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USING REFINED PHOSPHOGYPSUM TO REPLACE NATURAL GYPSUM IN PORTLAND CEMENT PRODUCTION IN VIETNAM

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ABSTRACT

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Keywords
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This study assessed the effects of different contents of two refined phosphogypsums (PG1, PG2) on standard consistency, setting times, compressive strength and sulfate resistance of cement. PG2 possesses higher water-soluble impurities such as P_2O_5, F content than PG1. The results were compared to those of cement containing natural gypsum (NG). The results showed that water demand of cement reduces when the content of the gypsums increases, especially with PG1 and NG. The phosphogypsums prolong the setting times of cement. The higher the gypsum content is, the more the 3-d compressive strength of cement can obtains. The low impurity phosphogypsum (PG1) accelerates the 3-d strength but lowers the 91-d strength of cement compared to the high impurity phosphogypsum (PG2). The strength of cement containing NG is always between those of the phosphogypsums at the ages of 3 and 91 days. There is a suitable content of gypsum to produce the highest strength of the cement at the ages of 28 and 91 days. Deterioration of the cement in sodium sulfate solution (50g/l) is more severely when increasing gypsum content. The sulfate resistance of cement containing PG1 is lower than that of cement containing PG2 or NG.

Contribution/Originality: This study is one of very few studies in Vietnam to investigatewhich have investigated the potential for using refined phosphogypsum to replace natural gypsum in cement for environmental protection in Vietnam. This study has reported that phosphogypsum content and impurities of P2O5 and F- significantly affect the properties of Portland cement.

1. INTRODUCTION

Phosphogypsum (PG) is a by-product from manufacturing process of phosphoric acid in phosphate fertilizer plants and chemical industries. About 5.4 tons of PG is generated when each ton of phosphoric acid is produced by the wet process. PG consists of 65÷70% gypsum, 25÷30% water and 5÷10% impurities, i.e. phosphoric acid and its salts, hydrofluoric acid and its compounds, R_2O_3 (Al_2O_3+ Fe_2O_3), quartz, apatite, alkali, organic matter, and others. The P_2O_5 and F impurities are found in three different forms: on the surface of gypsum crystals as water-soluble compounds (H_3PO_4, Ca $(H_2PO_4)_2 \cdot H_2O$, H_2SiF_6), substituted in the lattice of gypsum crystals (effectively solid solutions of $CaHPO_4 \cdot 2H_2O$, $SrSO_4$ or Na_2SiF_6) and as insoluble compounds, i.e. apatite and quartz. It has been estimated that approximately 100÷280 million tons of phosphogypsum has been disposed annually but only 15% is refined and reused (Leškevičienė and Nizevičienė, 2010). Phosphogypsum is one of the mineral wastes that is accumulated in large a mounts all over the world causing serious environmental problems. Using refined PG in the manufacture of building materials is economical and ecological.

The most volume of PG can be utilized in the construction industry. Refined PG can be used as an ingredient of plaster (Singh, 2002; Singh, 2005) or as a replacement of natural gypsum (NG) which plays the role of a set retarder in Portland cement (Tabikh and Miller, 1971; Mehta and Brady, 1977; Olmez and Erdem, 1989; Akın and Sert, 2004; Bhadauria and Thakare, 2006; Chandara *et al.*, 2009; Islam *et al.*, 2017). Basically, the role of PG in Portland cement is the same as NG. However, the impurities such as P_2O_5; F^-… in PG will effect on properties of cement, cement mortar and concrete. Akın and Sert (2004) studied the effect of PG or natural gypsum content on properties of Portland cement. The results showed that increasing content of the gypsums will increase the consistency and setting times of the cement. Both initial and final setting times of cement containing PG are significantly longer than that of cement containing NG. It seems that compressive strength at the ages of 7 and 28 days obtains maximum at the content of gypsum about 3-5%. Both the gypsums can induce the similar strength of sample at the same content of gypsum used. Islam et al. investigated the effect of phosphogypsum addition with cement clinker on properties of paste, mortar and concrete (Islam *et al.*, 2017). The results indicated that setting times of cement containing unprocessed PG (field condition with high impurities content) exceed the setting times of the control sample and strongly increase when the content of the PG increases. Meanwhile, when using processed phosphogypsum, the higher the content of the PG, the longer the setting times. The setting times of the sample containing 10% processed phosphogypsum are the same as those of the control sample. The flowability of mortar initially increases and then decreases when the content of the phosphogypsum in cement increases. Compressive strength of mortar and concrete containing processed phosphogypsum is always higher than that of sample containing unprocessed phosphogypsum. Processed sample conducted better or at least similar performance to the control samples (100% clinker) in paste, mortar and concrete at 10% addition level (Islam *et al.*, 2017).

