**Eco concrete made with phosphogypsum-based super sulfated cement**

**Nguyen Ngoc Lam**
Hanoi University of Civil Engineering, 55 Giai Phong Road – Hanoi – Vietnam

**Abstract.** Phosphogypsum is an important environmental issue for all countries with phosphate and phosphoric acid industries from phosphate rock. The problem mainly stems from the difficulty in storing phosphogypsum. Therefore, the reuse of phosphogypsum in producing construction materials plays an important role to protect human health, to decrease the environmental pollution and to reduce the building materials cost. This research aimed at developing an eco concrete using super sulfated cement (SSC) in which the phosphogypsum was recycled. The present paper deals with the experimental investigation on slump number of fresh concrete, 28-day compressive strength characteristics of concrete using only 10% cement, 30% - 60% phosphogypsum and granulated blast furnace slag in binders named super sulfated cement with 3 different water-binder ratios of 0.45, 0.50 and 0.55... It is shown that Portland cement can be replaced with super sulfated cement based on Vietnam phosphogypsum to develop a good and hardened concrete to achieve economy; The compressive strength of concrete can achieve 20-40MPa. This value is enough for the use of the eco-concrete in the construction industry. The results also indicate that the increase of replacement of phosphogypsum in concrete lead to reduction in the compressive strength but do not affect too much in the case of slump number.

**1. Introduction**

Concrete is an indispensable construction materials in the development of infrastructure, industry and housing. It is responsible for 5-7% of man-made carbon dioxide emissions [1]. Thus, the manufacture and utilization of eco-concrete is especially significant in construction to protect the environment against pollution. To make concrete an eco-material, ways of understanding the situation and of solving the specific problems become important. Eco-concrete can be defined as a type of concrete which contributes to reducing the burden on the global environment and which has ecologically conscious interfaces between concrete and all living things. We can produce this type of concrete by using effectively the resources such as reuse of waste, use of low-quality materials or recycling of demolished concrete [2].
The use of particular waste product will be economically advantageous usually at the place of abundant availability and production. Much of the literature is available on the use of fly ash, blast furnace slag, silica fume, rice husk, etc. in manufacture of cement concrete [3-6]. However, the number of research on the use of super-sulfated cement, especially phosphogypsum in construction industry is quite little. This paper tries to focus on the use of Vietnam phosphogypsum in super-sulfated cement in production concrete. Currently, there are 3 factories generating large sources of phosphogypsum waste, including: DAP factory of Dinh Vu joint stock company in Hai Phong, DAP joint stock company No. 2 in Lao Cai and at Duc Giang fertilizer chemical joint stock company in Lao Cai. It is estimated that by 2020, the whole country will have over 20 million tons. The conversion of toxic phosphogypsum waste into the environment and health into an admixture to produce construction materials (ceiling panels, wall panels, cement) not only reduces environmental pollution but also saves the cost cheaper than imported plaster. However, the fact shows that phosphogypsum waste has not been invested in research and widely used in the field of construction materials production. It is estimated that by 2020, phosphogypsum residues will be generated by 3,885,000 tons per year [7]. Some researches focus on the using the phosphogypsum or ground granulated blast-furnace slag in the construction of highways, runways, etc. [8-11] or recycled for manufacture of fibrous gypsum boards, blocks, gypsum plaster, composite mortars using Portland cement, masonry cement, [12]. Recently, the phosphogypsum have been studied in super-sulfated cement [13-15]. Also, the techno-economic feasibility of beneficiating phosphogypsum has been studied wherein the beneficiated phosphogypsum was used for making Portland cement and Portland slag cement, and the results favored use of phosphogypsum as an additive to cement clinker in place of natural gypsum [16]. The present paper deals with the experimental investigation on slump number, compressive strength characteristics of SSC concrete with water-binder ratios of 0.45, 0.50 and 0.55. The reuse of industrial byproducts such as phosphogypsum (PG) and ground granulated blast-furnace slag (GBFS) in producing SSC for concrete is necessary to make even “greener” concrete. In concrete, phosphogypsum particles can act as micro aggregates, while also can activate ground granulated blast-furnace slag to create more C-S-H minerals for binders. Meanwhile, GBFS will contribute to the strength of concrete because of its pozzolanic properties. Strength development of concrete using SSC binders is due to a chemical reaction between the GBFS, Phosphogypsum, calcium hydroxide and some other activators.

