact that the sample containing more QL will set quicker and improve the strength at early stage due to the activation of lime to the SSC hydration acceleration.

3.2 Compressive strength of SSC

The results of the compressive strength of 12 SSC samples and the control sample using 100% cement are shown in Table 6.

Table 6. Compressive strength of SSC samples at 3, 7, 28, 90 days

N°	Mix notation	Compressive strength of SSC samples in different curing conditions with time, MPa							
		At 3 days		At 7 days		At 28 days		At 90 days	
		Endogen	Water	Endogen	Water	Endogen	Water	Endogen	Water
1	CP1	2	2	22	18	32	33	43	38
2	CP2	5	5	30	29	46	38	45	39
3	CP3	5	5	31	32	45	40	60	55
4	CP4	8	8	35	32	51	50	69	55
5	CP5	3	3	14	11	21	21	24	22
6	CP6	5	5	18	15	25	26	26	24

7	CP7	6	6	20	20	29	31	35	32
8	CP8	10	10	24	25	39	32	45	39
9	CP9	4	4	14	14	28	23	35	29
10	CP10	7	7	18	16	33	28	50	43
11	CP11	9	9	19	19	38	34	53	47
12	CP12	8	8	27	28	43	41	51	49
13	CP13	28	28	34	41	50	48	55	53

Based on the results in the Table 6, the influence of raw materials content on the compressive strength of SSC samples will be analyzed in detail.

3.2.1 Effect of phosphogypsum content on compressive strength of the SSC

Based on the compressive strength results from 3 to 90 days under 2 curing conditions, the influence of phosphogypsum waste content on compressive strength of SSC samples is shown in Figure 4 and Figure 5.

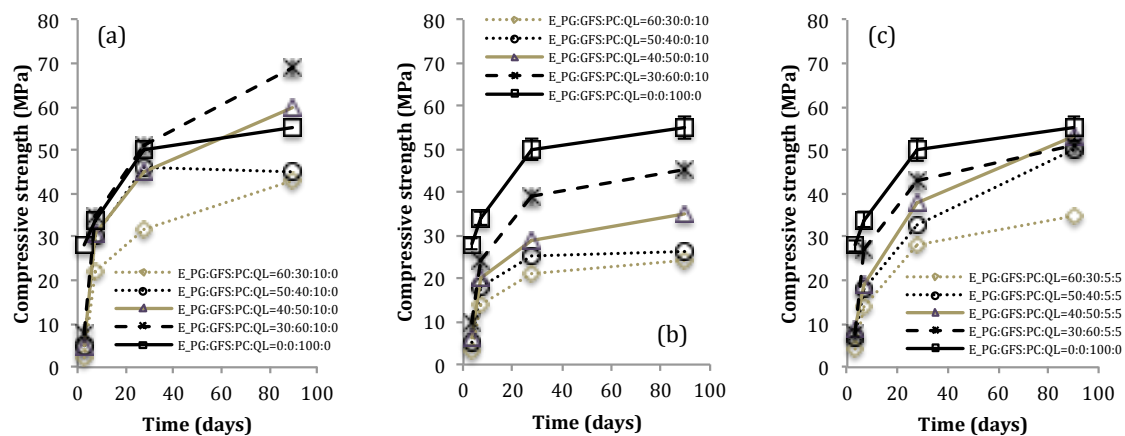
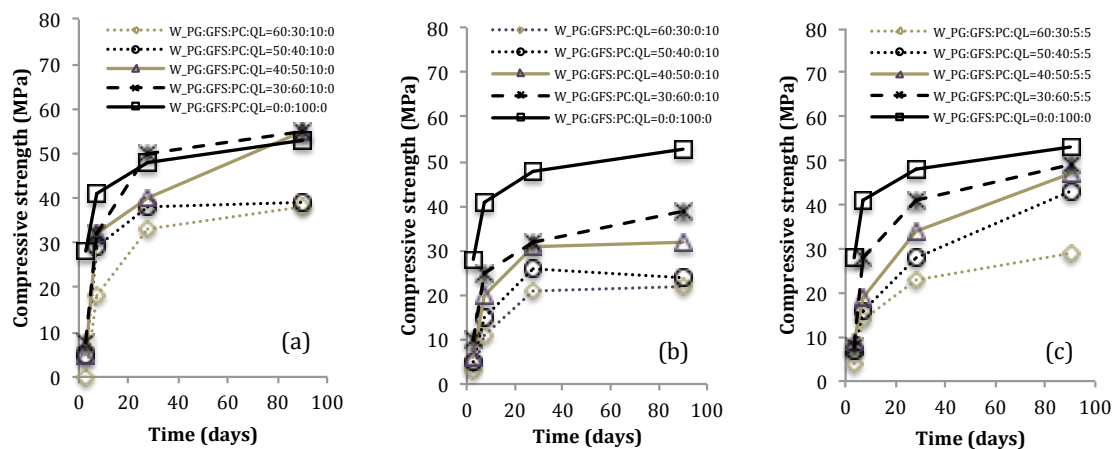