In Vietnam, PG is being disposed and stored into open areas with total about six million tons. It is estimated that annual production of PG from phosphoric acid and fertilizer plants in Vietnam in 2020 is approximately three and a half million tons. However, only about one million tons of PG are refined and reused in the construction industry. Meanwhile, Vietnam imports about four million tons of natural gypsum for producing of ninety million tons of cement in a year. Therefore, using PG to replace natural gypsum as a set retarder in Portland cement is needed to solve the environmental and disposal problems, and to get economical benefits.

This study investigated the effects of content of two types PG with different impurities content on the properties such as standard consistancy, setting times, compressive strength and sulfate resistance of Portland cement. The results were compared with those of sample containing natural gypsum. The study results are expected to promote the using of PG to replace natural gypsum in cement industry in Vietnam.

2. MATERIALS AND METHODS

2.1. Materials

A Portland cement clinker, natural gypsum and two types of phosphogypsum (PG1 and PG2) were used in this study. Chemical compositions of the clinker can be found in Table 1. PG1 and PG2 are samples taken from different stages of refinement process of Dinh Vu gypsum JSC. In Vietnam. PG2 is in powder form taken after water washing and drying. Meanwhile, PG1 is a commercial product which is completely processed and granulated to change the water-soluble impurities such as P_2O_5, F^-… into water-insoluble. Therefore, the difference in chemical compositions of PG1 and PG2 are mainly in the water-soluble content of P_2O_5 and F^- Table 2.

Table-1. Chemical compositions of clinker.

Materials	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	L.O.I
Clinker (wt%)	64.6	21.9	4.62	3.39	1.18	0.85

L.O.I- Loss on Ignition.

2.2. Experimental Methods

Fifteen Portland cement samples were produced by grinding clinker and the 3 gypsums in a batch vibration ball mill with the same material volume and grinding period. The gypsum contents in the cement samples are calculated based on the SO_3 content. The fineness of the samples is about 3010-3360 cm²/g Table 3.

Table-2. Chemical compositions of gypsums.

Materials	CaO	SO_3	H_2O	SiO_2	R_2O_3	P_2O_5(*)	F^- (*)	L.O.I	I.C
NG (wt%)	31.92	45.49	18.99	-	-	-	-	-	1.52
PG1 (wt%)	29.68	40.73	16.44	9.21	0.62	0.04	0.01	18.93	10.22
PG2 (wt%)	29.40	39.35	16.47	9.16	0.68	0.24	0.11	18.83	10.34

L.O.I- Loss on Ignition.
I.C- Insoluble Compound.
(*)- Water-soluble content.

Table-3. SO_3, gypsum content and fineness of different cement samples.

№	SO_3 content (%)	Gypsum content (%)			Fineness of cement (cm²/g)		
		NG	PG1	PG2	NG	PG1	PG2
1	1.32	2.9	3.24	3.35	3010	3160	3200
2	1.57	3.55	3.85	3.99	3180	3210	3360
3	1.82	4.0	4.47	4.6	3150	3210	3250
4	2.32	5.1	5.70	5.9	3200	3310	3150
5	2.82	6.2	6.90	7.2	3180	3220	3280

The standard consistency, setting times of the cement samples were tested with a Vicat needle as specified in the Vietnam Standard (2015) conforming to ISO 9597:2008. For compressive strength of cement, mortar samples (40x40x160mm³) were prepared with cement:sand:water ratio of 1:3:0.5 in accordance with the VS (2011) conforming to ISO 679:2009.

