PROPERTIES OF PASTES AND MORTARS CONTAINING AMMONIA CONTAMINATED FLY ASH

BY

SYAHRIL RAHMAT

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ABSTRACT

Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR) are widely used for NO_x emission control in coal-fired power plants. In the SCR and SNCR processes, liquid ammonia (NH_3(aq)) or urea is injected into the system or flue gas stream and reacts with NO_x in the flue gas to yield diatomic nitrogen (N_2) and water (H_2O). Unreacted ammonia in the flue gas after the NO_x reduction process is defined as slip and it contaminated the fly ash, yielding ammonia-contaminated fly ash. Ammonium sulfate $(NH_4)_2SO_4$ and ammonium carbonate $(NH_4)_2CO_3$ are the forms mostly found in ammonia-contaminated fly ash. This study is aimed to investigate the effects of ammonia that contaminate high CaO and low CaO fly ash on the properties of pastes and mortars. $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ solutions are set in a concentration range of 0 to 1000 ppm (mg of NH_3 per kg of fly ash). The results confirmed that both $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ reduced the normal consistency and led to less water requirement of fresh pastes. $(NH_4)_2SO_4$ decreased the compressive strength of the mortars. Oppositely, $(NH_4)_2CO_3$ increased the compressive strength of the mortars. The addition of $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ increased the autoclave expansion of pastes. Sulfate expansion test results showed that both of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ increased the sulfate expansion of the mortars, but the expansion was still lower than the OPC-only mortar. The formation of gypsum and ettringite was considered to cause the expansion of the paste and mortar specimens. The results of autogenous shrinkage indicated that $(NH_4)_2SO_4$ and $(NH_4)CO_3$ decreased autogenous shrinkage of the mortars.

Keywords: Ammonia-contaminated fly ash, Ammonium sulfate, Ammonium carbonate, Concrete, expansion

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Symbols/Abbreviations	Terms
ACFA	Ammonia contaminated Fly Ash
ASTM	American Society for Testing and Materials
CaO	Calcium oxide
EGAT	Electricity Generating Authority of Thailand
NC	Normal consistency
NCO	Ammonium carbonate
NO_x	Nitrogen oxide
NSO	Ammonium sulfate
s/b	Sand to binder ratio
SCR	Selective Catalytic Reduction
SNCR	Selective Non Catalytic Reduction
TIS	Thai Industrial Standard
w/b	Water to binder ratio

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CHAPTER 1

INTRODUCTION

1.1 Background

Coal is the most popular and largest source of fuel for producing electricity for the global energy system (about 40% of the total global electricity generation). The coal utilization is expected to remain for the next two to three decades. In coal-fired power plants, fly ash is a residue of the coal combustion process. Fly ash has been utilized as a material for partial Portland cement replacement in concrete production due to its pozzolanic properties. Thailand uses coal to generate electricity, especially lignite and bituminous coal, which come from Thailand itself and also from abroad, to generate electricity. However, fly ash is categorized as a waste material and a combustion byproduct (Tangtermsirikul, 2005). In addition, the coal combustion process causes several byproducts, such as coal ash boiler slag, bottom ash, etc.

In Thailand, 95% of the total fly ash production comes from the Mae Moh coal-fired power plant (Tangtermsirikul, 2005). The utilization of fly ash as a cement substitute has many advantages. It is known that partial replacement of ordinary Portland cement with fly ash improves many properties of the cementitious system. The process of combustion not only produces fly ash and bottom ash but also releases NO_x, which is a toxic gas. According to the regulation of environmental impact, coal-fired power plants desire to install the NO_x reduction technologies that are commonly used such as SNCR (Selective Non-Catalytic Reduction) and SCR (Selective Catalytic Reduction). Injection of ammonia or urea into the system and mixing it with flue gas to convert NO_x to nitrogen and water is the basic concept of SCR and SNCR. Reactions between NO_x and NH_3 are shown in Equations (1.1) and (1.2).

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{1.1}$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \tag{1.2}$$

Injection of liquid urea or ammonia results in unreacted liquid ammonia, known as ammonia slip. It occurs with an amount typically less than 1% of the total ammonia injection. Around 70% of the total ammonia slip is usually attached or adsorbed onto the fly ash in several forms, the common forms are ammonium salt or ammonia in gas form (Lindon & Jodie, 2011). There are several forms of ammonium salt that can be produced after the reaction between ammonia gas (NH_3) and sulfate trioxide (SO_3) in the exhaust gas, such as ammonium sulfate $(NH_4)_2SO_4$ and ammonium bisulfate (NH_4HSO_4). Also, by the reaction between ammonia gas (NH_3) and carbon dioxide (CO_2) that exists in the exhaust gas, ammonium carbonate, $(NH_4)_2CO_3$, can be produced. Reactions between ammonia and flue gas are shown in Equations (1.3)-(1.5).

$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4 \quad (1.3)$$

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \quad (1.4)$$

$$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3 \quad (1.5)$$

The limit of ammonia contamination in fly ash is 200 ppm for use in concrete (Larrimore, 2002). A high concentration of ammonia in fly ash may cause some odors that disturb and threaten workers' health and affect concrete properties. In a previous study, the researcher conducted an experiment on the effects of ammonia contaminated fly ash by partially substituting cement material with ammonia contaminated fly ash having ammonia contents from 0 to 620 ppm (Kim et al., 2011). The result of the test and experiment shows the compressive strength of the concrete decreased due to $(NH_4)_2SO_4$ ions. Increasing ammonia content in concrete mixture caused the delay of setting times of concrete (Kim et al., 2011).

In a previous study, ammonia contaminated fly ash was not used directly, but by adding ammonium salt solution to the fly ash (Kim et al., 2011). The experiment showed the same result that 28 days aged of compressive strength decreased when ammonium concentration was increased. Recently, researchers have paid attention on the effects of ammonia-contaminated fly ash on concrete properties. Recently, it is focused on ammonium salts, especially ammonium sulfate $(NH_4)_2SO_4$, ammonium bisulfate $(NH_4)HSO_4$, and ammonium carbonate $(NH_4)_2CO_3$.

A few studies about the effects of ammonia contaminated fly ash, containing ammonium sulfate and ammonium carbonate on mortars and concrete expansion properties have been conducted. Therefore, the aim of this study is to investigate the effects of ammonia-contaminated fly ash (ACFA) on the autoclave expansion of pastes and sodium sulfate expansion of mortars containing ammonia-contaminated fly ash. High CaO fly ash from the Mae Moh power plant and low CaO fly ash from the BLCP were utilized in this investigation. Instead of utilizing real ammonia contaminated fly ash from the power plant, ammonium sulfate and ammonium carbonate were added to the fly ash mixture in this study.

1.2 Statement of problem

SCR technology is already used by the Mae Moh power plant in Thailand and the power plant produces ammonia-contaminated fly ash (ACFA). Recently ammonia concentration is not high (Mae Moh), but it is possibly high in the future. The latest research that studied ACFA in Thailand was performed on flowability, setting times, compressive strength, and total shrinkage properties. Expansion properties of the pastes and mortars from the effects of ammonia-contaminated fly ash are still not provided yet. The research that studied properties of real (without addition in the laboratory) ACFA in Thailand is still not conducted yet. Real ACFA has still not been provided yet, and it needs more investigation on the effects of real ACFA on the properties of concrete.

There is another problem resulting from the changes in coal properties that use in power plants. The coal property changes affect the properties of the fly ash. For the Mae Moh power plant, high free lime and high SO_3 contents fly ash will be produced. A previous study shows that high CaO and high SO_3 contents of fly ash affect the expansion properties of mortars. There is no investigation about the combination of ammonia contaminated fly ash (ACFA) with high CaO, high free lime, and high SO_3 contents on properties of pastes and mortars. The investigation of the effects of ammonia contaminated fly ash with different concentrations of ammonium salts, using two types of fly ash, and the effects of ammonia contaminated fly ash with high free lime and SO_3 contents on properties of paste and mortars are necessary.

1.3 Objectives

The purpose of this research is to understand how ammonia-contaminated fly ash affects the properties of paste and mortars. To investigate the effects of ammonia-contaminated fly ash on properties of pastes and mortars, ammonia contamination was done by mixing ammonium sulfate and ammonium carbonate into the fly ash rather than using real ammonia-contaminated fly ash (ACFA) from the power plant.

The main objectives of this study are as follows:

1. To study the effects of different types and concentrations of ammonium salts on properties of pastes and mortars
2. To study the effects of blended ammonium salts on properties of pastes and mortars
3. To study the effects of ammonium salts with different fly ash types on properties of pastes and mortars
4. To study the effects of ammonium salts in fly ash with different free lime and SO_3 contents on properties of pastes and mortars

1.4 Scopes of study

In this study, various parameters are studied. The scopes of this study are as follows:

1. Materials
    - Cement type: Ordinary Portland Cement (OPC) type I
    - Fly ash type:
        - an original high CaO fly ash from Mae Moh power plant (CaO = 18.74%)
        - an original low CaO fly ash from BLCP power plant (CaO = 2.32%)
2. Materials variations
    - Ammonia concentration: 0, 100, 200, 400, 600, 1000 ppm

- Ammonium salts blend ratio: 0% - 100%, 25% - 75%, 50% - 50%, 75% - 25% and 100% - 0%
- Free lime content of fly ash:
    - Mae Moh fly ash: low (2.36%), medium (4%), and high (7%)
    - BLCP fly ash: low (0.19%), medium (4%), and high (7%)

- SO_3 content of fly ash:
    - Mae Moh fly ash: low (3.74%), medium (5%), and high (10%)
    - BLCP fly ash: low (0.28%), medium (5%), and high (10%)

3. Paste mixture
    - Water to binder ratio: at normal consistency
    - Amount of fly ash: 20 %
4. Mortar mixtures
    - Water to binder ratio: 0.5 and 0.55
    - Amount of fly ash: 30%
5. Experiment items
    - Normal consistency (ASTM C187)
    - Setting times (ASTM C191)
    - Compressive strength (ASTM C39)
    - Autoclave expansion (ASTM C151)
    - Sodium sulfate expansion (ASTM C1012)
    - Autogenous shrinkage (ASTM C1698)

CHAPTER 2
REVIEW OF LITERATURE

2.1 General

Fly ash is a byproduct of the coal combustion process in a power plant to generate electricity. As a byproduct or residue of the coal combustion process, fly ash commonly contains toxic constituents that can pose a hazard to the environment. In 2008, over 900 million tons of this byproduct were produced per year globally. The total amount is expected to increase to at least 2000 million tons by 2020 (Malhotra, 2008). Applications to reuse fly ash reached only about 43 percent. The rest of it has been disposed of as waste material. Massive environmental problems will occur when fly ash is disposed to open dumps. Groundwater contamination and soil contamination by heavy metals and dust will result in various health problems. So, making fly ash a useful product is very important for sustainable coal utilizing industry globally.

Many experiments and studies have been conducted in many countries to investigate effective ways to reuse fly ash. Using it in concrete as a partial substitute is the most popular application of fly ash. The American Society for Testing and Materials (ASTM) and TIS 2135 classify the main types of fly ash for several applications since fly ash has a wide range of chemical and physical characteristics similar to cement. The process of burning coal at a power generation plant is shown in Figure 1.

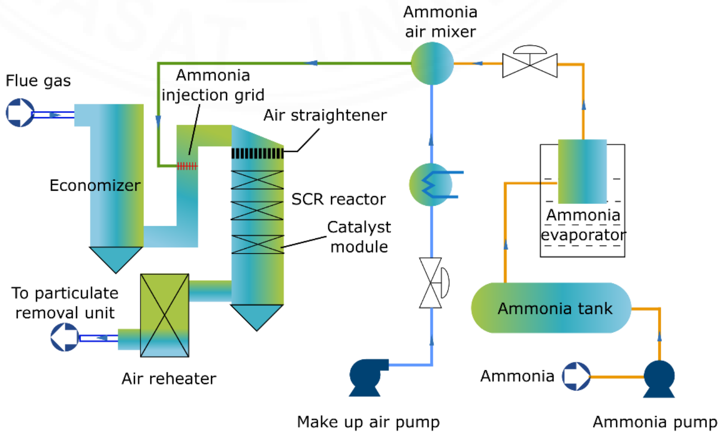


Figure 2.1 SCR process (Jenny, 2022)

Fly ash properties depend on several factors such as coal source, coal type, and chemical composition, boiler temperature boiler type, combustion process, and power plant emission control. These factors vary around the world, making the properties and characteristics of fly ash fluctuate. Due to the variations, it is a challenge to directly apply the standard from other countries. The Electricity Generating Authority of Thailand operates Mae Moh power plant and is the main producer of fly ash material in Thailand.

Researchers have been trying many strategies to utilize fly ash as a partial cement replacement material including the maximum percentage of replacement. Fly ash can be used up to 40% of the total binder in a concrete mix. Concrete containing fly ash and chemical additive consumes less water than regular concrete (Ashby, 1990). According to Ashby (1990), fly ash can be used in concrete in three ways: as a part of the cementitious material, as a fine aggregate, or as a mixture of cementitious material and fine aggregate. Thus, fly ash is good for the concrete industry that reduces the cement demand and, at the same time, reduces CO_2 emissions.

Coal is composed of many chemical substances, such as carbon, nitrogen, and sulfur. After the burning process of coal, the process releases CO_2, NO_x, and SO_2. NO_x and SO_2 are not allowed to be released directly into the environment due to their toxicity (Sarkar, 2015). Generally, in some coal-fired power plants, there is only fuel gas desulfurization to remove SO_2 or sulfur oxide without any process to reduce or remove $NO_{x.}$

The coal combustion process produces fly ash and bottom ash and releases NO_x, which is toxic to the environment. As for the environmental impact regulation, the coal-fired power plant desires to install the NOx reduction system either SNCR or SCR. The method to remove NO_x is done by injecting liquid ammonia into the exhaust gas which is from the boiler as shown in Figure 2.2. The purpose is to make ammonia and nitrogen oxide react at high temperatures.

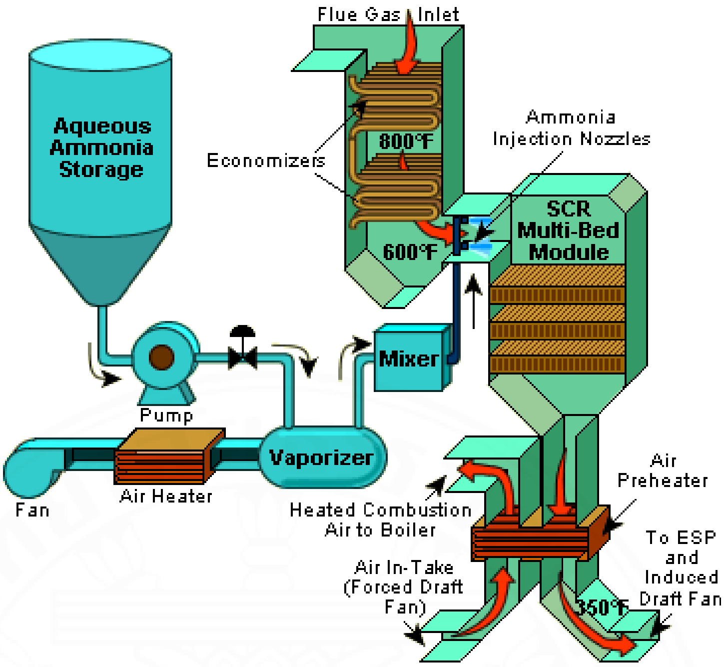


Figure 2.2 NO_x reduction process (Bosworth, 2012)

SNCR method utilizes reduction agent such as urea or ammonia in the systems. In the cyclone inlet or furnace, the injection of urea or liquid ammonia is done at high temperatures to reach the condition for all materials to react. Liquid ammonia reacts with the flue gas containing NO_x. The efficiency of this method varies between 20% - 70% depending on the design, capacity, and temperature of the boiler (Sarkar, 2015).

The main reaction expected from this method is that ammonia will react with nitrogen oxide and produce nitrogen and water that is not toxic to the environment. Usually, urea will convert to ammonia as a reduction agent before being injected into the selective catalytic reduction process, but urea is not the most common material used in this method. According to research, 80% of electricity utilities that operate selective catalytic reduction use an anhydrous and aqueous form of ammonia.

Selective catalytic reduction or SCR method has higher efficiency than the selective non-catalytic reduction or SNCR. Still, SCR gives more benefits, such as the system can be reinstalled in an existing boiler or a new boiler.

Selective catalytic reduction is the most efficient method to reduce nitrogen oxide. The SCR method is developed from the SNCR method by adding the catalyst to make the reaction faster. This method has an efficiency of up to 90% of nitrogen oxide reduction. The disadvantage of this method is that the initial cost is higher than SNCR, but it has a lower operational cost than SNCR.

2.2 SCR (Selective Catalytic Reduction)

Selective catalytic reduction or SCR is the upgraded version of SNCR and it uses the same technique to reduce nitrogen oxide by chemical reduction. However, the ammonia storage, injection grid, delivery system, and catalyst used in SCR are different from SNCR. The primary difference between SCR and SNCR is the metal catalyst to make the reaction faster and increase the reduction rate used in SCR.

At the specific temperature range, the nitrogen-based reducing agent will react with the post-combustion flue gas. The presence of oxygen and catalyst will speed up the urea or aqueous ammonia reaction with nitrogen oxide to produce water and nitrogen. The selective catalytic reduction has an advantage over SNCR because SCR reactions occur within a broader and lower temperature range. Therefore, the rate of reduction and efficiency of the SCR method is over the SNCR, but it makes the operational cost of SCR significantly higher than SNCR.

Catalyst replacement cost is the highest cost, and ammonia reagent cost is the most substantial selective catalytic reduction operational cost. These two reasons make the SCR cost increase, still the large volumes of catalysts that are needed in its process.

Generally, with compressed air or steam, the reagent is diluted to aid in injection. The flue gas downstream of the combustion unit will be injected with a reagent, and in the ductwork, it is an economizer with an injection grid. Both reagent and flue gas will be mixed into the reaction chamber containing the catalyst. The scheme of the SCR process is shown in Figure 2.3.

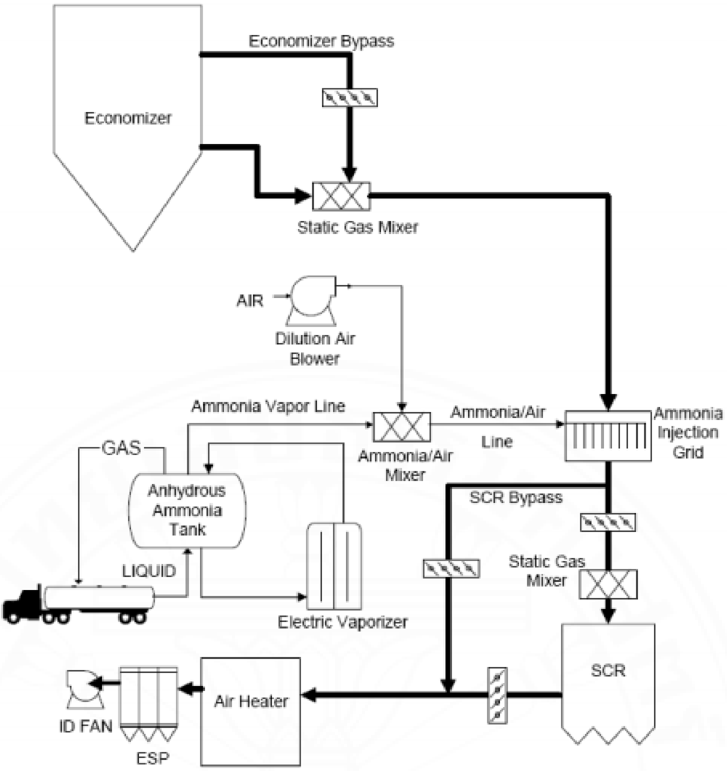


Figure 2.3 SCR scheme (Mladenović et al., 2017)

When the hot flue gas is diffused with ammonia through the catalyst and at the same time activated catalyst site, the water and nitrogen are produced when the nitrogen oxide is reduced. Therefore, the result of the reaction, such as water, nitrogen, and other fly ash constituent, will flow out of the reactor of selective catalytic reduction (Larrimore et al., 2015).

2.2.1 Reducing agent and catalytic reaction on SCR

To reduce NO_x, SCR uses urea and liquid ammonia as reducing agents and commonly there are two types of reducing agents in the SCR system:

- The first is ammonia in an aqueous form. This type of ammonia has the advantage of being easier to manage and less hazardous than pure anhydrous ammonia.
- The second is pure anhydrous ammonia. The disadvantage of this type of ammonia is that it needs a thick shell to store it because of its toxicity

The amount of ammonia injected into the system must be calculated because it can cause problems to the product during or after combustion. It has to be calculated, so there are enough and not over dosage of ammonia for reacting with NO_x.

2.2.2 Chemical reactions in SCR

Many chemical reactions in the SCR process depend on the NO_x and ammonia concentration. The main chemical reaction expected from the SCR system that uses ammonia injection is converting NO_x to water and nitrogen in the gas form (see Equations (2.1) to (2.5)). In addition, oxygen can involve in the reaction in the SCR process (Theotoki et al., 2015; Brendel et al., 2000).

$$6NO + 4NH_3 \rightarrow 5\ N_2 + H_2O \tag{2.1}$$

$$4NO + 4NH_3 \rightarrow O_2 + 4N2 + 6H_2O \tag{2.2}$$

$$6NO + 8\ NH_3 + 7N_2 + 12H_2O \tag{2.3}$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \tag{2.4}$$

$$NO + NO_2 + 2NH_3 \rightarrow O2 + 3H_2O \tag{2.5}$$

Ammonium nitrate is an explosive substance and is dangerous in high volume, and it is resulted from a reaction between ammonia and NO_x. The following reaction produced ammonium nitrate or NH_4NO_3:

$$2NH_3 + 2NO_2 + H_2O \rightarrow NH_4NO_3 + NH_4NO_2 \tag{2.6}$$

The catalyst's deactivation will happen because of liquid or solid ammonium nitrate formation in catalyst pores.

The present CO_2 will lead ammonia to slip into another reaction in the NO_x reduction process. There are two types of ammonium salt from the reaction between ammonia and carbon dioxide that is ammonium bicarbonate ($(NH_4)HCO_3$) and ammonium carbonate ($(NH_4)_2CO_3$).

$$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3 \qquad (2.7)$$

$$NH_3 + CO_2 + H_2O \rightarrow (NH_4)HCO_3 \qquad (2.8)$$

Ammonium bisulfate (NH_4HSO_4) and ammonium sulfate ($(NH_4)_2SO_4$) will be produced when there is sulfur in flue gas, and these reactions will occur when the temperature is lower than 250 °C. SO_3 or sulfate from this reaction comes from the oxidation of SO_2 or sulfur dioxide. Therefore, the sedimentation of the ammonium salt can attach to pipes, catalysts, and other equipment of SCR (James et al., 2007).

$$NH_3 + SO_3 + H_2O \rightarrow (NH_4)HSO_4 \qquad (2.9)$$

$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2HSO_4 \qquad (2.10)$$

SCR technologies have to put a system that can control the injection rate of ammonia because if the ammonia injection is too high, it will cause ammonia slip. But, on the other hand, when ammonia slips or ammonia that did not react is too high, the undesirable ammonia that releases into the environment is also high

2.2.3 Catalyst

The catalyst used for NO_x reduction, particularly for selective catalytic reduction technology, is vanadium pentoxide-based and zeolite-based.

- Vanadium based catalyst

In the process, V_2O_5 or Vanadium pentoxide cannot work alone because it needs support from TiO_2 or Titanium dioxide. Vanadium pentoxide and titanium dioxide is an active catalyst, but it needs physical and chemical promoter. WO_3 or Tungsten trioxide was used. For NO_x reduction catalyst, the vanadium-based catalyst is the first commercial catalyst. This catalyst is resistant to lubricant, sulfur, and hydrocarbon, with a temperature range of around 300-450 °C

- Zeolite based catalyst

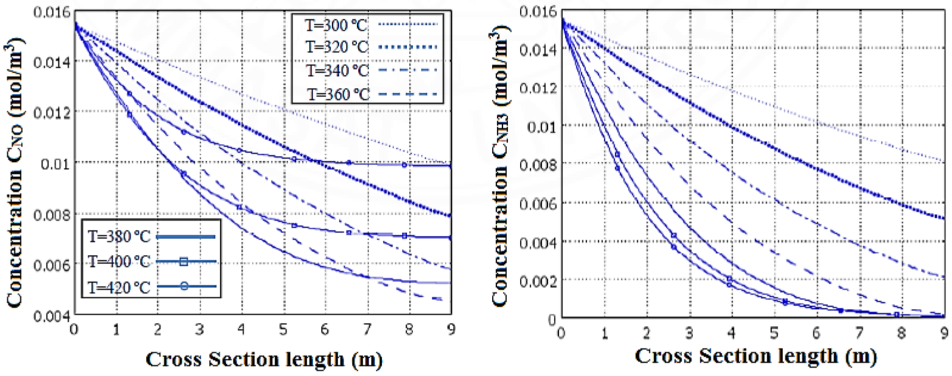
Vanadium-based catalyst has some weak points. At the required temperature, it needs to avoid reheating the exhaust gas in the system (Heede et al., 2014; Izquierdo et al., 2004). The advantages of zeolites compared to catalyst with vanadium based are as follows:

  - At a high temperature, it is high thermal durability.
  - It has better performance even with low temperature.
  - It is a nontoxic catalyst.
  - It has high selectivity to N_2.

In the process, the large molecule will trap a zeolite-based catalyst because with crystalline and its microporous structure, zeolite will allow only a small molecule to pass it.

2.2.4 Temperature

According to the simulation-based, the maximum NO_x conversion occurs when the temperature reaches 360°C. Xuan (2003) reported that NO_x conversion depends on increasing or decreasing temperature, and ammonia slip will decrease if the temperature increases. NO_x conversion projection over V_2O_5/TiO_2 as a catalyst based on knowledge of SCR kinetics is shown in Figure 2.4.



(a) Nitrogen oxide **(b)** Ammonia gas

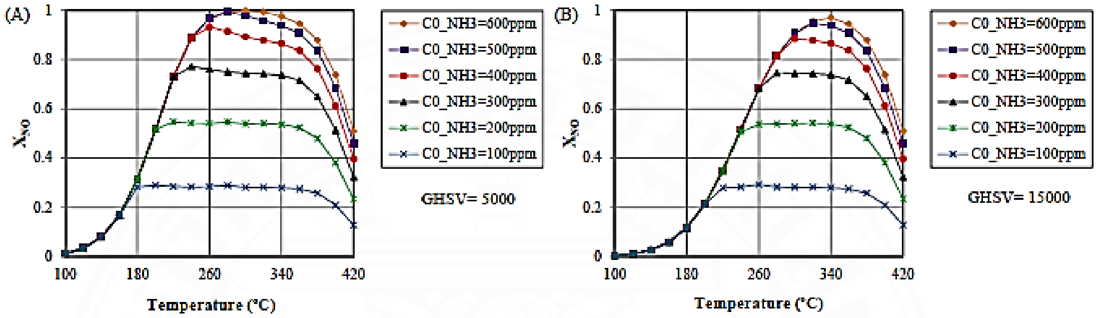
Figure 2.4 Temperature effects on NO_x conversion (Xuan et al., 2003)

2.2.5 Gases velocity

Conversion and residence time can be changed by variations such as GHSV or Gas Hourly Space Velocity. The NH_3 conversion or NO_x reduction depends on how much gas velocity changes. Generally, decreasing the residence time by gas velocity increased will reduce the conversion of NH_3 (Xuan et al., 2003).

2.2.6 Inlet of ammonia

Inlet ammonia and temperature in the process will affect the total amount of ammonia (Xuan et al., 2003).



(a) Inlet 5000 GHSV **(b)** Inlet 15000 GHSV

Figure 2.5 NH_3 inlet concentration on NO_x conversion at different temperature (Xuan et al., 2003)

From Figure 2.5, the different initial ammonia concentrations in the same temperature show that the conversion rate will be higher when the initial concentration is higher. At the difference of GHSV (Gas Hourly Space Velocity), the conversion is not different with the same concentration of initial ammonia. The conversion rate will decrease if the temperature is too high. From that result, the NO_x conversion rate is significantly affected by the temperature.

2.3 Ammonia slips

After the NO_x reduction process, not all ammonia will react with NO_x, and a part of the rest will attach to fly ash. Injection of ammonia into the SCR process to reduce NO_x may have some of them left the process called "ammonia slips”. The total of ammonia slips that are adsorbed by fly ash is up to 70% and in several forms, such as ammonia in gas form or ammonium salt. Slips of ammonia can also react with several chemicals from fly ash and form other types of chemical substances that affect the properties of concrete or become ammonia gas. This poisonous gas can harm humans and cause various health problems like eye irritation and asthma. However, compared with the amount of the initial ammonia injection, the total ammonia slip is very low (Lockert et al., 2009). Five ways of ammonia slip on the fly ash are as follows:

1. Ammonia slip absorbs on fly ash particles.
2. The total of ammonia that reacts with NO_x to produce N_2 and water is around 99%.
3. The total of ammonia slip that goes to the air heater is around 20%.
4. 70% of ammonium salts will attach to the surface of the fly ash, and 5% of it will go out as gases and pass-through air heater, and the rest is left in the equipment. Exhaust gases such as SO_2, and CO_2 will react with ammonia slip and result in several forms of ammonium salts such as (C. Lockert et al., 2009):
   - Ammonium bicarbonate
   - Ammonium carbonate
   - Ammonium bisulfate
   - Ammonium sulfate
5. The total of ammonia that reaches the environment is lower than 1%.

But ammonia in solid form or ammonium salt that is mostly found in this process is ammonium bisulfate $(NH_4)HSO_4$ or ammonium sulfate $(NH_4)SO_4$. Ammonium bisulfate and ammonium sulfate are quite favorable to form, the reason is the high temperature used in the process (sakar et al., 2015).

There is currently a lot of research to investigate the behavior of ammonia-contaminated fly ash, especially on the outer part or surface of ACFA. Still, the fly ash composition and ammonia concentration vary in each study depending on the coal source and NO_x reduction process. In many studies, ammonia residues' most common chemical substances are ammonia sulfate, including ammonium sulfate and bisulfate (Larrimore et al., 2002). However, there are still details about the other types of ammonium composition, namely ammonium carbonate, ammonium chloride, and ammonium nitrate, which affect concrete and mortar.

2.4 Ammonia adsorption on fly ash

2.4.1 Composition of fly ash

The solid surface acidity will change due to alumina content, according to the silica alumina zeoline molecular sieve study. That is, the mean ammonia absorption by fly ash particles will decrease due to the high Si/Al ratio (Zecchina et al., 1998; Barthomeuf et al., 1991).

2.4.2 Unburned carbon

In carbon particles, the generation of pore and tiny channels by devolatilization or dehydration will occur because the coal contains volatile matter and moisture content. It also occurs because oxygen diffuses into carbon particles, and ammonia gas is absorbed when coal is burned.

2.4.3 Fly ash surface area

The high absorption of ammonia gas is related to the large fly ash's surface area, the calculation is based on the BET (Brunauer, Emmet, and Teller) formula (Schure et al., 1985).

2.4.4 Fly ash porosity

Porosity directly affects the absorption of ammonia gas, and higher porosity leads to high adsorption of ammonia gas. IUPAC classified fly ash using the theory of Dubinin and Raduskevich (DR) to calculate porosity. There are three types of porosity (Schure et al., 1985; Rajwar et al., 2014):

- Micropores; the pore size is smaller than 20A
- Mesopores; the pore size is between 20 and 500A
- Macropores; the pore size is larger than 500A

2.4.5 Pressure

Increasing the pressure of gas injection on the NO_x reduction process increases the absorption of ammonia gas.

- Utilization and application of ammonia contaminated fly ash

The limits of ammonia concentration when working in good ventilation and not good ventilation conditions are different. The ammonia concentration limit for work in an unvented area is 100 ppmw and 200 ppmw for a vented area (Larrimore et al., 2002). The maximum limit of ACFA utilization in the concrete mixture is shown in Figure 2.6.

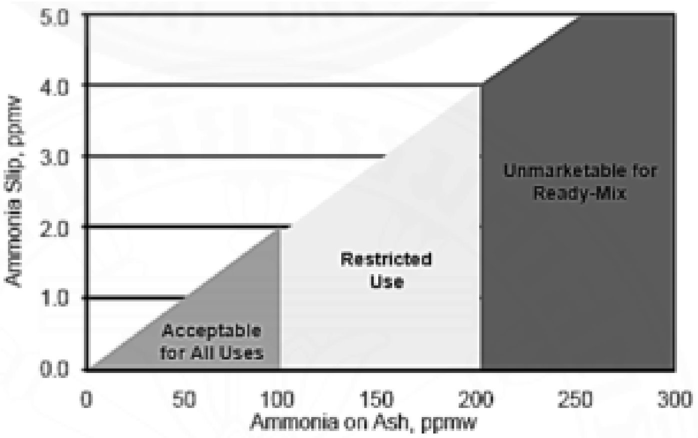


Figure 2.6 Acceptable limit of ammonia contaminated fly ash for use in concrete (Larrimore et al., 2002)

- Utilization and application of ammonia contaminated fly ash (ACFA)

  Ammonia will cause an environmental problem when the ammonia contaminated fly ash is disposed into soil and water. Ammonia is toxic that can cause health problems for living things that live on soil or in water.

2.5 Reaction between cement and ammonium salt

Several forms of ammonium salt, such as ammonium nitrate and ammonium sulfate, will cause deterioration in concrete and mortar structure. The reaction between ammonium salts and calcium hydroxide (($Ca(OH)_2$) is the main reaction that occurs in concrete and mixture (Ravindra et al., 2002). Because of that reaction, ammonium salt can change the properties of concrete and mortar structure.

- Ammonium sulfate (Star et al., 2013; Kumar et al., 1994):
  - Calcium hydroxide reaction

$(NH_4)_2HSO_4 + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O + 2NH_3$ (g) (2.11)

- C-S-H phase reaction

$CaO \cdot SiO_2 \cdot H_2O + (NH_4)_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O + 2NH_3$ (g) + SiO_2 (aq) (2.12)

- Ammonium bisulfate:

$NH_4HSO_4 + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O + 2NH_3$ (g) (2.13)

From the above reactions, it is known that gypsum will react with C-A-H or calcium aluminate hydrate and causes the expansion of the concrete. Ammonia gas is released in to the air when concrete is in a fresh state, but some are trapped in the capillary pores. As a result, large cracks and partial cleavage in the concrete and mortar occurs due to ettringite and gypsum formation (Bassuoni & Nehdi, 2012). High porosity and crack will have a direct impact on concrete properties, especially for compressive strength.

