Effect of Fly Ash as Partial Replacement of Cement in Aggressive Environment

I. R. Rahim¹, M. A. Caronge², and M.M. Amqhaar³

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ABSTRACT

Based on the Appendix I of Peraturan Pemerintah Republik Indonesia No. 101 year of 2014 on the management of Hazardous and Toxic waste, fly ash is categorized as Hazardous and Toxic waste with a waste code B409. Fly ash can be used as a cement replacement material in the manufacture of concrete because it contains alumina and silica which can be used as construction raw material. The cost of making fly ash mortar is slightly more expensive than conventional mortar. It is because of mortar fly ash uses chemical activators. Several literature reviews show that fly ashbased mortar having good mechanical character, power and good performance in acidic and sulfate environments. In this research, fly ash mortar was made using curing (treatment) that is 24 hour and 48 hours of curing oven. In this research simulated on aggressive environment that is 5% of H2SO4 and 10% of HCl for 0, 7, 14, and 28 days. Due to functioning as a building construction material, it is necessary to test the loss of compressive strength and weight loss. The test was performed for 0, 7, 14 and 28 days with the result: 1) fly ash mortar had loss of compressive strength and optimum weight loss at the age of 7 days each on the 24-hour of curing oven and 48-hour of curing oven.2) although the cost the production of fly ash mortar in general is slightly more expensive than cement mortar, but in terms of environmental aspects it has a significant effect on CO₂ reduction than the cement production using coal combustion.

1. Introduction

The world is currently exposed to the issue of global warming caused by carbon dioxide emissions. The construction industry is the second largest contributor of carbon dioxide emissions after electricity. In addressing this issue, research on green construction and green material has begun to be promoted as an effort to reduce carbon dioxide emissions.

The use of cement is part of the construction world which contributes the most emissions. Therefore, reducing the use of its development considers two important things both economically and environmentally. In economic terms, green material must consider the savings in construction costs that can be achieved. While environmental considerations in green material tend to focus on efforts to utilize waste that not only has economic value but also has environmental conservation efforts. One alternative material that can be used as a substitute for cement is

¹ Visiting Associate Professor & IALT member, Institute of Lowland Technology, Saga University, Saga 840-8502, JAPAN, geosuman@gmail.com

² Professor & IALT member, Institute of Lowland Technology, Saga University, Saga 840-8502, JAPAN, hino@ilt.saga-u.ac.jp

³ IALT member (if you are an IALT member, delete otherwise), organization, mailing address, COUNTRY, email address

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waste from coal combustion, namely fly ash. The use of fly ash waste into cement replacement material in the manufacture of concrete is expected to reduce waste that pollutes the environment, provide added value and reduce the use of cement. Substituting the use of cement with fly ash can reduce global warming arising from cement production because portland cement production has been releasing CO2 gas into the earth's atmosphere, where CO2 gas contributes the most to global warming.

In terms of economics, the cost of making fly ash mortar is slightly more expensive compared to conventional mortar. This is because chemical activators are expensive. The effect of the use of chemical activators on fly ash mortars is that they affect the resistance or strength of fly ash based mortars. Factors affecting the strength of fly ash mortars are the binder for the aggregate ratio, the sodium molarity molarity, sodium silicate, the sodium hydroxide ratio.

Mortar fly ash has several advantages, namely resistant to sulfuric acid attack, resistant to alkali-silica reaction, resistant to fire, reducing air pollution. Besides the advantages of fly ash mortar also has a disadvantage including making it a little more complicated than conventional mortar because the amount of material used is more than conventional and there is no exact mix design calculation. The objectives of this study are analyze the effect of using fly ash waste as a substitute for cement in an aggressive environment and analyzing the effect of the cost of utilizing fly ash instead of cement..

2. Literatur Review

Fly ash which is the remnants of coal combustion, which is flowed from the combustion chamber through a kettle in the form of smoke bursts, in the form of fine particles and is an inorganic material formed from changes in mineral materials due to the combustion process from the combustion process of coal in the generating unit Steam (boiler) will form a type of ash namely fly ash.

This solid waste is found in large enough quantities. The amount of fly ash produced is around 15% -17% of each tonne of coal combustion (Safitri et al. 2009).

Fly ash is generally disposed of in industrial landfills which will cause problems for the community and the environment such as the metal in fly ash is extracted and carried by water, the fly ash is blown by the wind so that it interferes with breathing such as the release of toxic elements into ground water, decreased microbial activity, and increased acidity of soil.

