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APPLICATIONS OF DUYEN HAI - 1 THERMAL POWER PANT'S FLY ASH AND HOA PHAT STEELMAKING PLANT'S BLAST FURNACE SLAG IN GEOPOLYMER CONCRETE FABRICATION

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Abstract. Currently, non-cement alkaline activated concretes, using fly ash instead of conventional cement binder, have been widely used in construction around the world. However, in Viet Nam researches on geopolymer concretes are still very limited. Meanwhile, coal-fired thermal power plants in Viet Nam annually generate about 13 million tons of fly ash, potentially causing environmental pollution. Therefore, the use of these raw materials for concrete making not only minimizes environmental pollution but also avoids wasting resources. This paper presents study results on the mechanical properties of geopolymer concrete using fly ash of the 1,245 MW Duyen hai - 1 thermal power plant and blast furnace slag of Hoa Phat steelmaking plant. The suitable ratio of liquid glass/NaOH used in this study was about 3.7. At this value, the compressive, flexural and tensile strengths of the geopolymer concrete have reached 43.2 MPa, 6.62 MPa and 87,780 N, respectively. In addition, geopolymer concrete samples were impervious and their mechanical properties were almost unchanged after soaking in various solutions for a period of 4 months. Furthermore, interlocking blocks were fabricated from this geopolymer concrete (with the same composition as sample M6), based on the TCVN 9901:2014 standard on Hydraulic structures and Requirements for sea dike design. These blocks were used to reinforce the sea dike against this year's typhoon season in central Viet Nam. The success of this project greatly contributes to the effective application of fly ash and reducing environmental pollution.

Keywords: Geopolymer, fly ash, blast furnace slag, concrete.

Classification numbers: 2.9.2, 2.10.2, 3.3.3.

1. INTRODUCTION

The development of alkaline activated cement has been mentioned by many scientists since the 1940s of the twentieth century. In the 1960s and 70s, Davidovits prepared mineral polymers by dissolving aluminosilicate oxides, alkali and colloidal silica in water at 120 °C. When synthesizing resin, feldspar and zeolite, he found that the hydrothermal process needed to be carried out in a dense alkaline environment and at temperatures below 150 ^{o}C. However, the products had poor mechanical properties [1]. Later, he had successfully invented a heat resistant mineral polymer with a smooth and hard surface [2]. In 1978, Davidovits coined the term "geopolymers" to describe amorphous mineral polymers with a three-dimensional silico-aluminate structure. They have the experimental formula of Mn{- (SiO_2)z - AlO2}.wH_2O, where M is a cation (K^+, Na^+ or Ca^{2+}), n is the condensing order and z is 1, 2 and 3 [3].

After Davidovits, this topic has been studied by many scientists [4, 5]. Recently, due to concerns about the increased degradation of the environment, researching and using fly ash and blast furnace slag based geopolymer concretes have been strongly developed in Australia, Japan, the United States and Europe [6]. Several studies have been successfully applied in practice. The geopolymer concrete block could be used as a slanted roof block or an interlocking block for sea dike in many countries. Rangan and colleagues at Curtin University have determined the composition of a high compressive strength alkaline activated concrete using fly ash as a binder [7, 8]. In addition, a large number of studies have been conducted on alkaline activated concretes using fly ash and blast furnace slag, however, these studies are still at experimental stages [9].

Palomo *et al*. [4] found that various fly ash samples, which were activated by NaOH of 8–12 M and cured at 85 °C for 24 hours, produced materials with a compressive strength of 35 to 40 MPa. If liquid glass was added ($SiO_2/Na_2O = 1.23$), the compressive strength reached nearly 90 MPa [4]. Other authors also indicated that the ratio of SiO_2/Na_2O is a very important parameter and the ratio of water to the binder should also be taken into account [10, 11].

In Viet Nam, there were few studies on the application of fly ash-based geopolymer concrete for construction. Furthermore, according to the statistics of the Ministry of Industry and Commerce, there are 25 coal power plants operating commercially nationwide. They generated about 13 million tons of fly ash per year. However, approximately 5 million tons have been used as raw materials to produce construction materials, such as bricks, cement, etc. [12]. As of last 2020, about 44.5 tons of fly ash were not used [13], leading to negative impacts on the environment. In 2017, the Prime Minister issued Decision No. 452 on encouraging the treatment and use of fly ash and plaster as raw materials for the production of construction materials. In addition, he also accepted the scheme “Development of construction materials for marine environment and island buildings” by Decision No. 126 in 2019 [14]. Thus, the investigation and application of fly ash in geopolymer concrete fabrication become urgent.