- Ammonium nitrate (T. Star e al., 2013; J. Scrivener et al., 1997; N. Alexander et al., 2012; M. Arafa et al., 2015):
  - C-S-H phase reaction
  - Calcium hydroxide reaction
  - Reaction on AFt phase
  - Reaction on AFm phase
- Ammonium carbonate (Matschei et al. 2007):

From the reaction shown in Equation (2.14), calcium carbonate is produced. It will increase the workability of the concrete or mortar, even without pozzolanic material. Ammonium carbonate will improve the early age compressive strength, and reduce the porosity of the concrete and mortar (Antoni et al., 2015; Gambhir et al., 2004). From the reaction, ammonia gas will also be produced and will generate air bubbles in concrete or mortar, increasing the workability of the concrete and mortar.

$(NH_4)_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O + 2NH_3$ (g) (2.14)

- Ammonium chloride (Yilmaz et al., 2004):

From the reaction shown in Equation (2.15), calcium chloride dihydrate is produced. Calcium chloride dihydrate is highly soluble in water, which will affect concrete properties. Ammonia gas will be produced, and this ammonia gas will generate bubbles in concrete or mortar, increasing the workability of the concrete and mortar. Therefore, ammonia will affect the properties of concrete and mortar.

$NH_4Cl + Ca(OH)_2 \rightarrow CaCl + 2H_2O + 2NH_3(g)$ (2.15)

2.6 Effects of ACFA on properties of mortar and concrete

There are currently several research conducted to investigate the behavior of ACFA. Still, the fly ash composition and ammonia concentration vary in each study depending on the coal source and NO_x reduction process. The potential shows how much ammonia is released on the surface of the fly ash. In many studies, ammonia residues' most common chemical substances are ammonia sulfate, including ammonium sulfate and bisulfate (Kim et al., 2007). However, there are still details about the other types of ammonium composition, namely ammonium carbonate, ammonium chloride, and ammonium nitrate, which affect concrete and mortar.

From the several studies that have already been conducted, experiments were carried out by adding ammonia solution at different concentrations to fresh concrete and mortar and then mixing properly. After that, the sample was taken to be formed for testing to observe the effects.

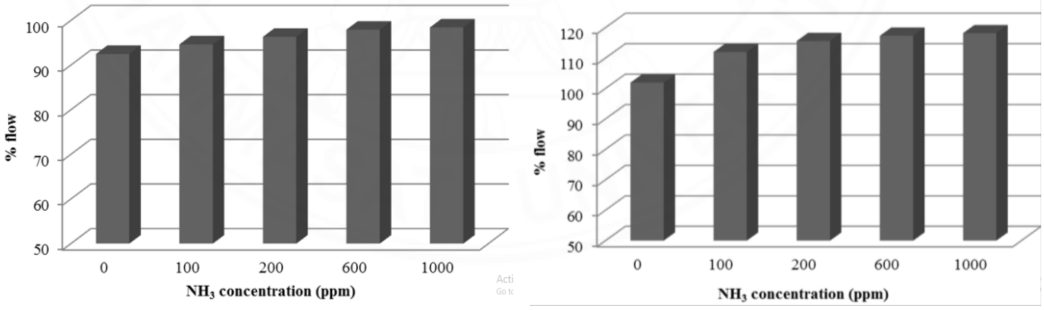
Fly ash used to be the cement replacement with the purpose to improve the properties of concrete and mortar due to the pozzolanic effect, at the same time to reach the lower cost of concrete. There are still some problems when the fly ash is contaminated with ammonia, which are properties that can be affected due to the ammonia contamination in fly ash (Shirazi et al., 2008).

When utilized as a cement substitution, Mae Moh fly ash has recently been found to have a high free lime content, resulting in undesired expansion and volume instability. Furthermore, fly ash from the Mae Moh power plant has a higher sulfur trioxide (SO_3) content, which affects the volume stability. A study to overcome the problems caused by high SO_3 and free lime contents in fly ash is needed.

From a previous study, several experiments have been already conducted on the effects of ammonia contaminated fly ash (Qin et al., 2019; Krerkchaiwan et al., 2017). In previous experiments, ACFA was made by adding fly ash with ammonium sulfate $(NH_4)SO_4$, ammonium carbonate $(NH_4)_2CO_3$, and ammonium bisulfate $(NH_4)HSO_4$. The properties that have already been investigated are workability, setting times, compressive strength, and total shrinkage. So, it needs to investigate more properties of concrete that used ammonia-contaminated fly ash, such as autogenous shrinkage, autoclave expansion, and sulfate expansion. In addition, the investigation of the properties of concrete that used high free lime and SO_3 has not been performed. The properties of ACFA from previous studies are given in the following section.

2.6.1 Workability

Krerkchaiwan et al. (2017) reported that increased ammonia concentration increased the workability of the concrete or mortar. Figure 2.7 shows that an increase in ammonium sulfate and ammonium carbonate concentration increased the workability of the concrete (Krerkchaiwan et al., 2017).



(a) Ammonium sulfate **(b)** Ammonium carbonate

Figure 2.7 Effects of ammonia concentration on flow percentage (Krerkchaiwan et al., 2017)

2.6.2 Setting times

For setting times, Qin, li, and Gao (2019) suggested that increasing the ammonium sulfate and ammonium bisulfate concentrations increased the concrete's initial and final setting times. Figures 2.8 and 2.9 show the effects of ammonia concentration on the initial and final setting times of pastes. From Figure 2.8, at 20% fly ash replacement, the delay was up to 22.6% for the initial setting time, and up to 12.8% for the final setting time. When pure fly ash was compared with fly ash with 3.0-6.0 % ammonium bisulfate, the initial setting time increased 20.4-25.2%, and the final setting time increased 13.5-19.7%. The values of the initial setting time of ammonia-contaminated fly ash pastes with 3.0-6.0% ammonium sulfate are 29.1-41.3% longer than that of the fly ash paste without ammonia, and the values of the final setting time of ammonia-contaminated fly ash pastes with 3.0-6.0% ammonium sulfate are 20.0-29.9% longer when compared to that of the fly ash paste without ammonia. It is known that paste setting times are affected when tricalcium silicate reacts and forms calcium silicate hydrate (Qin et al., 2019).

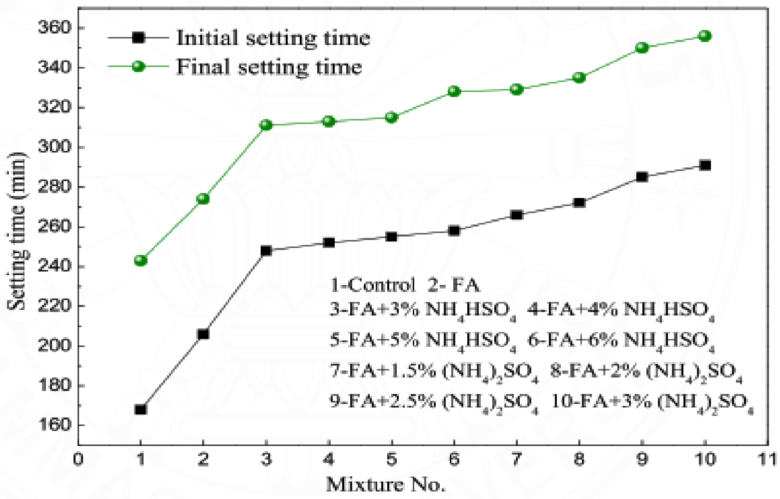
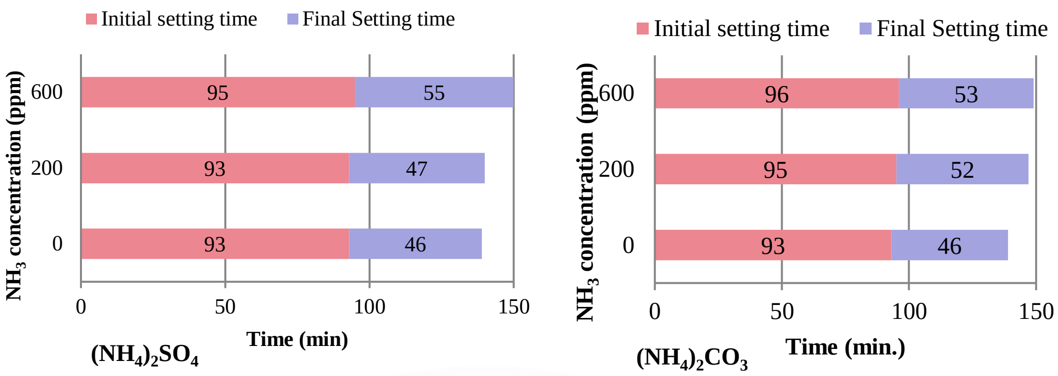


Figure 2.8 Effects of ammonia concentration on setting times (Qin et al., 2019)

From Figure 2.9, the initial and final setting times of paste with ammonium sulfate and ammonium carbonate were longer than those without ammonium salt. It can be seen that increased ammonia concentration in the form of ammonium sulfate or ammonium carbonate increased the setting times of pastes. The results show a similar tendency to the results reported by Qin, li, and Gao (2019), that ammonium sulfate increases the setting times of cement pastes.



(a) Ammonium sulfate **(b)** Ammonium carbonate

Figure 2.9 Effects of ammonia concentration on setting times (Krerkchaiwan et al., 2017).

When the ammonia-contaminated fly ash is added, the setting times are longer than normal fly ash paste because the reaction between the reaction of ammonium salts with calcium hydroxide has water as a product. So, the setting times are more delayed when ammonia concentration is increased (Zecchina et al., 1998; Barthomeuf et al., 1991).

2.6.3 Fly ash porosity

For porosity, as reported by Qin, li, and Gao (2019), when compared with cement paste, the porosity of the specimen increased up to 12.8% at the age of 28 days by the replacement of 20% fly ash. The increase became 24.4-29.1% when ammonium bisulfate was added at 3.0-6.0% and became 25.7-28.1% when 1.5-3.0 ammonium sulfate was added. Figure 2.10 shows that the addition of ammonium sulfate or ammonium bisulfate increased coarse pore formation with a size of diameter bigger than 1000 nm (Qin et al., 2019).

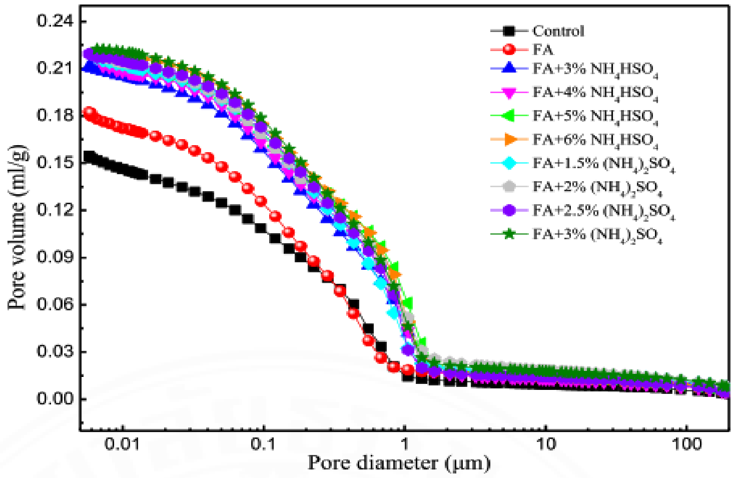


Figure 2.10 Effects of ammonia concentration on porosity (Qin et al., 2019)

2.6.4 Compressive strength

For compressive strength, Qin, li, and Gao (2019) suggested that fly ash with 3.0-6.0% ammonium bisulfate reduced the compressive strength by 4.3-10.4%. Likewise, fly ash with 1.5-3.0% ammonium sulfate caused a decrease in compressive strength by 6.3-8.9%, as shown in Figure 2.11 (Qin et al., 2019). Generally, higher content of ammonium sulfate and ammonium bisulfate leads to a more reduction in compressive strength of the paste specimen.

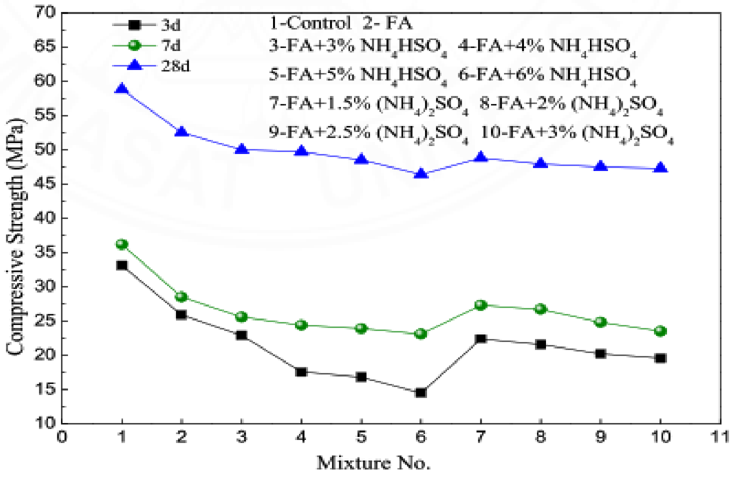
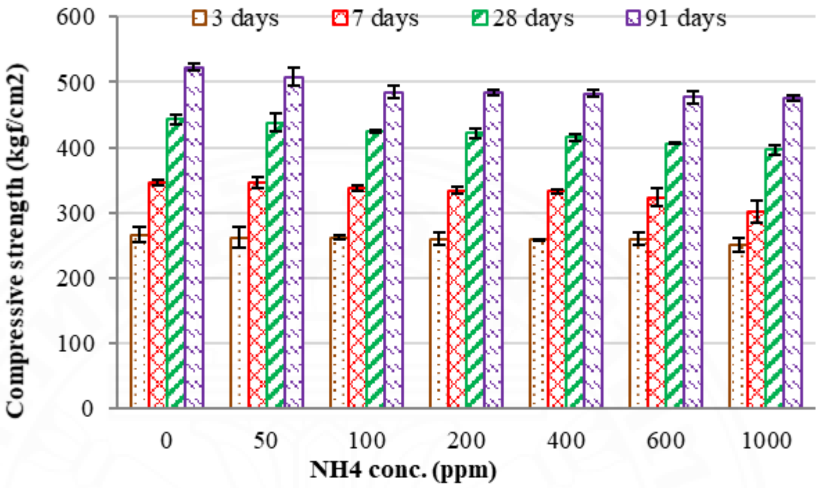
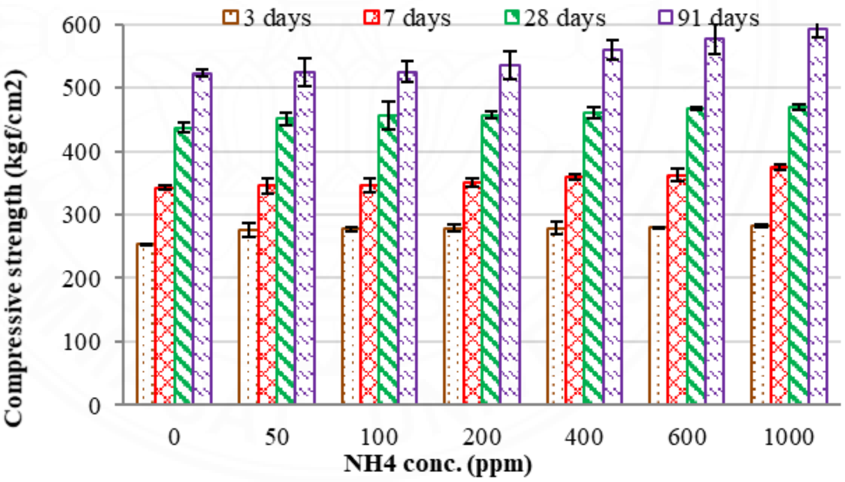


Figure 2.11 Effects of ammonia on compressive strength (Qin et al., 2019)

Krerkchaiwan et al. (2017) reports the same tendency of compressive strength decrease when ammonium sulfate concentration increased as illustrated in Figure 2.12. Ammonium carbonate shows the opposite tendency that increasing ammonium carbonate increased the compressive strength (Krerkchaiwan et al., 2017).



(a) Ammonium sulfate



(b) Ammonium carbonate

Figure 2.12 Effects of ammonium salt on compressive strength (Krerkchaiwan et al., 2017)

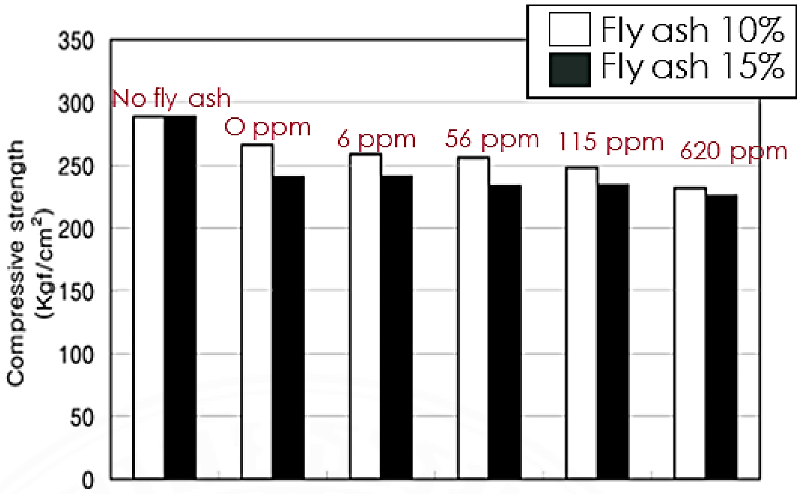


Figure 2.13 Compressive strength of concrete (Ki et al., 2007)

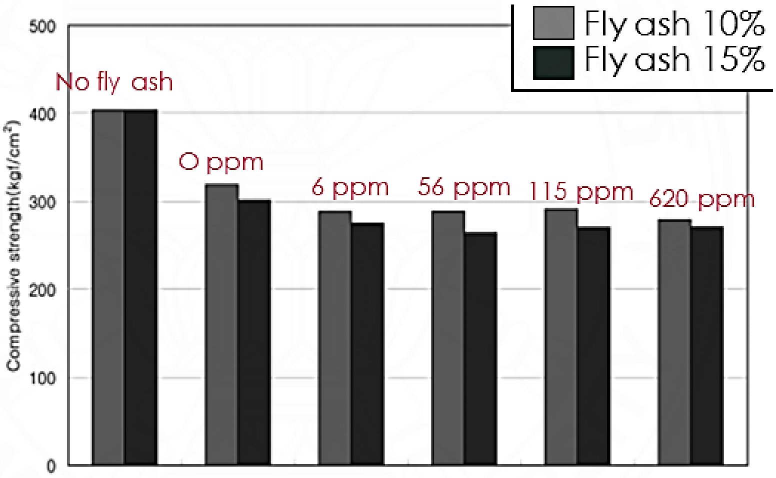
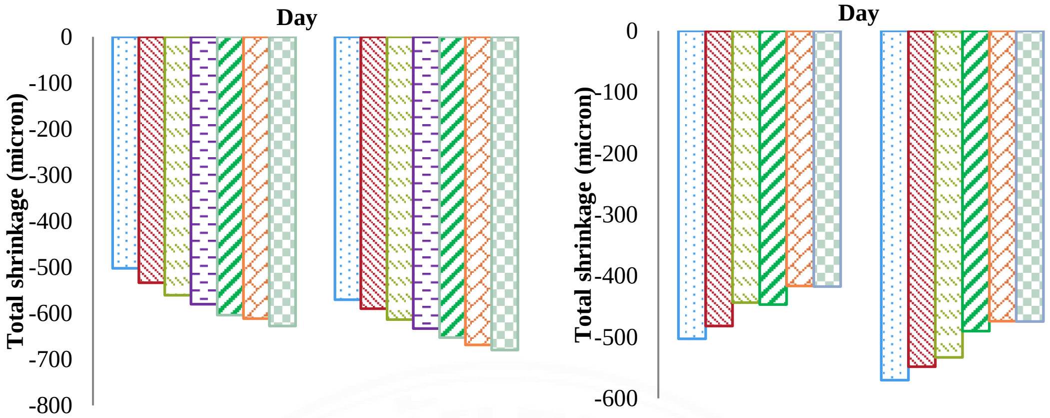


Figure 2.14 Compressive strength of mortar (Kim et al., 2007)

From Figures 2.13 and 2.14, the compressive strength decreased even with the same percentage of fly ash replacement, when increasing ammonia contamination (Kim et al., 2007).

2.6.5 Total shrinkage

Krerkchaiwan et al. (2017) reported that increasing ammonium sulfate concentration increased the total shrinkage as illustrated in Figure 2.15. Opposite to the ammonium sulfate, an increase in ammonium carbonate lowered the total shrinkage (Krerkchaiwan et al., 2017).



(a) Ammonium sulfate **(b)** Ammonium carbonate

Figure 2.15 Effects of ammonia concentration on total shrinkage (Krerkchaiwan et al., 2019)

2.6.6 Deteriorations and expansion

Deteriorations come from the ammonia sulfate salts ((NH_4) SO_4 / (NH_4) HSO_4) that react with calcium hydroxide ($Ca(OH)_2$) as shown in Equation (2.16). This reaction forms gypsum ($CaSO_4 \cdot 2H_2O$) and ammonium hydroxide NH_4OH, which has the acidity property that can make the mortar and concrete deteriorate (Kumar et al., 1994; Cwalina et al., 2008; Suleiman et al., 2014).

$$Ca\,(OH)_2 + (NH_4)_2\,SO_4 \rightarrow \underbrace{CaSO_4 \cdot 2H_2O}_{Gypsum} + \underbrace{2NH_4OH}_{Acid} \qquad (2.16)$$

The expansion comes from the reaction of the product of C_3A and gypsum from deterioration. It gets the ettringite as a product with high molecular weight, which leads to mortar and concrete expansion (Suleiman et al., 2014).

2.7 Ammonia gas released

The ammonia gas release detection indicates that the concentration of ammonia on surface concrete was higher than concentration in the air chamber. It was also found that the ammonia release rate was always continuing.

Generally, there are three periods when ammonia is released from concrete as follows:

a. Mixing period
b. Initial setting period
c. Curing period

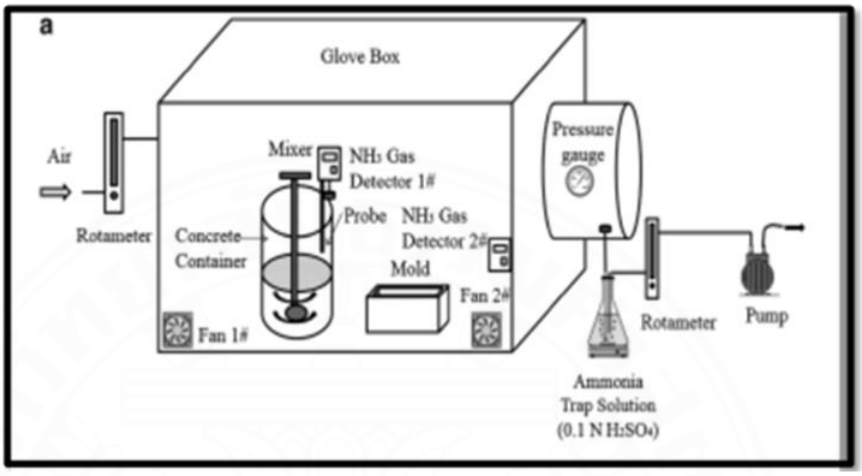


Figure 2.16 Mixing period and initial setting period experimental setup (Shou et al., 2014)

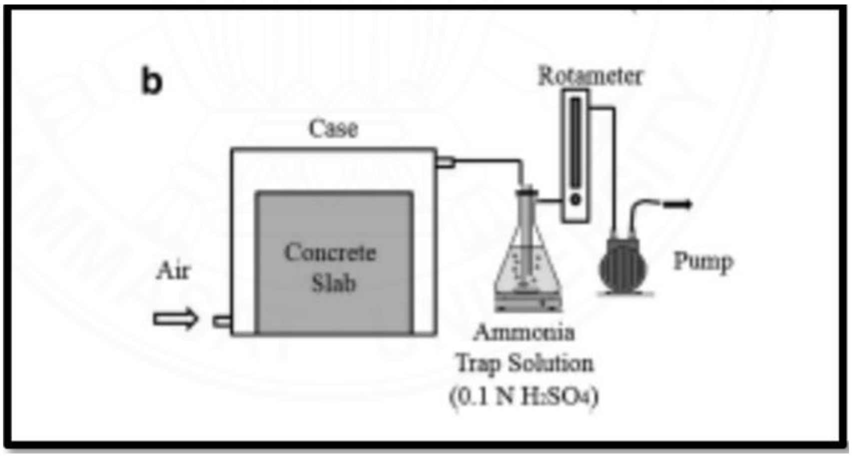


Figure 2.17 Curing period experimental setup (Shou et al., 2014)

Figures 2.16 and 2.17 show the experimental setup to observe the behavior of ammonia release from the concrete. The amount of released ammonia was measured using two real-time ammonia gas monitors. One stays 2-3 cm above concrete surface for measuring ammonia, and another is for the ambient ammonia concentration of the chamber. And before releasing the air from the chamber to the environment, the ammonia will be trapped by sulfuric acid solution and then analyzed by Ion chromatography. The ammonia concentration in the air at the chamber is always lower than ammonia in the concrete surface. It tells that the rate of ammonia release is continuous.

2.7.1 Mixing

For the Mixing period, the observation was around 20 minutes after the experiment started because the release of the ammonia will increase when the stirring process began, which can be explained by large diffusivity with some interface of air and convective mass transfer on liquid. And because the diffusion that occurred in the air is negligible compared to the convection effects by a wind from fans when this experiment was conducted.

2.7.2 Initial setting

For the initial setting period, the observation was started after the mixing period up until 8 hours. There was no stirring in this period, so ammonia was released from the liquid and air interface with constant diffusivity. Commonly ammonia is released from the water that evaporates from concrete.

The amount of ammonia released in gas form from mixing and the initial setting period measured by the real-time monitor is shown in Figure 2.18.

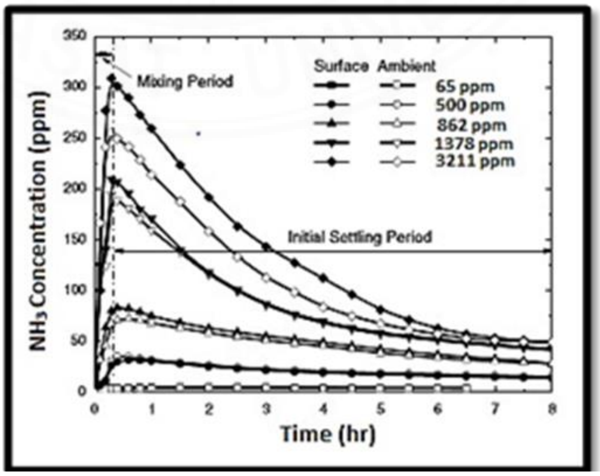


Figure 2.18 Real-time monitor of ammonia concentration measured during mixing and initial setting period of concrete (Shou et al., 2014)

2.7.3 Curing

Ammonia release from specimen occurred on the concrete's surface when it contacted with air or at the bleed water and air, for a period of curing of concrete is illustrated in Figure 2.19. The common way of ammonia released from the concrete specimen is evaporating at the same time with water. The convective mass transfer can explain by the diffusion process controlled by the solid mass transfer phase.

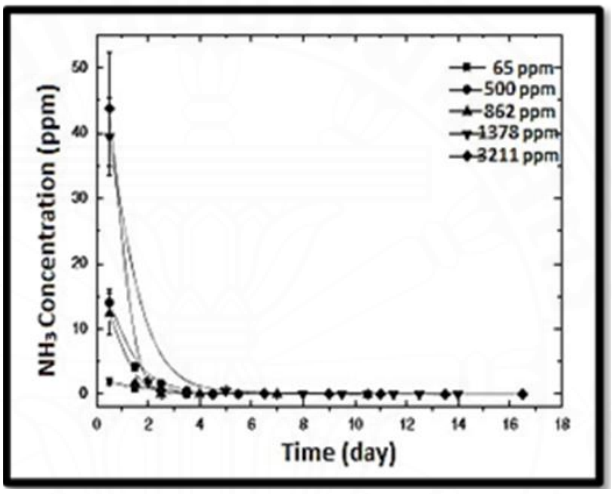


Figure 2.19 Real-time monitor of ammonia concentration during the curing period of concrete specimens (Shou et al., 2014)

2.8 Ammonia exposure limit

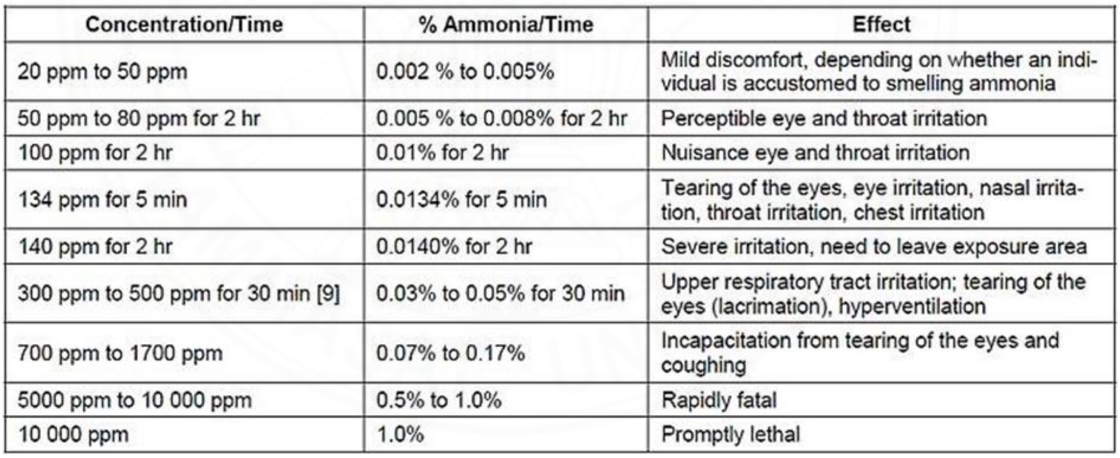
Ammonia's effects on humans depend on the limit of exposure. Ammonia in high concentration will affect human health. Although its smell is not good, this gas is also toxic (Issley et al., 2009). So, it is needed to know the limit of exposure when the people who have to work or deal with ammonia during their working period. There are three standards of ammonia exposure limits as follows:

1. Allowable limit of exposure by Occupational Safety and Health (OSHA):
   - Not more than 35 ppm or 27 mg/mg^3 as 15 minutes (should not excess during the workday)
   - 50 ppm for 8 hours for time average expose

2. Allowable limit of exposure by American Conference of Governmental Industrial Hygienists (AGIH):
   - o 17 mm/mg^3 or 25 ppm for 8 hours for average time expose per day
   - o 24 mg/mg^3 or 35 ppm for 15 minutes short term
3. Permissible exposure limit by National Institute for Occupational and Health (NIOSH) (Murphy et al., 2007):
   - o 17 mg/mg^3 or 25 ppm for 8 hours for average time expose per day
   - o 24 mg/mg^3 or 35 ppm for 15 minutes short term

Usually, in ammonia gas leakages, the first and the third standard will be used. But the situation of ammonia leakage is sometimes out of control, even though there is an ammonia exposure limit. The second standard is used for workers exposed during work to various concentrations of ammonia (Murphy et al., 2007). Table 2.1 shows the summary of ammonia exposure effects on humans.

Table 2.1 Summary of ammonia exposure effects on humans (Murphy et al., 2007).



Concentration/Time	% Ammonia/Time	Effect
20 ppm to 50 ppm	0.002 % to 0.005%	Mild discomfort, depending on whether an individual is accustomed to smelling ammonia
50 ppm to 80 ppm for 2 hr	0.005 % to 0.008% for 2 hr	Perceptible eye and throat irritation
100 ppm for 2 hr	0.01% for 2 hr	Nuisance eye and throat irritation
134 ppm for 5 min	0.0134% for 5 min	Tearing of the eyes, eye irritation, nasal irritation, throat irritation, chest irritation
140 ppm for 2 hr	0.0140% for 2 hr	Severe irritation, need to leave exposure area
300 ppm to 500 ppm for 30 min [9]	0.03% to 0.05% for 30 min	Upper respiratory tract irritation; tearing of the eyes (lacrimation), hyperventilation
700 ppm to 1700 ppm	0.07% to 0.17%	Incapacitation from tearing of the eyes and coughing
5000 ppm to 10 000 ppm	0.5% to 1.0%	Rapidly fatal
10 000 ppm	1.0%	Promptly lethal

2.9 Methods to apply ammonia contamination to fly ash in laboratory

There are two procedures to create ammonia-contaminated fly ash in the laboratory, which are blending and dissolving methods. Figure 2.20 illustrates the procedure of the blending method. The ammonium salts are blended with fly ash before being mixed with water and cement in this process. Because ammonium sulfate particles are crystallized, they must be crushed into powders before being mixed with fly ash. On the other hand, the particles of ammonium carbonate are powders, it can be combined with fly ash without being ground.

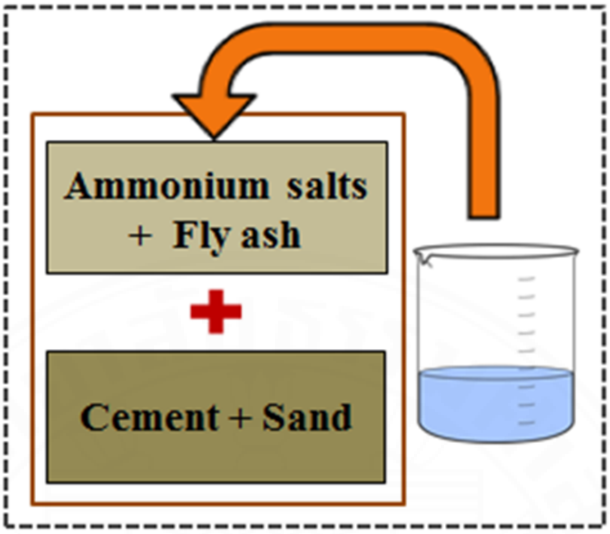


Figure 2.20 Blending method of ammonium salts in fly ash

Ammonium sulfate and ammonium carbonate were dissolved in water for the dissolving procedure. This method's mortar mixing procedure is illustrated in Figure 2.21.