The effects of different gypsum on sulfate resistance of the cement sample were tested in accordance with the VS (2007). 50x50x285mm³ samples were immersed in sodium sulfate 50g/l solution with the volume of the solution and mortar of 4 at 27±1°C. The weight and length changes of 3 specimens in the solution were measured after 1, 2, 3, 4 and 8 weeks. The solution was renewed after the length change measurement.

3. RESULT AND DISCUSSIONS

3.1. Standard Consistency and Setting Times

Standard consistency and setting times of cements containing different content of NG, PG1 and PG2 are showed in Table 4 and Figure 1, 2, 3. The results indicate that increasing NG or PG1 in cement results in reducing of the standard consistency of the cement. And the effect of NG on the standard consistency of the cement is more significantly than that of PG1 Figure 1. Meanwhile, the water demand of cement containing PG2 does not significantly change and is clearly lower than that of cement containing NG or PG1.

Table-4. Standard consistency and setting times of different cement samples.

№	SO_3 content (%)	Standard consistency (%)			Initial setting time (min)			Final setting time (min)		
		NG	PG1	PG2	NG	PG1	PG2	NG	PG1	PG2
1	1.32	30.0	29.5	26.0	120	85	135	215	165	270
2	1.57	29.5	29.0	25.0	115	110	130	210	220	280
3	1.82	28.5	29.0	25.5	125	120	145	195	230	285
4	2.32	26.5	28.5	26.5	120	155	145	200	265	285
5	2.82	25.5	27.0	25.5	115	205	155	210	310	290

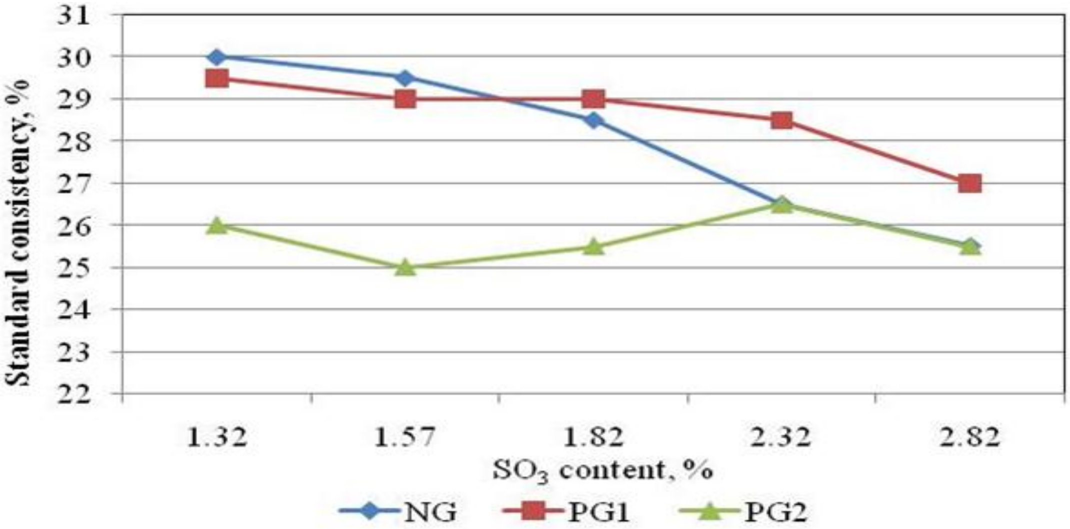

Figure-1. Effects of gypsum on standard consistency.