In many countries, fly ash and slag are considered as a resource of raw materials and many effective treatment methods have been developed and commercially available. In Viet Nam, coal-fired thermal power plants use different fuel sources. Therefore, the chemical composition of fly ash of each plant is different. To use fly ash of each plant for concrete making, it is clear that we need specific studies for suitable subjects. Although Duyen Hai - 1 thermal power plant with a capacity of 1,245 MW was built in 2015 and generated an amount of fly ash, there were few reports of its fly ash application.

In the literature, there were several studies on the effect of the fly ash chemical composition and the component ratio of geopolymer concrete on its mechanical properties. According to Phan Duc Hung and Le Tuan Anh [15], the flexural and tensile strengths of geopolymer concrete made from fly ash depend much on the ratio of liquid glass/NaOH, the ratio of active alkali/fly ash, and curing time, etc. According to these authors, when using a ratio of liquid glass/NaOH of 2.5, the flexural and tensile strengths of the concrete reached 4.85 MPa and 3.37 MPa, respectively, corresponding to the ratio of activated alkaline/fly ash of 0.6 and curing time of 4 hours.

In 2017, Tran Viet Hung *et al*. [16] fabricated geopolymer concrete from fly ash of Pha Lai thermal power plant. The research results showed that the elastic modulus of the geopolymer concrete was lower but its tensile strength was 7 - 27 % higher than that of conventional concretes.

For Duyen hai - 1 thermal power plant, it is necessary to investigate and apply its fly ash in eco-friendly product fabrication. In this paper, we report not only the results of Duyen hai – 1 plant's fly ash and Hoa Phat steelmaking plant's blast furnace slag based geopolymer concrete fabrication but also products of interlock geopolymer concrete block fabrication. The products of this study would be used to reinforce the sea dike against this year's typhoon season in central Viet Nam.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Fly ash

The fly ash used in this study was collected from Duyen Hai - 1 thermal power plant with the chemical composition as shown in Table 1.

Table 1. Fly ash chemical composition of Duyen Hai - 1 thermal power plant.

Composition	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	LOI
Ratio, %	46.12	19.93	6.68	3.60	1.09	18.70

According to Table 1, the loss on ignition (LOI) of Duyen Hai - 1 thermal power plant's fly ash was up to 18.70 %. However, according to the ASTM - C618 standard, fly ash for geopolymer concrete production should have an LOI content of < 6 %. Therefore, in order to reduce the actual LOI content, the research team has collaborated with the Department of Mineral Materials (Institute of Material Science, Vietnam Academy of Science and Technology) to clean the fly ash by a flotation process. Chemical analysis results of the floated fly ash are shown in Table 2.

Table 2. Floated fly ash chemical composition of Duyen Hai - 1 thermal power plant.

Composition	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	LOI
Ratio, %	55.99	24.10	7.21	4.05	1.11	3.89

From Table 2, it can be seen that:

- After flotation, the LOI content in the floated fraction of the fly ash was less than 4 %, equivalent to the fly ash quality of Group F according to ASTM standards, so it is perfectly suitable for use as raw materials for concrete production;

- The Si/Al ratio is approximately 2, which is very suitable for the polysilate structure (PS).

2.1.2. Blast furnace slag

The blast furnace slag used was a commercial product "GGBFS - S95" of Hoa Phat Group relevant to the TCVN 11586:2016 of Viet Nam quality standards.

2.1.3. Aggregates

- Sands (small aggregates)

Small aggregates were yellow sands provided by Song Da - Cao Cuong Joint Stock Company. In order to be used as aggregate, the sands were washed and deslimed by sedimentation and filtration to remove any clay. The clean sands then were sieved with a sieve of 0.15 - 1.25 mm aperture. Figure 1 presents a graph of particle size analysis of the sands.