Figure 4. Compressive strength of SSC samples using (a) 10% cement, (b) 10% QL, (c) 5% QL and 5% cement under endogenous condition with time



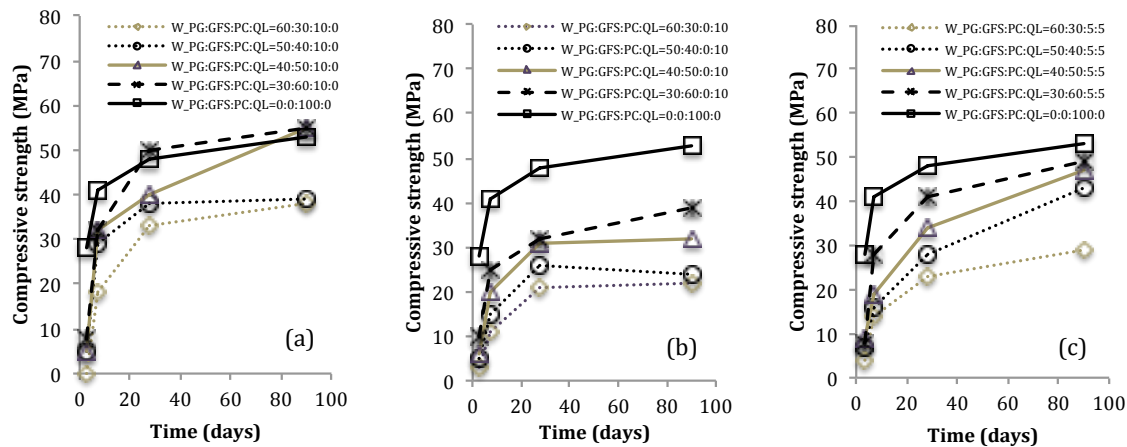


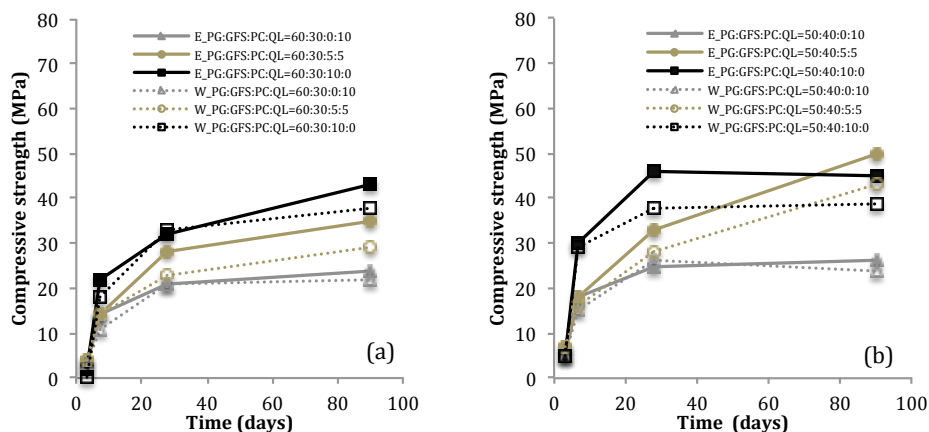
Figure 5. Compressive strength of SSC samples using (a) 10% cement, (b) 10% QL, (c) 5% QL and 5% cement under endogenous condition with time