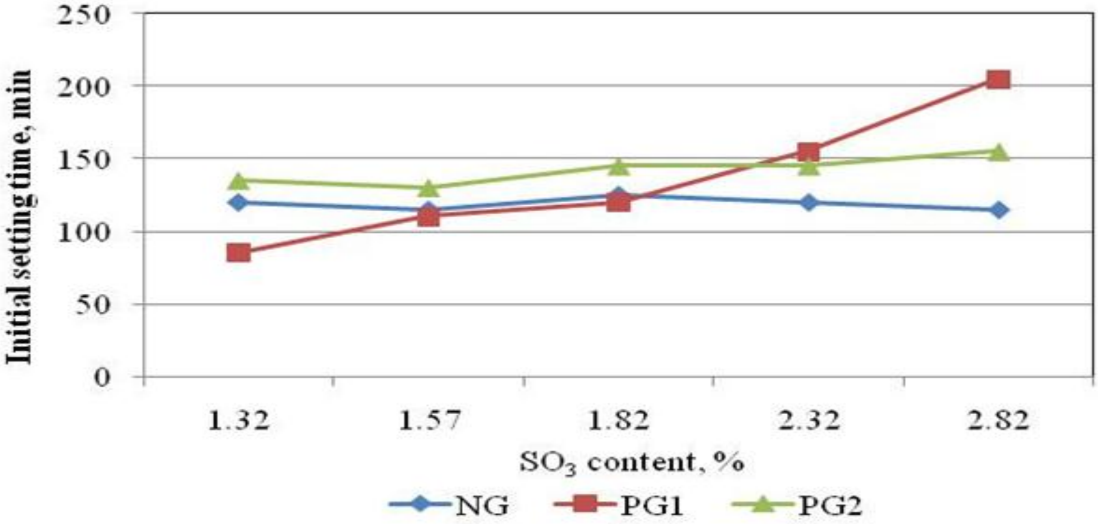

Figure-2. Effects of gypsum on initial setting time.

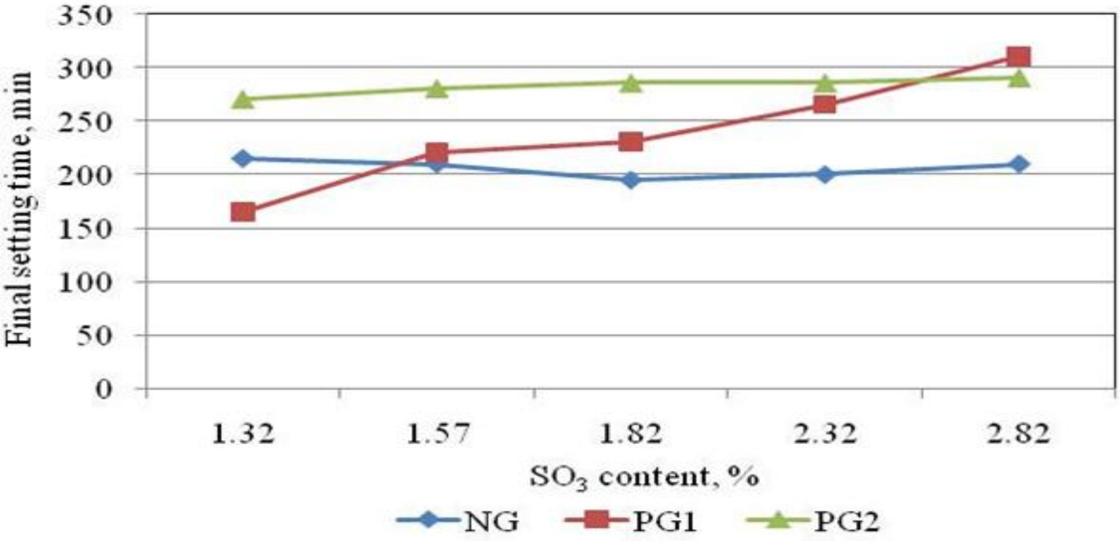

Figure-3. Effects of gypsum on final setting time.

Generally, the setting times of the cement increase when PG content in cement increases. But changing NG content in range of this study does not change both the setting times Table 4 and Figure 2, 3. For PG1, the initial and final setting times of cement containing 3.24% PG1 (1.32% SO_3) are 85 and 165 min, clearly shorter than those of cement containing NG and PG2, respectively. However, the setting times of the sample containing 6.9% PG1 (2.82% SO_3) increase up to 205 and 310 min, significantly exceed those of the samples containing NG or PG2. The cement containing 3.35% PG2 (1.32% SO_3) possesses the initial and final setting times of 135 and 270 min, respectively. When PG2 increases from 3.35% (1.32% SO_3) to 7.2% (2.82% SO_3), both the setting times of cement increase only 20 minutes Table 4.