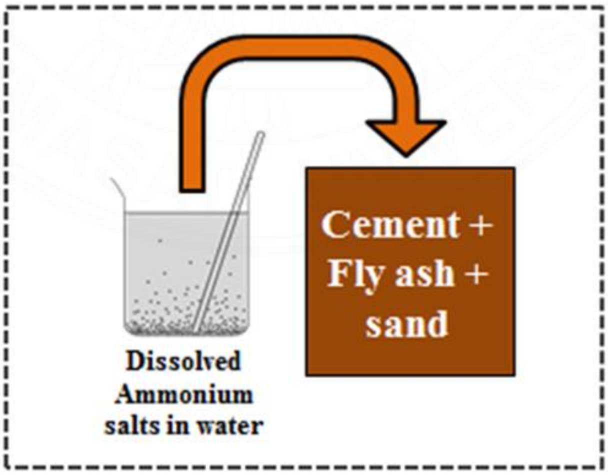


Figure 2.21 Dissolving method (Krerkchaiwan et al., 2017)

The flow test and compressive strength of mortars containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ prepared by blending and dissolving methods show that the dissolving method produces more obvious results than the blending method because the ammonium salts can be thoroughly mixed by dissolving rather than blending (Krerkchaiwan et al., 2017). The outcomes of these two mixing processes are just slightly different. The dissolving method is simpler and more convenient than the blending method. As a result, this study adopted the dissolving method of mixing ammonium salts in pastes and mortars.

Ref. code: 25646222040757RWH

CHAPTER 3
METHODOLOGY

3.1 General

To observe the effects of ACFA on properties of concrete, pastes and mortars were used as the representative of concrete to study the behavior, the properties, and the mechanisms. Fly ashes obtained from Mae Moh and BLCP power plants were used in the tests. Ammonium salts were used as the source of ammonia in the mortar mixtures.

Paste and mortar samples were used to study the properties and mechanisms of ammonia-contaminated fly ash in pastes and mortars.

There are 5 steps of testing:

1. Preparing the materials
2. Design the mix proportions of pastes and mortars.
3. Preparing the samples with different ammonia concentrations.
4. Testing the basic and durability properties of pastes and mortar samples.
5. Analyzing the results of all tests

3.2 Materials

3.2.1 Cement

All mixtures in this study were prepared by using Ordinary Portland Cement (OPC) type 1 following TIS 15. Table 3.1 shows the chemical compositions of the Ordinary Portland Cement type 1.

3.2.2 Fly ash

Fly ash was utilized to partially replace cement in percentage by weight of the total binder. According to TIS 2135, fly ash from Mae Moh power plant had a high CaO content while the BLCP fly ash had a low CaO content. Table 3.1 shows the chemical compositions of the Mae Moh and BLCP fly ashes. Table 3.2 shows the physical properties of the fly ashes used in this study.

Table 3.1 Chemical compositions of high CaO and low CaO fly ashes

Chemical compositions (%)	OPC Type I	Mae Moh fly ash (high CaO)	BLCP fly ash (low CaO)
SiO_2	18.93	36.18	61.09
Al_2O_3	5.51	20.21	20.35
Fe_2O_3	3.31	13.89	5.20
CaO	65.53	18.74	2.32
MgO	1.24	2.69	1.35
Na_2O	0.15	1.14	0.79
K_2O	0.31	2.29	1.36
SO_3	2.88	3.74	0.28
LOI	-	0.25	5.68
Free lime	0.87	2.36	0.19

Table 3.2 Physical properties of high CaO and low CaO fly ashes

Physical Properties	Ordinary Portland cement (OPC)	Mae Moh fly ash (high CaO)	BLCP fly ash (low CaO)
Specific gravity	3.15	2.57	2.17
Blaine fineness (cm^2/g)	3054	2254	2723
Median particle size (μm)	18.21	37.62	n/a

3.2.3 Ammonium salts

There are two types of ammonium salts used to contaminate fly ash in this research. Ammonium salts that are commonly found in the ammonia-contaminated fly ash are ammonium sulfate and ammonium carbonate. The concentrations of ammonia of 0, 100, 200, 400, 600, and 1000 ppm were varied for the investigation.

3.2.4 Fine aggregate

River sand was utilized as the fine aggregate. The river sand had a specific gravity of 2.61 g/cm^3 and an absorption of 1.03%. The gradation of the fine aggregate was in accordance with ASTM C 33.

3.3 Mixture proportions

Pastes and mortars with fly ash replacement were made by mixing them with ammonium salt solutions to evaluate the influence of ammonia concentration in different types of fly ash on properties of the pastes and mortars. The concentration of ammonia in the form of ammonium sulfate or ammonium carbonate solution was varied in the range of 0 to 1000 ppm. Table 3.3 shows the mix proportions of the tested pastes and mortars.

Table 3.3 Mix proportions to investigate the effects of ammonia concentration in different types of fly ash on properties of pastes and mortars

Test items	Paste/ mortar	Dimensions of specimens	Fly ash replacement ratio	w/b	s/b	Ammonia concentration (ppm)
Normal consistency	Paste	-	0.2	-	-	0, 100, 200, 400, 600, 1000
Compressive strength	Mortar	5 x 5 x 5 cm	0.3	0.5	2.75	600
Autoclave expansion	Paste	2.5 x 2.5 x 2.85 cm	0.2	NC	-	0, 100, 200, 400, 600, 1000
Sodium sulfate expansion	Mortar	2.5 x 2.5 x 28.5 cm	0.3	0.55	2.75	0, 100, 200, 400, 600, 1000
Autogenous Shrinkage	Mortar	2.5 x 2.5 x 28.5 cm	0.3	0.5	2.75	0, 100, 200, 400, 600, 1000

Remarks: w/b = water to binder ratio by weight, s/b = sand to binder ratio by weight

To investigate the effects of the contamination of fly ash with blended ammonium sulfate and ammonium carbonate on pastes and mortars, cement was partially replaced with fly ash and mixing them with water that contained the ammonium salt with varied concentrations. To see clearly the effects of blended ammonium salts, the highest ammonia concentration up to 1000 ppm was used. Table 3.4 shows the ammonia concentrations and ammonium salts ratios of pastes and mortars.

Table 3.4 Ammonia concentrations and ammonium salts ratios to investigate the effects of blended ammonium sulfate and ammonium carbonate on properties of pastes and mortars

Test items	Fly ash type	Ammonia concentration (ppm)	$(NH_4)_2SO_4$ - $(NH_4)_2CO_3$ ratio
Normal consistency Autoclave expansion Sodium sulfate expansion	High CaO and Low CaO	0 and 1000	0 - 1, 0.25 - 0.75, 0.5 - 0.5, 0.75 - 0.25 and 1 - 0

3.4 Methods to apply ammonia contamination to fly ash

The procedure of dissolving method of ammonium salts is shown in Figure 3.1. This method is to dissolve the ammonium salts into the water and use them as mixing water to be mixed with the binder. The amount of ammonium sulfate or ammonium carbonate added in the mixing water was calculated by using Equations (3.1) and (3.2). The process of dissolving ammonium salts into the water and mixing them with the binder has to be done as fast as possible in wind-free conditions. This is to avoid excessive ammonia gas release.

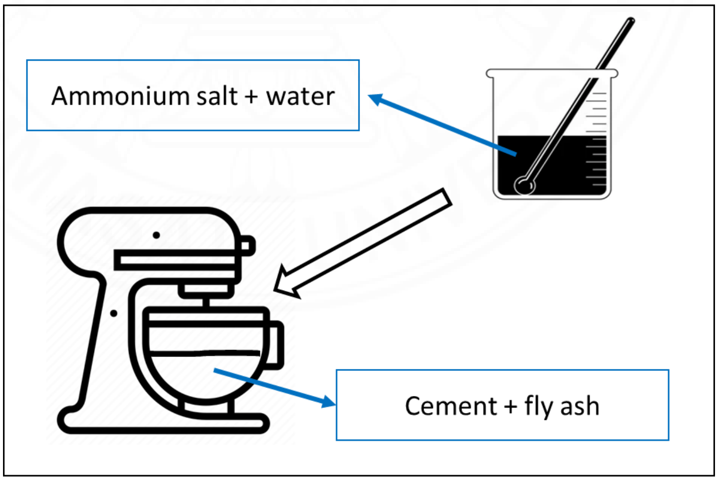


Figure 3.1 Dissolving method of ammonium salts

The amount of ammonium salts dissolved in the water were calculated using Equations (3.1) and (3.2) to get the concentration of ammonia in pastes and mortars.

$$W_{(NH_4)_2SO_4} = \frac{2\times132}{17}\times C_{NH_3}\times W_{FA} \quad (3.1)$$

$$W_{(NH_4)_2CO_3} = \frac{2\times96}{17}\times C_{NH_3}\times W_{FA} \quad (3.2)$$

Where, $W_{(NH_4)_2SO_4}$ = weight of ammonium sulfate (g)

$W_{(NH_4)_2CO_3}$ = weight of ammonium carbonate (g)

C_{NH_3} = NH_3 concentration in fly ash (ppm; mg/kg of fly ash)

W_{FA} = weight of fly ash in the mixture (g)

To investigate the effects of ammonia-contaminated fly ash with high free lime and SO_3 on properties of pastes and mortars, paste and mortar mixtures were prepared according to Table 3.5.

Table 3.5 Mix proportions to investigate the effects of ammonia contaminated fly ash with high free lime and SO_3 on properties of pastes and mortars

Test items	Fly ash type	Ammonia concentration (ppm)	Free lime content (%)	SO_3 content (%)
Normal consistency	High CaO and Low CaO	0 and 600	NF*, 4, 7	NS**, 5, 10
Compressive strength		0 and 600	NF*, 4, 7	NS**, 5, 10
Autoclave expansion		0 and 600	NF*, 4, 7	NS**, 5, 10
Sodium sulfate expansion		0 and 600	NF*, 4, 7	NS**, 5, 10

Remarks: NF* = 2.36% for high CaO fly ash and 0.19% for low CaO fly ash

NS** = 3.74% for high CaO fly ash and 0.28% for low CaO fly ash

3.5 Basic properties of mortar

The mortar samples used for the experiment are composed of Portland cement type I from a Thai cement company, fly ash from 2 power plants, Mae Moh Power plant, Lampang province and BLCP Power plant, Rayong province, sand, and water.

3.5.1 Flow test and water requirement

The mortar flow is related to workability. The change in flow shows the variability of materials that may not be observed by slump testing. The test was conducted following ASTM C 1437, the standard for flow of hydraulic cement mortar test method.

Figure 3.2 Flow tables, flow cones, tamping rod, and vernier caliper

3.5.2 Normal consistency

Normal consistency of pate is defined as the consistency (percentage of water) that allows the Vicat plunger to penetrate to a point 10 mm from the top of the Vicat mold. The typical range of values for dry cement is 22 to 30% by weight. Standard consistency is another term of normal consistency.

The normal consistency test was measured following ASTM C187. The tested paste mixtures had fly ash to binder ratio of 0.2. This method uses the Vicat apparatus to find a quantity of water to get exactly 10 mm of penetration, then continue testing for the initial and final setting times.

3.5.3 Setting times

This test was continued after getting the normal consistency value. The initial and final setting times were tested in accordance with ASTM C191.

3.5.4 Compressive strength

Ammonia was added into the mortar mixtures along with the non-ammonia contaminated fly ash by using ammonium salts which are ammonium sulfate and ammonium carbonate dissolved into the water following the specified concentration.

The 50x50x50 mm mortar cube samples were prepared following ASTM C109 and TIS 15 using cube molds. The samples were cured in high humidity for 24 hours and then in lime water after removing from the molds until the test ages of 3,7,28, and 91days.

Figure 3.3 Compressive strength test machine.

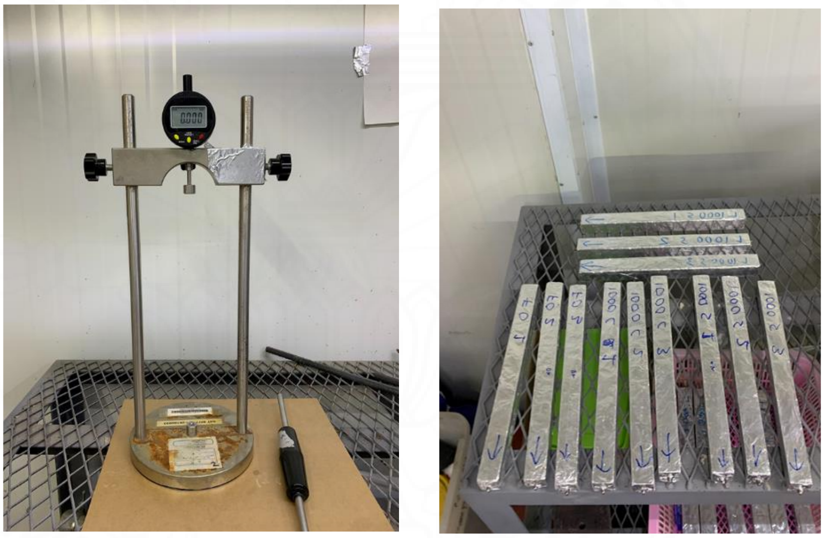
3.6 Durability properties of pastes and mortars

3.6.1 Autoclave expansion

In the autoclave expansion test, the sizes of prism paste specimens are 25x25x285 mm according to ASTM C151. The paste specimens at normal consistency were used. After 24 hours of casting, the specimens of autoclave expansion were demolded. After each sample was demolded, the initial measurement of sample length was conducted before being tested in the autoclave chamber. The test mixtures had a fly ash replacement of 20%.

3.6.2 Autogenous shrinkage

This test observes the macroscopic volume reduction, resulting in shrinkage right after the mortar’s final set (Tangtermsirikul, 2005). According to ASTM C1698, after the samples were removed from the molds, paraffin wax was applied to the samples, covered with plastic sheets, and then covered again with aluminum foils to prevent moisture loss to the environment. The covered specimens were taken to the controlled environment at 30°C with 70% relative humidity. Measurements of length change and weight loss were conducted for 120 days by measuring every two days for the first two weeks and then every week for the rest.



(a) Length comparator **(b)** Specimens

Figure 3.4 Length Comparator and autogenous shrinkage specimen

3.6.3 Total shrinkage

This test observes the length change due to combined autogenous and drying shrinkage. According to ASTM C596, the procedure and size of specimens are the same as the autogenous shrinkage test. When the specimens had been already cured for 24 hours, they were removed from the mold. The samples were immediately taken for the initial reading and weighting. The specimens were first cured in the water for seven days after removing the molds and then continued curing in a controlled environment with a temperature of 30 °C and relative humidity of 70 ± 5%. The length change and the weight loss were measured for 120 days by measuring every two days for the first two weeks and then every week for the rest.

Figure 3.5 Total Shrinkage specimens.

3.6.4 Sulfate expansion

Sulfate expansion test applied 25x25x285 mm mortar prisms with a w/b ratio of 0.55. Sodium sulfate was utilized to make a sulfate solution. The test method followed ASTM C1012. The samples were demolded after one day of casting and then cured in water until 28 days of age. At 28 days, the measurement of initial lengths of the samples was conducted and the specimens were subsequently immersed in a sodium sulfate ($NaSO_4$) solution, containing 50g of $NaSO_4$ per liter of water. Sodium sulfate solution was prepared 24 hours before use. The length comparator was used to measure the lengths of the samples at the specified ages of 1, 2, 3, 4, 8, 13, 15, and 16 weeks after the samples were submerged in the sodium sulfate solution.

CHAPTER 4

EFFECTS OF DIFFERENT AMMONIUM SALT TYPES AND CONCENTRATIONS ON PROPERTIES OF PASTES AND MORTARS

4.1 General

The effects of ammonium sulfate $(NH_4)_2SO_4$ and ammonium carbonate $(NH_4)_2CO_3$ with various concentrations on the properties of pastes and mortars are discussed in this chapter. In this investigation, two types of fly ash were used. High CaO fly ash produced by Mae Moh coal-fired power plant in Lampang and low CaO produced by BLCP coal-fired power plant in Rayong were used. Ammonia concentrations are 0, 100, 200, 400, 600, and 1000 ppm for ammonia-contaminated fly ash. The ammonia contamination was done by preparing each ammonium salt solution by dissolving the ammonium salt in water and using it as a part of mixing water. Several properties including basic and durability properties of paste and mortar mixtures containing fly ash with varying ammonia concentrations were considered. Normal consistency, autoclave expansion, sodium sulfate expansion, and autogenous shrinkage of mixtures containing fly ash contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ were conducted.

Effects of ammonia concentration were investigated on pastes and mortars containing FA with different ammonia concentrations by comparing the results for each concentration. A comparison of the pastes and mortars containing FA contaminated by ammonium sulfate $(NH_4)_2SO_4$ and ammonium carbonate $(NH_4)_2CO_3$ was conducted to investigate the effects of ammonium salt types. Pastes and mortars with OPC only and 0 ppm ammonia were used as the control mixtures in this study.

4.2 Normal consistency

The results of normal consistency of high CaO fly ash mixtures with different ammonia concentrations are shown in Figure 4.1. When ammonia concentrations are increased, the normal consistency of paste decreases for both mixtures containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ contaminated fly ash.

Less water is needed for $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ contaminated fly ash mixtures to achieve the normal consistency because the addition of ammonium sulfate and ammonium carbonate to cement paste results in dissolved ammonium ions (as demonstrated in Equations (4.1) and (4.2)) which can disturb the attractive intermolecular forces between water molecules. A decrease in the surface tension of water contributes to this reason. This reason is related to a previous study that water significantly lubricates the particles of cement, leading to a reduction of the force required for flow (Krerkchaiwan et al., 2017).

$$(NH_4)_2SO_4 \rightarrow 2NH_4^+ + SO_4^{2-} \quad (4.1)$$

$$(NH_4)_2CO_3 \rightarrow 2NH_4^+ + CO_3^{2-} \quad (4.2)$$

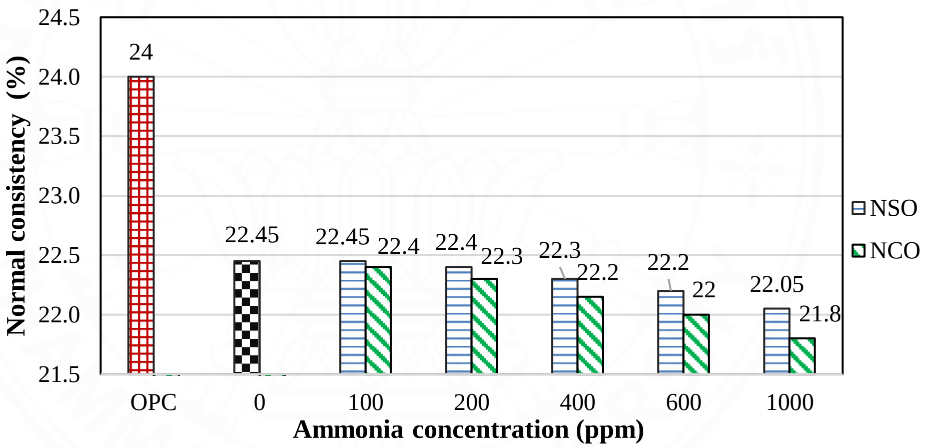


Figure 4.1 Normal consistency of high CaO fly ash pastes with different ammonia concentrations of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$

The results between normal consistency and ammonia concentration in the form of ammonium sulfate $(NH_4)_2SO_4$ and ammonium carbonate $(NH_4)_2CO_3$ on low CaO fly ash mixtures are illustrated in Figure 4.2. The normal consistency of pastes decreases as the ammonia concentration increases for mixtures containing fly ash contaminated with ammonium sulfate $(NH_3)_2SO_4$ or ammonium carbonate $(NH_4)_2CO_3$. $(NH_4)_2CO_3$ decreases normal consistency more significantly than $(NH_4)_2SO_4$ as shown in Figure 4.2.

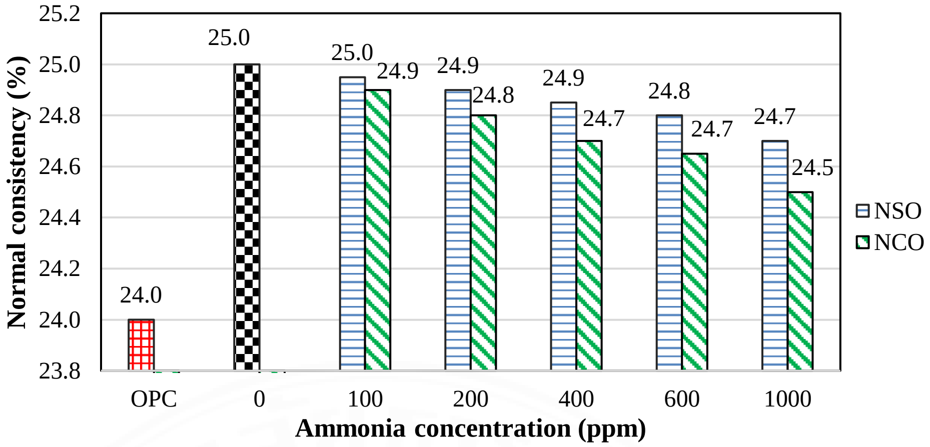


Figure 4.2 Normal consistency of low CaO fly ash pastes with different ammonia concentrations of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$

From Figures 4.1 and 4.2, it can be seen that $(NH_4)_2CO_3$ decreases normal consistency more significantly than $(NH_4)_2SO_4$ for both mixtures containing high CaO and low CaO fly ash. Normal consistency of paste without ammonia is higher than those with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ for both mixtures containing high CaO and low CaO fly ash. Ammonium salt addition to cement paste disturbs the attractive intermolecular forces between water molecules due to dissolved ammonium ions (reduces surface tension of water) and so, reduces the normal consistency of the pastes.

4.3 Autoclave expansion test

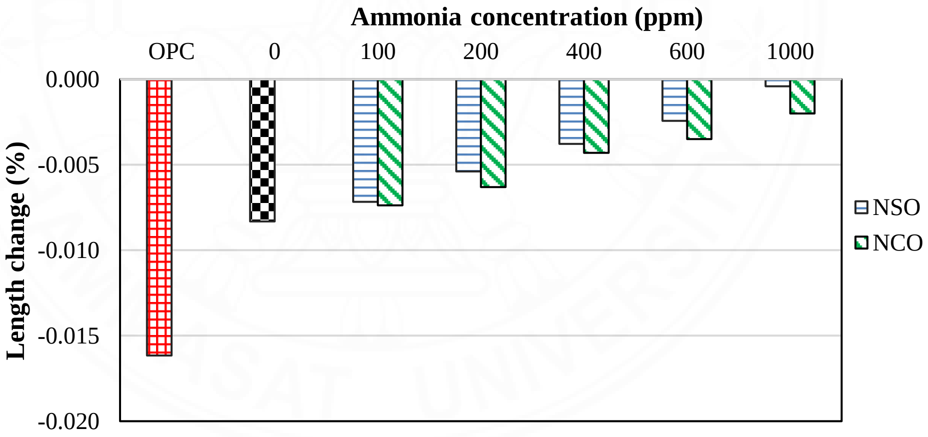
Figures 4.3a and 4.3b show the measured results of autoclave expansion of pastes containing high CaO and low CaO fly ash contaminated by ammonium sulfate $(NH_4)_2SO_4$ and ammonium carbonate $(NH_4)_2CO_3$ with 0-1000 ppm of ammonia concentration. The sample length after the autoclave test was measured by using a length comparator.

The relationship between autoclave expansion and ammonia concentration in the tested pastes containing high CaO and low CaO fly ash contaminated by ammonium sulfate $(NH_4)_2SO_4$ and ammonium carbonate $(NH_4)_2CO_3$ are illustrated in Figures 4.3. It can be observed that increasing the $(NH_4)_2SO_4$ concentration increases the autoclave expansion of ammonia contaminated high CaO and low CaO fly ash pastes. This may occur because the expansive products of $(NH_4)_2SO_4$ reactions are ettringite and gypsum, although the main cause of autoclave expansion is due to the reaction of free lime to form $Ca(OH)_2$. For $(NH_4)_2SO_4$, the liberated SO_4 ions into pore solution act as an initial sulfate source to react with hydration products to form gypsum. The addition of ammonium salt into the fly ash mixtures leads to the formation of gypsum and ettringite (as shown in Equations (4.3)-(4.5). The formation of gypsum is increased (Kumar & Rao, 1994), as shown in Equation (4.4). Gypsum partially reacts with alumina-bearing phases of cement paste, like tricalcium aluminate ($3CaO \cdot Al_2O_3$; C_3A), to generate ettringite, as illustrated in Equation (4.5). These products may be the reason for the increase in autoclave expansion of pastes with the ammonium salts.

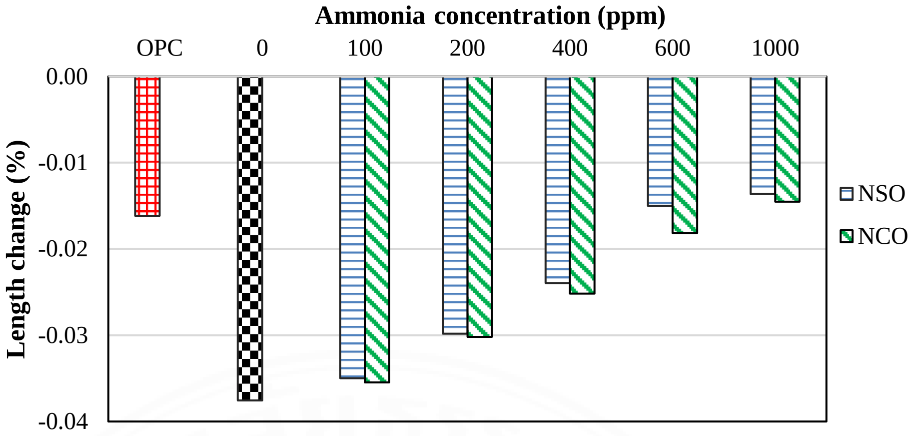
$$Ca(OH)_2+(NH_4)_2SO_4 \longrightarrow CaSO_4 \cdot 2H_2O + NH_3 \tag{4.3}$$

$$CaO \cdot SiO_2 \cdot 2H_2O+(NH_4)_2SO_4 \longrightarrow CaSO_4 \cdot 2H_2O + NH_3 + SiO_2 \tag{4.4}$$

$$3CaO \cdot Al_2O_3+3CaSO_4 \cdot 2H_2O+H_2O \longrightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot xH_2O + Ca(OH)_2 \tag{4.5}$$



(a) high CaO fly ash



(b) Low CaO fly ash

Figure 4.3 Autoclave expansion of high CaO and low CaO fly ash pastes with different ammonia concentrations of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$

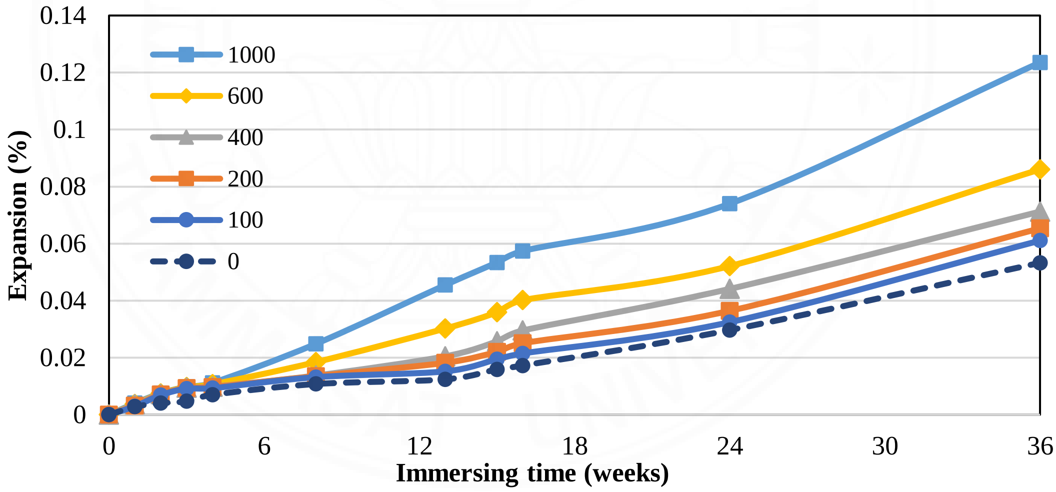
For ammonium carbonate, it can be seen that increasing the $(NH_4)_2CO_3$ concentration increases the autoclave expansion of the $(NH_4)_2CO_3$ contaminated fly ash pastes. The reason for the increase in autoclave expansion of paste is still not clear yet. The mechanism of the expansion of the $(NH_4)_2CO_3$ contaminated fly ash pastes in high pressure and high temperatures is still under investigation. Figure 4.3 shows that $(NH_4)_2SO_4$ reduces length change more significantly than $(NH_4)_2CO_3$ at the same concentration.

In Figure 4.3, the length change is below zero, which means all specimens are still in a state of shrinkage. However, when compared to the 0 ppm ammonia or non-ammonia fly ash mixture, the shrinkages of the mixtures with ammonium salts reduce, or the expansion is increased by the increase of ammonia concentration. The length changes from the autoclave test of pastes containing $(NH_4)_2CO_3$ contaminated high CaO or low CaO fly ash are not over the specified limit of 0.8%, as limited by ASTM C618.

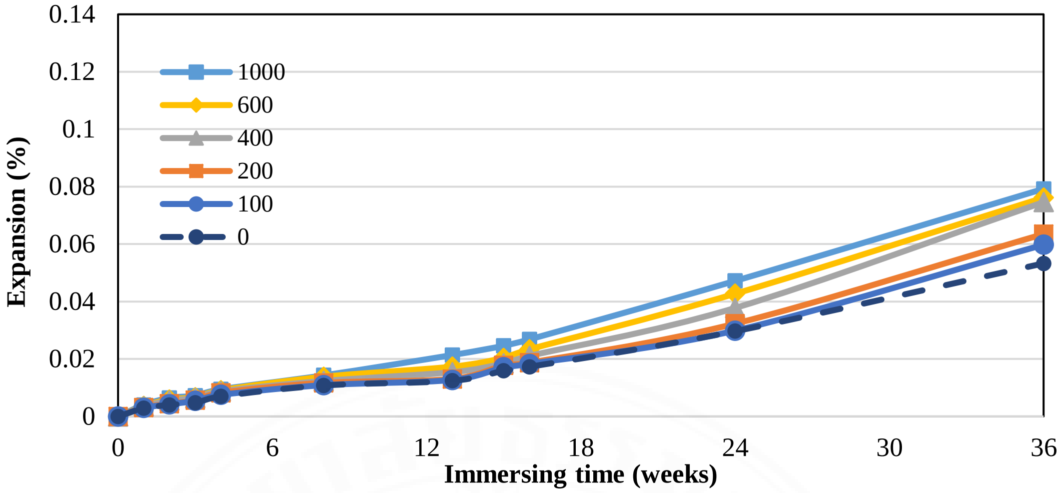
4.4 Sulfate expansion

The results of sulfate expansion of mortars containing high CaO and low CaO fly ash contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with ammonia concentrations of 0-1000 ppm are shown in Figures 4.4-4.6. For the sulfate expansion, 30% fly ash replacement was set for this test. The immersion period in sodium sulfate solution was up to 36 weeks.

The results of sulfate expansion of high CaO fly ash mortars contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are shown in Figure 4.4. From Figure 4.4(a), the sodium sulfate expansion of high CaO fly ash mortars increases when the ammonia concentration is increased. A significant increase can be seen from 600 ppm to 1000 ppm. Increasing the $(NH_4)_2SO_4$ concentrations increases the expansion of the mortar specimens due to the expansive products (gypsum and ettringite) that are formed by the reactions of the dissolved ammonium sulfate ions (as shown in Equations (4.3) - (4.5)). From Figure 4.4(b), it can be seen that increasing the $(NH_4)_2CO_3$ concentration increases the sulfate expansion of the $(NH_4)_2CO_3$ contaminated high CaO fly ash mortars. The hypothesis of expansion due to the increase of $(NH_4)_2CO_3$ concentration is probably the formation of $CaCO_3$. However, this still needs further investigation.



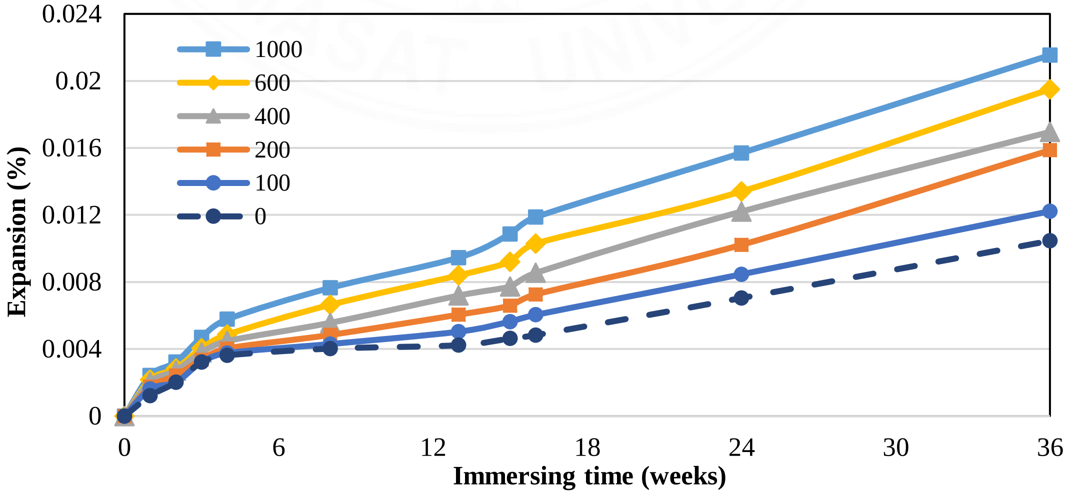
(a) $(NH_4)_2SO_4$



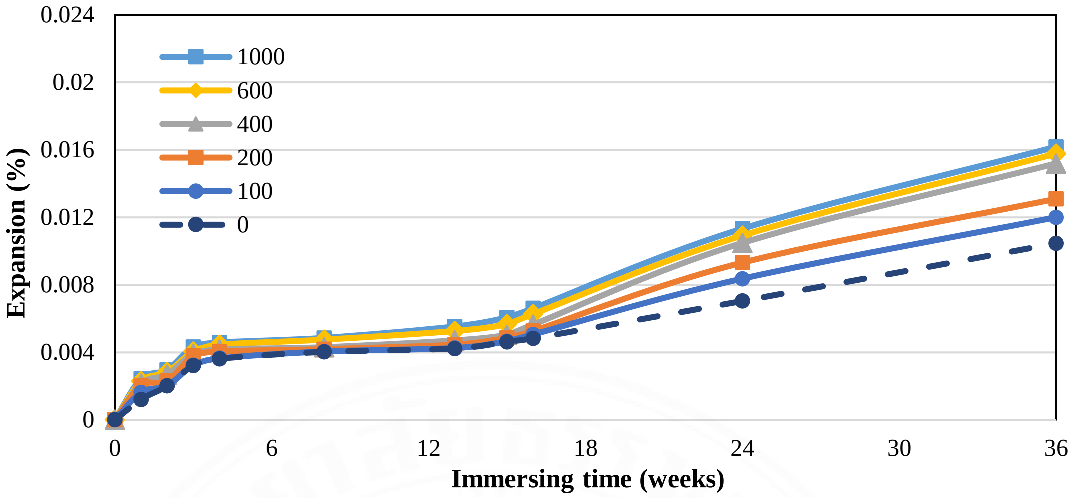
(b) $(NH_4)_2CO_3$

Figure 4.4 Sulfate expansion of high CaO fly ash mortars with different ammonia concentrations of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$

The results of the sulfate expansion of low CaO mortars contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are shown in Figure 4.5. The results show the same tendency to the high CaO fly ash. From Figure 4.5(a), it can be seen that the sodium sulfate expansion of low CaO fly ash mortars increases when the ammonia concentration is increased. From Figure 4.5(b), it can be seen that increasing the $(NH_4)_2CO_3$ concentration increases the sodium sulfate expansion of ammonia-contaminated fly ash mortars.



