Effect of Fly Ash as a Partial Replacement for Sand on Sulfate Resistance of Mortar

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Abstract. This study investigates the influence of fly ash as a partial replacing sand material on the sulfate resistance of mortar. Fly ash replacement are 0%, 10%, and 20% by volume of sand. Compressive strength and expansion of mortar due to sulfate attack were examined. In order to clarify the effect of fly ash as a fine aggregate on the sulfate resistance of mortar, the secondary electron images of cracked surface of mortar were analysed by SEM. Based on the test results, the compressive strength of mortar is enhanced by using fly ash when submerged in both water and sodium sulfate solution. The expansion due to sulfate attack of mortar is reduced when the amount of fly ash as a fine aggregate increased. Massive ettringite particles form and fill up the pore in the mortar matrix without fly ash, as seen in SEM images. Ettringite formation in small pores of mortar without fly ash leads to a higher expansion due to sulfate attack when compared to mortars with fly ash.

Keywords: Mortar · Fly Ash · Sulfate Resistance · Compressive Strength · SEM

1 Introduction

Sulfate attack is not a new issue but this is a factor to damage the durability of concrete structure and a significant concern for cement concrete. External sulfate attack occurs in both soil and ground water. However, sulfate ions in water easily enter into the porous concrete structure and react with products of cement hydration. External sulfate attack in hardened concrete, includes the formation of calcium sulfoaluminate (ettrngite) and gypsum. In external sulfate attack, the expansion reaction most important is the ettringite formation from monosulfate according to the following reaction [1]:

$$\begin{aligned} &C_4ASH_{12}(\text{Monosulfate}) + 2\,CSH_2(\text{Gypsum}) \\ &+ 16H\ (\text{Water}) \rightarrow C_6AS_3H_{32}(\text{Ettringite}) \end{aligned} \quad (1)$$

Gypsum formation is a reaction between sulfate and $Ca(OH)_2$. The reaction is described as follow [2]:

$$Na_2SO_4 + CH + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O\ (\text{Gypsum}) + 2NaOH \quad (2)$$

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However, the expansion due to ettringite or gypsum caused by many mechanisms such as the increase of the solid volume, topochemical reaction, oriented crystal growth, crystallization pressure, swelling phenomena [1]. There are three of the most effective strategies for combating sulfate attack. The first is limiting the C_3A content in cement material. The second is reducing the calcium hydroxide (CH) content. And the third is denser concrete structure. By lowering the water to binder ratio, the permeability of concrete is reduced, which makes it more resistant to sulfate attack [3]. Supplementary Cementitious Materials (SCMs) can improve sulfate resistance in concrete such as low CaO fly ash, slag, silica fume, metakaoline, etc.

Fly ash is a by-product of the thermal power plants. Fly ash is typically used in concrete as cement replacing material due to the pozzolanic reaction. The pozzolanic reaction of the fly ash is known as the chemical reaction between reactive silica or alumina in the fly ash and $Ca(OH)_2$ from cement hydration [4]. Therefore, the calcium hydroxide content is reduced in concrete containing fly ash due to the pozzolanic reaction.

In Vietnam, the quality of fly ash is not high. This is because fly ash has very high loss on ignition (LOI) content when compared to other countries. According to TCVN 10302:2014 [5], the maximum loss on ignition (LOI) of class F fly ash for heavy concrete with and without reinforcement is 12% and 15%, respectively. The LOI limit for normal concrete at 6% is specified in ASTM standard [6]. Japan Industrial Standard JIS A 6201 classified fly ash to 4 types based on their LOI content and fineness [7]. The LOI limits of the 4 types are from 3% to 8%. So, the amount of Vietnamese fly ash used in concrete is limited. Moreover, the demand of using natural sand in concrete continually increases. However, the supply of the natural sand is not adequate. Many researches used other materials to replace sand in concrete such as crushed stone and demolition waste, bottom ash, copper slag, steel slag, etc., as fine aggregates in concrete [8–10]. However, the use of these materials as replacing sand still has existed several limitations:

- Difficult to control the input of material properties.
- Sea sand has just studied in some studies. The results obtained are still unclear.
- The use of crushed sand is quite popular today. However, this crushed sand is also from natural stone materials. Finally, the rock source will also be exhausted.