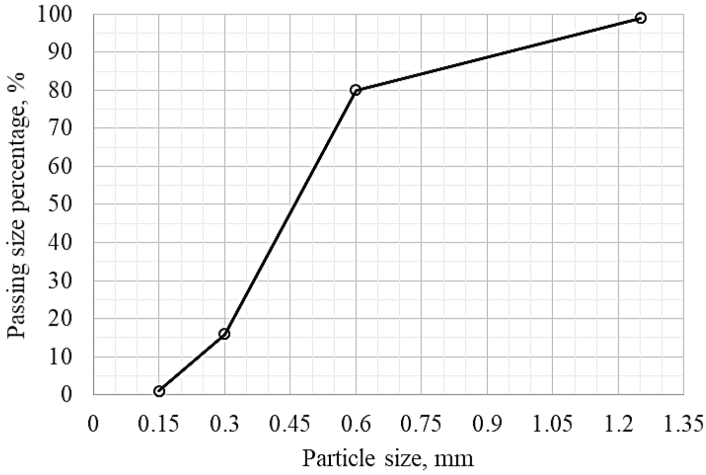

Figure 1. Particle size analysis of the sand.

- Gravels (large aggregates)

The large aggregates used in the study were construction gravels provided by Toan Trung Co. Ltd. with 3 types with the top sizes of 20, 14 and 7 mm, respectively, the mixing ratio of each aggregate are presented in Figure 2. The used mixing ratios of the large aggregates in the concrete were: 21.5 % (20 mm) + 28.5 % (14 mm) + 50 % (7 mm). Similar to the sands, gravels were also washed before being used for mixing.

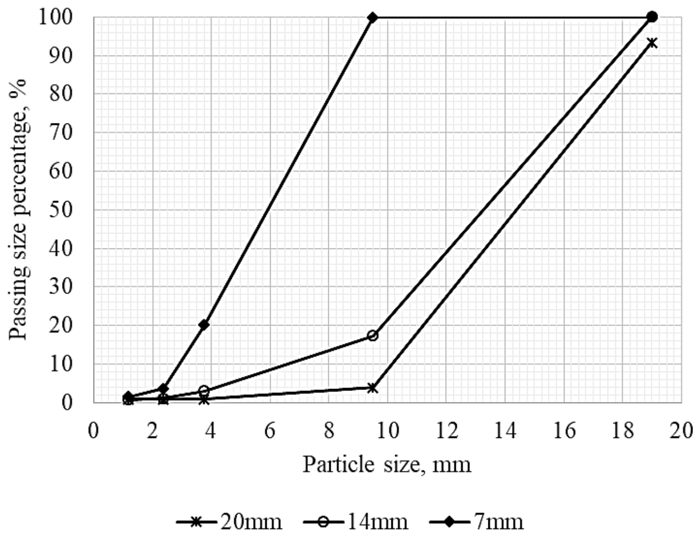

Figure 2. Particle size analysis of the gravel.

2.1.4. Alkaline solution

The alkaline solution and the liquid glass were mixed for 30 minutes and let stand for at least 1 day before using. The alkaline solution was made from dry flake NaOH with a purity of 98 % and a concentration of 18 mol/L. The liquid glass had a ratio of $Na_2O/SiO_2/H_2O$ by weight of 11.8/28.5/59.7 %. The ratios between anhydrous NaOH, water and liquid glass are given in Table 4.

2.2. Methods

The purpose of this study is to determine the optimal ratio of activated alkaline solution in the geopolymer concrete. Therefore, the material mixing ratios were kept constant as given in Table 3 and only the activated alkaline solution ratios were changed as shown in Table 4. In addition, for comparative purposes, some concrete samples were made as follows: M7 included 90 kg of liquid glass mixed with 5 kg of silica fume (Silica 90 is a commercial product of Neomax Viet Joint Stock Company); M9 was a plain concrete (without NaOH and Na_2SiO_3, with the ratio of water/cement of 180/440); M10 had no blast furnace slag (the amount of blast furnace slag was replaced by additional fly ash), and M11 was concrete with untreated fly ash.

Table 3. Geopolymer concrete mixing ratio.

Material	Gravel	Yellow sand	Fly ash	Blast furnace slag
Ratio (kg/m^3)	1040	740	310	50

Table 4. Ratio of activated alkaline solution in the studied samples and experimental conditions.