2. Materials and Experimental methods

2.1. Materials

All concrete materials used in this current study were locally sourced. Figure 1 shows the chemical composition of the raw materials determined using the X-ray fluorescence (XRF). Typical ordinary Portland cement that complied with TCVN 2682-2016 suitable for general-purpose construction was used. The chemical composition and physical properties of the cement are shown in Table 1 and Table 2. The phosphogypsum was collected from waste disposal sites at DAP Dinh Vu fertilizer plant, Hai Phong, Viet Nam has particle size finer than 11μm. The specific gravity of PG is 2.34 g/cm³. Physical properties and chemical composition of finely GBFS used in this study are shown in Table 3. The natural fine and coarse aggregate used during this research work were commercially obtained. The natural sand of 5 mm maximum particle size having its particle size grading conforming to TCVN 7570:2006 while the gravel having a maximum size of 20 mm was used in this study. The physical properties of both the sand and gravel aggregate materials are presented in Table 4 and Table 5. The particle size gradation for the glass sand, natural sand and gravel aggregate were carried out using sieve analysis and are presented in Figure 2. The Hardening activator (Na₂SO₄) was added into the mixture of binder containing GBFS to combine with SiO₂ in the slag for the formation of the C-S-H product. The Na₂SO₄ content is fixed at 1%. Concrete mixing water meets all the technical requirements of TCVN 4506-2012. To improve the workability of concrete, the polycarboxylate
superplasticizer of Basf Vietnam, Glenium ACE388 SureTec was used (liquid, amber, specific gravity 1.07g/cm³, content chloride ion <0.1).

Table 1. Chemical composition of raw materials

| Raw material | Chemical composition, % by weight |
|--------------|-----------------------------------|
|              | SiO₂ | Fe₂O₃ | Al₂O₃ | CaO   | MgO   | Na₂O  | K₂O  | SO₃  | TiO₂ | L.O.I |
| PC           | 20.3 | 5.05  | 3.51  | 62.81 | 3.02  | -     | -    | 2.0  | -    | 1.83  |
| GBFS         | 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 |

Table 2. Properties of the PC40 But Son cement used in this study

| Blaine fineness cm²/g | Mean particle size, µm | Consistency, % | Specific gravity, g/cm³ | Compressive strength at 3 days, MPa | Compressive strength at 28 days, MPa |
|-----------------------|------------------------|----------------|------------------------|--------------------------------------|---------------------------------------|
| 3890                  | 11.0                   | 29.5           | 3.15                   | 29.8                                 | 52.2                                  |

Table 3. Properties of ground-granulated blast-furnace slag used in this study

| N° | Physical properties | Unit | Value |
|----|---------------------|------|-------|
| 1  | Specific gravity    | g/cm³| 2.94  |
| 2  | Strength activity index | % | 104.3 |
| 3  | The mean particle size | µm | 10.2  |
| 4  | L.O.I               | %    | 0.96  |

Table 4. Properties of fine aggregate used in the study

| N° | Characteristic                  | Unit | Value | Testing method          |
|----|---------------------------------|------|-------|-------------------------|
| 1  | Specific density                | g/cm³| 2.66  | TCVN 7572:2006          |
| 2  | Bulk density                    | kg/m³| 1510  | TCVN 7572:2006          |
| 3  | Void Percentage of bulk Aggregates | % | 0.43  | TCVN 7572:2006          |
| 4  | Saturated surface dry           | %    | 1.05  | TCVN 7572:2006          |
| 5  | Fineness Modulus                |      | 3.06  | TCVN 7572:2006          |
| 6  | Content of dust, mud and clay   | %    | 0.2   | TCVN 7572:2006          |
| 7  | Particle size distribution      |      | Qualified | TCVN 7572:2006  |

Table 5. Properties of coarse aggregate Dₘₐₓ = 20mm used in the study

| N° | Characteristic                  | Unit | Value | Testing method          |
|----|---------------------------------|------|-------|-------------------------|
| 1  | Specific density                | g/cm³| 2.70  | TCVN 7572:2006          |
| 2  | Bulk density                    | kg/m³| 1460  | TCVN 7572:2006          |
| 3  | Void Percentage of bulk Aggregates | % | 45.9  | TCVN 7572:2006          |
| 4  | Saturated surface dry           | %    | 0.5   | TCVN 7572:2006          |
2.2. Experimental method