The main components of coal fly ash from power plants are silica (SiO2), alumina, (Al2O3), iron oxide (Fe2O3), the rest are carbon, calcium, magnesium and sulfur (Nurhayati et al, 2012).

According to ASTM C 168-87 / AASHTO M 295-90 standards, fly ash from coal combustion is classified according to the type of coal used for combustion. There are two types of fly ash, namely: 1. Class F

Fly ash is produced from burning anthrasite or bituminous coal.

2. Class C

Fly ash is produced from the burning of lignite or sub-bituminous coal.

Mortar geopolymers are an alternative environmentally friendly building material products. The raw material used in the manufacture of geopolymer mortars is waste ash from coal combustion which is a substitute for cement.

The term geopolymer was first used by Professor Davidovits in 1978 (Davidovits, 1988) to describe polymers produced through geochemistry. Geopolymers are organic forms of alumina-silica synthesized through many materials containing silica (Si) and Alumina (Al) originating from nature or from industrial byproducts. The chemical composition of geopolymer material is similar to Zeolite, but it has an amorphous microstructure (Davidovits, 1999). During the synthesis process, silica and alumina atoms fuse and form blocks that chemically have structures similar to natural rocks.

Geopolymers are ceramic-like materials produced through the reaction of alumina-silica as a raw material in the environment. Geopolymers are categorized as environmentally friendly materials because the manufacture of geopolymer base materials requires a low amount of energy when compared to the production of portland cement which produces large amounts of CO2 (Pan et al, 2009).

Generally fly ash has the main chemical composition in the form of silica (SiO2), alumina (Al2O3) and ferric oxide (Fe2O3). Other chemical ingredients such as calcium oxides (CaO), magnesium (MgO), sulfur (SO3), alkaline (Na2O, K2O), phosphorus (P2O5), manganese (Mn2O3) and titanium (TiO2). Fly ash is divided into three categories based on ASTM C618-03 namely class N, class F and class C as in Table 1 and Table 2.

Table 1. Physical Necessity of Fly Ash (ASTM C618-
03,2003)

Kebutuhan	Kelas			
Residunan	N	F	С	
Jumlah lolos saringan 4 mm (No.325) kondisi	34	34	34	
Basah				
Dengan semen Portland pada umur 7 hari	75°	75°	75°	
Dengan semen Portland pada umur 28 hari	75°	75°	75°	
Kebutuhan air maksimum	115	105	105	
Ekspansi atau perubahan bentuk, max%	8.0	0.8	0.8	
Berat jenis maksimum variasi dari rata-rata, %	5	5	5	
Persentasi lolos saringan 45 mm (No.325),maks	5	5	5	
variasi dari rata-rata	5	5	5	

Table 2. Chemical content needs Fly Ash (ASTM C618-03, 2003)

Kabudukan	Kelas		
Kebutunan	N	F	С
Silicon dioxide (SiO_2) plus aluminium oxide (Al_2O_3) plus iron oxide (F_2O_3), min, $\%$	70	70	50
Sulfur trioxide (SO ₃), maks, %	4,0	5,0	5,0
Moisuture, maks, %	3,0	3,0	3,0
Loss on ignition (LOI), maks, %	10,0	6,0	6,0

Compressive strength is the ability of a mortar to accept the compressive force of a broad unity which causes it to break if it is burdened with a certain compressive force by a press machine. Based on SNI 03-6825-2002, to determine the compressive strength used the formula:

To determine the compressive strength of a mortar the formula is used:

$$\sigma m = \frac{Pmaks}{A}$$

Description:

σm = Force Press Mortar (MPa)

Pmaks = Max Press Force (N)

A = area of cross section of test items (mm2)

In general, cement is widely used as a material in making concrete. but today the impact of environmental sustainability considerations has influenced the use of cement in the construction industry. According to experts involved in observations on global warming, 7% of the production of CO2 emissions in natural gas is derived from cement production and each reduction of 1 ton of cement production results in a reduction of 1 ton of CO2 gas emissions (Malhotra, 1999) so this has encouraged experts in the field of building construction engineering to find alternative materials to replace cement.

(Sujivorakul, et al. 2011) stated that substitution of cement by 10-20% by artificial pozolan namely fly ash resulted in an increase in bending strength, bending toughness, and water absorption from a concrete mixture with glass fiber (glass fiber-reinforced concrete). Thus this material is recommended to be used as a commercial product in concrete construction, namely as a cement substitution material up to 20% of the weight of the mixture. Some of the advantages of using this material are saving construction costs, improving the mechanical properties of the mixture and reducing the production of CO2 emissions from cement production. If all the use of cement in construction projects in the world replaces the use of cement by 25-30% with fly ash or other pozolan material, then there will be a 2% reduction in CO2 emissions in cement production. This is a major contribution to achieving the Kyoto protocol agreement as stipulated by

the United Nations, where each member country must reduce CO2 emissions of at least 5% below 1990 levels in the 2008-2012 period (Kyoto Protocol, 2012). In this study cement was replaced by fly ash by 100%.