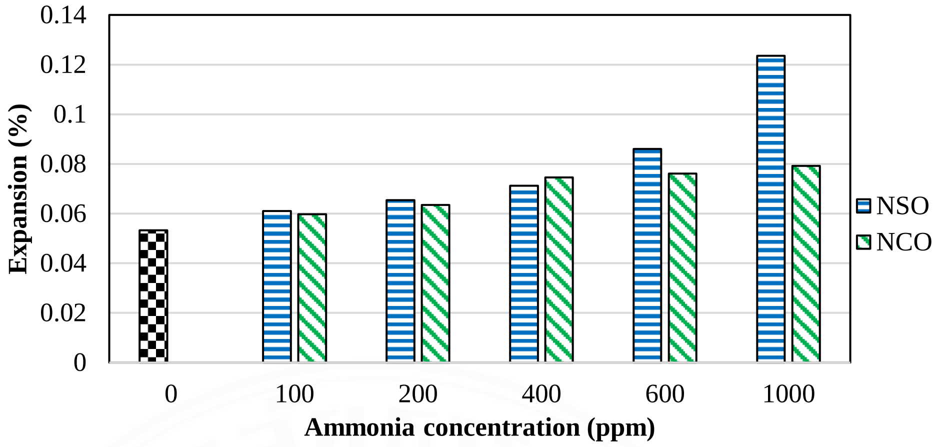
(a) $(NH_4)_2SO_4$



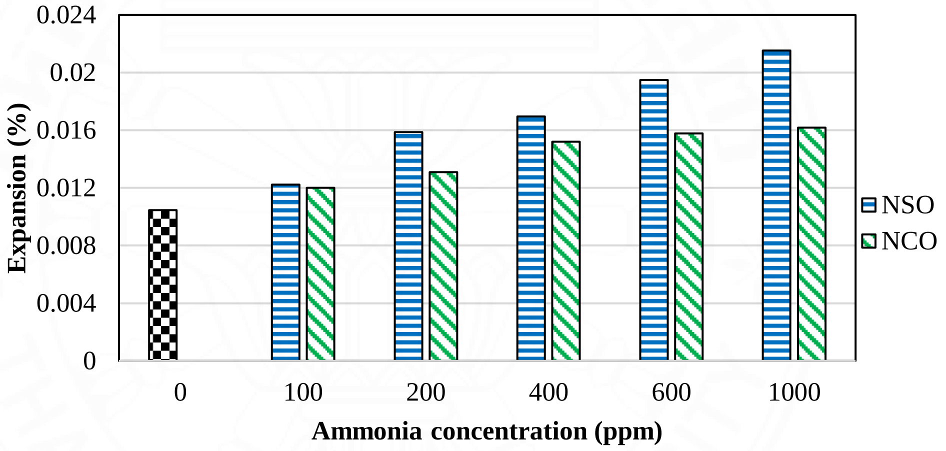
(b) $(NH_4)_2CO_3$

Figure 4.5 Sulfate expansion of low CaO fly ash mortars with different ammonia concentrations of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$

The comparison of sulfate expansion of mortars containing ACFA using ammonium sulfate and ammonium carbonate can be seen at 36 weeks of mortars immersion in a sodium sulfate solution. Figures 4.6(a) and 4.6(b) show the sulfate expansion of high CaO fly ash and low CaO fly ash mortars, respectively, with different $(NH_4)_2SO_4$ concentrations. From Figure 4.6(a), the results show that the expansion of high CaO fly ash mortars with $(NH_4)_2SO_4$ is higher than those with $(NH_4)_2CO_3$. It is due to the expansive products (gypsum and ettringite) that are formed by reactions of the dissolved ammonium sulfate ions present in the mixtures with $(NH_4)_2SO_4$ contaminated fly ash. Figure 4.6(b) shows a similar trend of the results of low CaO fly ash to that of the high CaO fly ash that the expansion of low CaO fly ash mixtures with $(NH_4)_2SO_4$ is higher than the mixtures with $(NH_4)_2CO_3$.



(a) high CaO fly ash



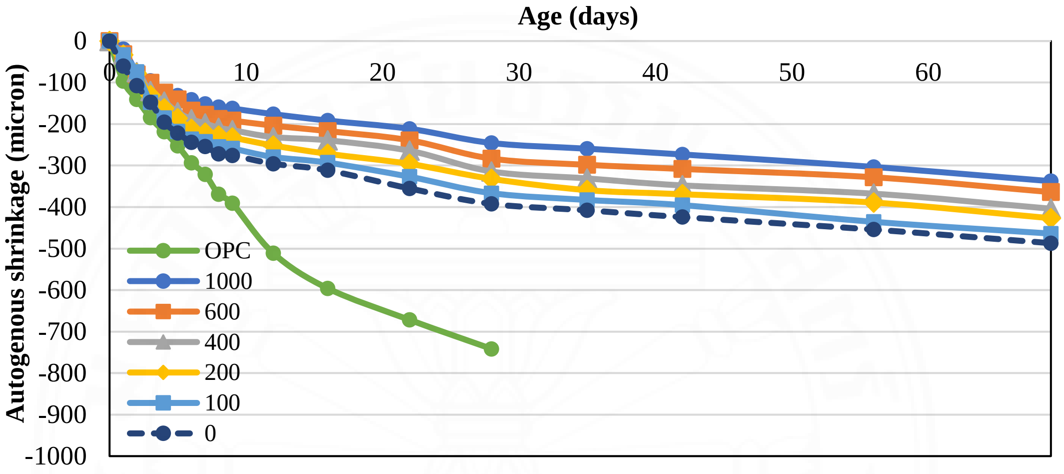
(b) low CaO fly ash

Figure 4.6 Sulfate expansion of high CaO and low CaO fly ash mortars with different ammonia concentrations of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at 36 weeks

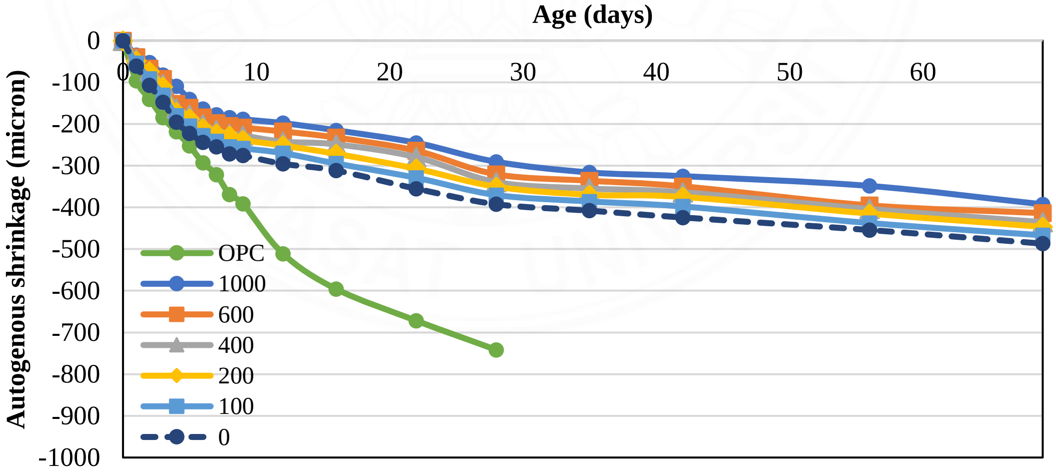
4.5 Autogenous shrinkage

The results of autogenous shrinkage of mortars containing high CaO and low CaO fly ash contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with concentrations of 0-1000 ppm are shown in Figures 4.7-4.9. The shrinkage was tested for up to 69 days. For the autogenous shrinkage tests, 30% fly ash replacement was fixed for all tested mixtures.

The results of the autogenous shrinkage of mortars containing high CaO fly ash contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are shown in Figure 4.7. From Figure 4.7(a), the autogenous shrinkage of high CaO fly ash mortars decreases when the ammonia concentration is increased. Increasing the $(NH_4)_2SO_4$ concentration decreases the shrinkage of mortar specimens due to the expansive products (gypsum and ettringite) that are formed by the reactions of the dissolved ammonium sulfate ions (as shown in Equations (4.3)-(4.5)). From Figures 4.7(b), it can be seen that increasing the $(NH_4)_2CO_3$ concentration decreases the autogenous shrinkage of the $(NH_4)_2CO_3$ contaminated fly ash mortars.



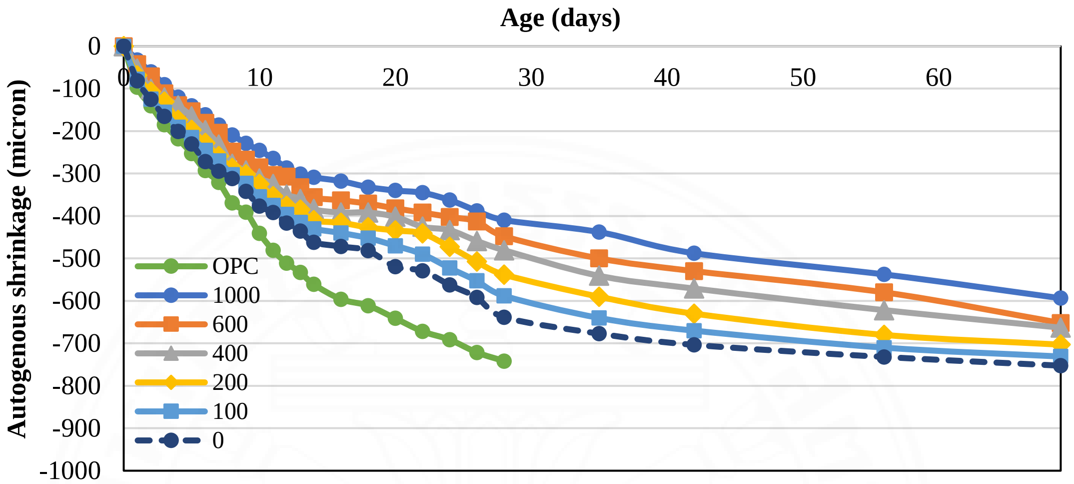
(a) $(NH_4)_2SO_4$



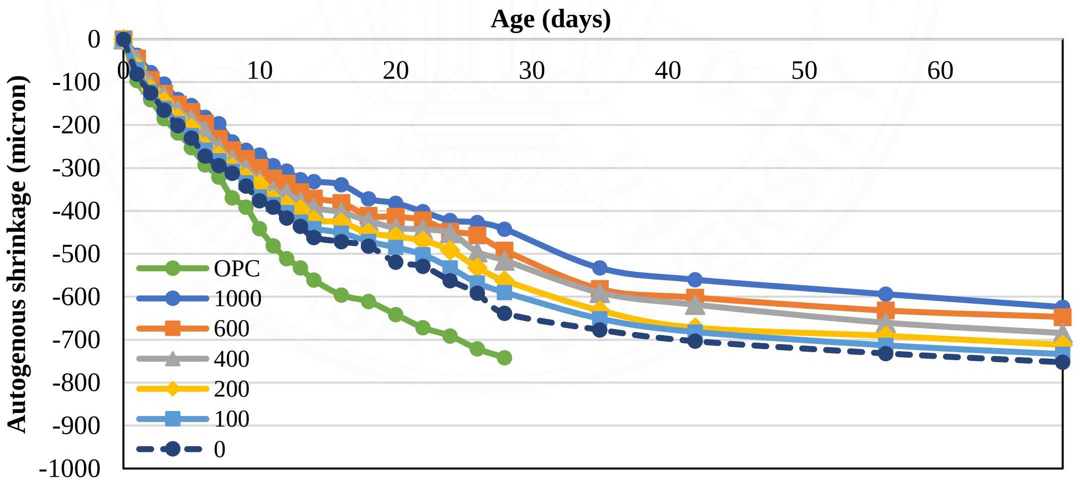
(b) $(NH_4)_2CO_3$

Figure 4.7 Autogenous shrinkage of high CaO fly ash mortars with different ammonia concentrations of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$

The results of the autogenous shrinkage of mortars containing low CaO fly ash contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are shown in Figure 4.8. The results show the same tendency as the results of the high CaO fly ash mortars. From Figures 4.8(a) and 4.8(b), the autogenous shrinkage of the low CaO fly ash mortars decreases when the ammonia concentration is increased.



(a) $(NH_4)_2SO_4$

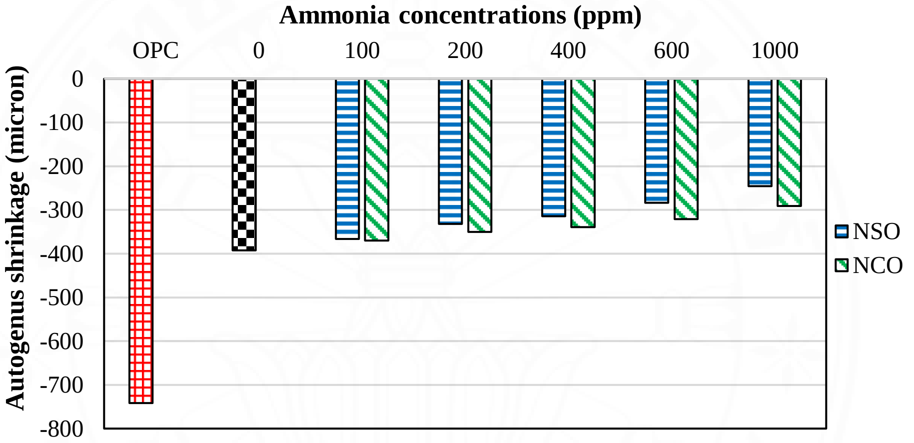


(b) $(NH_4)_2CO_3$

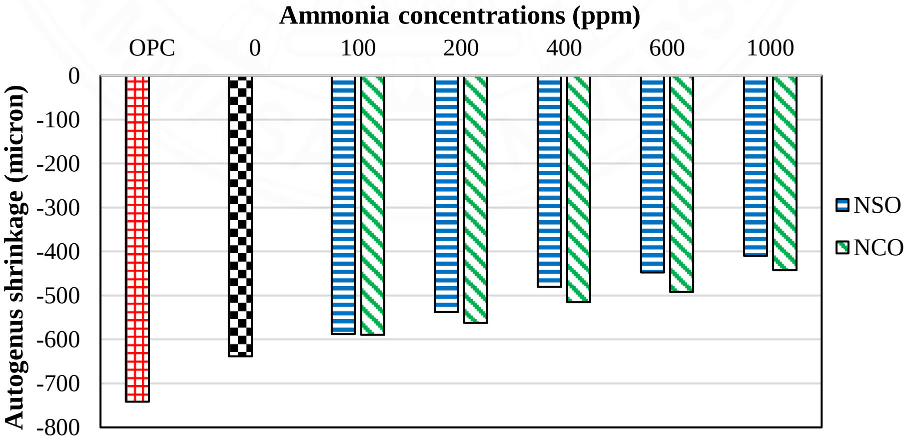
Figure 4.8 Autogenous shrinkage of low CaO fly ash mortars with different ammonia concentrations of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$

The comparison of autogenous shrinkage of mortars containing ACFA with ammonium sulfate and ammonium carbonate was conducted at 28 days. Figure 4.9

shows the autogenous shrinkage of high CaO fly ash and low CaO fly ash mortars with different ammonia concentrations using ammonium sulfate and carbonate. From Figure 4.9(a), the shrinkage of the mortar mixtures containing high CaO fly ash with $(NH_4)_2SO_4$ is lower than those with $(NH_4)_2CO_3$, and it is due to the expansive products (gypsum and ettringite) that are formed by reactions of the dissolved ammonium sulfate ions. Figure 4.9(b) shows a similar trend of results of low CaO fly ash to that of the high CaO fly ash that the shrinkage of mortars containing low CaO fly ash with $(NH_4)_2SO_4$ is lower than those with $(NH_4)_2CO_3$.



(a) High CaO fly ash



(b) Low CaO fly ash

Figure 4.9 Autogenous shrinkage of high CaO fly ash mortars with different ammonia concentrations of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$

CHAPTER 5

EFFECTS OF BLENDED $(NH_4)_2SO_4$ AND $(NH_4)_2CO_3$ ON PROPERTIES OF PASTES AND MORTARS

5.1 General

The effects of blended ammonium sulfate $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ contamination in fly ash with various concentrations on the properties of pastes and mortars are discussed in this chapter. There are two types of fly ash that are used in this research, high CaO fly ash from the Mae Moh power plant and low CaO fly ash from BLCP power plant. For blended ammonium salts, the $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ solutions were prepared with an ammonia concentration of 1000 ppm only (mg of NH_3 per kg of fly ash) for normal consistency and autoclave expansion. For sulfate expansion tests, the $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ solutions were prepared with an ammonia concentration of 600 ppm (mg of NH_3 per kg of fly ash). The blending ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ were 0, 0.25, 0.5, 0.75, and 1.

5.2 Normal consistency

Figure 5.1 shows normal consistency values of the tested mixtures with blended ammonium salts with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in high CaO and low CaO fly ashes. For the normal consistency test, 20% fly ash replacement was used. Normal consistency values of pastes containing $(NH_4)_2CO_3$ are lower than those containing $(NH_4)_2SO_4$. For blended ammonium salts with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, it can be seen that increasing the proportion of $(NH_4)_2CO_3$ decreases the normal consistency of both high CaO and low CaO fly ash pastes. On the other hand, an increasing proportion of ($(NH_4)_2SO_4$ increases the normal consistency of the mixtures.

The results show that normal consistency values of pastes containing fly ash with blended $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are in between the values of pastes containing fly ash with single ammonium salt i.e. pure $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$. The presence of ammonium ions in water can interrupt the attractive intermolecular forces between the water molecules. The surface tension of both ammonium salt solutions is lower than that of pure water. When compared between $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ solutions, the surface tension of $(NH_4)_2CO_3$ solution is lower than that of $(NH_4)_2SO_4$ solution. Therefore, water lubricates cement particles better, which leads to decreasing the required force for flow (Krerkchaiwan et al., 2017). The effects of blended $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ on normal consistency properties are similar in high CaO and low CaO fly ash pastes.

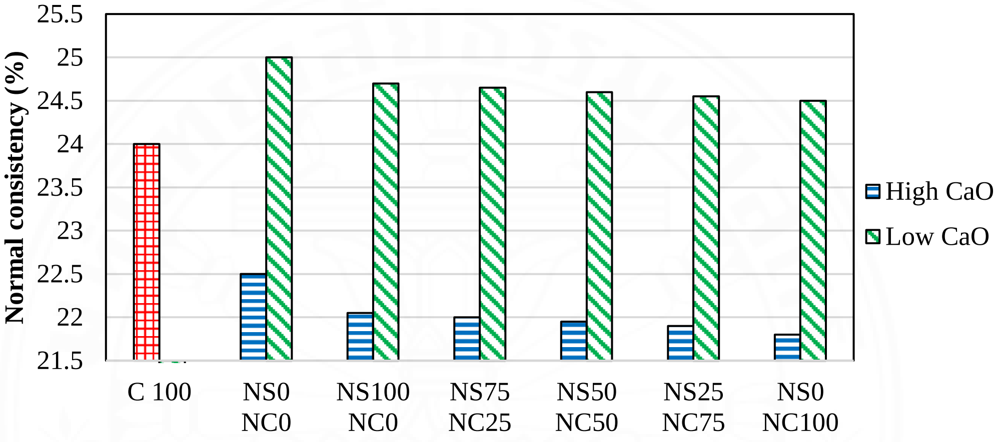


Figure 5.1 Normal consistency of high CaO and low CaO fly ash pastes with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 1000 ppm

5.3 Autoclave expansion

Figure 5.2 shows the length change from the autoclave test of the high CaO and low CaO fly ash pastes containing blended ammonium salts with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$. For the autoclave expansion test, 20% fly ash replacement was used. As all of the tested paste mixtures do not show positive values of the % length change (expansion), here, the higher autoclave expansion is represented by the lower shrinkage percentage. Autoclave expansion of fly ash paste containing pure $(NH_4)_2SO_4$ is higher than that containing pure $(NH_4)_2CO_3$ (showing lower shrinkage). For blended ammonium salts with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, increasing the concentration of $(NH_4)_2SO_4$ increases the autoclave expansion of the pastes (expressed by lower shrinkage). On the other hand, increasing the concentration of $(NH_4)_2CO_3$ decreases the expansion of blended ammonium salt pastes (expressed by higher shrinkage). The results show that autoclave expansion of high CaO fly ash pastes with the blended $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ show the trend to be in between the values of pastes with pure $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$. It is noted that the test results of NS0NC100 may need to be varied as they do not follow the trend of the rests. The autoclave expansion of low CaO fly ash pastes with the blended $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are lower than fly ash pastes with pure $(NH_4)_2SO_4$ and pure $(NH_4)_2CO_3$ (expressed by higher shrinkage).

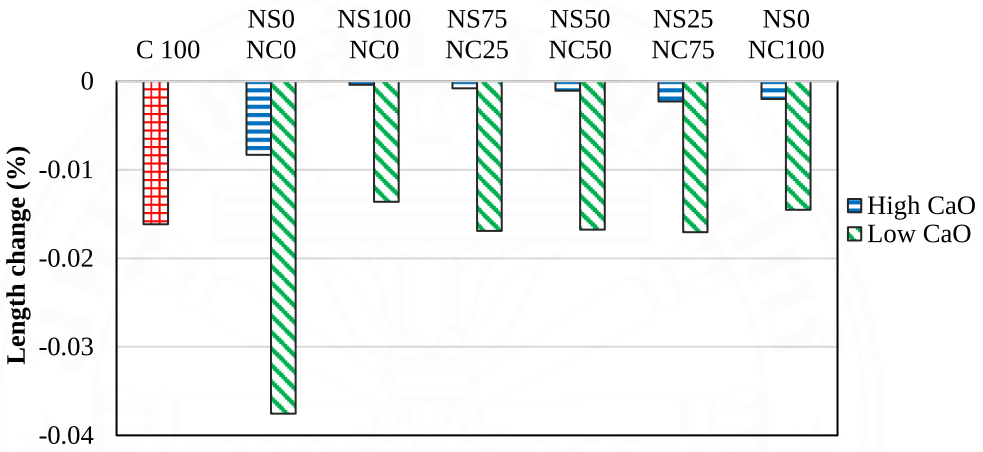


Figure 5.2 Autoclave expansion of high CaO and low CaO fly ash pastes with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 1000 ppm

5.4 Sulfate expansion

Figures 5.3 and 5.4 show the comparison between sulfate expansion results of high CaO and low CaO fly ash mortars containing ammonium salts with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ and the control mortar without ammonium salt up to 36 weeks of immersion in a sodium sulfate solution. For the sulfate expansion test, 30% fly ash replacement, 0.55 water to binder ratio, and 2.75 sand to binder ratio were applied.

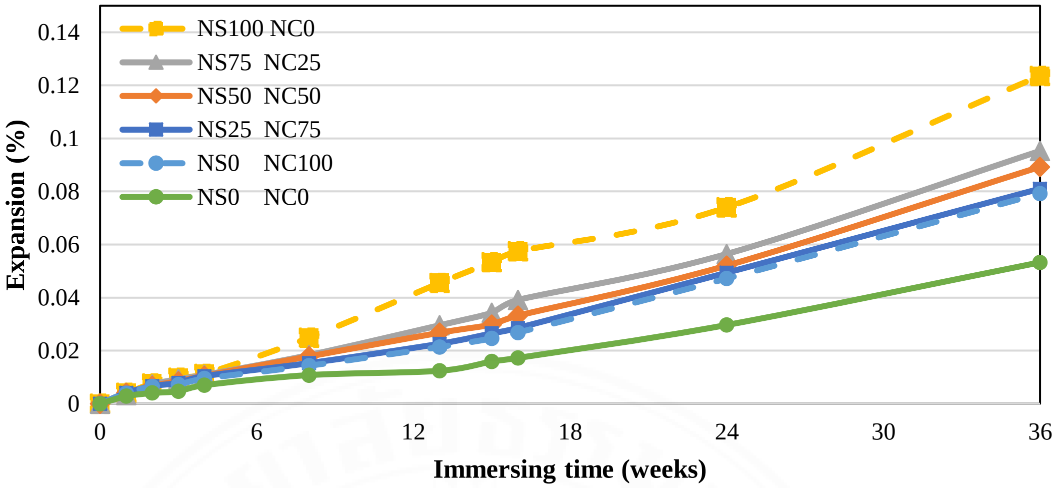


Figure 5.3 Sulfate expansion of high CaO fly ash mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 600 ppm

Expansion of mortar containing only $(NH_4)_2SO_4$ is higher than that containing only $(NH_4)_2CO_3$. For blended ammonium salts with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, increasing the concentration of $(NH_4)_2SO_4$ increases the expansion of the mortars. On the other hand, increasing the concentration of $(NH_4)_2CO_3$ decreases the expansion of blended ammonium salt mortars.

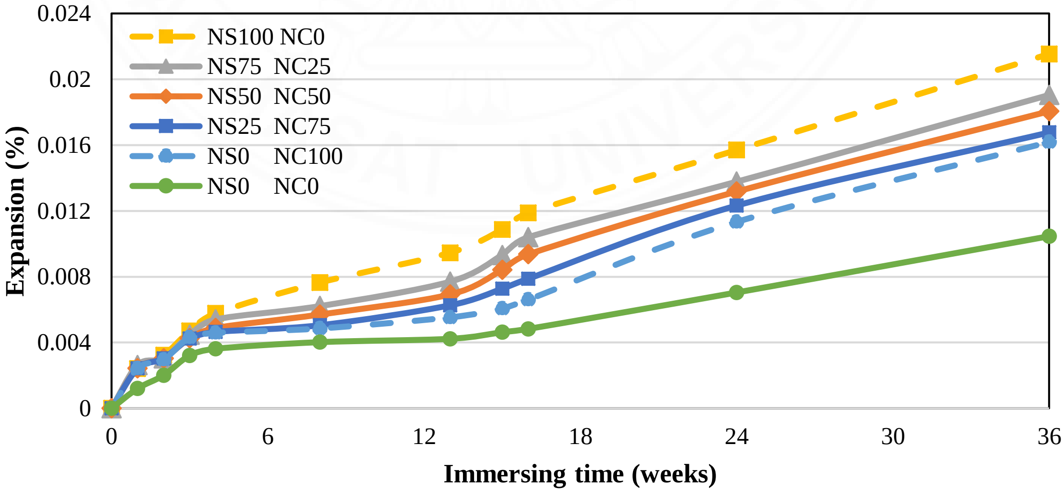


Figure 5.4 Sulfate expansion of low CaO fly ash mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 600 ppm

Figure 5.5 compares the sulfate expansion of mixtures of blended ammonium salts at 36 weeks of immersion. Figure 5.5 shows that the expansion results of mixtures with a combination of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are in between the results of the mortar specimens with the single ammonium salt (pure ammonium sulfate $(NH_4)_2SO_4$ and pure ammonium carbonate $(NH_4)_2CO_3$).

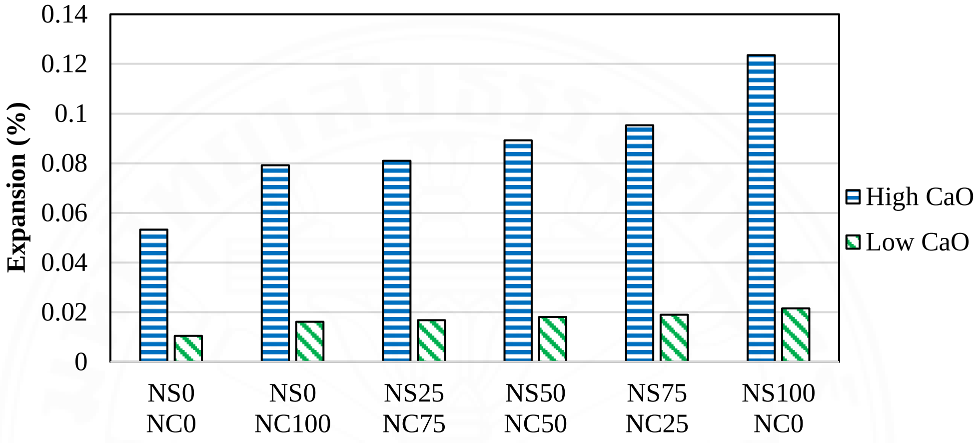


Figure 5.5 Sulfate expansion of high CaO and low CaO fly ash mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 600 ppm at 36 weeks of immersion

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CHAPTER 6

EFFECTS OF AMMONIUM SALTS WITH DIFFERENT FLY ASH TYPES ON PROPERTIES OF PASTES AND MORTARS

6.1 General

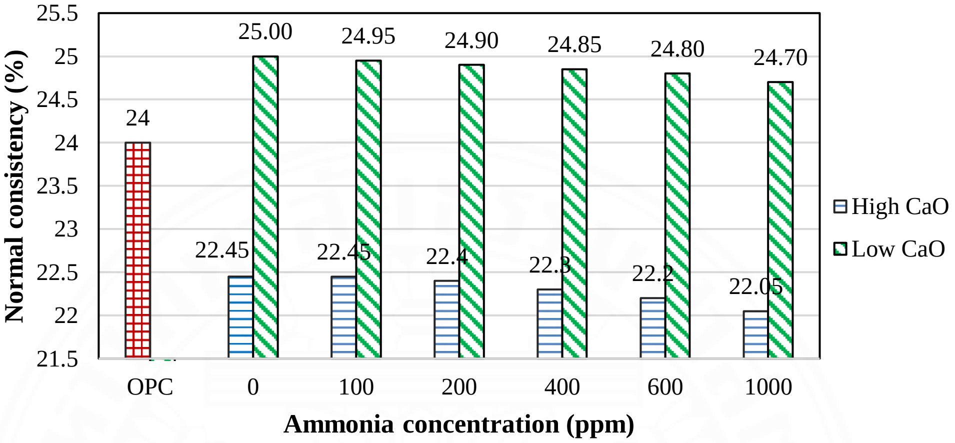
The effects of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in various concentrations with different fly ash types on the properties of pastes and mortars are discussed in this chapter. There are two types of fly ash that are used in this study, high CaO fly ash from the Mae Moh power plant and low CaO fly ash from the BLCP power plant. Ammonia concentrations are 0, 100, 200, 400, 600, and 1000 ppm (mg of NH_3/ kg of fly ash) for the ammonia-contaminated fly ash. The ammonia contamination was done by preparing ammonium salt solutions with dissolved ammonium salts in water and used them as a part of mixing water. Some basic and durability properties of ammonia contaminated fly ash mixtures with various concentrations of ammonium sulfate and ammonium carbonate were considered. Normal consistency, autoclave expansion, sodium sulfate expansion, and autogenous shrinkage were tested and compared for the effects of ammonium salts between high CaO and low CaO fly ash.

6.2 Normal consistency

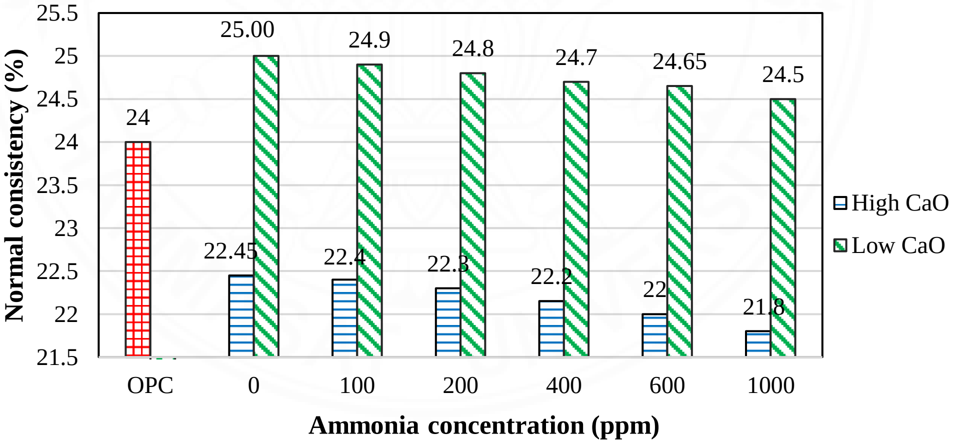
The results of normal consistency of pastes containing high CaO and low CaO fly ashes contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with ammonia concentrations of 0-1000 ppm are shown in Figure 6.1. The normal consistency of the paste decreases when the ammonia concentration is increased for both of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$. It can be seen that both of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ show the same behavior for high CaO and low CaO fly ash mixtures.

Less water is needed to achieve a normal consistency value, due to the addition of ammonium sulfate and ammonium carbonate to the pastes. The reasons are the same as those explained in section 4.2 (as shown in Equations (4.1) and (4.2)).

It is obvious that the normal consistency of pastes with the high CaO fly ash is lower than that of the pastes with the low CaO fly ash for all ammonium salt contamination types and levels, and it has the same trend as the pastes without ammonium salt. It is generally known that the high CaO fly ash from Mae Moh has better particle shape and lower LOI content than the low CaO fly ash from BLCP, causing lower water requirement and so lower normal consistency.