One of methods to solve the pollution due to fly ash and lack of amount of natural sand is the use of fly ash as a partial sand replacing material. Siddique [11] studied fly ash as a partial replacement for fine aggregate to enhance the compressive strength of concrete. The results showed that the highest compressive strength of concrete mixture containing 20% fly ash to replace sand. Moreover, concrete using fly ash has outstanding environmental performance. Ravina [12] also studied the replacement of fine sand by fly ash in concrete. The results showed that the compressive strength at later ages and elastic modulus of concrete containing fly ash are higher than the control concrete.

Surangi et al. [13] investigated the effect of fly ash (class F) as natural sand on the properties and durability of concrete at different curing temperatures. The test results found that the compressive strength of concrete at both early and late ages were increased by the use of fly ash. The durability including the carbonation resistance, chloride penetration resistance, and sulfate resistance of concrete using fly ash are all improved when compared to the controlled concrete without using fly ash. Hossack and Thomas [14] studied the effect of temperature on the sulfate reaction rate of mixed cement. At a high temperature, the mixed cement containing fly ash clearly improves the resistance to sulfate. However, at low temperatures, the sulfate resistance does not change much.

To solve the problem of lacking of natural sand and the environmental pollution caused by fly ash, the purpose of this study is to investigate the effects of fly ash with high LOI content as a partial sand replacing material on the sulfate resistance of mortar.

2 Experiment Program

2.1 Materials and Mix Proportions

In this study, the ingredients include Ordinary Portland cement (PC40), fly ash, and sand. Fly ash was used as partial sand replacement material. Specific gravity values of cement, fly ash, and sand are 3.10 g/cm^3, 2.22 g/cm^3, and 2.62 g/cm^3, respectively. The chemical compositions of cement and fly ash are presented in Table 1. Fly ash is classified into Class F with low CaO content. However, the loss on ignition of fly ash is quite high when compared to the its limitation mentioned in some standards for fly ash [6, 7].

The mix proportions of mortar are shown in Table 2. Water to cement ratio was controlled at 0.5 and fine aggregate to cement ratio of controlled mixture (F00) was and 3.0. Fly ash was used as partial sand replacement material. The replacing sand ratios are 0%, 10%, and 20% by volume to keep the same volume of F00 mixture.

Table 1. Chemical compositions of cement and fly ash

No	Chemical compositions	Content (% by weight)	
		Cement	Fly ash
1	SiO_2	15.18	50.26
2	Al_2O_3	3.25	22.51
3	Fe_2O_3	3.83	6.96
4	CaO	71.52	2.58
5	MgO	1.36	1.17
6	Na_2O	0.07	0.31
7	K_2O	0.72	3.98
8	SO_3	3.18	0.55
9	LOI	–	9.70

Table 2. Mix proportions

Mixtures	Cement (g)	W/C	Sand/Cement by weight	Fly ash/ Fine aggregate by volume
F00	500	0.5	3:1	0
F10			–	10%
F20			–	20%

2.2 Test Methods

This study investigated the effect of fly ash as partial sand replacement material in mortar when mortar samples were immerged in the sodium sulfate solution. The sodium sulfate solution contained 50 g of Na_2SO_4 dissolved in one liter of the solution. The compressive strength, expansion in sodium solution, and SEM analysis of mortar were examined.

The compressive strength of mortar was tested when mortar samples were immerged in the water and in the sodium sulfate solution. The cubes with size 5 × 5 cm were used in this study. The casting and prepared samples was followed ASTM C109 [15]. The compressive strength of mortar was measured by the compression testing machine at 28 days, 91 days, and 180 days of age.

The expansion of mortar due to sulfate attack was measured by the length comparator. Mortar bars with a dimension of 285 × 285 mm were used. Mortar samples were cured in water until the compressive strength of mortars reached 20MPa. The development of compressive strength of mortar with fly ash have is faster than that of mortar without fly ash due to their lower w/b ratio (3 mixtures in the mix proportions controlled w/c ratio at 0.5, when fly ash is used as a sand replacing material, the w/b ratios of 3 mixtures are different). Therefore, the curing age to reach 20MPa of compressive strength of mortar with fly ash is 3 days while that of mortar without fly ash is 7 days, as seen in Table 3. And then, mortar bars were immersed in the sodium sulfate solution. The initial length of mortar specimens was measured by the length comparator at the last day in water curing. The expansion of the mortar bars was measured according to ASTM C1012 [16].

To clarify the effect of fly ash as a partial sand replacing material in mortar, the secondary electron images of cracked surface of mortar were analysed by SEM. Samples submerged in the sulfate solution at 24 weeks were selected for this test.