(calculated for 1 m^3 of concrete products)

Samples	Activated alkaline solution				Experimental Conditions
	NaOH (kg)	H_2O (liter)	Liquid glass (kg)	Cement (kg)	
M 1	21.2	29	125	0	Autoclave curing
M 2	21.2	29	150	0	Autoclave curing
M 3	21.2	29	175	0	Autoclave curing
M 4	21.2	29	200	0	Autoclave curing
M 5	25.0	34	110	0	Autoclave curing
M 6	30.0	41	110	0	Autoclave curing
M 7	30.0	41	90 + 5 kg of silica fume	0	Autoclave curing
M 8	30.0	41	110	0	without Autoclave curing
M 10	30	41	110	0	Autoclave curing
M 11	30	41	110	0	Autoclave curing

Geopolymer concrete mixtures with an alkaline solution were fabricated in cylindrical shapes according to ASTM C39 and ASTM C78. After casting, samples were left in the open air for 2 h, then they were cured in an autoclave at a steam temperature of 80 ºC for 8 h.

Compressive strength, flexural strength, tensile strength, and waterproofing ability of the activated alkaline geopolymer concrete were tested in accordance with the standards: TCVN-3118:1993, DIN 1015-11:2007-05, TCVN-3116:1993, TCVN-3119:1993, and TCVN-3105:1993. These tests were conducted by the Laboratory for Testing and Auditing of building materials LAS-XD1234 (University of Civil Engineering). In addition, samples were also tested for waterproofing and durability in sulphate environments. TCVN 9901:2014 standard was used as a reference for the design and fabrication of interlock geopolymer concrete blocks.

3. RESULTS AND DISCUSSION

3.1. Results in compressive strength

3.1.1. Effect of liquid glass/NaOH ratio on strength of the geopolymer structure

According to previous studies [16, 17], the strength of Si-O-Si bond depends mainly on SiO_2 and Al_2O_3 content in fly ash, the ratio of liquid glass/fly ash, the ratio of activated solution/fly ash, and the ratio of liquid glass/NaOH. Because of different types of fly ash in chemical composition, it is necessary to determine the above ratios when changing the type of fly ash for geopolymer concrete making. The ratio of liquid glass/NaOH is one of the most decisive factors affecting the mechanical strengths of the geopolymer concrete. For optimal ratio determination when using fly ash and blast furnace slag for geopolymer concrete making, ratios of liquid glass/NaOH were changed for concrete samples from M1 to M6. These samples were treated under the same autoclave curing conditions and mix ratio, only changes in the ratios of liquid glass/NaOH were made as presented in Table 4. Experimental results to determine the compressive strength are shown in Figure 3.

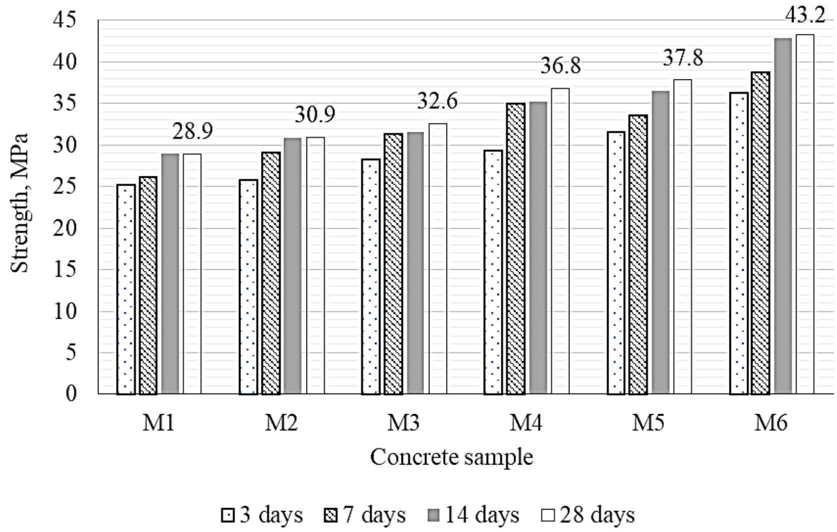

Figure 3. Compressive strength of the concrete samples with different ratios of liquid glass/NaOH.

From the experimental results, it could be found that the M6 sample provided the highest compressive strength of 43.2 MPa at the age of 28 days, corresponding to the liquid glass/NaOH ratio of 3.7 (110/30). The compressive strength of other concrete samples decreased gradually from M6 to M1. This could be explained by the effect of the liquid glass/NaOH ratio. With ratios greater than 3.7 (110/30), the excessive content of the liquid glass retarded the geopolymerization process. So, the efficiency of the geopolymer concrete reaction decreased with increasing the liquid glass/NaOH ratio. The M5 samples had the same amount of liquid glass as the M6, however, they had less than 5 kg of NaOH and presented a smaller compressive strength of about 5 MPa at the age of 28 days. Samples M1 to M4 had a higher amount of liquid glass and a lower amount of NaOH than both above samples. Consequently, earlier samples (M5 and M6) provided a higher compressive strength. It means that the ability to enhance bonding in the geopolymer chain depends not only on the presence of liquid glass and NaOH addition but also on their ratio and dosage. In other words, the strength of geopolymer structure depends mainly on the ratio of liquid glass/NaOH and the dosage of NaOH.