(a) $(NH_4)_2SO_4$



(b) $(NH_4)_2CO_3$

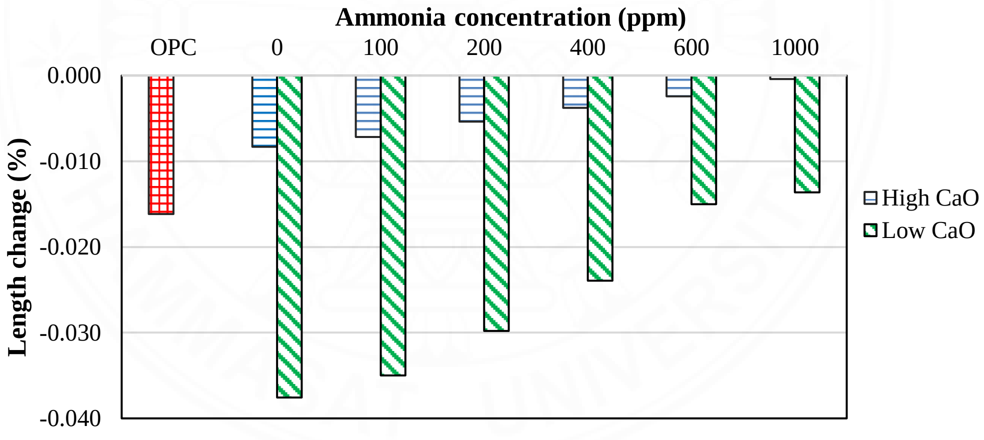
Figure 6.1 Normal consistency of high CaO and low CaO fly ash pastes with different ammonia concentrations using $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$

6.3 Autoclave expansion

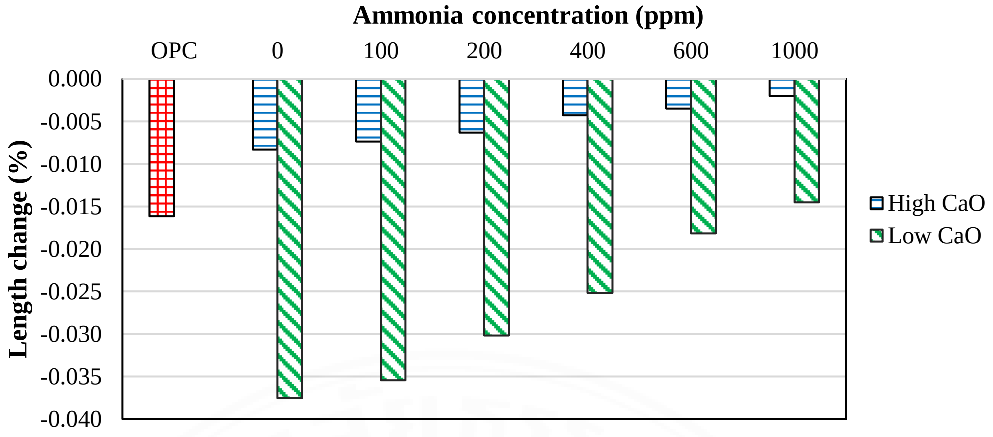
The results of autoclave expansion of pastes containing high CaO and low CaO fly ash contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with ammonia concentrations of 0-

1000 ppm are shown in Figure 6.2. Again, as all of the tested paste mixtures do not show positive values of percentage length change (expansion), here, the higher autoclave expansion is represented by the lower shrinkage percentage. The autoclave expansion increases when the ammonia concentration is increased for both $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$. It can be seen that both $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ cause the same behavior to high CaO and low CaO fly ash pastes.

Figure 6.2 show that all mixtures are in a state of shrinkage. Mixtures with ammonia contaminated fly ash have lower shrinkage (larger expansion) than those without ammonia. Higher concentration of ammonia results in lower shrinkage (larger expansion) among the pastes with ammonia contaminated fly ash, which means that ammonia causes the expansion of the pastes. The results show that ammonia-contaminated fly ash by using ammonium sulfate and ammonium carbonate increases the autoclave expansion for both high CaO and low CaO fly ashes.



(a) $(NH_4)_2SO_4$

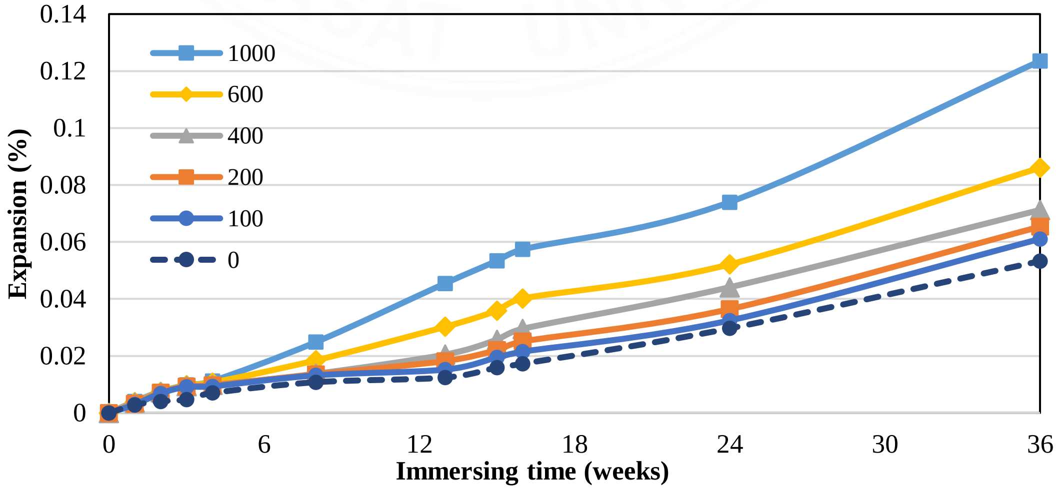


(b) $(NH_4)_2CO_3$

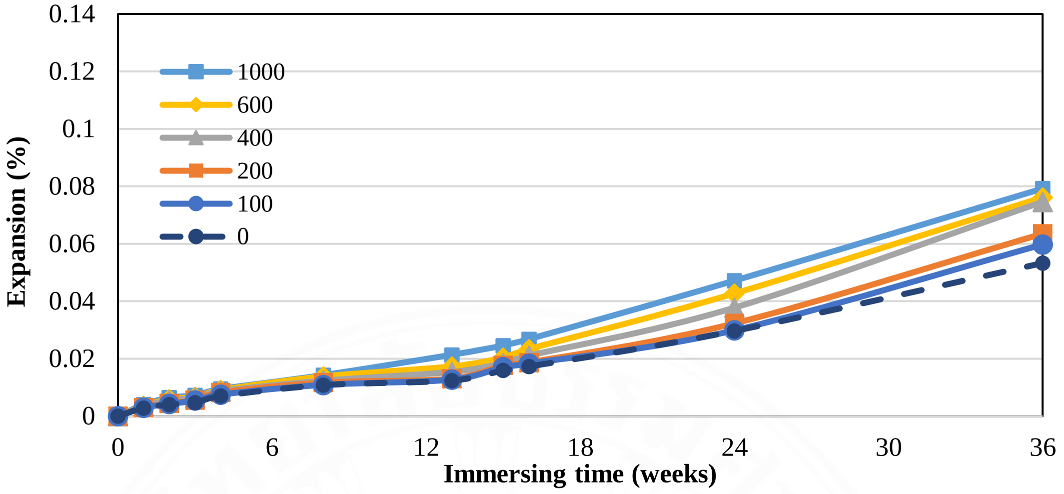
Figure 6.2 Autoclave expansion of high CaO and low CaO fly ash pastes with different $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ concentrations

6.4 Sulfate expansion

The results of sulfate expansion of mortars containing high CaO and low CaO fly ash contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with ammonia concentrations of 0-1000 ppm are shown in Figures 6.3 and 6.4. The immersion period in sodium sulfate solution was up to 36 weeks. The sulfate expansion of the mortars increases when the ammonia concentration is increased for both of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$. It can be seen that both of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ result in the same behavior for high CaO and low CaO fly ash mortars.

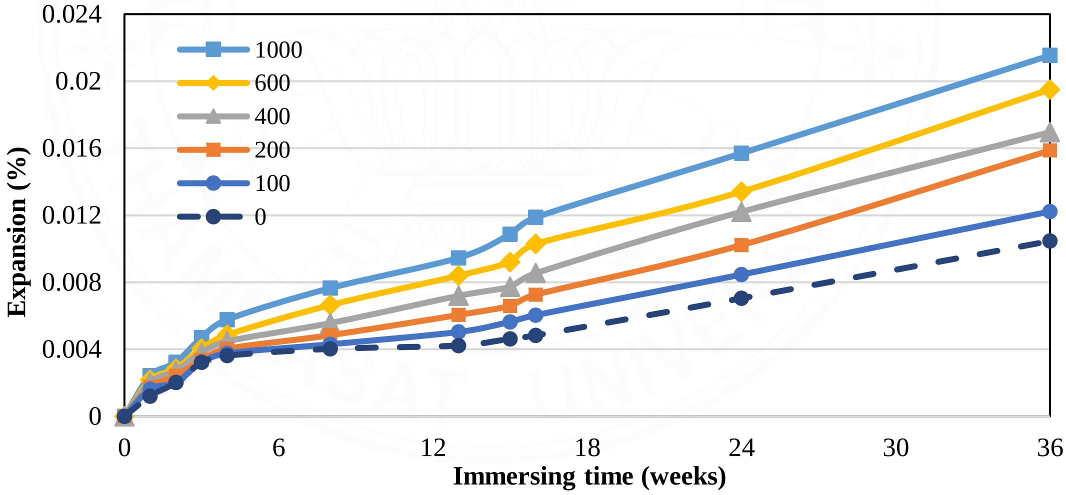


(a) $(NH_4)_2SO_4$

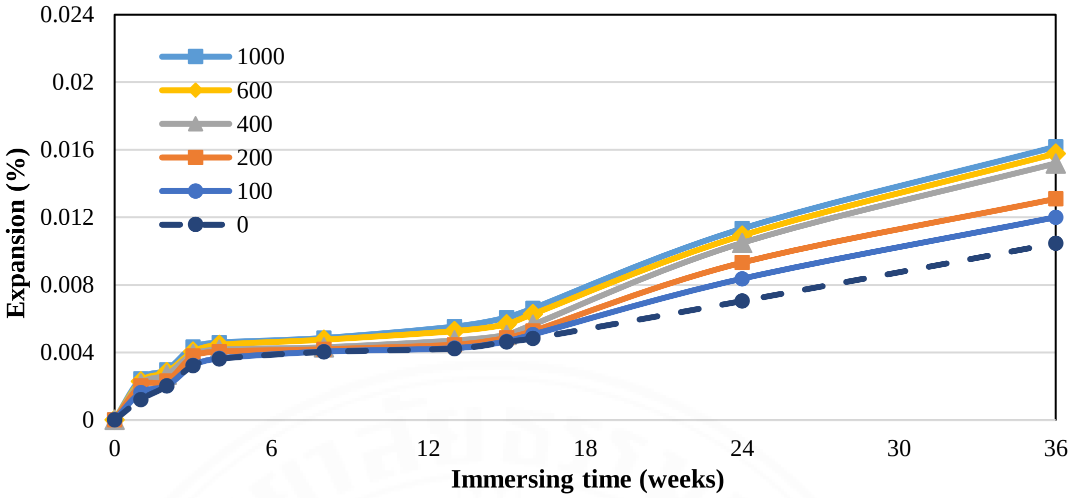


(b) $(NH_4)_2CO_3$

Figure 6.3 Sulfate expansion of high CaO fly ash mortars with different ammonia concentrations using $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$



(a) $(NH_4)_2SO_4$

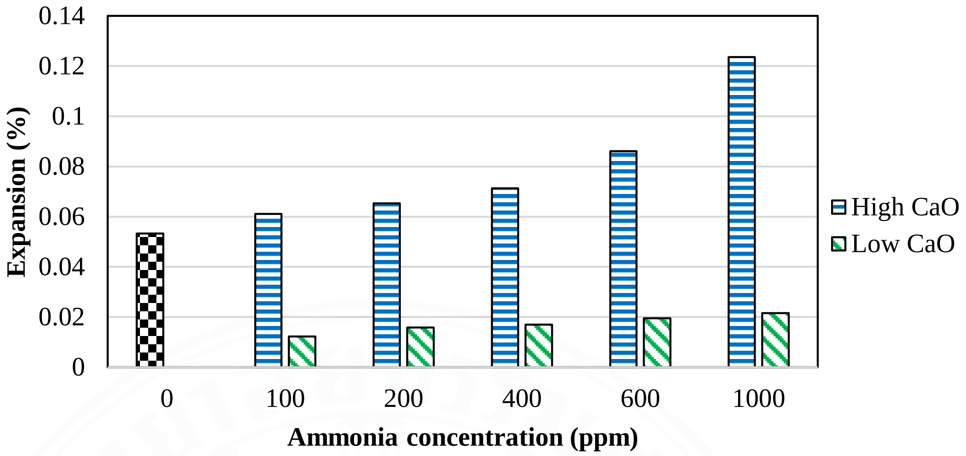


(b) $(NH_4)_2CO_3$

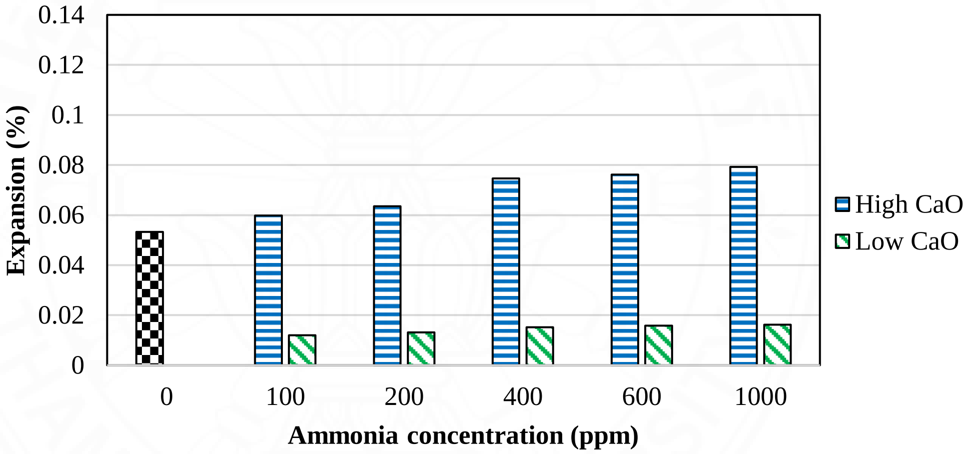
Figure 6.4 Sulfate expansion of low CaO fly ash mortars with different ammonia concentrations using $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$

A clear comparison of sulfate expansion of mortars containing ACFA using ammonium sulfate can be seen at 36 weeks of mortar immersion in a sodium sulfate solution. Figure 6.5(a) shows the sulfate expansion of high CaO and low CaO fly ash mortars with different ammonia concentrations using ammonium sulfate. The results show that the expansion of high CaO fly ash mixtures with or without ammonia is higher than low CaO fly ash mixtures, due to higher CaO, free lime and SO_3 contents of the high CaO fly ash. The increase of ammonia contamination concentration of fly ash leads to the increase in the sodium sulfate expansion of both high CaO and low CaO fly ash mortars. The sulfate expansion due to $(NH_4)_2SO_4$ on high CaO fly ash is more significant than on low CaO fly ash, and it can be clearly seen at the 1000 ppm concentration.

Figure 6.5(b) shows the sulfate expansion of high CaO and low CaO fly ash mortars with different ammonia concentrations using ammonium carbonate. The results show that the expansion of high CaO fly ash mixtures with or without ammonia is higher than low CaO fly ash mixtures. The increase of ammonia contamination concentration of the fly ash leads to the increase in the sodium sulfate expansion of both high CaO and low CaO fly ash mortars. The sulfate expansion due to $(NH_4)_2CO_3$ on high CaO fly ash is also more significant than on low CaO fly ash.



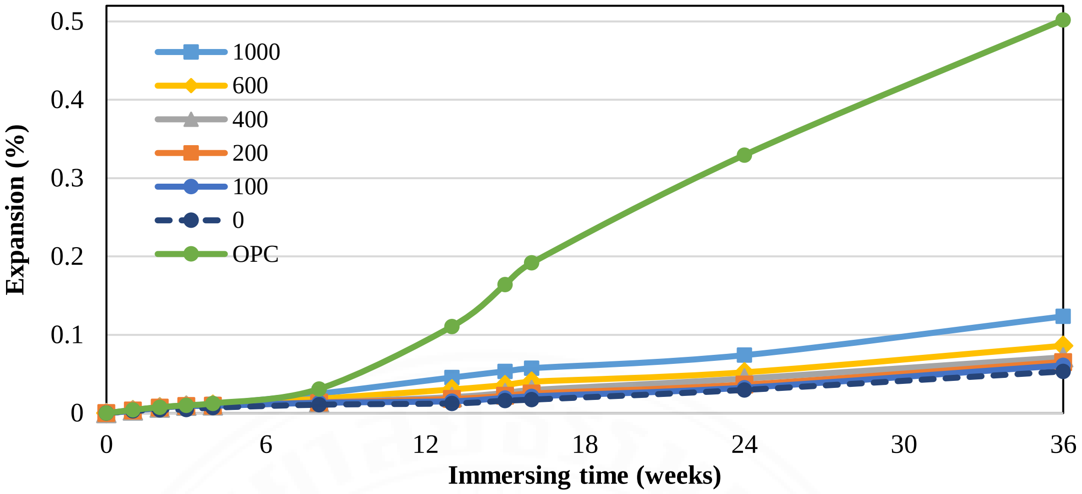
(a) $(NH_4)_2SO_4$



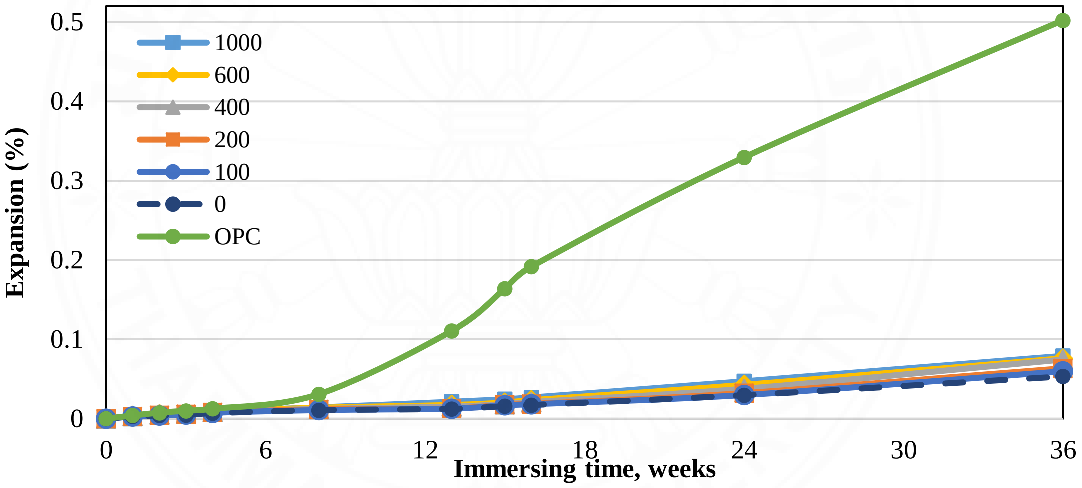
(b) $(NH_4)_2CO_3$

Figure 6.5 Sulfate expansion of high CaO and low CaO fly ash mortars with different ammonia concentrations using $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at 36 weeks

From Figures 6.6 and 6.7, it can be seen that sulfate expansion of mortars containing high CaO fly ash with ammonia is higher than low CaO fly ash mortars but still far lower than mortars with OPC only.

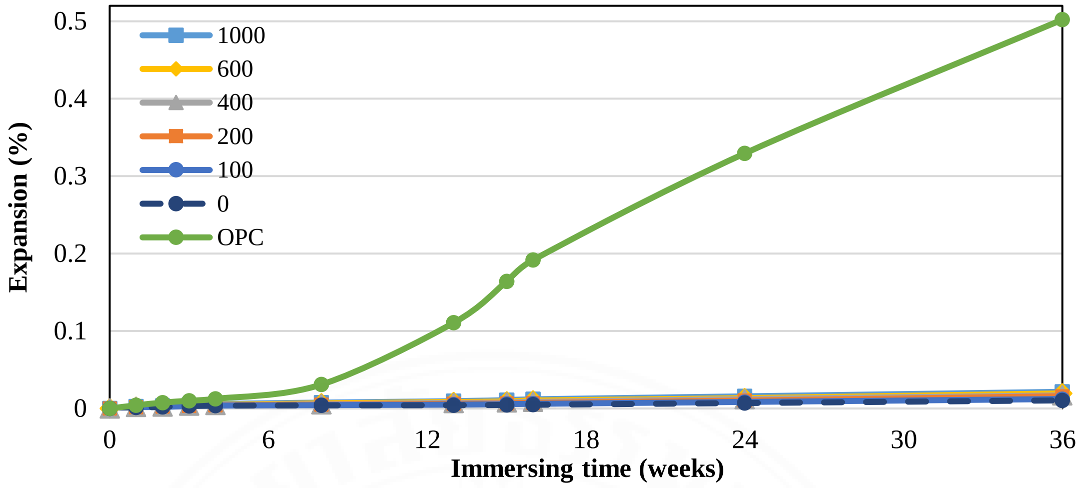


(a) $(NH_4)_2SO_4$

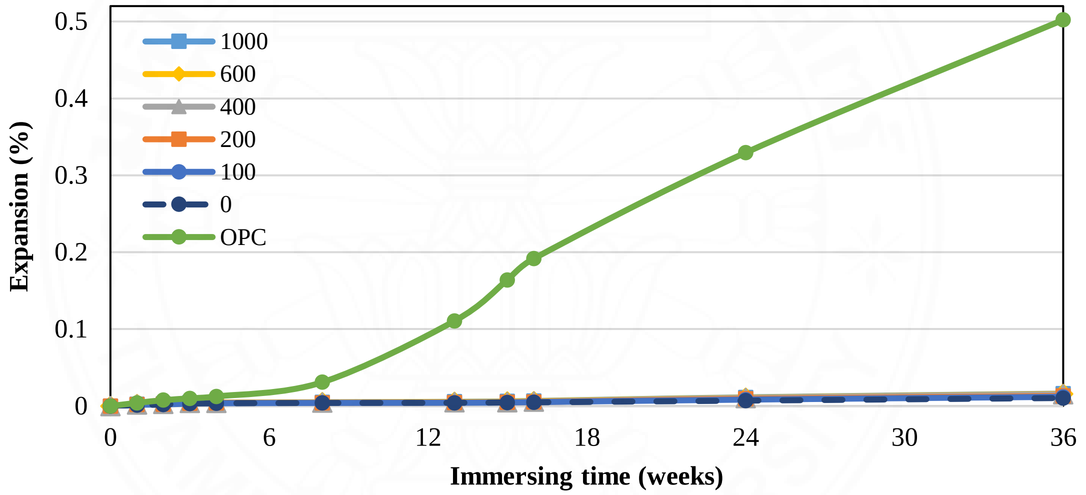


(b) $(NH_4)_2CO_3$

Figure 6.6 Sulfate expansion of high CaO fly ash mortars with different ammonia concentrations using $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ compared to OPC-only mortars



(a) $(NH_4)_2SO_4$



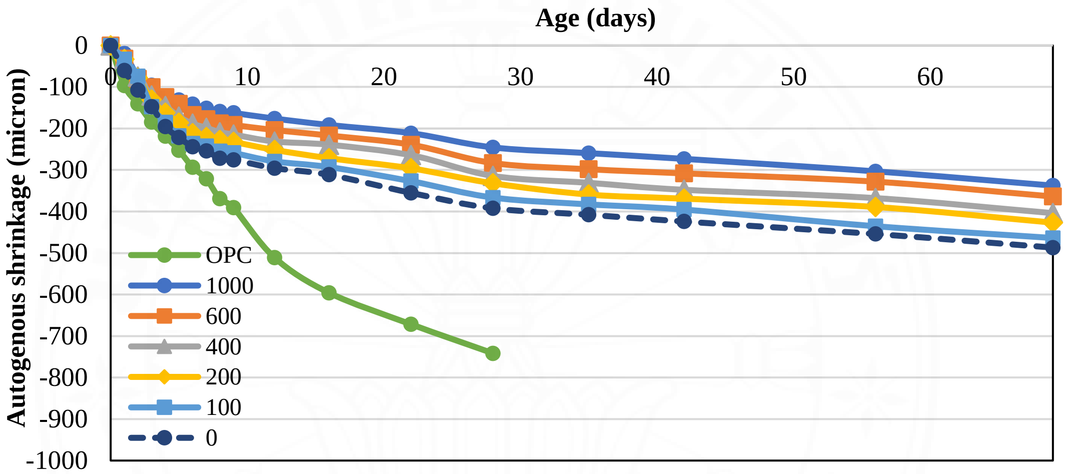
(b) $(NH_4)_2CO_3$

Figure 6.7 Sulfate expansion of low CaO fly ash mortars with different ammonia concentrations using $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ compared to OPC-only mortars

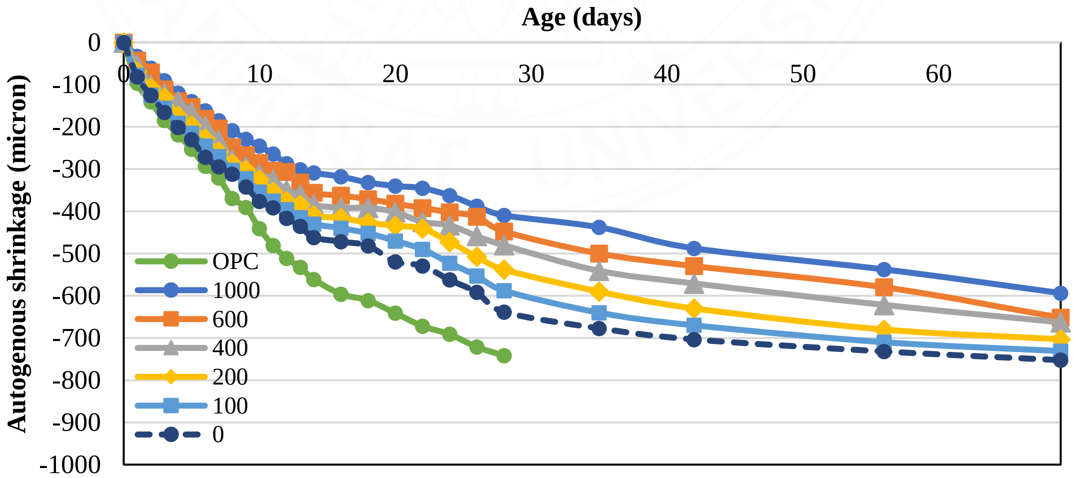
6.5 Autogenous shrinkage

The results of autogenous shrinkage of mortars containing high CaO and low CaO fly ash contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with ammonia concentrations of 0-1000 ppm are shown in Figures 6.8 and 6.9. The shrinkage was measured up to 69 days. The autogenous shrinkage of the mortars decreases when the ammonia concentration is increased for both of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$. It can be seen that both of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ show the same behavior for high CaO and low CaO fly ash mortars.

Figures 6.8 and 6.9 show the autogenous shrinkage of high CaO and low CaO fly ash mortars with different ammonia concentrations using ammonium sulfate and ammonium carbonate, respectively. The results show that the shrinkage of mortars containing high CaO fly ash with or without ammonia is lower than low CaO fly ash mortars and lower than mortars with OPC only.

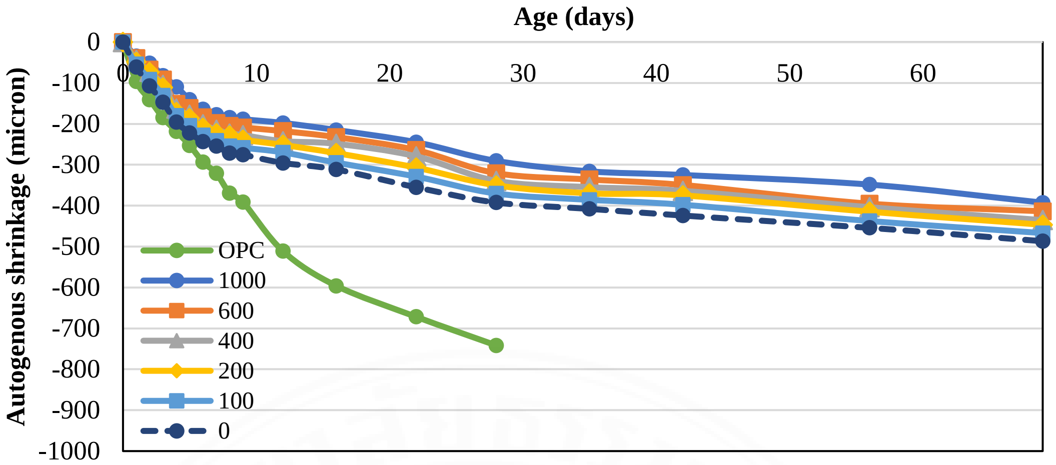


(a) high CaO fly ash

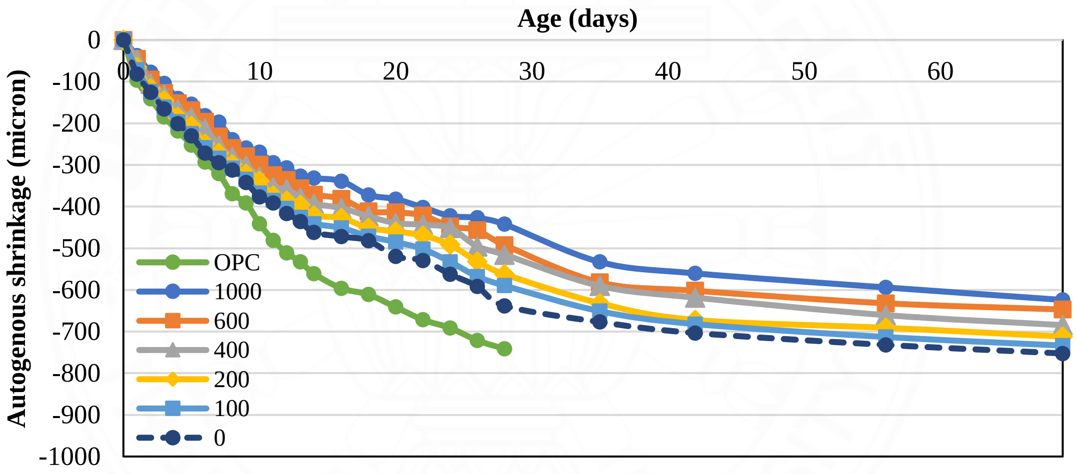


(b) Low CaO fly ash

Figure 6.8 Autogenous shrinkage of low CaO fly ash mortars with different ammonia concentrations using $(NH_4)_2SO_4$



(a) high CaO fly ash



(b) Low CaO fly ash

Figure 6.9 Autogenous shrinkage of low CaO fly ash mortars with different ammonia concentrations using $(NH_4)_2CO_3$

CHAPTER 7

EFFECTS OF AMMONIA CONTAMINATED FLY ASH WITH DIFFERENT FREE LIME AND SO_3 CONTENTS ON PROPERTIES OF PASTES AND MORTARS

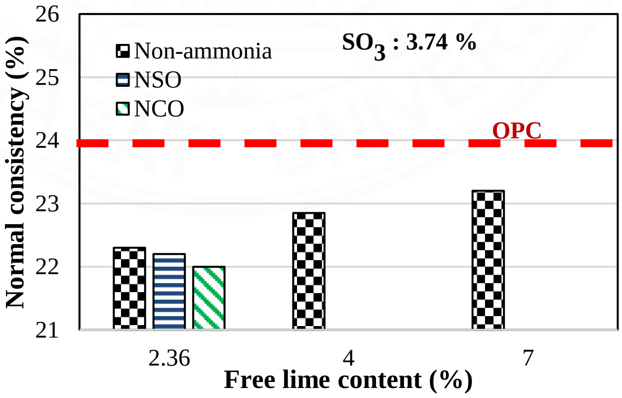
7.1 General

The effects of different free lime content and different SO_3 content in fly ash contaminated with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are discussed in this chapter. There are two types of fly ash that are used in this study, high CaO fly ash from the Mae Moh power plant and low CaO fly ash from BLCP power plant. Free lime contents in the fly ash were varied at normal (2.36% for Mae Moh fly ash and 0.19% for BLCP fly ash), medium (4%), and high (7%). There are three conditions of SO_3 in fly ash in this study, which are normal (3.74% for Mae Moh fly ash and 0.29% for BLCP fly ash), medium (5%), and high (10%). Some basic and durability properties of mixtures with various free lime and SO_3 contents and contamination using ammonium sulfate ($(NH_4)_2SO_4$) and ammonium carbonate ($(NH_4)_2CO_3$) were compared. Normal consistency, setting times, compressive strength, autoclave expansion, and sodium sulfate expansion of pastes and mortars containing fly ash with different free lime and SO_3 contents, with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ were tested and compared with normal free lime and SO_3 fly ash mixtures and also OPC-only mixtures as a control.

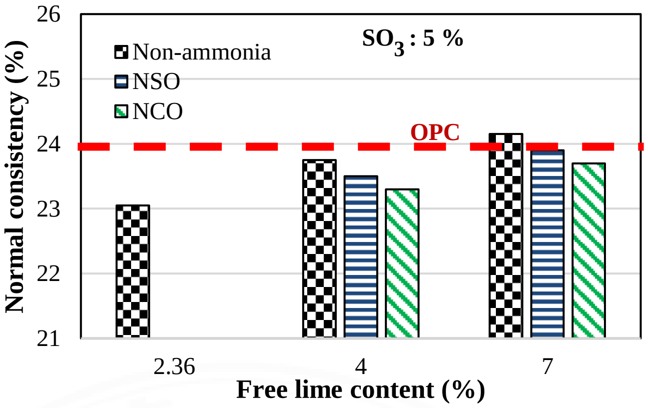
7.2 Normal consistency

The results of the normal consistency of pastes incorporating low SO_3 fly ash having high CaO and low CaO contents containing different free lime content, and contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are shown in Figure 7.1. For the normal consistency test, 20% fly ash replacement was used. In the comparison, the high CaO and low CaO fly ashes were contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with ammonia concentrations of 600 ppm. From Figure 7.1, it can be seen that the normal consistency of high CaO fly ash pastes decreases when ammonia concentration, either $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$, is increased. The tendency is the same for normal, medium, and high SO_3 fly ash mixtures. From Figure 7.1, it can be seen that $(NH_4)_2CO_3$ decreases normal consistency more significantly than $(NH_4)_2SO_4$ for high CaO fly ash pastes with different contents of free lime and SO_3 in the fly ash. From Figure 7.1, the results show that the normal consistency of high CaO fly ash paste increases when the free lime content in the fly ash is increased in normal, medium, and high SO_3 fly ash mixtures. When the SO_3 content in the fly ash is increased, the normal consistency of high CaO fly ash pastes increases. The pastes containing high CaO fly ash that is contaminated by ammonia and has high free lime and high SO_3 contents have higher normal consistency compared to the OPC-only paste.

