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Improving the durability of pozzolan concrete using alkaline solution and geopolymer coating

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Abstract

Durability is a major concern for concrete, therefore initiatives are needed to improve the durability of concrete. One way to improve concrete durability is improving its surface quality. This study focuses on the improvement of the surface durability of pozzolan concrete by applying coating of alkali solution or geopolymer paste. There were two different pozzolanic materials used to manufacture the pozzolan concrete, i.e. class-F fly ash and calcined volcanic mud with two different particle sizes. The alkaline solution was a combination of NaOH and sodium silicate solution. Fly ash-based geopolymer paste was prepared for the geopolymer coating. Concrete specimens were exposed to 10% sulphuric acid solution by applying the wet-dry cycles to accelerate the damage process, and to chloride solution to evaluate its penetration depth. The results show that applying the alkaline solution and geopolymer coating improves the durability of pozzolan concrete.

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1. Introduction

Concrete is one of the main materials for building construction. The consistent increasing demand for concrete, increases the demand for cement. Cement production is a major contributor on the release of carbon dioxide emissions of CO₂ gas to the atmosphere that causing the global warming [1]. One alternative measure to overcome the problem is the use of waste materials, such as fly ash and calcined Sidoarjo volcanic mud, as cement replacement

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material. Fly ash and calcined Sidoarjo volcanic mud can be used because of its high content of SiO_2 and Al_2O_3 and its pozzolanic properties [2].

Geopolymer is a polymeric material with polymer frame and AlO_4SiO_4 tetrahedral bonding [3]. The source material for geopolymer is the one with high SiO_2 and Al_2O_3 content and amorphous [4]. Geopolymer material possesses excellent durability properties in aggressive environment, including in acid environment [5]. Geopolymer has also been developed as a coating material to resist high heat environment to above 1000°C [6].

Previous study showed that the application of alkaline solution on the surface of concrete with fly ash content of up to 80% of the total cementitious material, by mass, significantly increases the concrete durability [7]. However, in that study, the compressive strength of concrete samples are low, less than 30 MPa, causing difficulty in analysing the decline of the compressive strength of concrete.

In this study, concrete with higher compressive strength is used to better analyze the impact of applying coating, i.e. alkaline coating or geopolymer paste coating, on the durability properties of concrete containing pozzolanic materials. Two types of pozzolanic materials are utilized, i.e. type-F fly ash or low calcium fly ash and calcined Sidoarjo volcanic mud.

2. Materials

Sidoarjo volcanic mud used in this study was collected directly from the mud pond in Sidoarjo, East Java, Indonesia. The fresh volcanic mud was then treated to improve its reactivity, by applying drying, calcination and milling process. The details of the treatment have been explained elsewhere [8,9,10]. Fly ash type F was obtained from Paiton Power Station, Probolinggo, Indonesia.

The oxides compositions of Sidoarjo volcanic mud and fly ash as measured by X-ray Fluorescence (XRF) are shown in Table 1. Particle size of Sidoarjo mud was taken as one of the variables. Different particle sizes were obtained by varying the milling time from 8 to 12 hours. The details on the particle sizes can be seen from Table 2.

Table 1. The composition of Sidoarjo volcanic mud and fly ash as measured by XRF (% by mass)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	K ₂ O	MgO	SO_3	TiO_2	Mn_3O_4	Cr_2O_3	Na_2O
Sidoarjo Mud	56.70	23.30	7.37	2.13	1.04	2.95	0.96	0.38	0.14	0.01	2.7
Fly Ash	51.12	18.90	17.7	5.54	0.82	3.17	0.63	0.98	0.14	0.01	0.47

Table 2. Details of particle sizes of Sidoarjo volcanic mud

Duration of Milling (hours)	d(10) (μm)	d(50) (μm)	d(90) (μm)	SSA (m^2/g)
8 hours	1.069	5.611	36.687	2.018
12 hours	0.982	4.484	27.865	2.308

The total content of SiO_2 , Fe_2O_3 , and Al_2O_3 within the mud is bigger 70%, and thus it can be classified as pozzolanic material according to ASTM C 618-05 [11]. From Table 2, it can be seen that prolonged the milling time reduces the particle size of the calcined mud, and increases its specific surface area (SSA) significantly from 2.018 m^2/g to 2.308 m^2/g . Reducing the particle size of calcined Sidoarjo volcanic mud and other pozzolanic material improves its reactivity [8,12].