The results in Figure 4 and Figure 5 show that the compressive strength development of all SSC samples is very low at early ages. However, the long-term compressive strength increases significantly due to the accelerated hydration process. In fact, the strength development is related to the formation of C-S-H caused by the possibility to activating GFS of cement, lime and phosphogypsum. The compressive strength of SSC samples increase rapidly from 3 to 28 days, but becomes slow down after that, i.e. from 28 to 90 days.

In addition, the results also indicate that when the amount of cement or lime in binder is kept constant, the compressive strength of SSC samples increases with the decreasing the ratio of PG or with the increasing amount of GFS in binders. This can be explained by the fact that F possesses hydraulic properties, thus, this can be activated in the presence of activators such as cement or lime in binder, whereas PG basically acts as an inert filler, only a small portion of sulfate ions are involved in the slag activation process. However, it can be seen that the compressive strength of the CP4 sample (PG: GFS: PG : PC: QL = 30: 60 : 10: 0) attains the highest value, even greater than that of the control sample containing 100% cement. The CP6 sample (PG: GFS: PC: QL = 60: 30: 0: 10) has the lowest compressive strength value under both endogenous condition and water immersion condition.

3.2.2 Compressive strength of SSC samples under different curing conditions

Due to the high amount of PG in the SSC, it is necessary to evaluate the water resistance of this type of binder to ensure its practical application. As mentioned in the research methodology, the mortar samples after demolding will be cured in a sealed plastic bag or immersed in water until the testing age for the compression test. The results are shown in Figure 6.



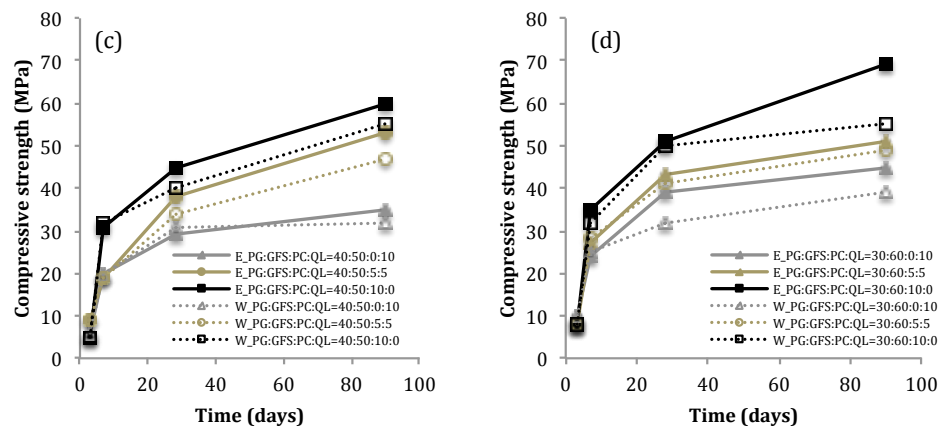
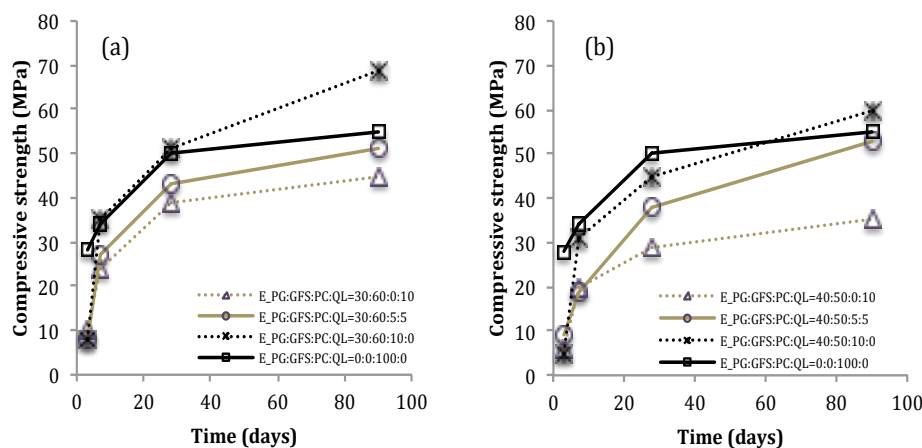