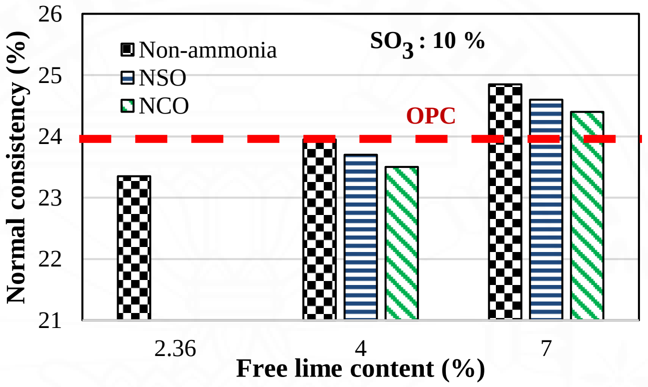
The normal consistency tests of ACFA with 4% and 7% of free lime contents with 3.74% SO_3 content (as shown in Figure 7.1(a)) were not conducted because the tendency was expected to be similar to the tendency of the medium SO_3 content (5% SO_3 as shown in Figure 7.1(b)) and high SO_3 content (10% SO_3 as shown in Figure 7.1(c)). The same case was expected for ACFA containing low free lime content (2.36% free lime) with medium SO_3 content (5% SO_3 as shown in Figure 7.1(b)) and high SO_3 content (10% SO_3 as shown in Figure 7.1(c)) which resulted in the same tendency as the ACFA containing low free lime (2.36% free lime) with low SO_3 content (3.74% SO_3 as shown in Figure 7.1(a)). A similar explanation was applied to normal consistency results of low CaO fly ash pastes.



(a) 3.74% SO_3 content



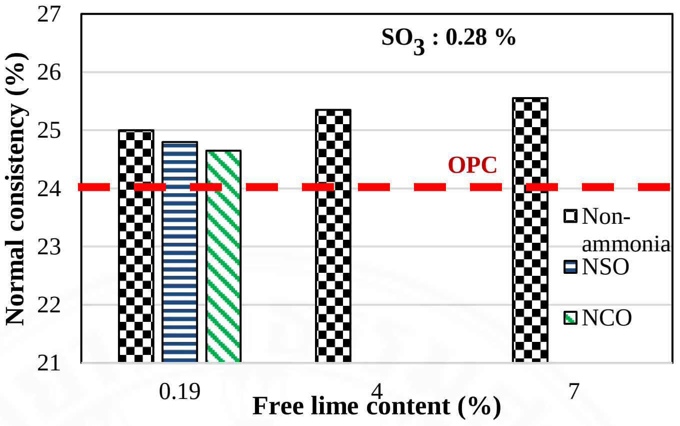
(b) 5% SO_3 content



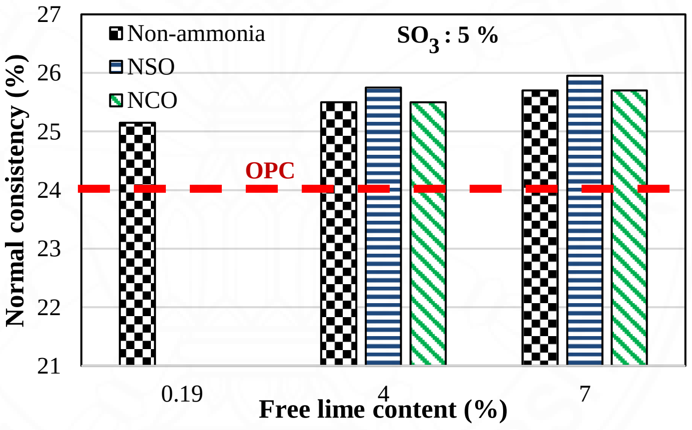
(c) 10% SO_3 content

Figure 7.1 Normal consistency of high CaO fly ash pastes with varied free lime and SO_3 contents

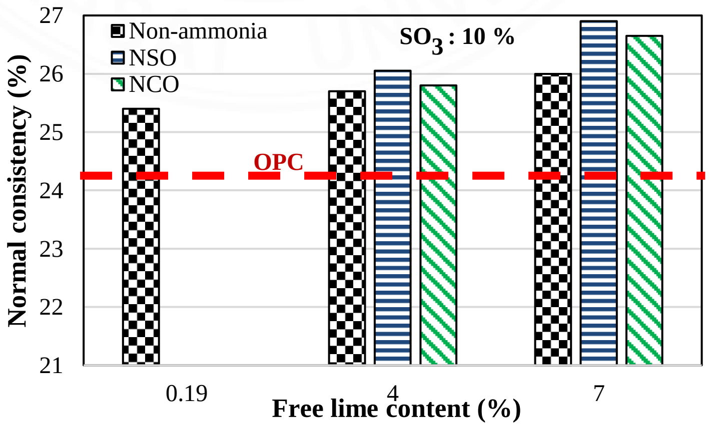
The results of the normal consistency of low CaO-low SO_3 fly ash pastes containing fly ash with different free lime contents contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ show a similar tendency to high CaO fly ash. From Figure 7.2, it can be seen that the normal consistency of low CaO fly ash paste decreases when contamination of $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ is increased. The tendency is the same for normal, medium, and high SO_3 conditions. From Figure 7.2, it can be seen that $(NH_4)_2CO_3$ decreases normal consistency more significantly than $(NH_4)_2SO_4$ for high CaO fly ash pastes with different contents of free lime and SO_3. From Figure 7.2, the results show that the normal consistency of low CaO fly ash paste increases when the free lime content is increased in normal, medium, and high SO_3 conditions. When the SO_3 content is increased, the normal consistency of low CaO fly ash paste increases. The pastes that contained low CaO fly ash that was contaminated by ammonia with medium and high free lime and SO_3 contents have higher normal consistency values compared to the OPC-only pastes.



(a) 0.28% SO_3 content



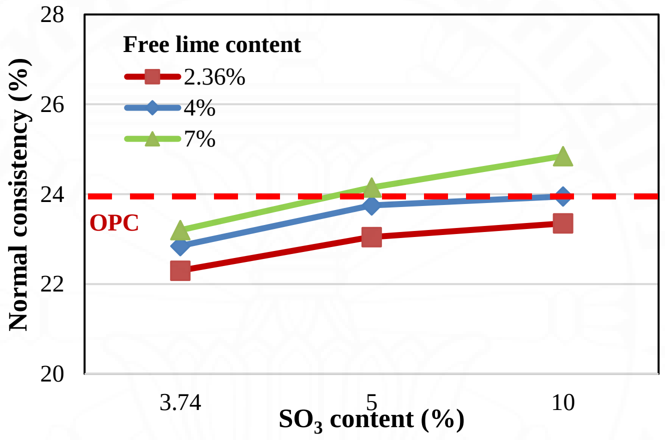
(b) 5% SO_3 content



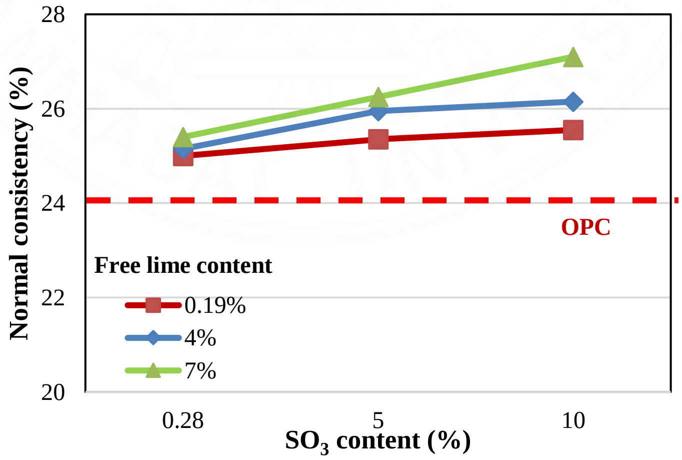
(c) 10% SO_3 content

Figure 7.2 Normal consistency of low CaO fly ash pastes with the varied free lime and SO_3 contents

Figures 7.3(a) and 7.3(b) show that non-ammonia pastes containing high CaO and low CaO fly ash with low, medium and high free lime content and varied SO_3 contents lead to increase of the normal consistency of pastes when SO_3 content was increased. Figures 7.4(a) and 7.4(b) show that ACFA pastes containing high CaO and low CaO fly ash with medium and high free lime contents and varied SO_3 contents show similar tendency with non-ammonia pastes (as shown in Figures 7.3(a) and 7.3(b)). It can be seen that the normal consistency of pastes increases when SO_3 content increases.

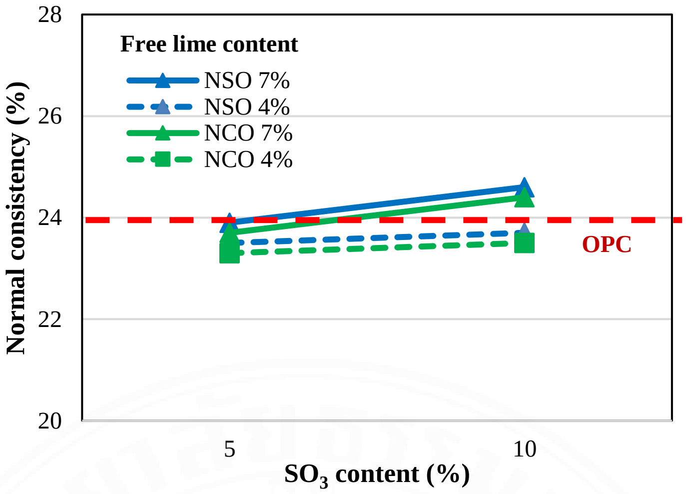


(a) High CaO fly ash

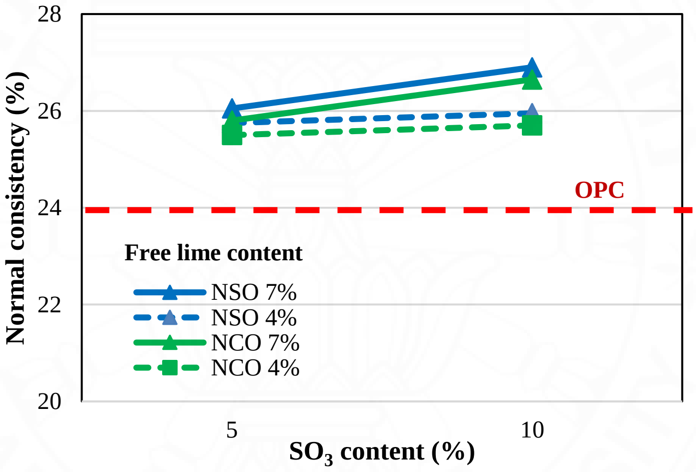


(b) Low CaO fly ash

Figure 7.3 Normal consistency of non-ammonia fly ash pastes with varied free lime and SO_3 contents



(a) High CaO fly ash



(b) Low CaO fly ash

Figure 7.4 Normal consistency of ammonia contaminated fly ash pastes with varied free lime and SO_3 contents

7.3 Setting times

The results of the setting times of low SO_3 with high CaO and low CaO fly ash paste containing different free lime contents contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are shown in Figures 7.5-7.12. For the tests of setting times, 20% fly ash replacement was used. In this comparison result, high CaO and low CaO fly ashes were contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with an ammonia concentration of 600 ppm and different contents of free lime and SO_3 were utilized.

The results of the setting times of high CaO-low SO_3 fly ash paste containing different free lime contents contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are shown in Figures 7.5-7.7. From Figure 7.5, the initial and final setting times of pastes containing high CaO fly ash with 4% free lime and 3.74% SO_3 content increase when the concentration of $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ is increased. The tendency is similar for other conditions of free lime (2.36% and 7%) and SO_3 (5% and 10%). From Figure 7.6, it can be seen that the initial and final setting times of pastes containing high CaO fly ash with 5% SO_3 content and using $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ decrease when free lime content is increased (4% to 7%). From Figure 7.7, the initial and final setting times of pastes containing high CaO fly ash with 4% free lime content contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ decrease when SO_3 content is increased (5% to 10%).

Free lime increases the amount of calcium hydroxide to react with fly ash, resulting in faster reaction and setting times. The hydration reaction of free lime also consumes water, resulting in lowering workability. In fly ash, calcium can be found in the form of glassy phase and free lime. External calcium in the form of free lime is primarily found outside the fly ash particles, whereas internal calcium is primarily found in the glassy phase. Because the internal calcium in the glassy phase may not dissolve completely at an early age, free lime particles are more easily available and undergo fast hydration. As a result, the external calcium system would have more calcium products than the internal calcium system. As a result of the rapid hydration of free lime, the setting times decrease (Nawaz et al., 2015).

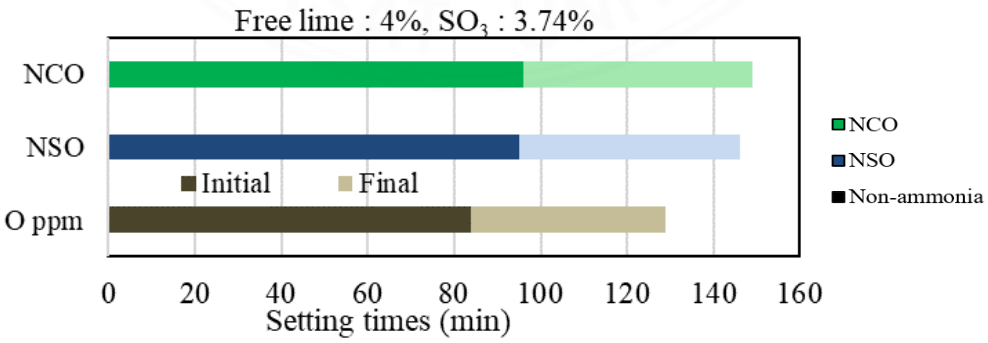


Figure 7.5 Setting times of high CaO fly ash pastes with low free lime and normal SO_3 content

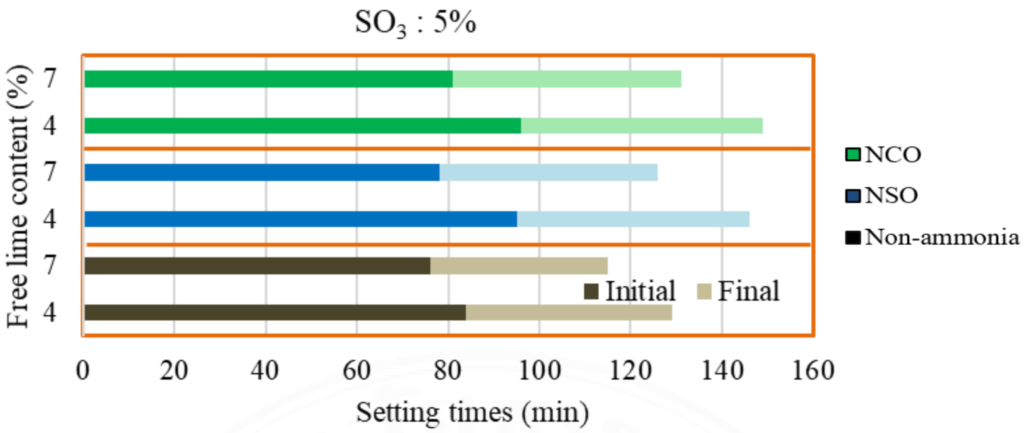


Figure 7.6 Setting times of high CaO fly ash pastes with varied free lime and medium SO_3 content

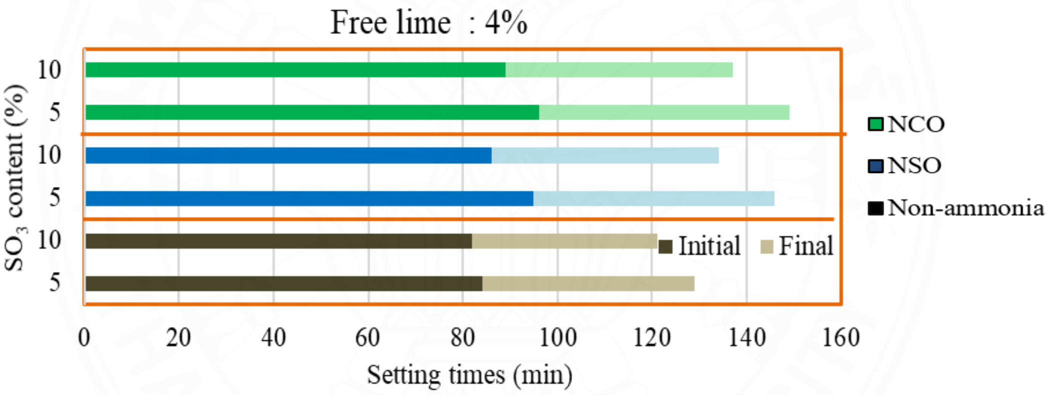


Figure 7.7 Setting times of high CaO fly ash pastes with low free lime and varied SO_3 content

The results of the setting times of low CaO fly ash pastes containing different free lime contents and low SO_3 content contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are shown in Figures 7.8-7.10. The results show that the behavior of pastes incorporating low CaO-low SO_3 fly ash containing different free lime contents, contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, is similar to that of the high CaO fly ash pastes. From Figure 7.8, the initial and final setting times of pastes containing low CaO fly ash with 4% free lime and 0.28% SO_3 content increases when concentration of $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ is increased. From Figure 7.9, the initial and final setting times of pastes containing low CaO fly ash with 5% SO_3 content, using $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, decrease when free lime content is increased (4% to 7%). From Figure 7.10, the initial and final setting times of low CaO fly ash with 4% free lime content, using $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, decrease when SO_3 content is increased (5% to 10%).

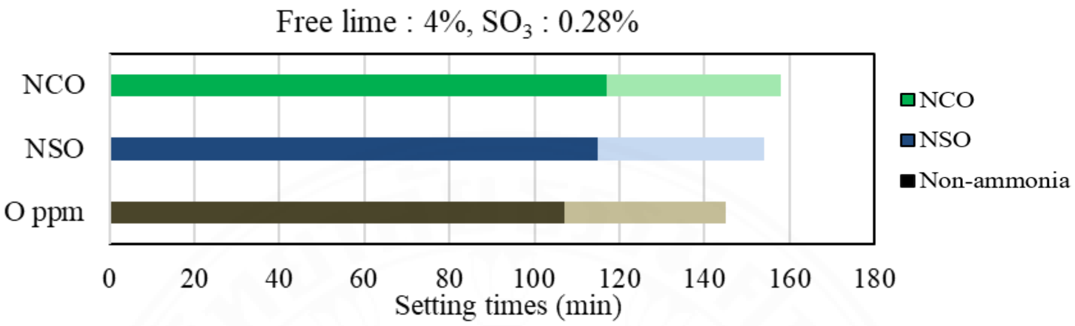


Figure 7.8 Setting times of low CaO fly ash pastes with medium free lime and medium SO_3 content

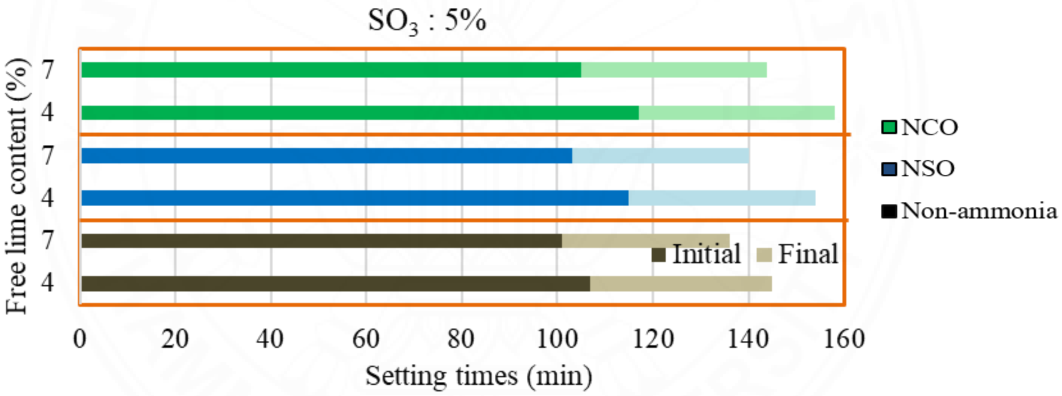


Figure 7.9 Settings time of low CaO fly ash pastes with varied free lime and normal SO_3 content

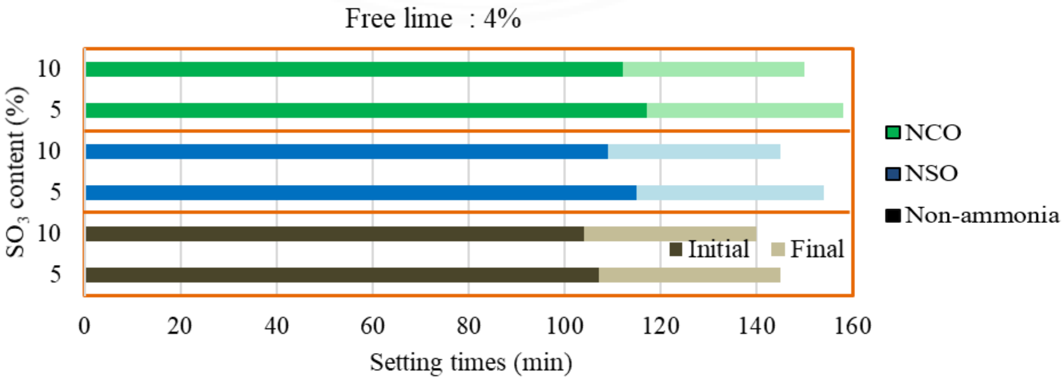
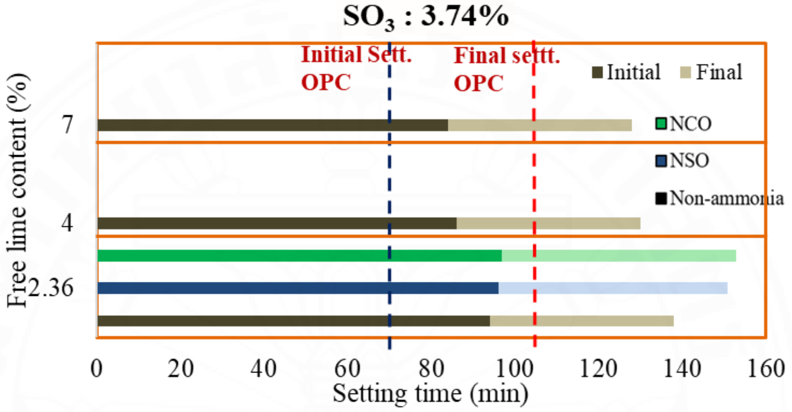
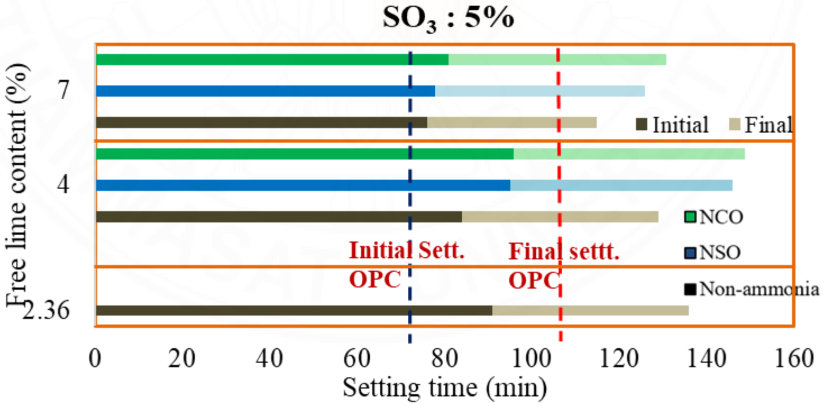


Figure 7.10 Setting times of low CaO fly ash pastes with medium free lime and varied SO_3 content

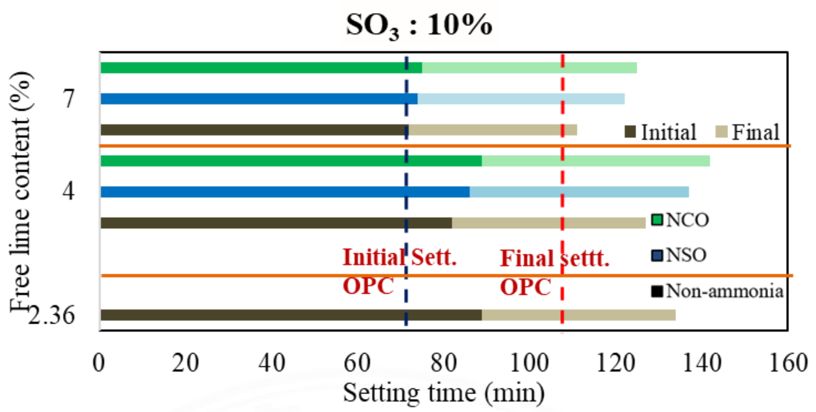
Comparisons of setting times of pastes containing low SO_3 fly ash having high CaO and low CaO contents, with different free lime contents, and contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are shown in Figures 7.11 and 7.12. All of the pastes that contain high CaO and low CaO fly ashes with varied free lime and SO_3 contents and are contaminated by ammonia have longer initial and final setting times compared to OPC-only pastes.



(a) 3.74% SO_3 content

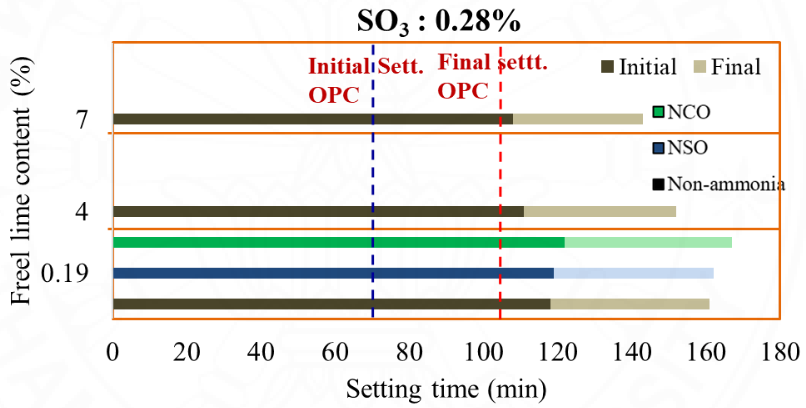


(b) 5% SO_3 content

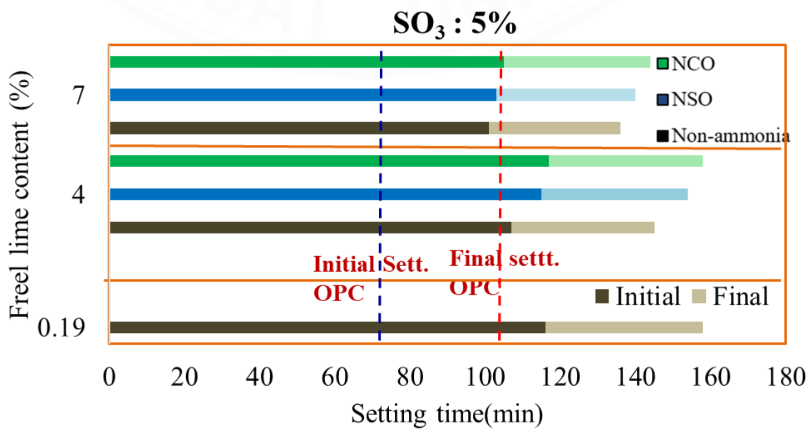


(c) 10% SO_3 content

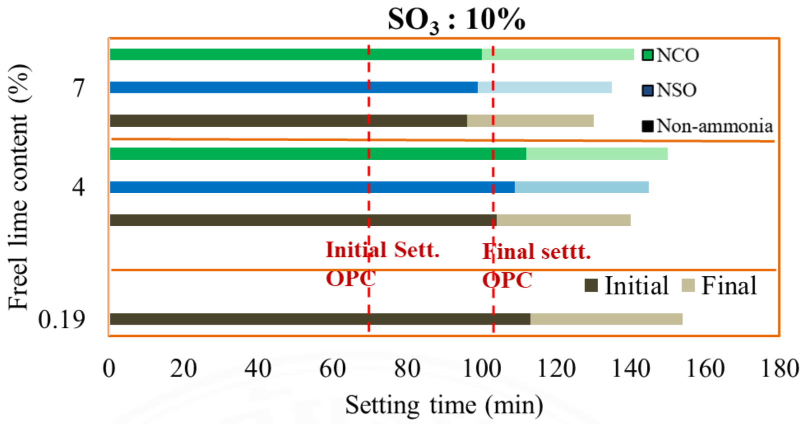
Figure 7.11 Setting times of high CaO fly ash pastes with varied free lime and SO_3contents



(a) 0.28% SO_3 content



(b) 5% SO_3 content



(c) 10% SO_3 content

Figure 7.12 Setting times of low CaO fly ash pastes with varied free lime and SO_3 contents

7.4 Compressive strength

The relations between compressive strength and free lime and SO_3 contents of fly ash contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are shown in Figures 7.13-7.24. In this study, high CaO and low CaO fly ashes were contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with an ammonia concentration of 600 ppm. For the compressive strength test, 30% fly ash replacement, 0.5 water to binder ratio, and 2.75 sand to binder ratio were utilized. The compressive strength was measured at 3, 7, 28, and 91 days of the mortar age.

The results of compressive strength of ammonia contaminated high CaO fly ash mortars containing different free lime and SO_3 contents at 3 days are shown in Figure 7.13. From Figure 7.13, the early age compressive strength of high CaO fly ash mortars decreases when $(NH_4)_2SO_4$ is added. On the other hand, the early age compressive strength of high CaO fly ash mortars increases when $(NH_4)_2CO_3$ is added. The tendency is the same in normal, medium, and high SO_3 conditions. The results obtained from this research show a similar trend to a previous study (Marchand et al., 2003). For the explanation, the liberated SO_4 ions into pore solution act as an initial sulfate source, which can react with hydration products to form gypsum (as shown in Equations (7.1)-(7.2)). Then, gypsum partially reacts with alumina-bearing phases of cement paste, like tricalcium aluminate ($3CaO{\cdot}Al_2O_3$; C_3A), to generate secondary ettringite, as illustrated in Equation (7.3). A large amount of gypsum and ettringite is the deleterious effect that may cause micro-cracking, which reduces the strength of mortars (S. Kumar et al., 1994). More gypsum to react with C_3A also leads to less C–A–H formation, reducing compressive strength.

$$Ca(OH)_2 + (NH_4)_2SO_4 \rightarrow CaSO_4{\cdot}2H_2O + NH_3 \qquad (7.1)$$

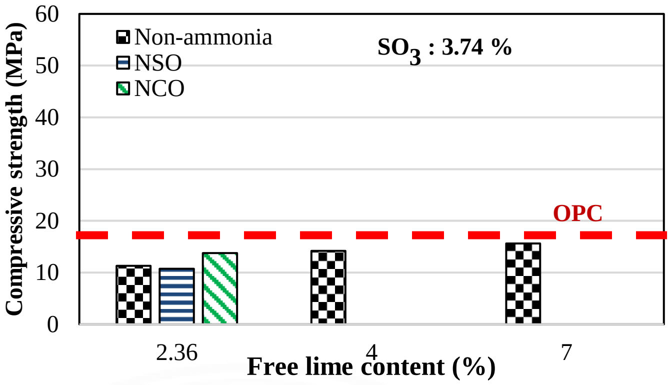
$$CaO{\cdot}SiO_2{\cdot}H_2O + (NH_4)_2SO_4 \rightarrow CaSO_4{\cdot}2H_2O + NH_3 + SiO_2 \qquad (7.2)$$

$$4CaO{\cdot}Al_2O_3{\cdot}xH_2O + 3CaSO_4{\cdot}2H_2O + H_2O \rightarrow$$

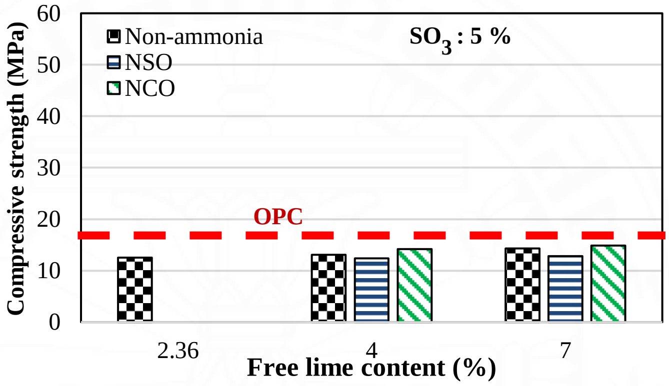
$$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}xH_2O + Ca(OH)_2 \qquad (7.3)$$

From Figure 7.13, the results show that the early-age compressive strength of high CaO fly ash mortars increases when the free lime content is increased in normal and medium SO_3 conditions. The early-age compressive strength of high CaO fly ash mortars increases when the free lime content in fly ash increases in high SO_3 conditions. When the SO_3 content in fly ash is higher, the early age compressive strength of high CaO fly ash mortars decreases (as shown in Figure 7.13).

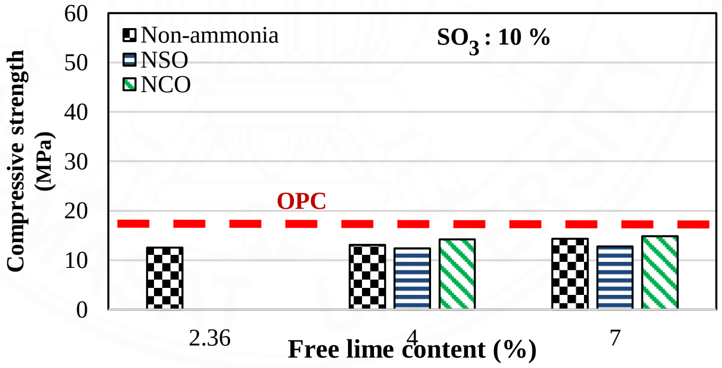
The compressive strength tests of ACFA with 4% and 7% of free lime contents with 3.74% SO_3 content (as shown in Figure 7.13(a)) were not conducted because the tendency was expected to be similar to the tendency of medium SO_3 content (5% SO_3 as shown in Figure 7.13(b)) and high SO_3 content (10% SO_3 as shown in Figure 7.13(c)). The same case was expected for ACFA containing low free lime content (2.36% free lime) with medium SO_3 content (5% SO_3 as shown in Figure 7.13(b)) and high SO_3 content (10% SO_3 as shown in Figure 7.13(c)) which resulted in the same tendency as the ACFA containing low free lime (2.36% free lime) with low SO_3 content (3.74% SO_3 as shown in Figure 7.13(a)). A similar explanation was applied to compressive strength results of high CaO and low CaO fly ash mortars at 7, 28, and 91 days.