3. Research Methodology



Fig 1. Research Methodology

This study was designed to determine the effect of aggressive environments on resistance to mortar geopolymers with $5 \times 5 \times 5$ cm cube molds. The number of test specimens in this study can be seen in Table 3 and

Table 4. The mixing methods used in this study are as follows:

- 1. Sand + fly ash, dimix in dry conditions for 1 minute (slow speed)
- Add the Na2SiO3 solution and water, mix for 2 minutes (slow speed)
- Add the NaOH solution, Mix for 5 minutes (slow speed)
- 4. Stir manually for 1 minute and after that sand, fly ash, activator solution and water mix for 5 minutes (high speed). So that the total mixing time is 14 minutes.

 Table 3. Number of research test objects for strong press

 loss testing

Jenis. Larutan.	Variasi Curing	Jumlah benda uji untuk umur. rendaman lacutan asam		Bentuk Benda Uji	Jenis. Pengujian	
		7 Hari	14 Hari	28 Hari		
H ₂ SO ₄ 5%	24 Jam	3	3	3	Kubus 5 x 5 x 5cm	Kehilangan
	48 Jam	3	3	3	1	Kuat Jekan
HCL 10%	24 Jam	3	3	3		
	48 Jam	3	3	3		
Total		36				
Subu		55±3°C				

 Table 4. Number of research test items for weight loss testing

Jenis Larutan	Variasi Curing	Jumlah benda uji untuk rendaman larutan asam	Bentuk Benda Uji	Jenis Pengujian
H ₂ SO ₄ 5%	24 Jam	3	Kubus 5 x 5 x 5cm	Kehilangan
	48 Jam	3		Berat
HCL 10%	24 Jam	3		
	48 Jam	3		
Total		12		
Suhu		55±3°C		

4. Results and Discussion

4.1 Measurement of pH Solution

4.1.1 The pH value of sulphuric acid (H2SO4) 5%

Based on Figure 14 the pH value of sulphate acid solution 5% before soaking the mortar fly ash on the curing oven 24 hours by 1.7 and 1.4 for oven curing 48 hours of 1.4. After 28 days the pH was increased for a 24-hour curing oven of 2.6 and 2.7 for an oven curing 48 hours.



Fig 2. The pH value of sulphuric acid (H2SO4) 5%

It can be seen in Figure 14 that immersion by using sulphuric acid (H2SO4) solution of 5% against mortar fly ash gives pH change in sulfuric acid solution. Acid content that is owned by very high sulphuric acid solution is concentrated to mortar fly ash. Changes in the pH of sulphuric acid solution occur as a result of sulfuric acid with a mortar.

4.1.2 pH value of hydrochloric acid (HCI) 10%

Based on Figure 15 the pH value of a 10% hydrochloric acid solution before soaking the mortar fly ash at a 24-hour curing oven of 2.0 and 1.6 for oven curing 48 hours. After 28 days the pH was increased for a 24-hour curing oven of 3.3 and 3.1 for an oven curing 48 hours.



It can be seen in Figure 15 that immersion by using hydrochloric acid (HCI) solution of 10% against mortar fly ash gives pH change in hydrochloric acid solution. Acid content that is owned by a very high solution of hydrochloric acid is concentrated to the mortar. The pH of hydrochloric acid solution occurs due to the reaction between hydrochloric acid and the content of CaO.

4.2 Loss of Strong press

In testing against strong loss of mortar press due to the acid sulphate attack obtained results as seen in the following graph:



Fig 4. Comparison chart between strong loss press Mortar Fly Ash with cement Mortar at sulfuric acid Attack (H2SO4) 5%

Based on Figure 16 we can see that mortar fly ash loses strong press curing oven 24 hours at the age of 7 days by 2%, at the age of 14 days by 27% and at the age of 28 days by 16%. For mortar fly ash loses strong press curing oven 48 hours at the age of 7 days by 14%, at the age of 14 days of 46% and at the age of 28 days of 48%. For mortar cement lost strong press at the age of 7 days by 27%, at the age of 14 days of 45% and at the age of 28 days amounted to 73%.