Table 3. Curing age of mortar samples to reach 20MPa of compressive strength

Mixtures	Curing ages (days)	Compressive strength (MPa)
F00	7	20.52
F10	3	20.57
F20	3	20.45

3 Results and Discussion

3.1 Compressive Strength

Figures 1 and 2 show the compressive strength of mortar immerged in the normal water and the sodium sulfate solution, respectively. It can be seen that the compressive strength of mortar cured in normal water is enhanced when fly ash is used as a partial sand replacement material. At later ages, when the fly ash to fine aggregate ratio increases, the improved compressive strength of mortar is obvious. In the case of mortar immerged in the sodium sulfate solution, at 28 days of age, the compressive strength of mortar with fly ash slightly decreases. However, at later ages, the compressive strength of mortar also is improved by using fly ash to replace a part of sand. There are two hypotheses to explain the compressive strength. The first, fly ash has the pozzolanic reaction in mortar fly ash. This pozzolanic reaction can increase the calcium silicate hydrate product to enhance the strength and also consume Portlandite in mortar to inhibit the sulfate attack. And the second, fly ash shows the filling effect as a fine aggregate. It makes the mortar matrix denser and leads to a higher compressive strength.

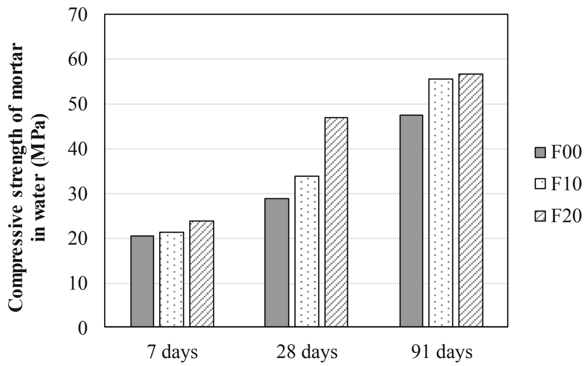


Fig. 1. Compressive strength of mortar in water

3.2 Sulfate Resistance

The influence of fly ash on the sulfate resistance of mortar is shown Fig. 3. It is seen obviously that the expansion of fly ash mortar is lower when compared to that of mortar without fly ash. When the replacing sand ratio increases, the expansion of mortar decreases. Moreover, the speed of expansion is slow when mortar uses fly ash to partially replace sand.

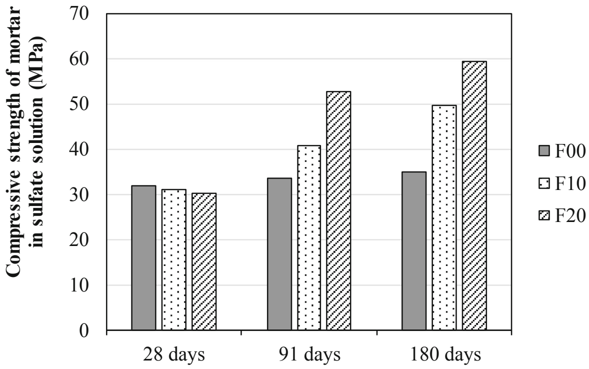


Fig. 2. Compressive strength of mortar in sulfate solution

The expansion of mortar containing fly ash as a fine aggregate is decreased due to a denser matrix mortar. This explanation is described by four reasons. The first reason is an effect of w/b ratio. Three mixtures in this study were controlled w/c ratio at 0.5. However, the mixtures use fly ash such as F10 and F20, the water to binder (cement and fly ash) w/b ratio are changed to 0.45 and 0.38, respectively. Figure 4 shows the relationship between w/b ratio and the expansion of mortar. The mortar matrix is denser when the w/b ratio is reduced. It leads to the lower expansion of mortar due to sulfate attack. The second reason is a filling effect of fly ash as a fine aggregate. Fly ash with very fine particles easily fills in the pore to make mortar matrix denser, as seen in SEM images (Fig. 5b and 5c). It delays the sulfate attack from sodium sulfate solution into mortar. The third reason is an effect of pozzolanic reaction of fly ash. Fly ash consumes a part of $Ca(OH)_2$ to form calcium silicate hydrate during the pozzolanic reaction. So, the sodium sulfate attacking $Ca(OH)_2$ process shown in Eq. 2 is decreased. And the fourth reason is a crystallization pressure due to the formation of ettringite and gypsum within small pores. The expansion of mortar due to sulfate attack occurs when the crystallization pressure is too much, especially ettringite or gypsum particles in small pores. The SEM images of cracked surface mortar samples are presented in Fig. 5. Massive ettringite particles are formed and they fill up the pore in the mortar matrix without fly ash (F00), as seen in Fig. 5a. It leads to a higher expansion of mortar. In the case of mortar containing fly ash (F10 and F20), ettringite particles formed less in the pores than F00 mortar. On the other hand, large amount of gypsum particles is formed in F10 and F20 mortars. However, gypsum particles with small size are scattered in the mortar matrix, as seen in Fig. 5b and 5c. Ettringite-triggered expansion is more prevalent than gypsum-generated expansion due to its low solubility [1]. Therefore, the crystallization pressure from gypsum is not enough to make high expansion of mortar.