The concrete mixtures were proportioned based on the unit volume of 1 m$^3$. The SSCs binder were successfully prepared in different combinations of cement, GBFS and phosphogypsum while the total aggregate content was kept constant. The water-to-binder-ratio (W/B) varied from 0.45 to 0.55. The ingredient contents of binder were calculated based on their weight ratio. The total volume of aggregates was the residual volume except binder volume. The formulations of concrete using SSC binder in this study are shown in Table 6:

Table 6. Formulation of eco-concrete using SSC

| N° | W/B ratio | Proportion of materials in SSC | PC kg/m$^3$ | PG, kg/m$^3$ | GBFS, kg/m$^3$ | Sand, kg/m$^3$ | Gravel, kg/m$^3$ | Water, kg/m$^3$ | Na$_2$SO$_4$, kg/m$^3$ | Super plasticiser, kg/m$^3$ |
|----|-----------|-------------------------------|-------------|--------------|---------------|----------------|-----------------|----------------|----------------------|------------------------|
| 1  | 0.45      | 30% PG + 60% GBFS +10% PC    | 361.8       | 0.0          | 0.0           | 825.0         | 1090.0          | 162.8          | 3.62                 | 3.62                   |
| 2  | 0.45      | 40% PG + 50% GBFS +10% PC    | 34.6        | 103.7        | 207.3         | 825.0         | 1090.0          | 155.5          | 3.46                 | 3.46                   |
| 3  | 0.45      | 50% PG + 40% GBFS +10% PC    | 34.2        | 136.8        | 171.0         | 825.0         | 1090.0          | 153.9          | 3.42                 | 3.42                   |
| 4  | 0.5       | 30% PG + 60% GBFS +10% PC    | 33.8        | 169.2        | 135.4         | 825.0         | 1090.0          | 152.3          | 3.38                 | 3.38                   |
| 5  | 0.5       | 30% PG + 60% GBFS +10% PC    | 340.3       | 0.0          | 0.0           | 825.0         | 1090.0          | 170.1          | 3.40                 | 3.40                   |
| 6  | 0.5       | 40% PG + 50% GBFS +10% PC    | 32.6        | 97.8         | 195.5         | 825.0         | 1090.0          | 162.9          | 3.26                 | 3.26                   |
| 7  | 0.5       | 50% PG + 40% GBFS +10% PC    | 32.3        | 129.1        | 161.3         | 825.0         | 1090.0          | 161.3          | 3.23                 | 3.23                   |
| 8  | 0.5       | 30% PG + 60% GBFS +10% PC    | 32.0        | 159.8        | 127.8         | 825.0         | 1090.0          | 159.8          | 3.20                 | 3.20                   |
| 9  | 0.55      | 30% PG + 60% GBFS +10% PC    | 321.2       | 0.0          | 0.0           | 825.0         | 1090.0          | 176.7          | 3.21                 | 3.21                   |
| 10 | 0.55      | 30% PG + 60% GBFS +10% PC    | 30.8        | 92.5         | 185.0         | 825.0         | 1090.0          | 169.6          | 3.08                 | 3.08                   |
2.3. Testing procedures

The mixing method of eco-concrete is presented as follows. All the materials (Cement, GBFS and phosphogypsum, fine aggregate and coarse aggregate) were weighed and dry-mixed for 5 min to ensure homogeneity of the mixture. Water and superplasticizer after measuring exactly were added into the dry mixture and mixed for another 3 min until a homogeneous mix is achieved.

After the mixing procedure, slump test was performed according to Vietnamese standard TCVN 3106-1993, and then all specimens were cast in the mold 10x10x10 cm and covered with the plastic sheets, followed by storage in the laboratory for 24 h. The specimens were demolded and cured in water until the day of testing. At the end of the 7 and 28 days, to determine the hardened properties of specimens, compressive strength tests according to TCVN 3118-1993 were performed on 100-mm cube specimens.