It should be noted that the water-soluble form of P_2O_5 and F^- in PG2 are higher than those in PG1 and NG. It means that water-soluble P_2O_5 and F^- in phosphogypsum induce longer setting times of cement. The water demand of cement reduces or the workability of cementitious mixture increases when the content of gypsum or impurities in cement increases. These results are in good agreement with those of previous studies (Akın and Sert, 2004; Islam *et al.*, 2017) where the setting times of cement containing high water-soluble P_2O_5 and F^- impurities are longer. For instance, Sadiqul Islam showed that the water demand of the mortar initially decreases when the content of the phosphogypsum in cement increases (Islam *et al.*, 2017).

3.2. Compressive Strength

Compressive strength at the ages of 3, 28 and 91 days of mortar can be found in Table 5 and Figure 4, 5, 6. The 3-d compressive strength results at Figure 4 show that increasing the gypsum content in cement will accelerate the early strength of the mortar. Comparing to natural gypsum, the low impurities content in phosphogypsum (PG1) enhances the strength of the mortar at the early age but it will be reduced by phosphogypsum with high impurities content PG2, Figure 4. In contrast, compressive strength of samples containing PG2 exceeds that of samples containing NG and PG1 possesses the lowest 91-d compressive strength Figure 6. There is an optimum gypsum content in cement which produces the highest strength of the mortar at the ages of 28 and 91 days Figure 5 and 6. These results are also similar to those reported by Akın and Sert (2004).

Table-5. Compressive strength of different cement samples.

N°	SO_3content (%)	3-d compressive strength (MPa)			28-d compressive strength (MPa)			91-d compressive strength (MPa)		
		NG	PG1	PG2	NG	PG1	PG2	NG	PG1	PG2
1	1.32	19.0	27.6	18.0	42.9	41.8	44.0	51.5	49.0	56.2
2	1.57	21.3	31.6	20.2	43.5	43.5	44.3	55.2	52.8	57.0
3	1.82	24.9	32.5	21.8	43.7	45.1	45.0	55.5	53.4	60.7
4	2.32	25.2	33.0	22.6	44.6	44.6	45.1	54.1	50.7	58.3
5	2.82	27.7	34.4	23.5	40.2	44.1	44.2	52.5	47.1	57.7

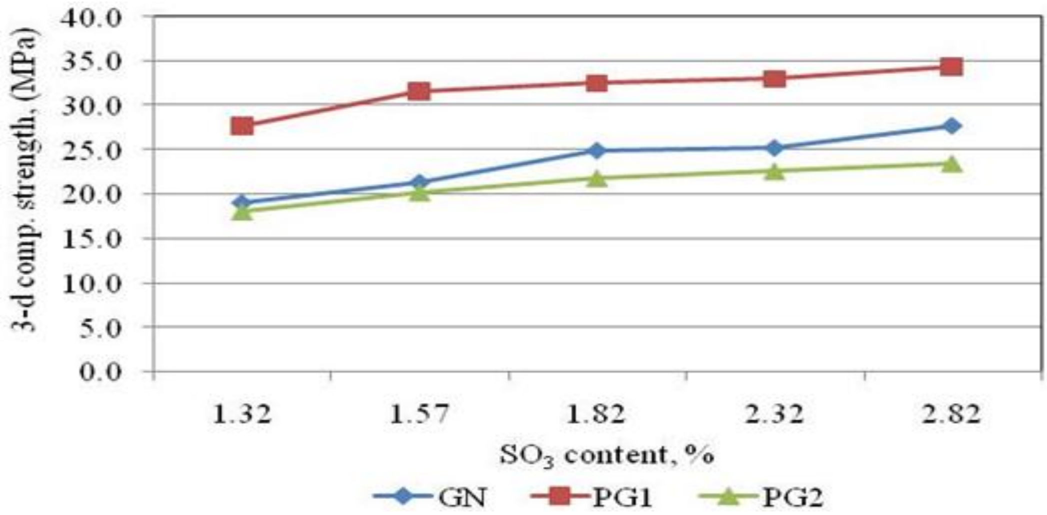

Figure-4. Effects of gypsum on 3-d compressive strength.