For curing the oven 24 hours and 48 hours experienced strong press optimum at the age of 7 days but for an oven curing 24 hours There is a strong decline of press at the age of 7 days and 14 days, then increased at the age of 28 days. The decline at the age of 7 days occurs due to acid sulphate reaction with mortar. Sulfuric acid attacks the bonding of mortar structures from the edges of the surface until it breaks into damage and weakens the bonding of particles in the mortar. However, an increase of the age of 28 days. These results are different data from previous research because it should be strong press to decrease according to age increase. This increase may be due to the reduction of acid attack strength of mortar.

Comparison of strong resistance to the attack on sulphuric acid between mortar fly ash with cement mortar is very much different, based on Figure 16 cement mortar is very weak against sulfuric acid attack where the percentage of the decline is very large at the age of 7, 14 and 28 days, different from the mortar fly ash which has decreased slightly.

From the test results to strong press mortar due to hydrochloric acid attacks obtained results as seen in Figure 5 follows:



Fig 5. Comparison chart between strong loss press Mortar Fly Ash with cement Mortar in hydrochloric acid (HCl) attack 10%.

Based on Figure 17 we can see that mortar fly ash loses strong press curing oven 24 hours at the age of 7 days by 16%, at the age of 14 days is 47% and at 28 day of age is 48%. For mortar fly ash loses strong press curing

oven 48 hours at the age of 7 days by 10%, at the age of 14 days of 45% and at the age of 28 days of 35%. For mortar cement lost strong press at the age of 7 days by 27%, at the age of 14 days of 45% and at the age of 28 days amounted to 73%.

For curing oven 24 hours and 48 hours experienced strong press optimum at the age of 7 days but for an oven curing 48 hours There is a strong decline in press at the age of 7 days and 14 days, then increased at the age of 28 days. The decline at age 7 days occurred due to the reaction of hydrochloric acid with mortar. Hydrochloric acid invades the mortar structure from the edges of the surface until it breaks into damage and weakens the binding of particles in the mortar. However, an increase of the age of 28 days. This increase may be due to the reduction of acid attack strength of mortar.

Comparison of strong durability of the press against hydrochloric acid attacks between mortar fly ash and cement mortar is very much different, based on Figure 17 cement mortar is very weak against hydrochloric acid attack where the percentage of the decline is very large at the age of 7, 14 and 28 days, different from the mortar fly ash which has decreased slightly. Table 10 shows the results of a strong press test data.

Table 5. Strong press Test Data results

Umur	H_2SO_4		HCI	
(Hari)	Curing Oven 24 Jam	Curing Oven 48 Jam	Curing Oven 24 Jam	Curing Oven 48 Jam
0	23.466	22.986	23.466	22.986
7	22.885	19.676	19.624	20.673
14	17.162	12.324	12.458	12.752
28	19.660	11.901	12.244	14.846

A mortar fly ash caused by the lack of CaO content in the mortar fly ash caused by acid attack, because fly ash has a CaO content that is the catalytic. CaO's fly ash has resistance to acid attacks that make the pHnya increase, for the pH measurement results can be seen in the pictures 14 and 15. Keroposnya particles on the mortar fly ash resulting in decreased strong press that has a mortar to the age.

4.3 Acid Attack damage

Based on immersion result of the 24-hour oven-curing test object and 48 hours on acid sulphate aqueous solution (H2SO4 5%) and hydrochloric acid (HCI 10%) With time 0, 7, 14 and 28 days, here is a photo of the test piece damage:

• Marinated acid Sulphate (H2SO4 5%)

Curing Oven 24 Jam		
0 Hari	7 Hari	14 Hari
	28 Hari	

Marinate hydrochloric acid (HCl 10%)



Fig 6. Visual Curing Oven 24 Hour Acid Sulphate attack (H2SO4 5%)



Fig 8. Visual Curing Oven 24 hour Hydrochloric acid attack (HCI 10%)



Fig 7. Visual Curing Oven 48 hours of acid sulphate attack (H2SO4 5%)

Mortar fly ash resistance at sulfuric acid attacks, at a 24 hour curing oven is lower than the 48-jam oven curing. This is due to the reaction between sulfuric acid solution and mortar which causes the inner mortar or outer surface. The reaction occurs resulting in the particles damaged and irrespective of the bonding between the particles in the mortar

Fig 9. Visual Curing Oven 48 hours of hydrochloric acid attack (HCl 10%)

Mortar fly ash resistance on hydrochloric acid attacks, at a 24 hour curing oven is lower than the 48-hour curing oven. This is due to the reaction of a solution of hydrochloric acid with a mortar that causes mortar for both the inside and outer surface. The reaction occurred resulting in the particles damaged and detached from the bonding between the particles in the mortar.