To control the workability of the fresh mortar, a superplasticiser (SP) from polycarboxylate type, Glenium ACE 8590 produced by BASF, was employed. The amount of superplasticiser used was determined by a target flow diameter of the fresh mortar of 17 ± 2 cm.

Sand was obtained from Lumajang, East Java, Indonesia. The characteristics of the sand are as follows; specific gravity (G_s) = 2.79, water content (W_c) = 1.582%, and the fineness modulus (FM) = 2.41. Crushed granite stone was used as the coarse aggregate. The maximum particle size was 20mm, specific gravity (G_s) = 2.62, and water

content (W_c) = 2.95. Cement of Pozzolan Portland Cement (PPC) type, produced by Semen Gresik, was used. Alkaline solution was a mix of sodium hydroxide (NaOH) and sodium silicate solution. The sodium silicate solution was characterized by Na_2O content of 17.14% and SiO_2 content of 36.71% .

3. Experimental Details

The mixture composition of concrete specimens were determined to follow the previous study [2]. Pozzolanic material, either Sidoarjo volcanic mud or fly ash, was taken as 50% of the total cementitious materials. HVSM stands for high volume Sidoarjo mud concrete, while HVFA stand for high volume fly ash concrete. The details of the mixture compositions can be seen in Table 3.

Table 3. Concrete mixture compositions

Type	Cement (kg/m ³)	Sidoarjo Mud (kg/m ³)	Fly Ash (kg/m ³)	Sand (kg/m ³)	Coarse Aggregate (kg/m ³)	Water (kg/m ³)	Super Plasticizer (% by mass)
Conventional concrete	423	-	-	910	986	169.2	0.1% of cement
HVSM	211.5	211.5	-	910	986	169.2	1.5 – 2% of cementitious materials
HVFA	211.5	-	211.5	910	986	169.2	-

Two forms of concrete specimens were manufactured. The first one was concrete cubes of 10x10x10 cm³ for evaluating its durability in the sulfuric acid environment. The second one was in the form of concrete cylinders, with the diameter of 10 cm and the height of 20 cm. The composition of the alkaline solution and the geopolymer paste for coating are shown in Tables 4 and 5, respectively. Geopolymer paste was prepared by using fly ash as the source material.

Table 4. Composition of the alkaline solution

NaOH (solid) (kg/m ³)	Na ₂ SiO ₃ (liquid) (kg/m ³)	Water (kg/m ³)
57.1	114.21	178.125

Table 5. Composition of geopolymer paste for coating

Molarity of NaOH solution	Fly Ash (kg/m ³)	NaOH (kg/m ³)	Na ₂ SiO ₃ (kg/m ³)	Water (kg/m ³)
10M	1920	61.12	428	152.88

Concrete specimens were left to harden in room temperature. After 24 hours, they were removed from the moulds. Alkaline coating was then applied by using brush in two layers, horizontally and vertically. After being coated, concrete specimens were left for aging at room temperature.

The application of geopolymer paste coating was performed at the same day as for the alkaline coating. Right after coating application, concrete specimens were cured in an oven, with a temperature of 60°C for 24 hours. Curing in the oven was carried out to ensure the polymerization reaction to take place. Concrete specimens were then left in room temperature until the day of soaking in 10% sulfuric acid solution at the seventh day.

To accelerate the damaging process, a wet-dry cycle process was employed in accordance to Darwin's Theory, as explained by Browning, Gong, and Hughes [8,9,10]. The illustration of the wet-dry cycle process can be seen in Figure 1.a. During soaking in 10% sulfuric acid solution, concrete specimens were positioned as shown in Figure 1.b.

Sulfuric acid solution was replaced periodically in every 4 weeks to ensure the desired acid concentration was maintained. Mass losses of concrete specimens were measured periodically on weekly basis. Weighing was carried out after cleaning the specimens surface and left it for surface dry. Compressive strength tests were done at the ages

of 28 days, 56 days and 90 days. Visual inspections was also performed in every stage of experiment, especially prior to compressive strength test.