(a) 3.74% SO_3 content



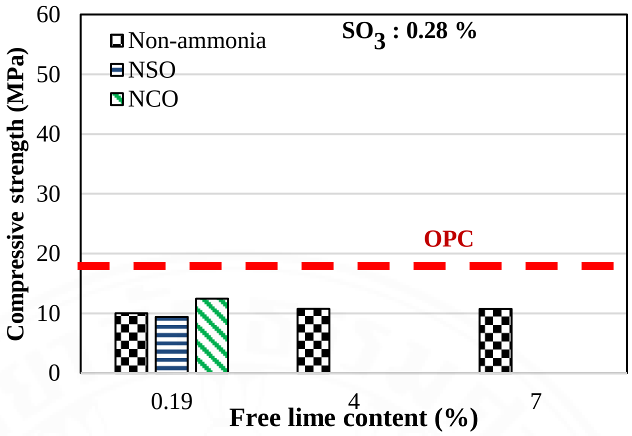
(b) 5% SO_3 content



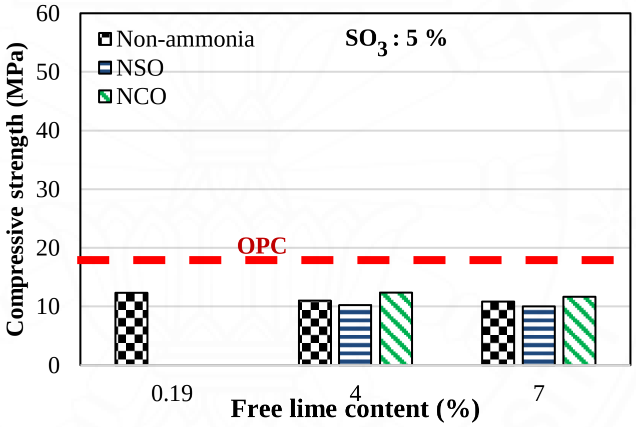
(c) 10% SO_3 content

Figure 7.13 Compressive strength at 3 days of high CaO fly ash mortars with varied free lime and SO_3 contents

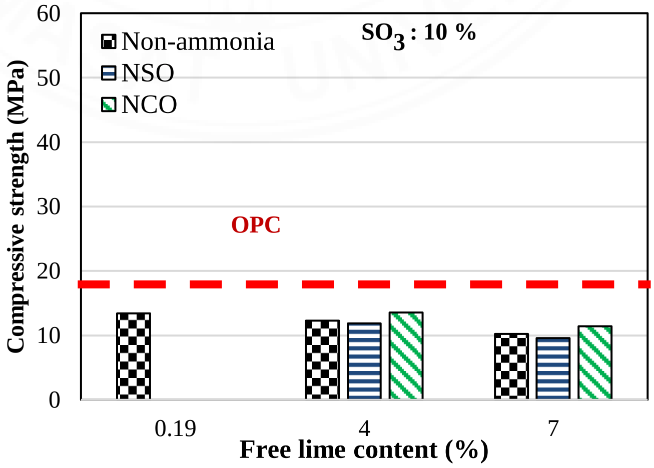
The results of compressive strength of ammonia contaminated low CaO fly ash mortars containing different free lime and SO_3 contents at 3 days are shown in Figure 7.14. From Figure 7.14, the effects of $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, free lime, and SO_3 on compressive strength of mortars with low CaO fly ash contaminated by ammonia with varied free lime content and varied SO_3 contents have the same behavior as the high CaO fly ash mortars.



(a) 0.28% SO_3 content



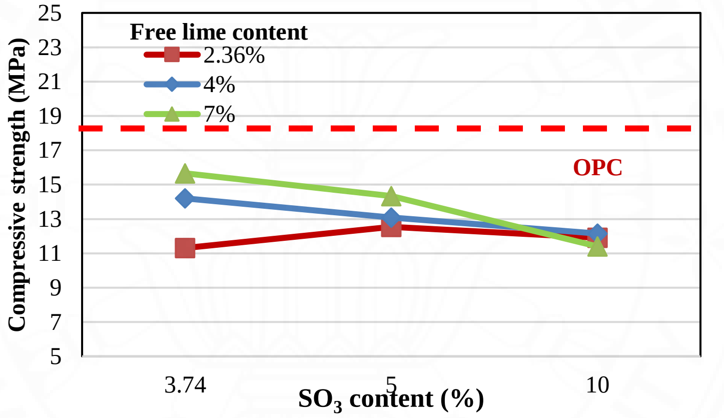
(b) 5% SO_3 content



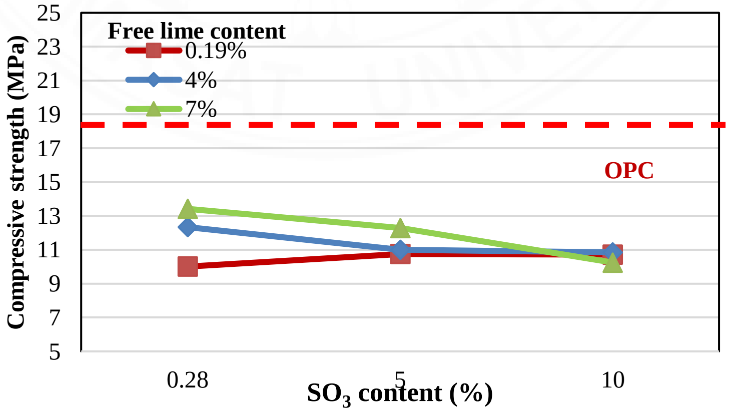
(c) 10% SO_3 content

Figure 7.14 Compressive strength at 3 days of low CaO fly ash mortars with varied free lime and SO_3 contents

Figures 7.15(a) and 7.15(b) show that the non-ammonia mortars containing high CaO and low CaO fly ash with high (7%) and medium (4%) free lime contents and varied SO_3 contents lead to a decrease in the early-age compressive strength of mortars when SO_3 content of the fly ash increases. On other hand, the mortars containing high CaO and low CaO fly ash with low free lime content (2.36% for high CaO fly ash and 0.19% for low CaO fly ash) lead to an increase in the early-age compressive strength of the mortars when SO_3 content increases (up to 5% SO_3 content), but the compressive strength decreases when SO_3 content is higher than 5%, as shown in Figures 7.15(a) and 7.15(b). Figures 7.16(a) and 7.16(b) show that ACFA mortars containing high CaO and low CaO fly ash with medium and high free lime contents lead to a decrease in the compressive strength of mortars when SO_3 content increases.

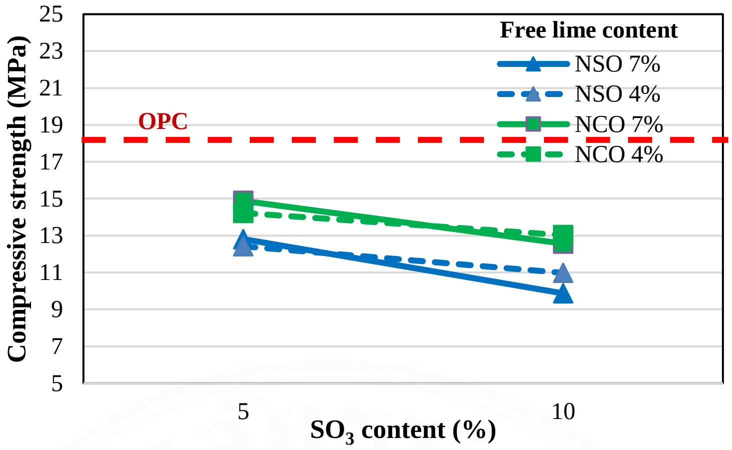


(a) High CaO fly ash

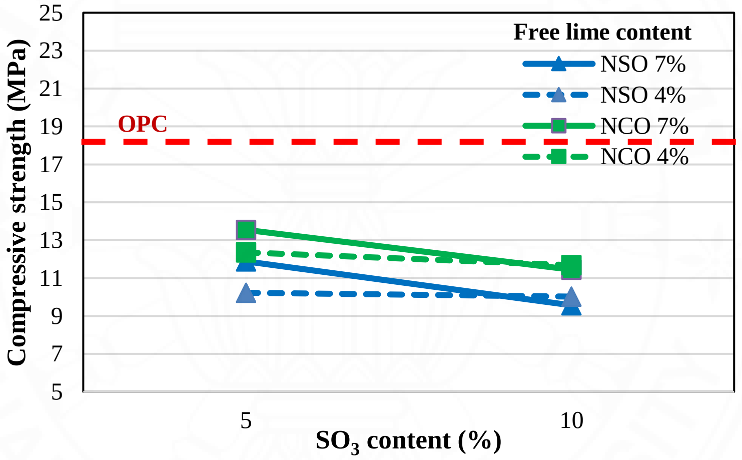


(b) Low CaO fly ash

Figure 7.15 Compressive strength at 3 days of non-ammonia fly ash mortars with varied free lime and SO_3 contents



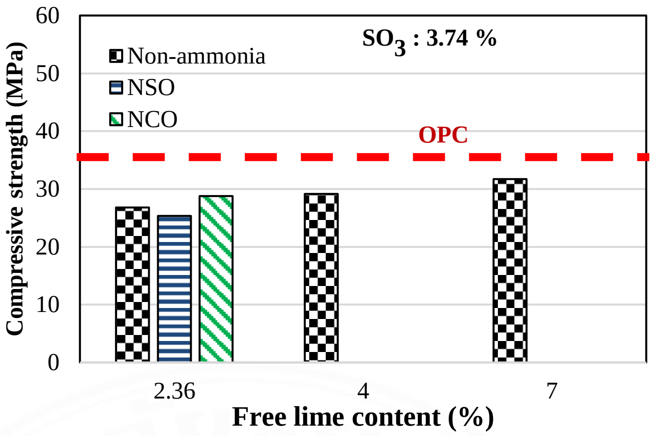
(a) High CaO fly ash



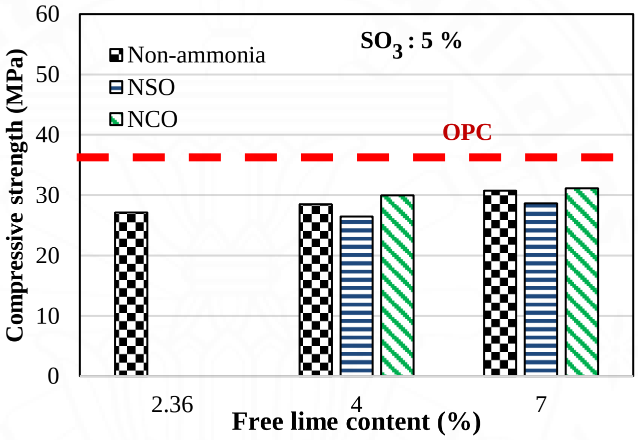
(b) Low CaO fly ash

Figure 7.16 Compressive strength at 3 days of ammonia-contaminated fly ash mortars with varied free lime and SO_3 contents

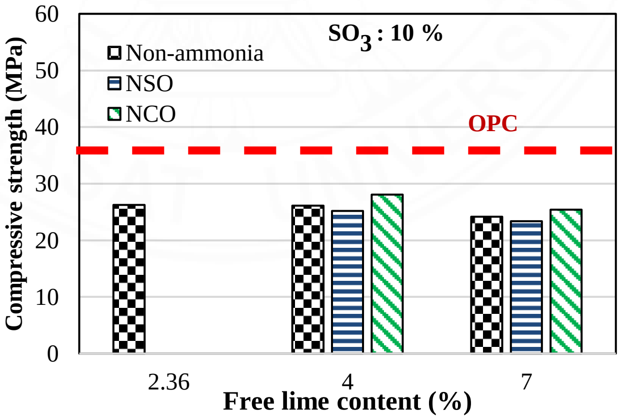
The results of compressive strength of ammonia contaminated high CaO fly ash mortars containing different free lime and SO_3 contents at 7 days are shown in Figure 7.17. From Figure 7.17, the effects of $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, free lime, and SO_3 on compressive strength of mortars with high CaO fly ash contaminated by ammonia with varied free lime content and varied SO_3 content at 7 days have the same tendency as the results at 3 days.



(a) 3.74% SO_3 content



(b) 5% SO_3 content

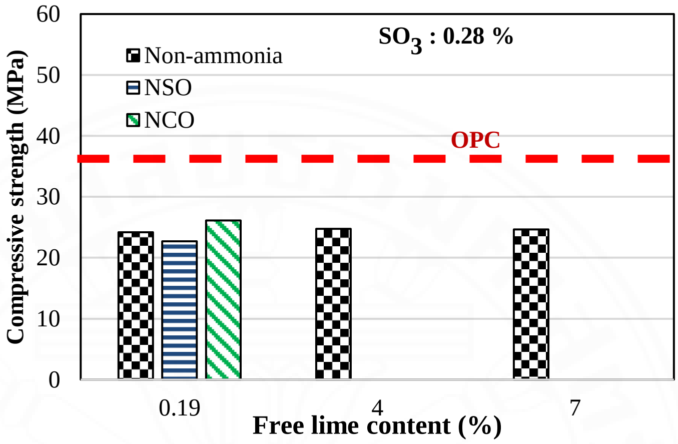


(c) 10% SO_3 content

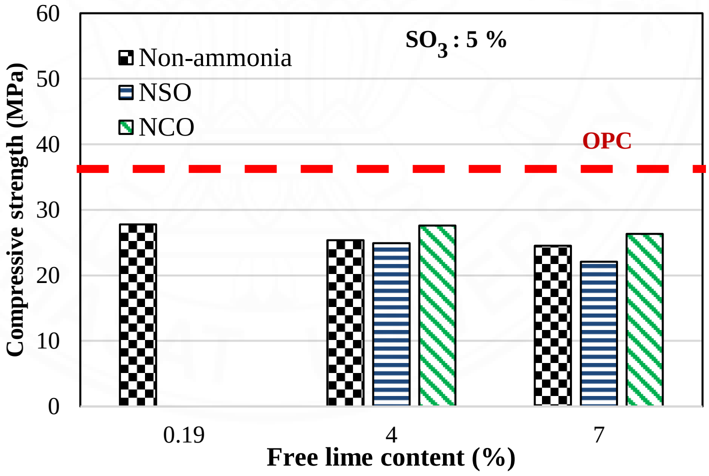
Figure 7.17 Compressive strength at 7 days of high CaO fly ash mortars with varied free lime and SO_3 contents

The compressive strength of ammonia contaminated low CaO fly ash mortars containing different free lime and SO_3 contents at 7 days are shown in Figure 7.18.

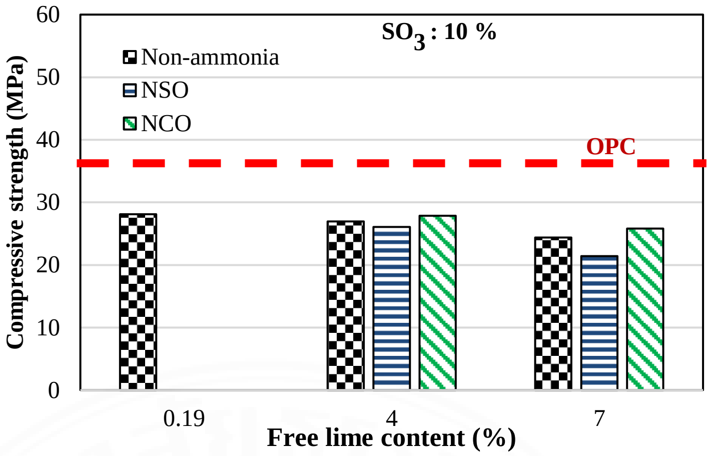
From Figure 7.18, the effects of $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, free lime, and SO_3 on compressive strength of mortars with low CaO fly ash contaminated by ammonia with varied free lime content and varied SO_3 content have the same behavior as the high CaO fly ash mortars.



(a) 0.28% SO_3 content



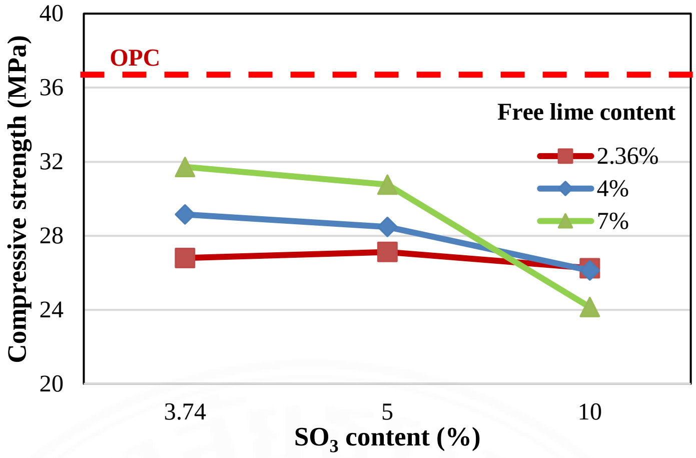
(b) 5% SO_3 content



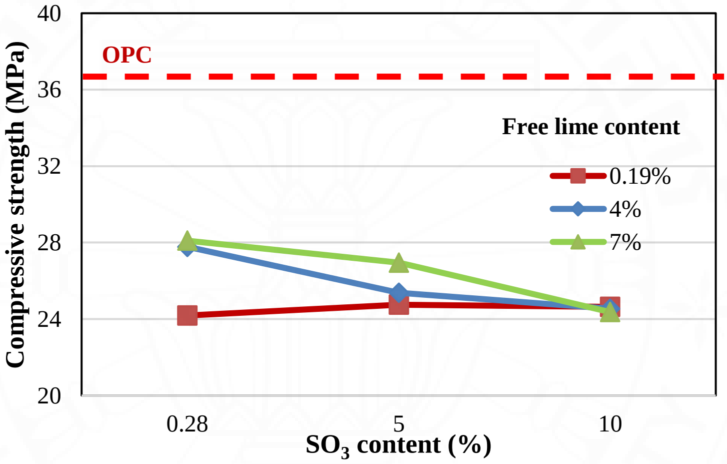
(c) 10% SO_3 content

Figure 7.18 Compressive strength at 7 days of low CaO fly ash mortars with varied free lime and SO_3 contents

Figures 7.19(a) and 7.19(b) show that the non-ammonia mortars containing high CaO and low CaO fly ash with high (7%) and medium (4%) free lime contents and varied SO_3 content lead to a decrease in compressive strength of the mortars at 7 days when SO_3 content increases. On other hand, the mortars containing high CaO and low CaO fly ash with low free lime content (2.36% for high CaO fly ash and 0.19% for low CaO fly ash) lead to an increase in the early-age compressive strength of the mortars when SO_3 content increases (up to 5% SO_3 content), but the compressive strength decreases when SO_3 content is higher than 5%, as shown in Figures 7.19(a) and 7.19(b). Figures 7.20(a) and 7.20(b) show that ACFA mortars containing high CaO and low CaO fly ash with medium and high free lime contents lead to a decrease in the compressive strength of mortars when SO_3 content increases.

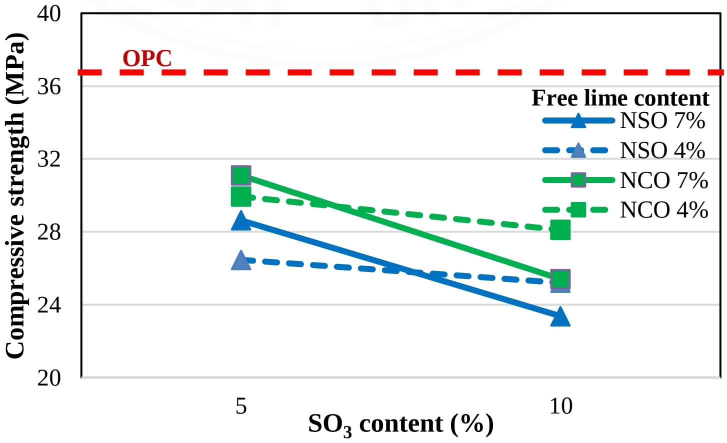


(a) High CaO fly ash

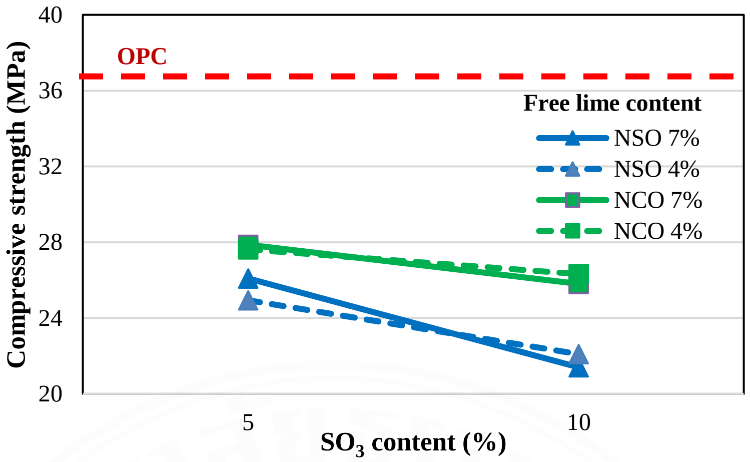


(b) Low CaO fly ash

Figure 7.19 Compressive strength at 7 days of non-ammonia mortars with varied free lime and SO$_3$ contents



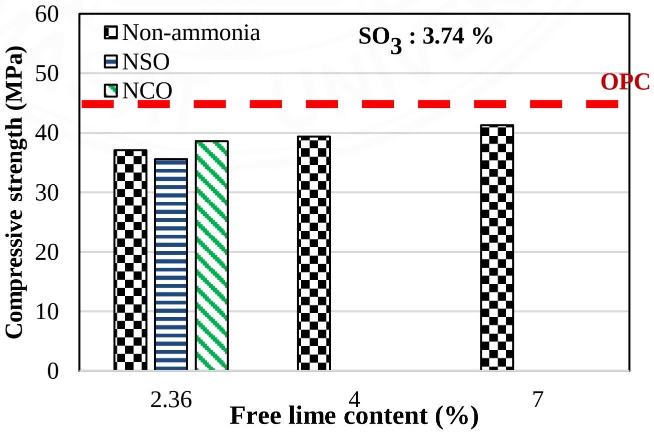
(a) High CaO fly ash



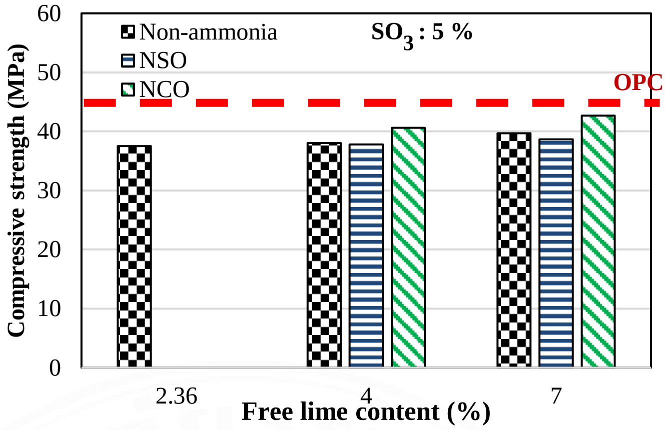
(b) Low CaO fly ash

Figure 7.20 Compressive strength at 7 days of ammonia-contaminated fly ash mortars with varied free lime and SO_3 contents

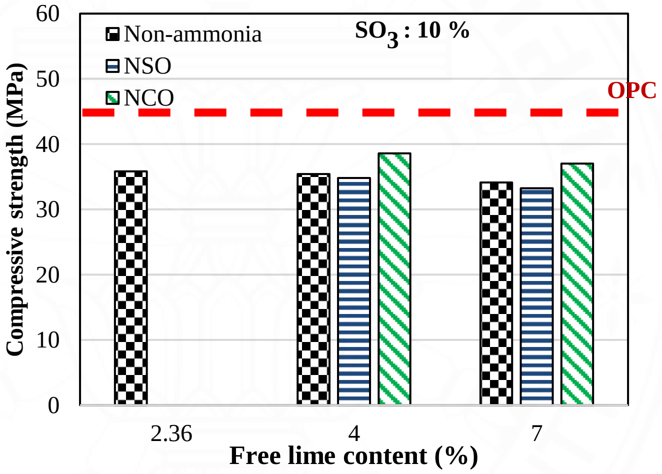
The results of compressive strength of ammonia contaminated high CaO fly ash mortars containing different free lime and SO_3 contents at 28 days are shown in Figure 7.21. It can be seen that the effects of $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, free lime, and SO_3 on compressive strength of mortars with high CaO fly ash contaminated by ammonia with varied free lime and SO_3 contents at 28 days have the same tendency as the results at 3 and 7 days.



(a) 3.74% SO_3 content



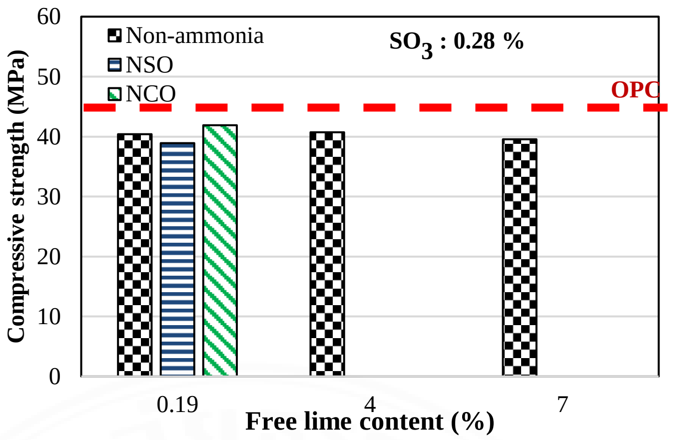
(b) 5% SO_3 content



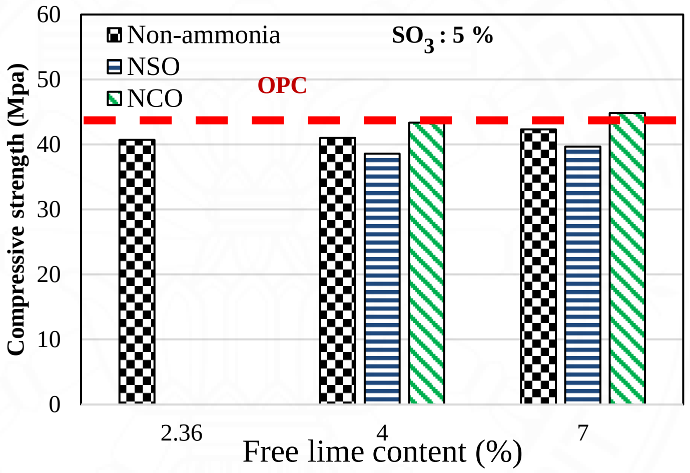
(c) 10% SO_3 content

Figure 7.21 Compressive strength at 28 days of high CaO fly ash mortars with varied free lime and SO_3 contents

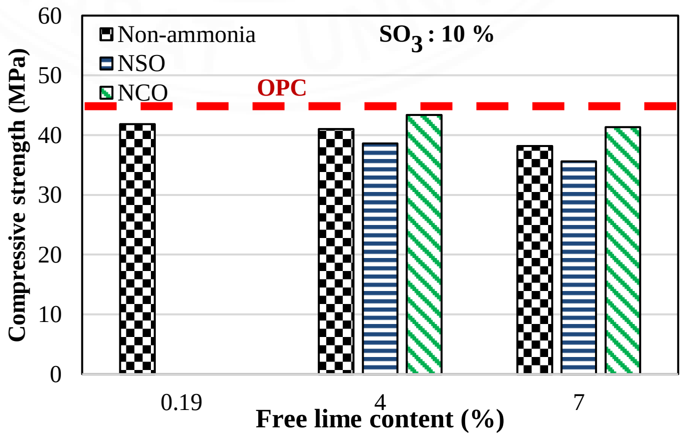
The results of compressive strength of ammonia contaminated low CaO fly ash mortars containing different free lime and SO_3 contents at 28 days are shown in Figure 7.22. It can be seen that the effects of $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, free lime, and SO_3 on compressive strength of mortars with low CaO fly ash contaminated by ammonia with varied free lime and SO_3 contents have the same behavior as the high CaO fly ash mortars.



(a) 0.28% SO_3 content



(b) 5% SO_3 content

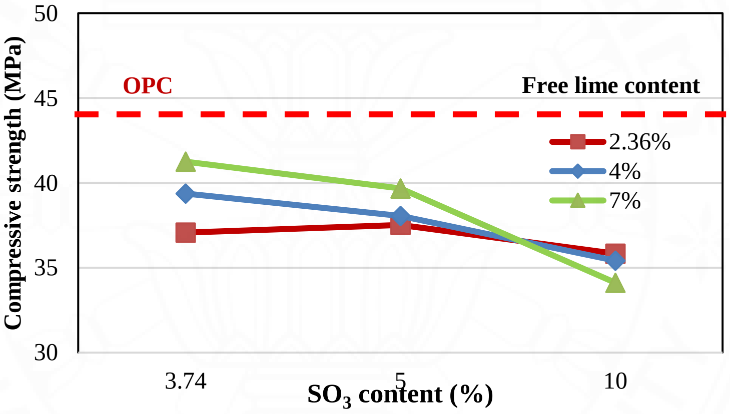


(c) 10% SO_3 content

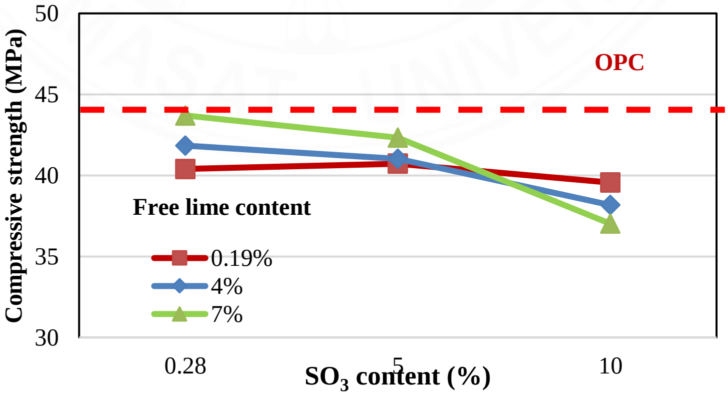
Figure 7.22 Compressive strength at 28 days of low CaO fly ash mortars with varied free lime and SO_3 contents

Ref. code: 25646222040757RWH

Figures 7.23(a) and 7.23(b) show that the non-ammonia mortars containing high CaO and low CaO fly ash with high (7%) and medium (4%) free lime contents and varied SO_3 contents lead to a decrease in compressive strength of the mortars at 28 days when SO_3 content increases. On other hand, the mortars containing high CaO and low CaO fly ash with low free lime content (2.36% for high CaO fly ash and 0.19% for low CaO fly ash) lead to an increase in the compressive strength of the mortars when SO_3 content increases (up to 5% SO_3 content), but the compressive strength decreases when SO_3 content is higher than 5%, as shown in Figures 7.23(a) and 7.23(b). Figures 7.24(a) and 7.24(b) show that ACFA mortars containing high CaO and low CaO fly ash with medium and high free lime contents lead to a decrease in the compressive strength of mortars when SO_3 content increases.

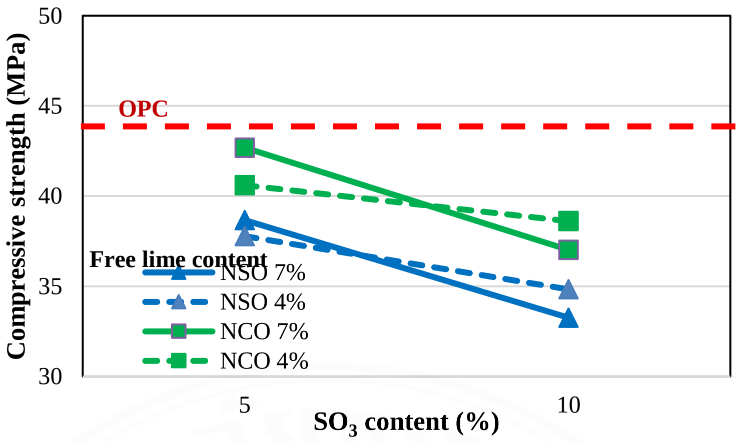


(a) High CaO fly ash

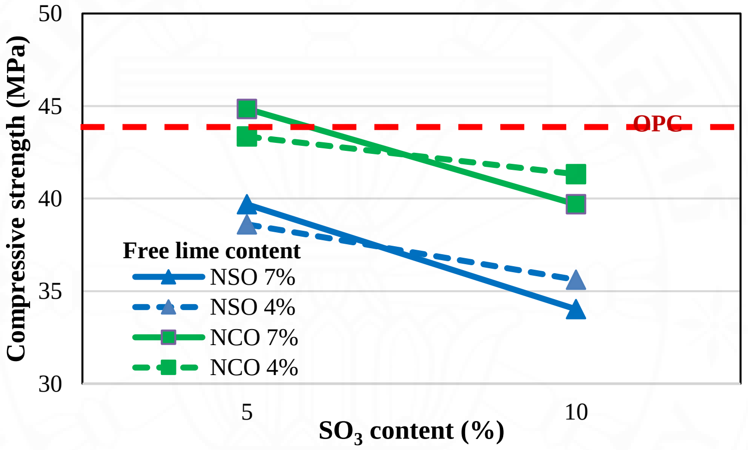


(b) Low CaO fly ash

Figure 7.23 Compressive strength at 28 days of non-ammonia mortars with varied free lime and SO_3 contents



(a) High CaO fly ash

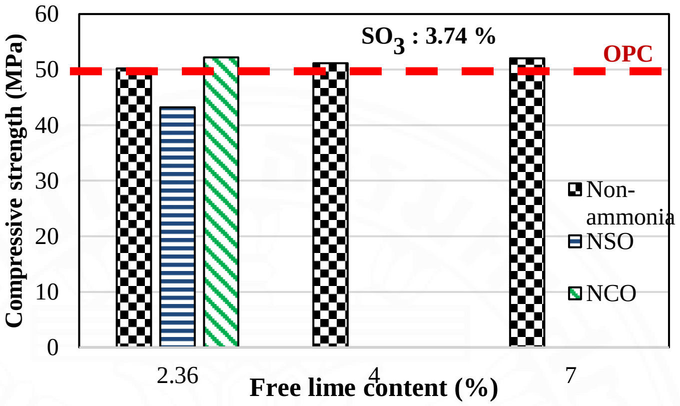


(b) Low CaO fly ash

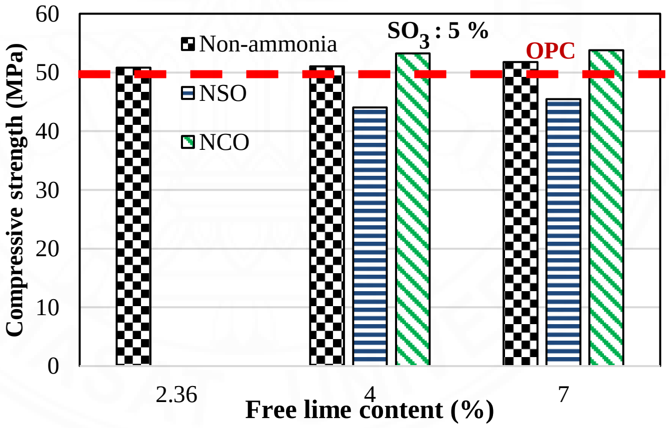
Figure 7.24 Compressive strength at 28 days of ammonia-contaminated fly ash mortars with varied free lime and SO_3 contents

The results of compressive strength of ammonia contaminated high CaO fly ash mortars containing different free lime and SO_3 contents at 91 days are shown in Figure 7.25. It can be seen that the long-term (91-day) compressive strength of high CaO fly ash mortars decreases when $(NH_4)_2SO_4$ is added. On the other hand, the long-term compressive strength of high CaO fly ash mortars increases when $(NH_4)_2CO_3$ is added. The tendency is the same in normal, medium, and high SO_3 fly ash conditions. Figures 7.26 show the same effects of free lime content on the compressive strength of the mortars with low CaO fly ash.