3. Test results and Discussion

3.1. Test results of Properties of fresh concrete and hardened concrete

In order to clarify the feasibility and high applicability of green concrete using SSC in this research, two important technical properties of concrete are workability and compressive strength were studied. Experimental results are shown in Table 7:

Table 7. Slump number of fresh concrete and compressive strength of hardened concrete

| №  | W/B ratio | Proportion of materials in SSC                     | Slump, cm | Compressive strength at 28 days, MPa |
|----|-----------|---------------------------------------------------|-----------|-------------------------------------|
| 1  | 0         | 0                                                 | 7         | 41.5                                |
| 2  | 0.45      | 30% PG + 60% GBFS +10% PC                         | 4.5       | 35.9                                |
| 3  | 0.45      | 40% PG + 50% GBFS +10% PC                         | 4         | 34.6                                |
| 4  | 0.45      | 50% PG + 40% GBFS +10% PC                         | 4         | 30.8                                |
| 6  | 0         | 0                                                 | 8         | 32.1                                |
| 7  | 0.5       | 30% PG + 60% GBFS +10% PC                         | 6.5       | 31.8                                |
| 8  | 0.5       | 40% PG + 50% GBFS +10% PC                         | 6         | 30.3                                |
| 9  | 0.5       | 50% PG + 40% GBFS +10% PC                         | 6         | 26.9                                |
| 10 | 0.55      | 0                                                 | 9.5       | 29.6                                |
| 11 | 0.55      | 30% PG + 60% GBFS +10% PC                         | 7.5       | 28.7                                |
3.2. Slump of fresh concrete

Results of measuring slump number of fresh concrete with different proportions according to TCVN 3118 – 1993 are shown in Table 7 and Figure 1:
As expected, the increase of W/B ratio resulted in increase of slump of all mixtures. At the same W/B ratio, the slump of fresh control concrete using 100% cement is the highest. While the mixtures using super-sulfated cement was almost the same and varied from 4.0 cm to 4.5 cm (with W/B=0.45), 6.0 cm to 6.5 cm (with W/B=0.50), and 6.5 cm to 7.5 cm (with W/B=0.55). The lowest slump was noticed in composition containing 50% PG in binder while the compositions with 100% of cement have the highest slump. Decreased slump probably could be attributed due to the higher water holding capacity and the smoother surface relating to the glass phases of GBFS although phosphogypsum has a lower specific surface area when compared to blast furnace slag.

3.3 Compressive Strength of concrete

Because of the low cement content, compressive strength is an extremely important indicator that should be considered with this green concrete. Compressive strength results can be used for quality control especially the durability of the concrete structures and for increase the practicality of applying research results; The compressive strength development of mixtures using different percentage replacements of phosphogypsum at water/binder ratios of 0.45, 0.50 and 0.55 is presented in Table 7 and Figure 2.
W/B = 0.45

W/B = 0.50

Compressive strength, MPa

a)

b)
The results in Figure 2, the W/B ratio has a significant effect on the compressive strength, whereas the difference in compressive strength of various mixtures at the same W/B ratio is quite little. As expected, the mixture using 100% PC have the highest compressive strength. Further replacement of super-sulfated cement with phosphogypsum leads to drastic reduction in the compressive strength. Phosphogypsum is not a pozzolanic material. For that reason, GBFS increases the compressive strength via the filler effect and pozzolanic effect; Meanwhile the role of PG is to be filler and to activate the GBFS.

The proportion of binder used for eco concrete is 30%PG:60%GBFS and 10% PC can be taken as the optimum possible replacement of cement with SSC. However, in conventional concrete structures, concrete strength ranges between 20-40 MPa. Therefore, depending on the compressive strength, it can be used any appropriate replacement of cement by SSC binders with appropriate water-binder ratio of 0.45-0.55. Par example, for concrete with grade designations M25 all the mixtures above can be used, but grade designations M30 only the mixture using 30%PG:60%GBFS and 10% PC is affordable.

4. Conclusion

Based on the experimental investigation conducted and the analysis of test results, the following conclusions are drawn:

- Industrial waste such as phosphogypsum, GBFS can be used in construction industry for preparation of eco - concrete replacing large quantity of cement, which is a valuable ingredient of concrete, to achieve economy.

- With only 10% cement with 30-60 % phosphogypsum, or 60-30%GBFS the compressive strength at 28 days can reach 80-90% of the strength value of concrete samples using 100% cement.

- Depending on mixture proportion, Eco – concrete using SSC can achieve grade M20, M30, M35 which is similar to conventional concrete, suitable for manufacturing basic bearing structures in construction.

- Further research is needed on waterproofing, corrosion resistance, tensile strength and exterior behavior of SSC concretes.
bending strength of concrete to increase the feasibility of applying this type of concrete to different structures such as concrete for marine constructions, concrete pavements and roads.

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