Figure 6. Compressive strength of SSC samples using different ratios of PC and QL; PG&GFS were fixed at (a) 60&30%, (b) 50&40%, (c) 40&50%, (d) 30&60% by weight of binder, respectively, under different curing conditions

The results show that the compressive strength of samples cured in the water is slightly lower than that of samples cured under endogenous condition. This difference may be caused by the fact that the binder samples cured in water are always under saturated condition, resulting in reducing the compressive strength of the sample in comparable with the samples under the endogenous condition. It also can be seen that there is no decline of the compressive strength of samples cured in the water over time. This is very important to prove the water resistance of this binder.

3.2.3 Influence of the cement and lime content on compressive strength of the SSC

Compressive strength of SSC samples from 3 to 90 days when using the same amount of PG and GFS but different amounts of PC and QL is demonstrated in Figure 7 and Figure 8.



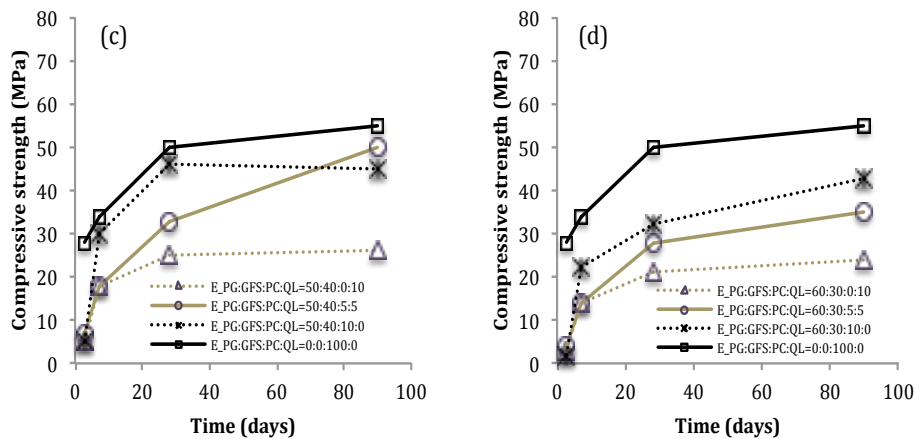


Figure 7. Compressive strength of SSC samples using different ratios of PC and QL with time under endogenous condition, PG&GFS were fixed at (a) 30&60%, (b) 40&50%, (c) 50&40%, (d) 60&30% by weight of binder, respectively