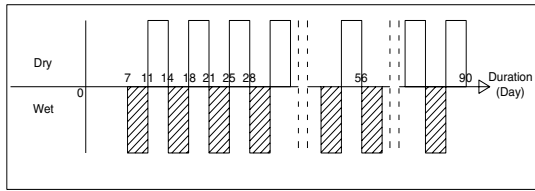
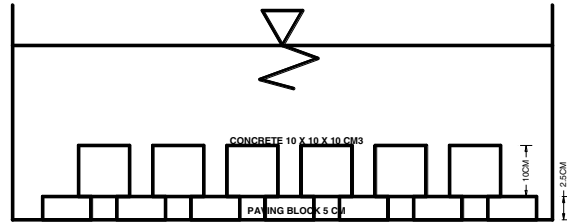


Fig.1. (a) Wet-and-dry cycles of sulfuric acid exposure



(b) Immersion of concrete specimens in sulfuric acid solution

Chloride ion penetration test was performed following the NordTest NT Build 492. This test aims to measure the permeability of concrete soaked in 10% sodium chloride solution, charged with electric current of 30V. The sample used in this experiment was in the form of concrete cylinder with a diameter of 10 cm and 20 cm high. Concrete cylinder was cut into three parts with the same thickness of 5 cm. Concrete samples were coated on its upper or lower surfaces, i.e. the ones exposed to the solution directly, either by alkaline solution or geopolymer paste.

Chloride ion penetration test was started at the age 28. The schematic diagram of the test is shown in Figure 2. The duration of the test was 24 hours. Temperature of the chloride solution was monitored throughout the test. Once the test completed, the specimen was cut into two equal halves, cleaned, and sprayed with 0.3M silver nitrate (AgNO₃) solution. After approximately 15 minutes, due to precipitation of silver chloride, the depth of chloride ion penetration can be measured easily using calipers. Then, the coefficient of chloride ion penetration can be calculated.

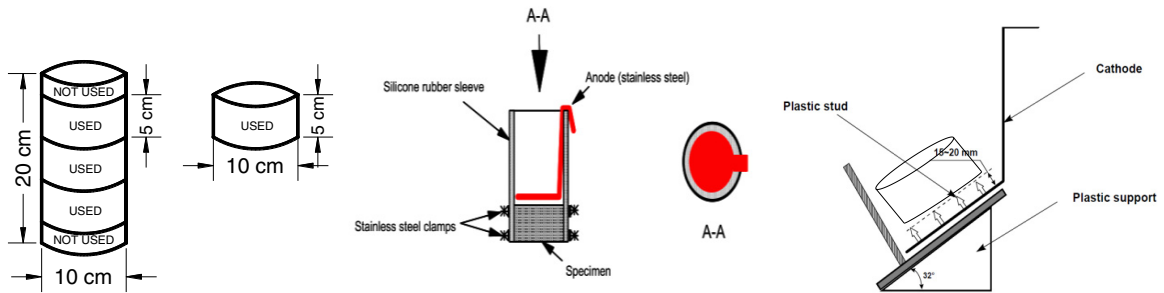


Fig.2. Illustration of Chloride Penetration Test Using NT BUILD 492 Standard

4. Result and Discussion

The term HVFA denotes high volume fly ash concrete containing 50% fly ash; HVSM indicates high volume Sidoarjo mud concrete utilizing 50% calcined mud, while ‘conventional’ designates concrete with no pozzolan content. Number 8 or 12 after HVSM states the milling duration of the calcined mud. The word ‘control’ is applied to the coated concrete specimens immersed in tap water, while the word ‘soaked’ represents concrete specimens without any coating, soaked in sulfuric acid solution.

After immersion in 10% sulfuric acid (H₂SO₄) solution for 90 days, concrete specimens experienced mass loss. However, all HVFA concrete specimens showed excellent performance, compared to conventional concrete with no pozzolan content (see Figure 3). Application of coating does not really affect the performance.

Figures 4(a) and (b) show the performance of HVSM after being soaked in 10% sulfuric acid solution up to 90 days. In general, HVSM performs significantly better than conventional concrete in terms of its mass loss. Application of geopolymer coating significantly improves the durability of HVSM concrete, comparable to HVFA concrete. Prolong the milling duration of calcined Sidoarjo mud from 8 to 12 hours slightly improves the durability performance.