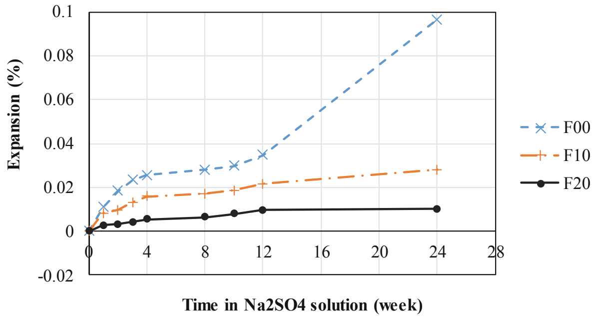


Fig. 3. Expansion of mortar

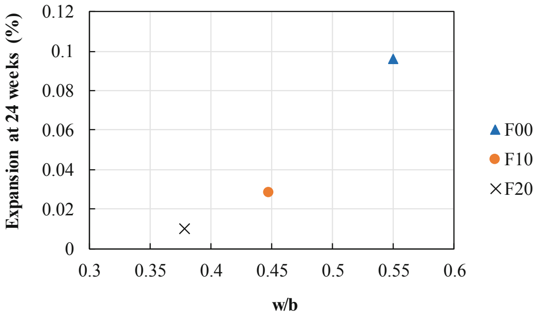
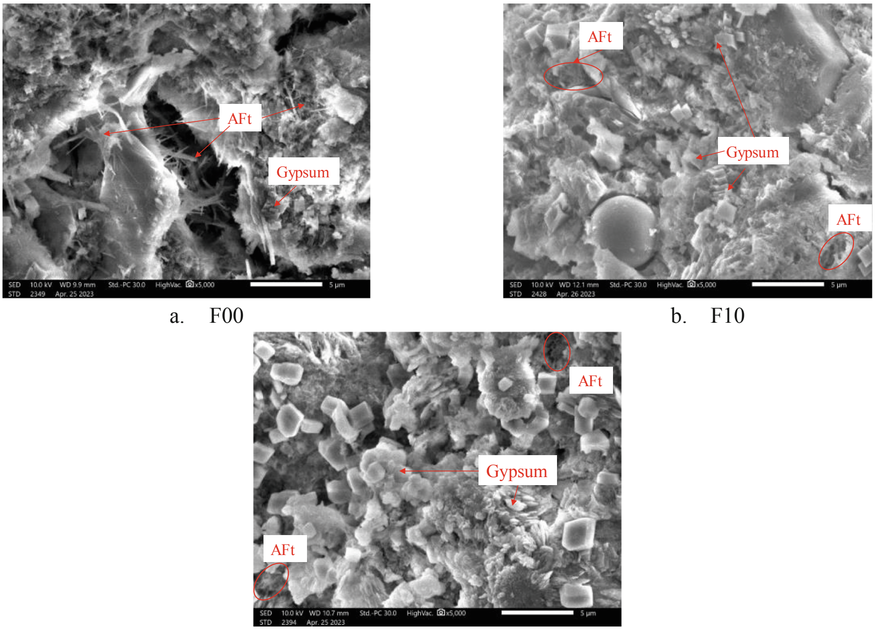


Fig. 4. Relationship between w/b ratio and expansion at 24 weeks of mortar

4 Conclusions

This study focused on the effect of fly ash as fine aggregate on the compressive strength and the sulfate resistance of mortar immerged in sodium sulfate solution. The following conclusions can be drawn:

1. The compressive strength of mortar is enhanced by using fly ash as a fine aggregate when mortar samples are immerged in normal water for all of the curing period, but at later ages in sodium sulfate solution.
2. The expansion of mortar due to sulfate attack is decreased rapidly when mortar uses fly ash as a fine aggregate.



a. F00

b. F10

c. F20

Fig. 5. SEM images of mortar samples

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