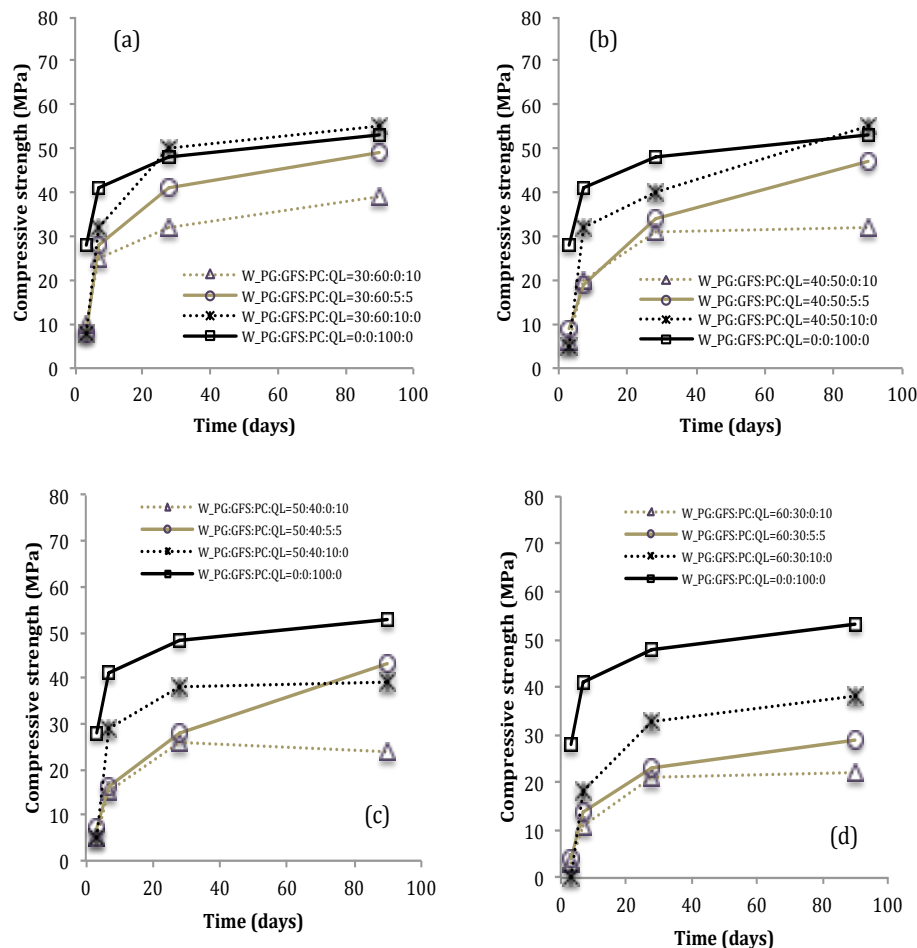


Figure 8. Compressive strength of SSC samples using different ratios of PC and QL with time under immersion condition, PG&GFS were fixed at (a) 30&60%, (b) 40&50%, (c) 50&40%, (d) 60&30% by weight of binder, respectively

The effect of the (PC and QL) content on compressive strength of SSC binders shows that the development of compressive strength from 3 days to 28 days is also very significant; and then becomes slow down. The compressive strength of sample using 10% PC is higher than that of mortar sample using 5% PC, 5% or 10% QL. This can be explained by the fact that calcium silicate hydrate (C-S-H) is the main product at early ages of the hydration of Portland cement and is primarily responsible for the strength of binder, while PC containing $\text{Ca}(\text{OH})_2$ also can react with GFS to produce C-S-H but with a smaller amount of product, and this reaction occurs slowly at early ages. In addition, the $\text{Ca}(\text{OH})_2$ formed by the hydration of cement also can react with GFS to generate more C-S-H, which refines the pore structure of SSC. Therefore, the compressive strength of SSC increases with increasing of the PC content used in binder.

4. Conclusion

In this study, the setting time and development of compressive strength of SSC using a high volume phosphogypsum have been studied. These experimental results prove a high feasibility of research into PG applications in the manufacture of a new binder as well as other non-fired building materials, especially in the context that our country is looking for developing sustainable construction. Some conclusions can be drawn as follows:

- The setting time of the SSC paste is much longer than that of the control mixture containing only Portland cement; this disadvantage can be compensated by using quicklime due to the higher amount of $\text{Ca}(\text{OH})_2$, C-S-H and ettringite formed and promoted a denser matrix and shortened the setting time.
- Compressive strength of SSC is influenced by the amount of PG used in binder; the strength increases with decreasing of the PG content or with increasing of the GFS content in binder.
- All SSC samples are stable in water and the compressive strength of SSC using only 10% cement is higher than that of the control sample using only cement. The compressive strength of the SSC samples of 45-50 MPa, and 69 MPa can be obtained at 28 days and at 90 days, respectively. This value even exceeds the compressive strength of the PC40 cement.

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