On the other hand, applying alkali solution for coating does not really affect the durability performance of HVSM in an sulfuric acid environment. Without curing in elevated temperature, it seems that geopolymerisation does not take place between the alkali solution and the calcined Sidoarjo mud.

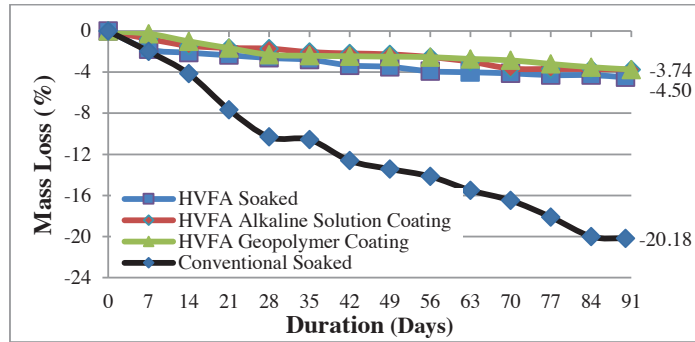


Fig.3. Mass Loss of HVFA Concrete after Immersion in 10% Sulphuric Acid Solution

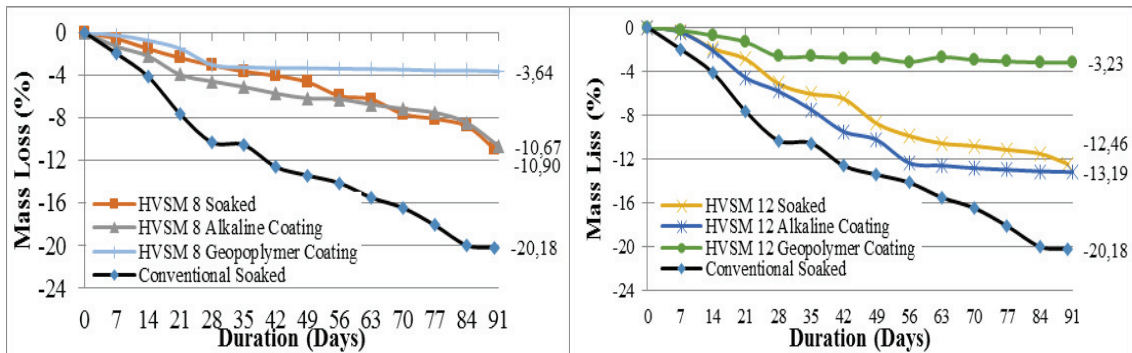


Fig.4. (a) Mass Loss of HVSM 8 Concrete after Immersion in 10% Sulphuric Acid Solution; (b) Mass Loss of HVSM 12 Concrete after Immersion in 10% Sulphuric Acid Solution

Compressive strength tests were conducted at the age of 28-days, 56-days and 90-days. Each data represents the average compressive strength from three concrete specimens. Figure 5 shows that the compressive strength of HVFA concrete soaked in tap water increases with the age. Soaking in an acid solution decreases the compressive strength due to decomposition, as it was confirmed by the loss of mass. Applying alkaline coating on HVFA concrete soaked in an acid solution improves its compressive strength, especially on later age. Applying geopolymer coating improves the compressive strength of HVFA concrete exposed to acid environment. On 56-day of age, the compressive strength increased 20%, while on later age at 90 days, the strength almost double compared to the ones without coating and soaked in the same environment. This increase is attributed to the better durability performance of HVFA concrete with geopolymer coating due to reduced decomposition rate.