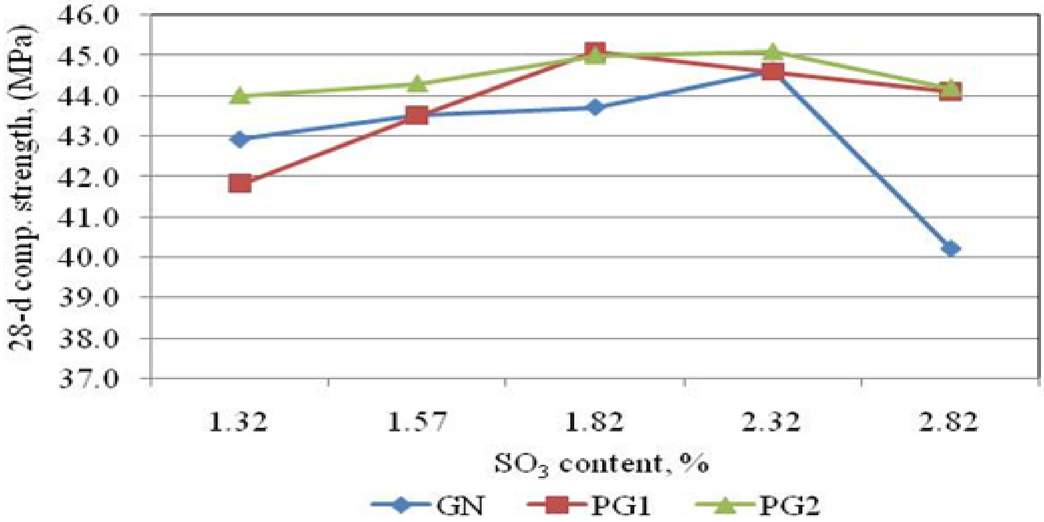

Figure-5. Effects of gypsum on 28-d compressive strength.

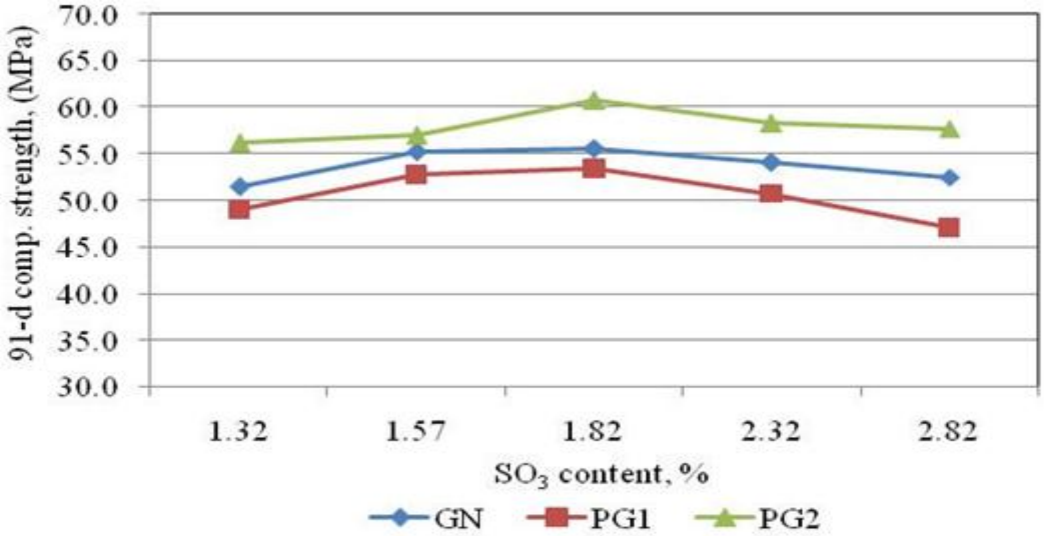

Figure-6. Effects of gypsum on 91-d compressive strength.