3.1.2. Effects of other factors on compressive strength

The strength of geopolymer structure depends on many factors such as blast furnace slag and silica fume, LOI content in fly ass, and geopolymer concrete fabrication process. For experimental proves, geopolymer concrete samples from M7 to M11 were manufactured in different compositions to find out the effect of these factors. The composition of these samples was, of course, based on that of the control sample M6 (see Table 4). The experimental results of their compressive strength are shown in Figure 4.

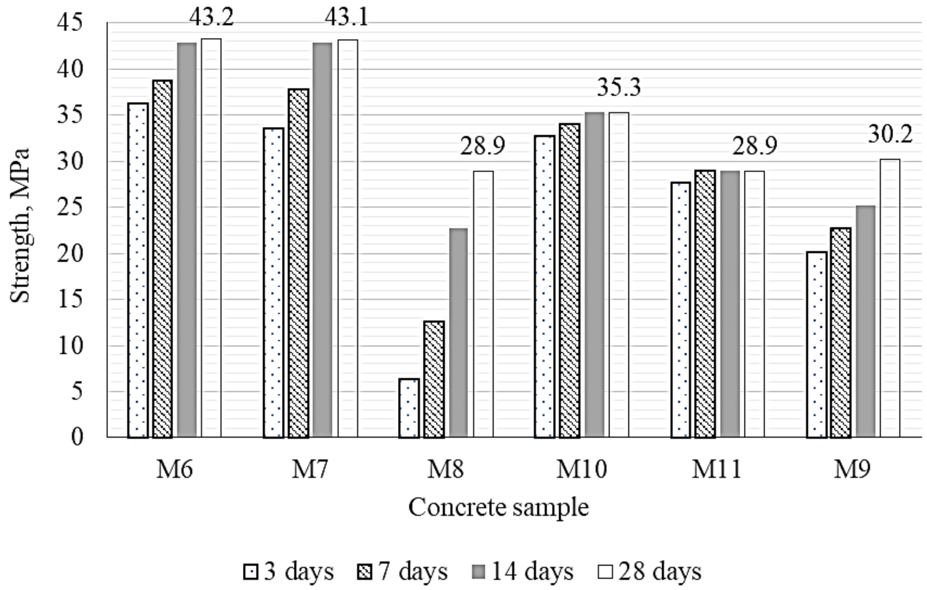

Figure 4. Compressive strength development of concrete samples with different binders.

From the experimental results, it could be found that samples M6 and M7 after 14 days of age reached a similar compressive strength of 42.8 MPa. At the age of 28 days, M6 and M7 had a little difference in compressive strength, 43.2 MPa for M6 and 43.1 MPa for M7, respectively. Thus, when using 5 kg of silica fume mixed with liquid glass, the strength of concrete was not significantly reduced, but the dosage of liquid glass was reduced to 90 kg compared to 110 kg. This requires further research to determine the reasonable ratio between liquid glass and silica fume to reduce the production cost of fly ash-based geopolymer concrete. Sample M8 was produced under non-autoclaved conditions, after 28 days, its strength was only 28.9 MPa, equal to about 70 % of the M6 sample's strength and lower than that of normal concretes (sample M9 reached 30.2 MPa after 28 days).

According to the experimental results of sample M10, without the blast furnace slag, this sample provided a lower compressive strength than sample M6 (35.3 MPa vs. 42.3 MPa). Because of the chemical composition of blast furnace slag with high alkaline activity and CaO content ranging from 40 to 48 %, therefore it has a self-curing ability like Portland cement. This ability is higher when activated by alkali. That is the main cause of the decrease in compressive strength of sample M10.