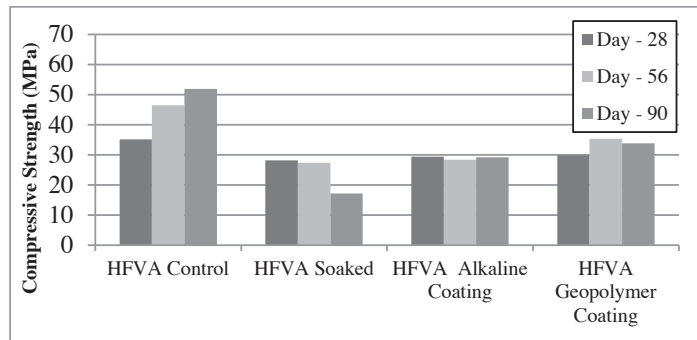


Fig. 5. Concrete Compressive Strength of HVFA Concrete after Immersion in Acid Solution for 90 Days

Finer particle size of calcined Sidoarjo mud produced higher compressive strength of HVSM concrete, as can be seen in Figure 6 for HVSM control. HVSM 12 control, utilizing calcined Sidoarjo mud milled for 12 hours, shows approximately similar compressive strength with the one of HVFA. This confirms that calcined Sidoarjo mud possesses pozzolanic properties, and thus also its potential as construction material.

The compressive strength of HVSM concrete reduced significantly after being immersed in an acid solution for up to 90 days. Applying alkali coating or geopolymer coating increases the compressive strength of HVSM concrete. There is not much different on the compressive strength of concrete coated with two different coating materials (see Figures 6(a) and (b))

Chloride ion penetration test results showed that with the application of alkaline coating or geopolymer coating on the surface of concrete lowers the penetration coefficient of chloride ion in concrete, as shown in Figure 7. This shows the improvement of the durability properties of concrete.

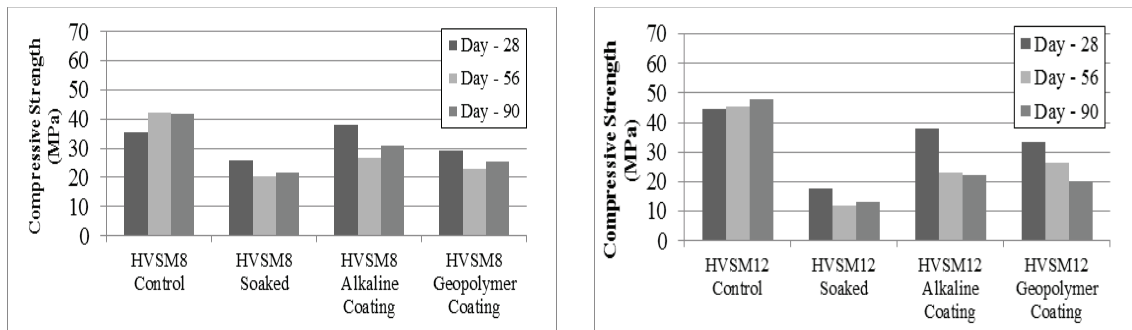


Fig.6. (a) Compressive Strength of HVSM 8 Concrete after Immersion in Acid Solution for 90 Days; (b) Compressive Strength of HVSM 12 Concrete after Immersion in Acid Solution for 90 Days

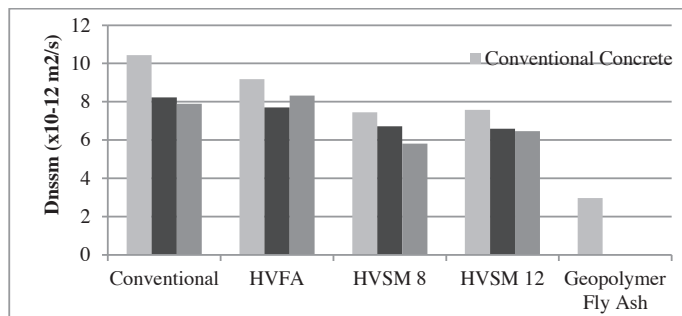


Fig.7. Chloride Ion Penetration Coefficient of HVFA and HVSM Concrete

5. Conclusion

Based on the data presented and analysed, several conclusions have been drawn, i.e.:

- HVFA concrete and HVSM concrete with 50% pozzolanic material content show significantly better durability in acid environment when compared to conventional concrete with no pozzolanic material content
- Applying coating, either alkaline solution or geopolymer, improves the durability of concrete, especially HVSM concrete with geopolymer coating.
- There is a decrease in chloride ion penetration coefficient of HVFA and HVSM concrete, compared to conventional concrete. Applying coating, especially geopolymer paste, further reduced the coefficient. Lowering the chloride ion penetration improves the durability properties of concrete.

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