3.3. Sulfate Resistance

Results of weight and length changes of samples containing different contents of gypsums in the sodium sulfate solution (50g/l) up to 8 weeks are given in Figure 7 to Figure 9. It shows clearly that the longer the sample is in the solution, the more the weight increases and the larger the length changes. The increasing gypsum content in cement induces lower durability of the sample in the solution, i.e. absorbing more Na_2SO_4 and showing larger expansion. It should be noted that the expansion of the samples containing 1.32 SO_3 of phosphogypsums begins to exceed that of the sample containing 1.82 SO_3 of phosphogypsums after 8 weeks in the solution Figure 8 and 9.

Comparing the results of the samples at the same SO_3 content between different gypsums (i.e. NG, PG1 and PG2 in Figure 7 to Figure 9) indicates that there is no significant difference in weight change between the three gypsums. The expansion of the samples containing PG1 is largest Figure 8. The samples containing low contents of NG (i.e. 1.32% and 1.82% SO_3) have the length change slightly higher than the samples containing low contents of PG2, respectively. Meanwhile, the length change of the sample containing high content of NG (i.e. 2.82% SO_3) is lower than that of the sample containing high content of PG2.

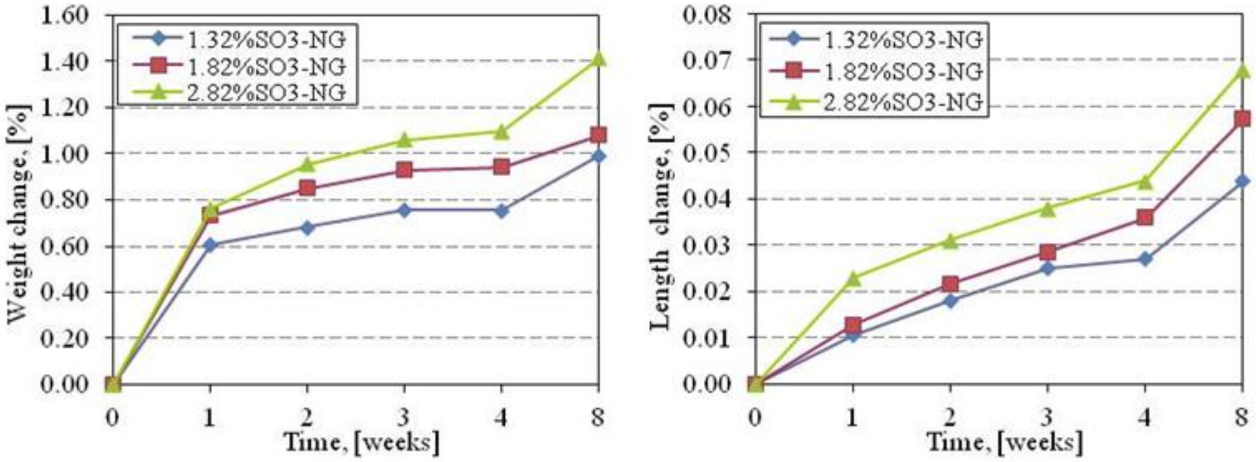

Figure-7. Effects of NG content on weight and length change of mortar sample.