Regarding the results for the non-treated fly ash-based M11 sample (with LOI content of 18.7 %), its compressive strength was lower than that of treated fly ash-based M6 (LOI content of 3.89 %). The explanation of this result is the non-hydration of LOI during geopolymerization, producing an amount of pores in M11 and thus, reducing the compressive strength of this sample. According to the test results, the M6 sample presented better mechanical performance in compression. So, the composition of M6 was selected for producing geopolymer concrete with fly ash from Duyen Hai - 1 thermal power plant in the next experiments.

3.2. Flexural and indirect tensile strength determination

Geopolymer concrete samples with composition corresponding to that of sample M6, after 28 days, were tested under flexural force at three points according to the standard DIN 1015-11:2007-05. The average flexural strength at three points for a group of 30 samples was 6.62 MPa. The standard deviation for this tensile strength was 0.625 MPa, corresponding to a percentage coefficient of 9.44 %. Destruction force and breaking pull force of a ϕ14 steel bar had average values of 37,000 N and 87,780 N, respectively.

3.3. Waterproofness and durability in sulphate environment test

M6 was tested for waterproofness according to the TCVN-3116:1993 standard. The water was pressurized incrementally, each level 2 daN/cm^2, the time period between two pressure levels was 16 h. At the maximum pressure of level 23 of the testing device, the test samples were still not seeped.

Samples with dimensions of $\Phi150 \times 300$ mm was submerged into solutions of 2 % NaCl; 2 % NaOH; 2 % Na_2SO_4; 2 % H_2SO_4; and 2 % $MgSO_4$. Sulphate resistance was assessed by observing external destructions and changes in length and weight as well as changes in compressive strength after soaking in sulphate solution for a period of 4 months. After a 4-month cycle, it was found that:

- Samples soaked in solutions of 2 % NaCl; 2 % NaOH; 2 % Na_2SO_4; and 2 % $MgSO_4$, were unchanged, showing no signs of corrosion or cracking. But the sample immersed in 2 % H_2SO_4 solution was corroded on the outside surface of the sample because it was not covered by geopolymer layer;
- The difference in length of samples before and after soaking was only less than 0.016 %;
- The mass of concrete did not change after soaking;

- Samples soaked in 2 % NaCl, 2 % NaOH, 2 % Na_2SO_4, and 2 % $MgSO_4$ were unchanged in compressive strength. But the sample soaked in 2 % H_2SO_4 had a lower compressive strength, only 80% of that before soaking.

3.4. Fabrication of interlock geopolymer concrete blocks

Based on the TCVN 9901:2014 standard on Hydraulic structures and Requirements for sea dike design, interlock geopolymer concrete blocks were designed and fabricated with the same compositions and experimental conditions as for the M6 sample. The interlocking block had the shape of the number eight with dimensions of 1000 mm × 1000 mm × 150 mm (length × width × thickness). However, depending on the type of application (loading level), the thickness of these blocks can be increased or decreased according to the calculation. Figure 5 presents the mold design for these interlock blocks (Fig. 5a) and as-cast products (Fig. 5b).

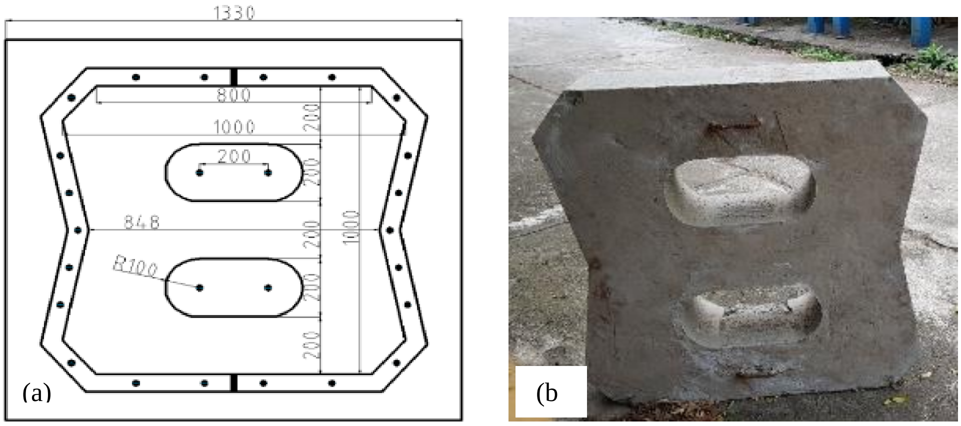

Figure 5. Mold design for interlocking geopolymer concrete blocks (a) and as-cast products (b).