4.4 Environmental cost Analysis

In general, the cement industry in Indonesia has a GHG emission capacity of 0.833 tons of CO2/ton of cement (IGD Atmaja, 2015). By looking at the data above that the CO2 produced in cement production is large enough that it needs efforts to overcome the magnitude of CO2 in cement production. The use of fly ash of 100% in lieu of cement has affected CO2 gas emission reduction by 100% or 1 ton of CO2 in the production of 1 ton of cement.

The use of fly ash can reduce the emissions of CO2 exhaust gas in the cement industry because of its production using coal. If fly ash can replace cement as construction material then cement production factories can be reduced for CO2 emissions can be reduced.

 Table 6. Cost between conventional Mortar use and

 Mortar Fly Ash

				Biaya		
Material	Mortar Konvensional	Mortar Fly Ash	Volume	-		
				Mortar Konvensional	Mortar Fly ash	
Pasir	V	V	1 m ³	Rp. 200,000.00	Rp. 200,000.00	
Semen	V	-	40 kg	Rp. 44,000.00	-	
Fly Ash	-	\checkmark	1 ton	-		
Air	V	\checkmark	1 liter	-	-	
Alkali Aktivator						
· Sodium Silikat	-	1	1 kg	-	Rp. 25,000.00	
· Sodium Hidroksida	-	\checkmark	1 kg	-	Rp 25,000.00	
Total Biaya				Rp. 244,000.00	Rp. 250,000.00	

The use of fly ash in this research uses waste from PT. Semen Tonasa. Turbine Boiler Generator Power plant PT. Semen Tonasa is a steam power plant by using coal as the main fuel. The combustion of coal in boilers besides producing steam, also produces ash. The function of BTG at PT. Semen Tonasa as the driver of its supporters and is one of the supporting units of cement production which is owned by PT. Semen Tonasa. From the burning resulted in solid waste in the form of fly ash (Eka, 2017).

The use of coal and the amount of ash produced in BTG Power plant PT. Semen Tonasa, which is the number of coal consumed for 1 month by BTG I amounting to 23,840.11 tons and produce a solid waste of fly ash as much as 1,471.79 tons. At BTG I in a day coal consumed by BTG 1 as much as 794.67 tonnes and the effluent of fly ash produced about 58.87 tonnes (Eka, 2017).

At BTG II consume coal as much as 29,406.00 tonnes in 1 month with average consumption daily around 980.20 tonnes and produce waste fly ash about 818.30 ton with average daily about 48.14 tons (Eka, 2017). In the day total fly ash on BTG I and BTG II is 107.01 tons, then if in 1 Zak of 40 kg then it can produce 97,077,839 kg/day Flya Ash or 2426 zak.

The manufacture of mortar fly ash in terms of economy is slightly more expensive than conventional mortar, the high cost is basically because of mortar fly ash using chemical activator. The use of alkaline activator can affect resistance or strength from fly ash based mortar. In terms of environmental aspects, if all the use of cement on the construction project in the world replaced the use of cement as a construction material with the use of fly ash, there will be a reduction of CO2 emissions resulting from one industry that uses coal burning process for example in cement industry.

5. Conclusion

- 1. Fly ash mortar on sulfuric acid for 24 hours and 48 hours curing oven experienced optimum compressive strength loss at the age of 7 days by 2% and 14% while cement mortar at 7 days was 27% and the optimum weight loss that occurred in curing oven 24 hours and 48 hours occurred at the age of 7 days by 1.75% and 1.42% while the mortar of cement at the age of 7 days was 17%.
- 2. Fly ash mortar on hydrochloric acid for 24 hour and 48 hour curing oven experienced optimum compressive strength loss at the age of 7 days by 16% and 10% while cement mortar at 7 day age was 27% and the optimum weight loss that occurred in 24 hour curing oven and 48 hours occurred at the age of 7 days by 1.63% and 1.38% while cement mortar at the age of 7 days amounted to 16%.
- 3. Manufacture of fly ash mortars in economic terms is somewhat more expensive than conventional mortars, the costs are high basically because fly ash mortars use chemical activators. The use of alkaline activators can affect the durability or strength of fly ash based mortars. In terms of environmental aspects, if all the use of cement in the construction project in the world replaces the use of cement as construction material with the use of fly ash, there will be a reduction in CO2 emissions resulting from one industry that uses the coal combustion process, for example in the cement industry.

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