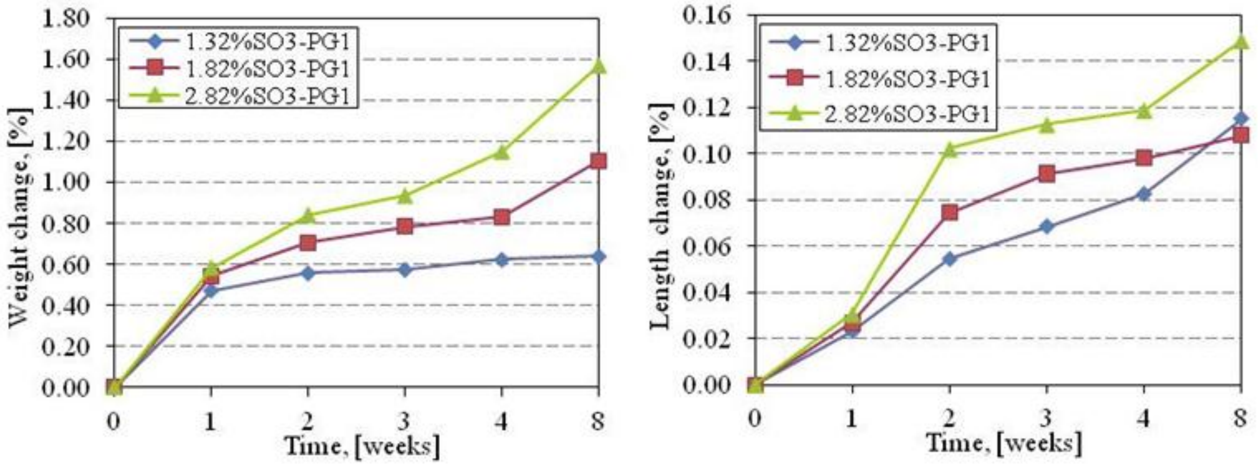

Figure-8. Effects of PG1 content on weight and length change of mortar sample.

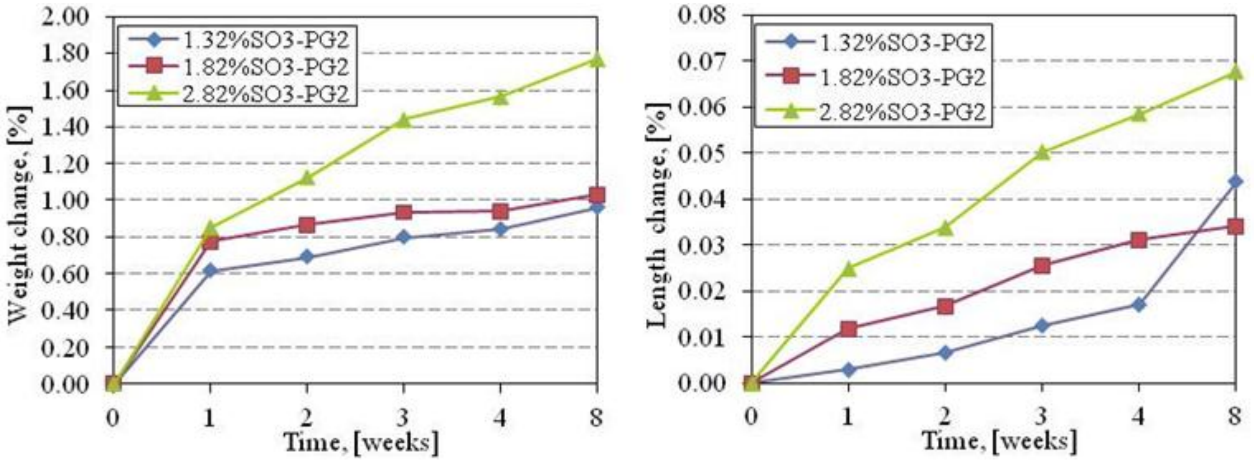

Figure-9. Effects of PG2 content on weight and length change of mortar sample.

4. CONCLUSIONS

The following conclusions can be drawn from the results of this study:

- Increasing the content of the gypsums with low impurities of P_2O_5 and F^- (i.e. NG and PG1) will decrease the water demand of the cement. Impurities of P_2O_5 and F^- in gypsums prolong the setting times of cement. The phosphogypsum containing low impurities of P_2O_5 and F^-(PG1) increases the setting times of the cement more significantly than the gypsum with the high content of the impurities (PG2);

- The 3-d compressive strength of cement will be accelerated by gypsum content but there is a suitable content of gypsum to induce the highest strength of the cement at the ages of 28 and 91 days. At the age of 3 days, cements containing PG1 possesses the highest strength and PG2 induces the lowest strength. However, the higher impurity phosphogypsum (PG2) enhances the long term strength comparing to PG1 and NG.
- The higher the content of the gypsums, the lower the sulfate resistance of the cement. The durability of cement containing PG1 is lower than that of cement containing PG2 or NG.

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