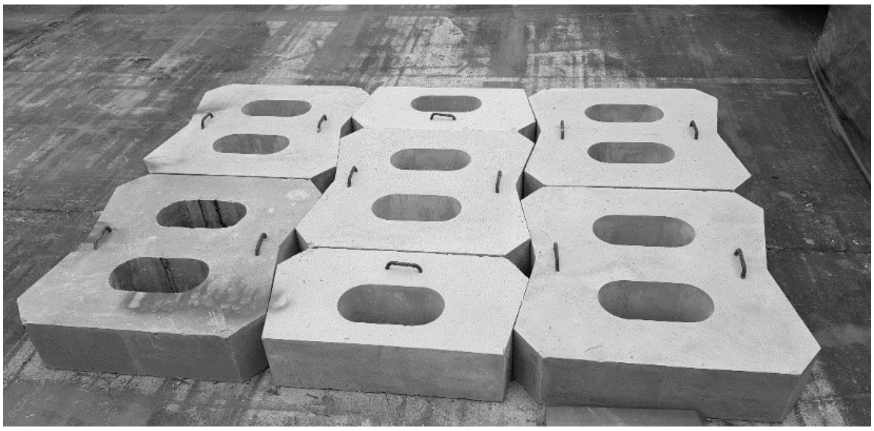

Figure 6. The arrangement of interlocking geopolymer concrete blocks in field.

These interlock geopolymer concrete blocks were tested to identify several properties as permeability and water tightness, durability and weathering, drying shrinkage and potential for cracking in some cases of transportation and construction. The results showed that these blocks ensured all critical values according to TCVN 9901:2014 standard. Furthermore, blocks and semi-blocks can pave a surface (assembled side by side as a system) as presented in Figure 6. So, these blocks could be used as a wave damping layer on the surface to protect the sea dike. The interlocking block has two holes to ensure evapotranspiration of the underlying material (soil, sand, etc.). The advantages of these blocks are their durability and good weather resistance because of their high mass and dimension. However, their use encounters some difficulties in construction.

Currently, these interlock geopolymer concrete blocks are used to reinforce sea dike against this year's typhoon season in central Viet Nam. This project was implemented in cooperation with the Irrigation University to test these products. Therefore, practical effectiveness of these products will be assessed after this year's typhoon season. The succeed of this plan could become the basis for commercializing our products. This also contributes to the efficient application of fly ash and the reduction of environmental pollution.

4. CONCLUSIONS

This paper presents experimental results on the fly ash of Duyen Hai - 1 thermal power plant with a capacity of 1,245 MW and blast furnace slag of Hoa Phat steelmaking plant, as well as corresponding geopolymer concrete. The application of this geopolymer concrete to fabricate interlocking blocks for sea dike reinforcement is also presented. As a result, the following conclusions can be drawn for this paper:

- Chemical composition of fly ash of Duyen Hai - 1 thermal power plant and blast furnace slag of Hoa Phat steelmaking plant has been identified and analyzed. It is necessary to reduce the LOI content to less than 4 % for use in geopolymer concrete.
- The parametric study on the ratio of fly ash/blast furnace slag/NaOH/liquid glass showed that this ratio strongly affected the mechanical properties of geopolymer concrete. As a result, with the ratio of fly ash/blast furnace slag/NaOH/liquid glass of 310/50/30/110, the geopolymer concrete sample (M6) reached the highest compressive strength.
- M6 geopolymer concrete samples were tested according to the TCVN standards, achieving compressive strength of 43.2 MPa, flexural strength of 6.62 MPa, and tensile strength of 87,780 N.
- The compressive, tensile and flexural strengths, waterproofness and durability in sulphate environment of geopolymer concrete are all higher than the standard 14 TCVN 63:2002 for concrete in breakwaters blocks. Thus, it is completely possible to use this type of concrete in construction works, especially those in seawater construction.
- Interlocking geopolymer concrete blocks were designed and fabricated according to the TCVN 9901:2014 standard. These products were used to reinforce the sea dike in central Viet Nam against this year's typhoon season.

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CRediT authorship contribution statement. The article was written through contributions of all authors. Le Tuan Minh: Conceptualization, methodology, writing-original draft preparation. Nguyen Anh Minh: Investigation, Formal analysis, writing-review and editing, supervision. Nguyen Xuan Truong: Lab testing. Nguyen Thanh Ha: Funding acquisition. All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest. The authors declare no conflicts of interest.

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