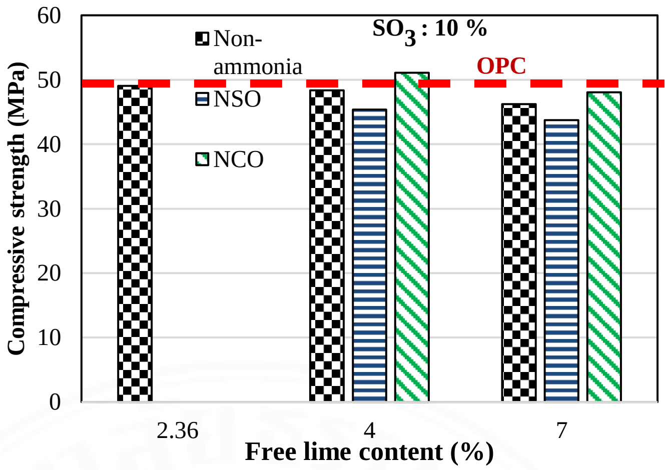
From Figure 7.25, the long-term compressive strength of high CaO fly ash mortars increases when the free lime content is increased in normal and medium SO_3 conditions. The long-term compressive strength of high CaO fly ash mortars decreases when the free lime content is increased in high SO_3 (SO_3=10%) condition.



(a) 3.74% SO_3 content



(b) 5% SO_3 content

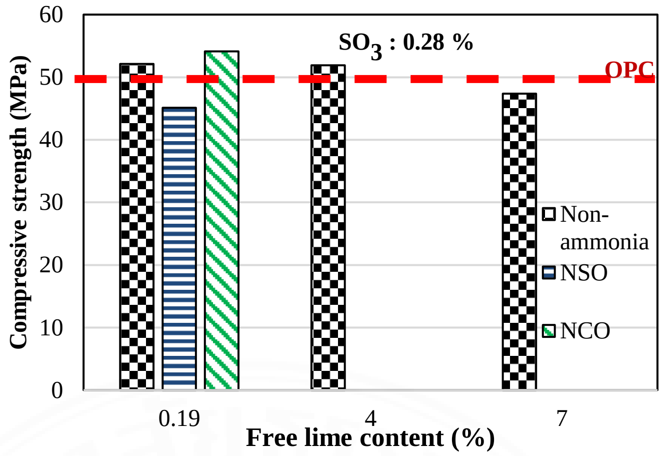


(c) 10% SO_3 content

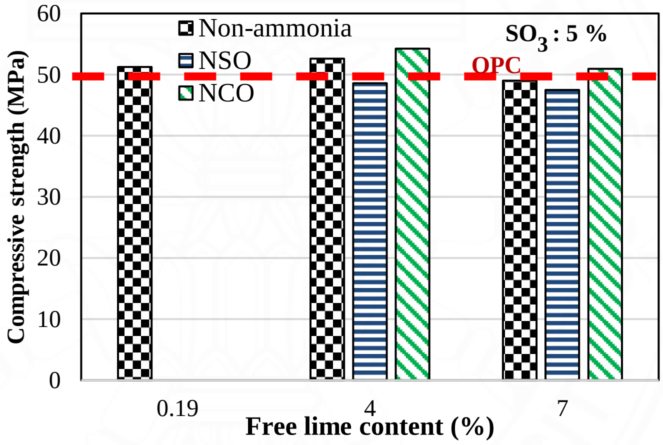
Figure 7.25 Compressive strength at 91 days of high CaO fly ash mortars with varied free lime and SO_3 contents

The results of compressive strength of ammonia contaminated low CaO fly ash mortars containing different free lime and SO_3 contents at 91 days are shown in Figure 7.26. It can be seen that the effects of $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, free lime, and SO_3 on compressive strength of mortars with low CaO fly ash contaminated by ammonia with varied free lime and varied SO_3 contents have the same behavior with the high CaO fly ash mortars.

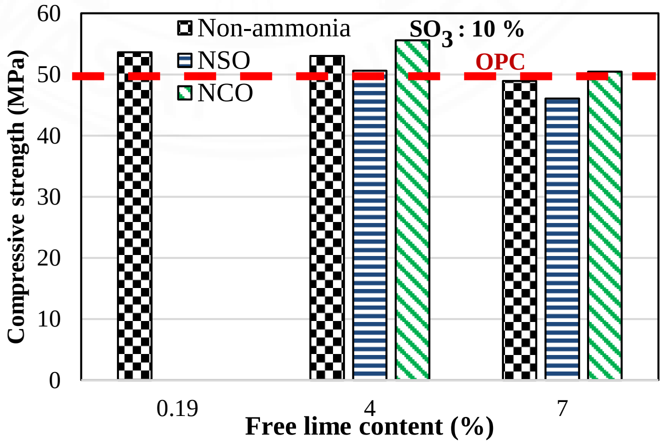
In the condition of high SO_3, an increase of free lime content reduces the compressive strength of mortars with high CaO or low CaO fly ash because SO_3 gives a more significant negative effect to decrease compressive strength compared to the positive effect of free lime to increase the compressive strength of mortars.



(a) 0.28% SO_3 content



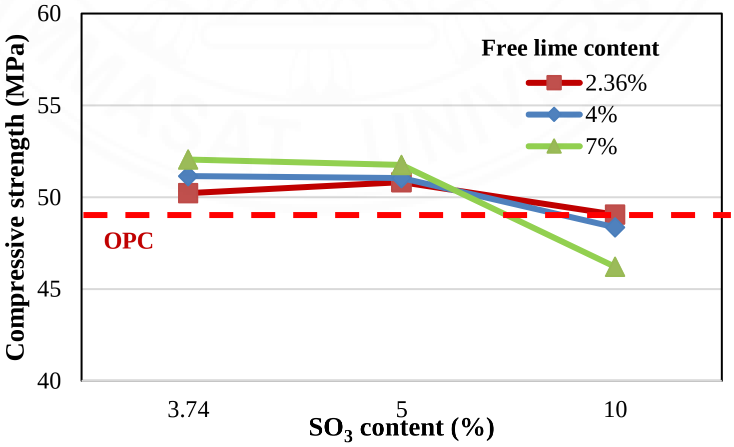
(b) 5% SO_3 content



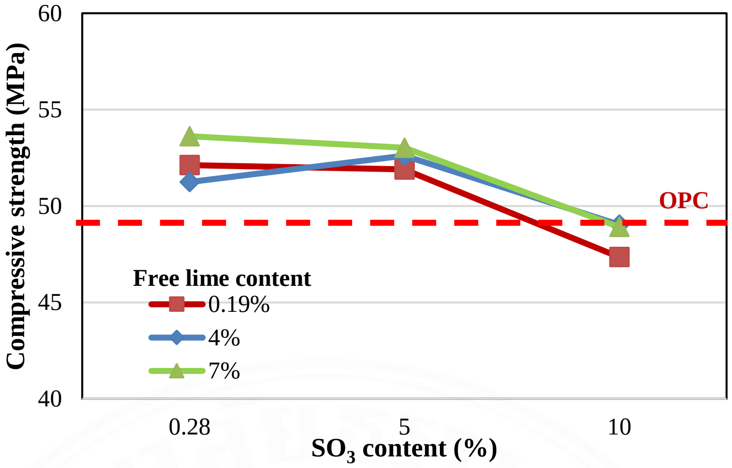
(c) 10% SO_3 content

Figure 7.26 Compressive strength 91 days of low CaO fly ash mortars with varied free lime and SO_3 contents at

Figures 7.27 (a) and 7.27(b) show that the non-ammonia mortars containing high CaO fly ash with high (7%) and medium (4%) free lime contents lead to a decrease in the long-term compressive strength of the mortars when SO_3 content increases. On other hand, the mortars containing high CaO fly ash with low free lime content (2.36%) lead to an increase in the long-term compressive strength of the mortars when SO_3 content increases (up to 5% SO_3 content), but the compressive strength decreases when SO_3 content is higher than 5%, as shown in Figure 7.27(a). The mortars containing low CaO fly ash with high (7%) and low (0.19%) free lime contents lead to a decrease in the long-term compressive strength of the mortars when SO_3 content increases. The mortars containing low CaO fly ash with medium free lime content (4%) lead to an increase in the long-term compressive strength of the mortars when SO_3 content increases (up to 5% SO_3 content), but the compressive strength decreases when SO_3 content is higher than 5%, as shown in Figure 7.27(b). Figures 7.28(a) and 7.28(b) show that ACFA mortars containing high CaO and low CaO fly ash with medium and high free lime contents lead to a decrease in the compressive strength of mortars when SO_3 content increases, except mortar containing high CaO fly ash with 4% free lime content contaminated by $(NH_4)_2SO_4$ that shows the increase in compressive strength when SO_3 increases.

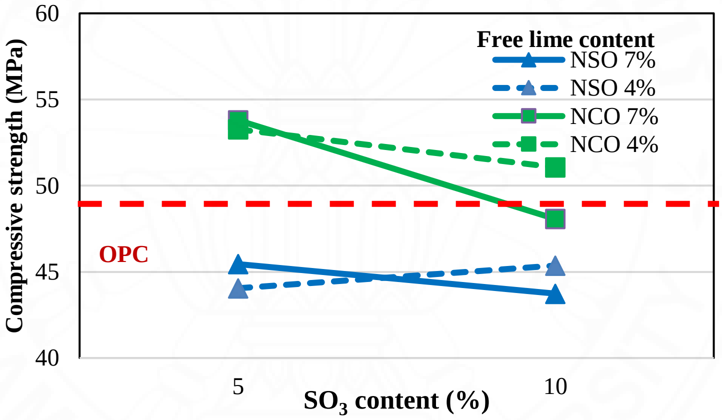


(a) High CaO fly ash

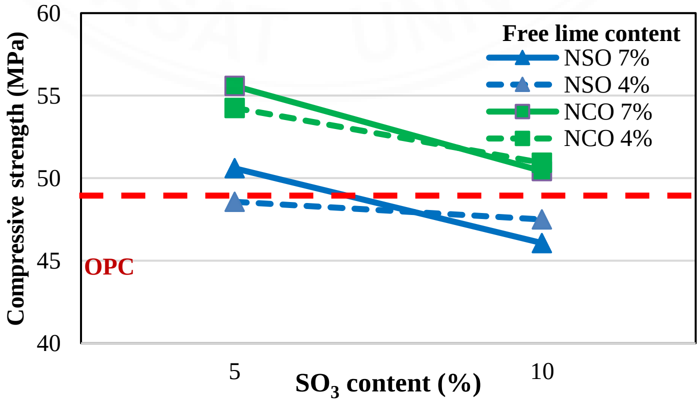


(b) Low CaO fly ash

Figure 7.27 Compressive strength at 91 days of non-ammonia fly ash mortars with varied free lime and SO_3 contents



(a) High CaO fly ash



(b) Low CaO fly ash

Figure 7.28 Compressive strength at 91 days of ammonia-contaminated fly ash mortars with varied free lime and SO_3 contents

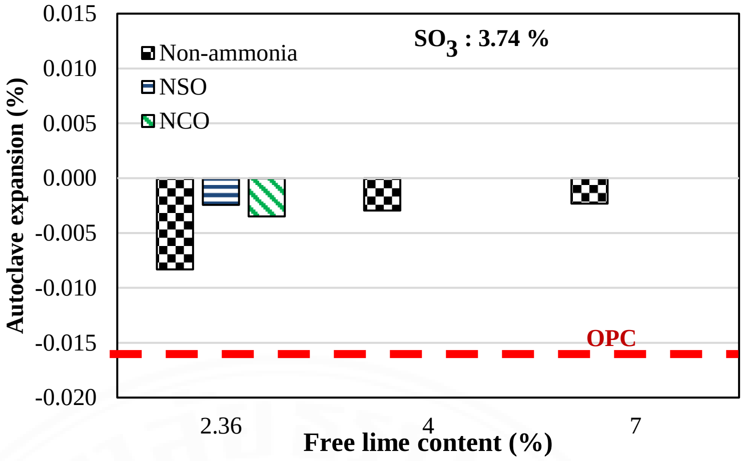
7.5 Autoclave expansion

The results of the autoclave expansion of pastes with high CaO and low CaO fly ash contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ and containing different free lime content and low SO_3 content are shown in Figures 7.29 and 7.32. For the autoclave expansion tests, 20% fly ash replacement was used. In this study, high CaO and low CaO fly ashes were contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with an ammonia concentration of 600 ppm.

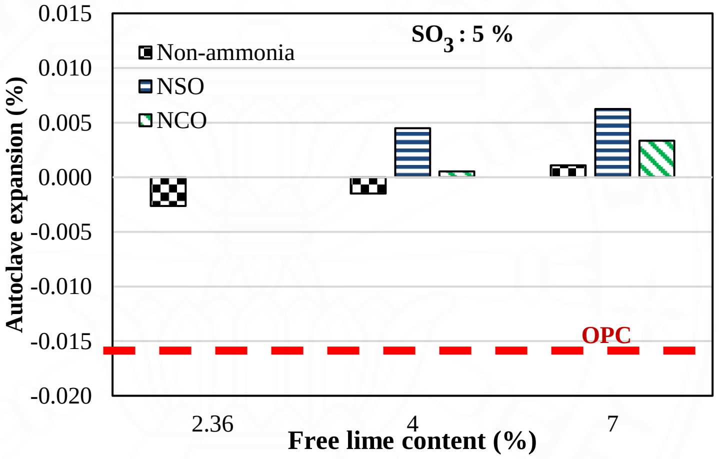
Autoclave expansion results of ammonia contaminated high CaO fly ash pastes containing different free lime and SO_3 contents are shown in Figure 7.29. It can be seen that autoclave expansion of high CaO pastes decreases when ammonia concentration by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ is increased. $(NH_4)_2SO_4$ has more significant effects on autoclave expansion than $(NH_4)_2CO_3$. The tendency is the same for normal, medium, and high SO_3 conditions.

From Figure 7.29, the results show that autoclave expansion of high CaO fly ash pastes increases when the free lime content is increased in normal, medium, and high SO_3 conditions. When the SO_3 content is increased, autoclave expansion of high CaO fly ash pastes increases. The pastes that contained high CaO fly ash that was contaminated by ammonia with varied free lime and SO_3 contents have higher autoclave expansion compared to OPC-only pastes.

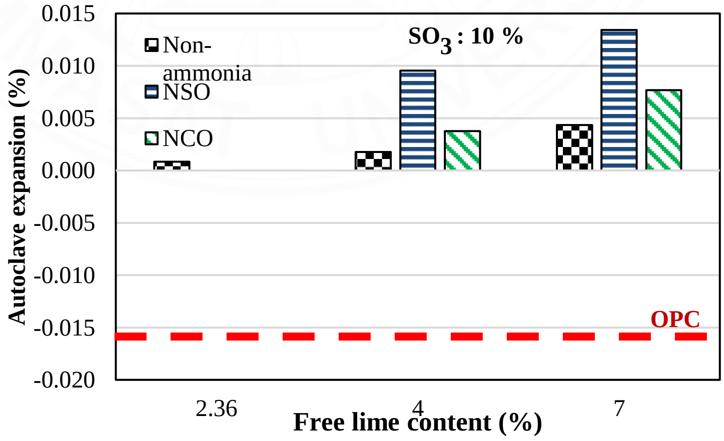
The autoclave expansion tests of ACFA with 4% and 7% of free lime contents with 3.74% SO_3 content (as shown in Figure 7.29(a)) were not conducted because the tendency was expected to be similar to the tendency of medium SO_3 content (5% SO_3 as shown in Figure 7.29(b)) and high SO_3 content (10% SO_3 as shown in Figure 7.29(c)). The same case was expected for ACFA containing low free lime content (2.36% free lime) with medium SO_3 content (5% SO_3 as shown in Figure 7.29(b)) and high SO_3 content (10% SO_3 as shown in Figure 7.29(c)) which resulted in the same tendency as ACFA containing low free lime (2.36% SO_3) with low SO_3 content (3.74% SO_3 as shown in Figure 7.29(a)). A similar explanation was applied to autoclave expansion results of low CaO fly ash pastes.



(a) 3.74% SO_3 content



(b) 5% SO_3 content

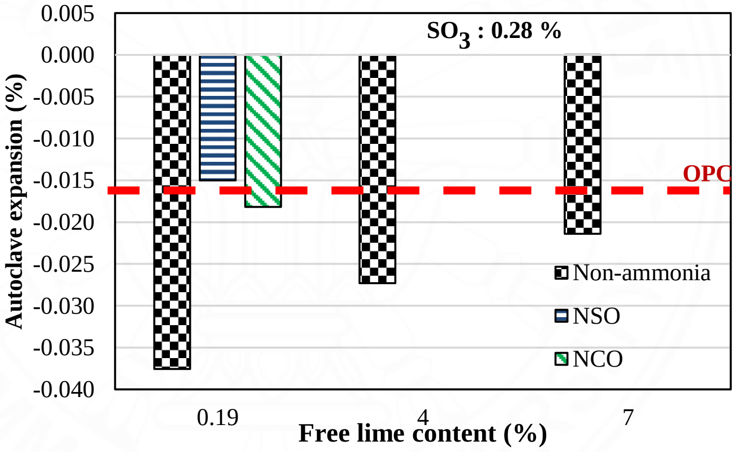


(c) 10% SO_3 content

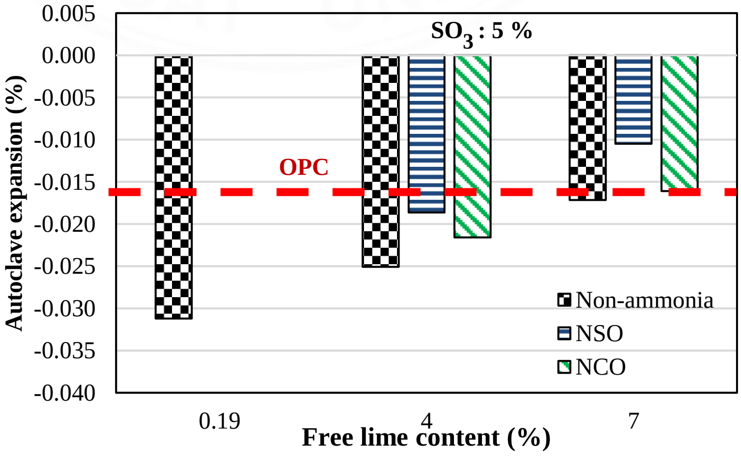
Figure 7.29 Autoclave expansion of high CaO fly ash pastes with varied free lime and SO_3 contents

Autoclave expansion results of ammonia contaminated low CaO fly ash pastes containing different free lime and SO_3 contents are shown in Figure 7.30. It can be seen that the effects of $(NH_4)_2SO_4$, $(NH_4)_2CO_3$, free lime, and SO_3 on autoclave expansion of pastes with low CaO fly ash contaminated by ammonia with varied free lime content and varied SO_3 content have the same behavior as the high CaO fly ash pastes. $(NH_4)_2SO_4$ has more significant effects on autoclave expansion than $(NH_4)_2CO_3$.

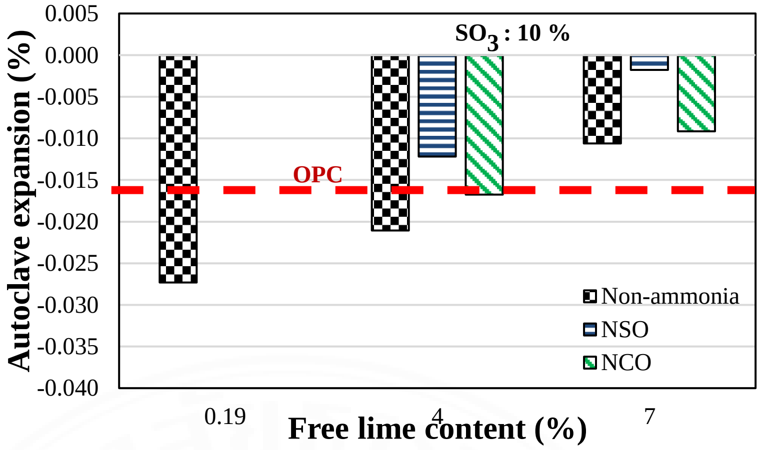
From Figure 7.30, the results show that autoclave expansion of low CaO fly ash pastes increases when the free lime content is increased in normal, medium, and high SO_3 conditions. When the SO_3 content is increased, autoclave expansion of low CaO fly ash pastes increases. The pastes that contained low CaO fly ash that was contaminated by ammonia with high free lime and high SO_3 contents have higher autoclave expansion compared to OPC-only pastes.



(a) 0.28% SO_3 content



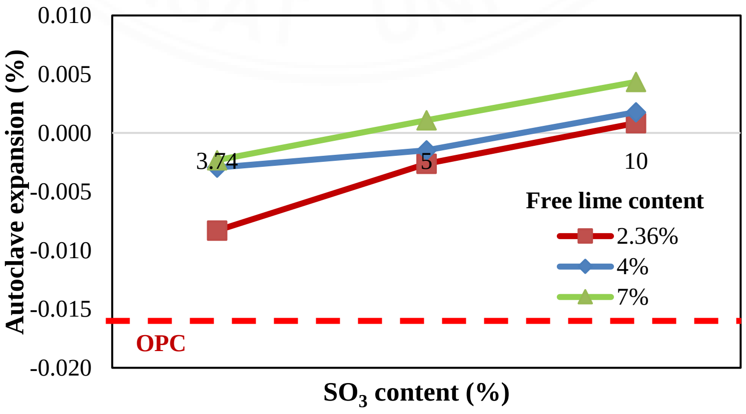
(b) 5% SO_3 content



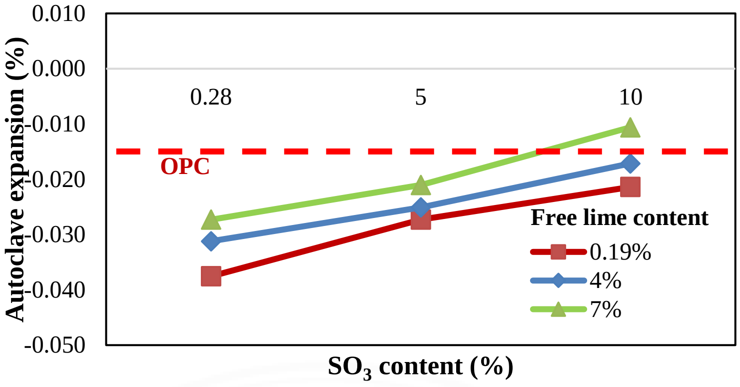
(c) 10% SO_3 content

Figure 7.30 Autoclave expansion of low CaO fly ash pastes with varied free lime and SO_3 contents

Figures 7.31(a) and 7.31(b) show that the non-ammonia pastes containing high CaO and low CaO fly ash with low, medium, and high free lime contents lead to an increase in the autoclave expansion or specifically decrease the shrinkage of pastes when SO_3 content increases. Figures 7.32(a) and 7.32(b) show that ACFA pastes containing high CaO and low CaO fly ash with medium and high free lime contents show a similar tendency with non-ammonia pastes (as shown in Figures 7.31(a) and 7.31(b)). It can be seen that the autoclave expansion of pastes increases when SO_3 content increases.

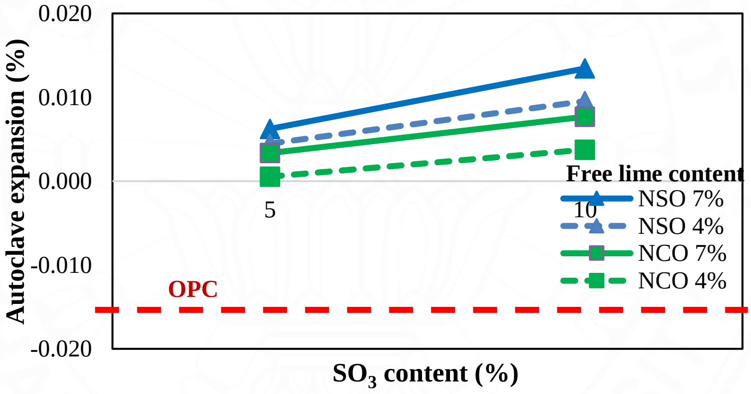


(a) High CaO fly ash

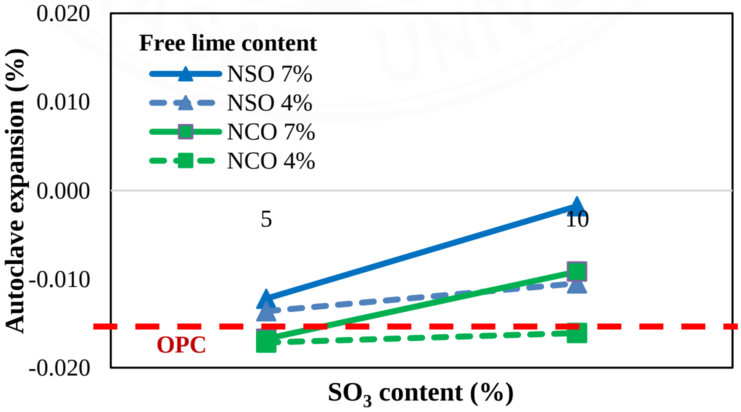


(b) Low CaO fly ash

Figure 7.31 Autoclave expansion of non-ammonia high CaO and low CaO fly ash pastes with varied free lime and SO_3 contents



(a) High CaO fly ash



(b) Low CaO fly ash

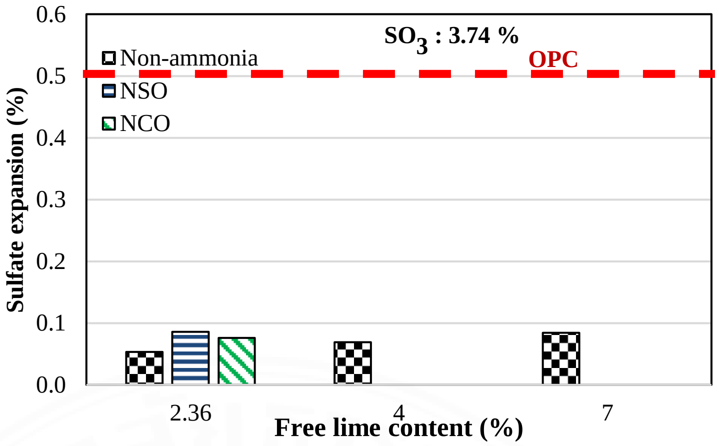
Figure 7.32 Autoclave expansion of ammonia-contaminated fly ash mortars with varied free lime and SO_3 contents

7.6 Sulfate expansion

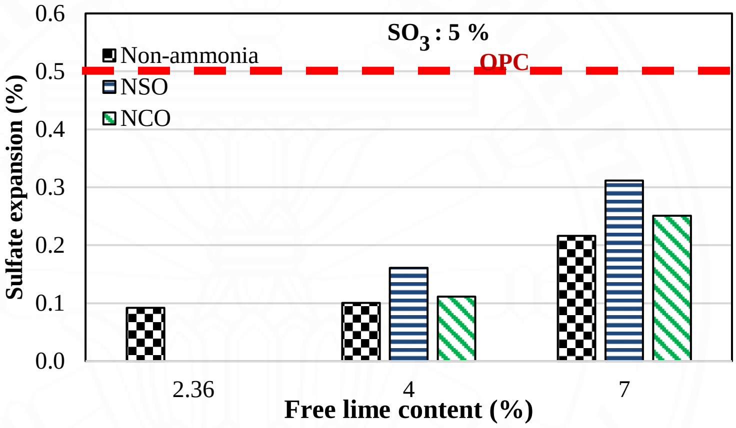
The results of sulfate expansion of mortars with high CaO and low CaO fly ash contaminated by ammonia containing different free lime and SO_3 contents, with only OPC as a control reference, are shown in Figures 7.33 and 7.36. A clear comparison of sulfate expansion of high CaO and low CaO fly ash mortars containing different free lime content and low SO_3 content can be seen at 36 weeks of mortars immersion in a sodium sulfate solution. For the sulfate expansion test, 30% fly ash replacement, 0.5 water to binder ratio, and 2.78 sand to binder ratio were applied. In this study, high CaO and low CaO fly ashes were contaminated by $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with an ammonia concentration of 600 ppm.

Figure 7.33 shows that the sulfate expansion of mortars containing high CaO fly ash contaminated by ammonia with different free lime and SO_3 contents increases when $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are added. The tendency is the same in normal, medium, and high SO_3 conditions. The results show that sulfate expansion of high CaO fly ash mortars increases when the free lime content is increased in normal, medium, and high SO_3 conditions. When the SO_3 content is increased, sulfate expansion of high CaO fly ash mortars increases. The mortars containing high CaO fly ash that is contaminated by ammonia with the varied free lime and SO_3 contents have lower sulfate expansion compared to OPC-only mortars at 36 weeks, except for the mortars with both high CaO and high SO_3 fly ash that is contaminated by $(NH_4)_2SO_4$.

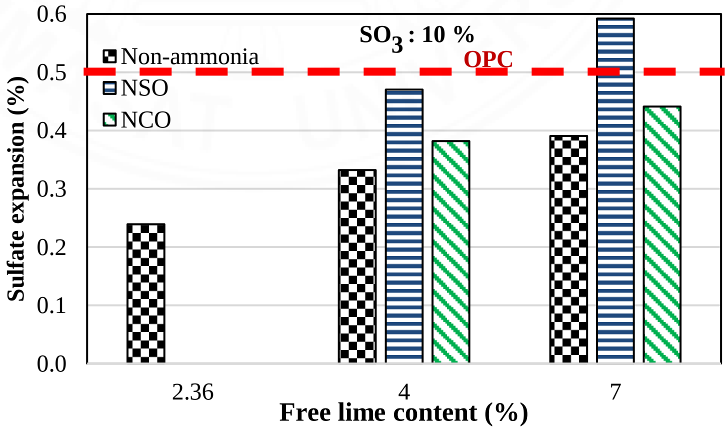
The sulfate expansion tests of ACFA with 4% and 7% of free lime contents with 3.74% SO_3 content (as shown in Figure 7.33(a)) were not conducted because the tendency was expected to be similar to the tendency of medium SO_3 content (5% SO_3 as shown in Figure 7.33(b)) and high SO_3 content (10% SO_3 as shown in Figure 7.33(c)). The same case was expected for ACFA containing low free lime content (2.36% free lime) with medium SO_3 content (5% SO_3 as shown in Figure 7.33(b)) and high SO_3 content (10% SO_3 as shown in Figure 7.33(c)) which resulted in the same tendency as ACFA containing low free lime (2.36% SO_3) with low SO_3 content (3.74% SO_3 as shown in Figure 7.33(a)). A similar explanation was applied to sulfate expansion results of low CaO fly ash mortars.



(a) 3.74% SO_3 content



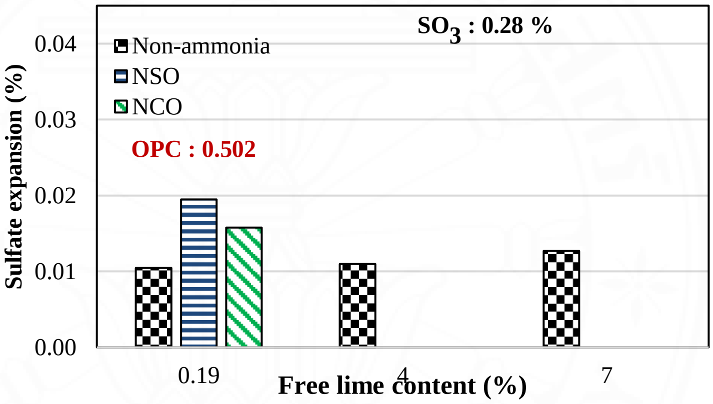
(b) 5% SO_3 content



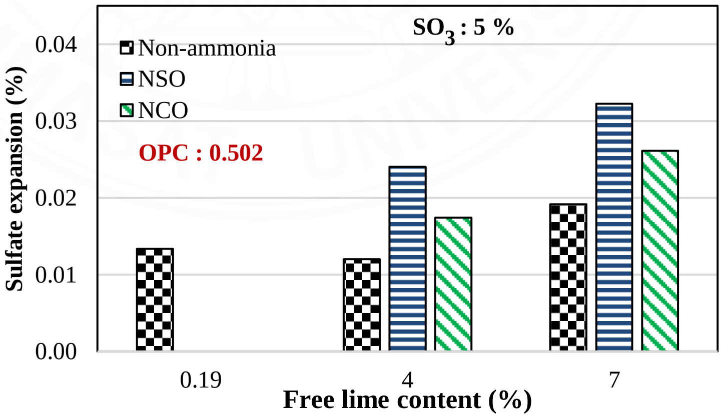
(c) 10% SO_3 content

Figure 7.33 Sulfate expansion of high CaO fly ash mortars with varied free lime and SO_3 contents

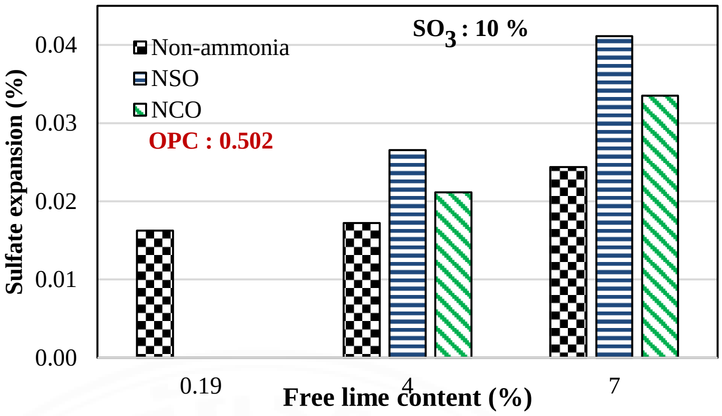
Figure 7.28 shows that the sulfate expansion of mortars containing low CaO fly ash mortars contaminated by ammonia with different free lime and SO_3 contents increases when $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are added. The tendency is the same in normal, medium, and high SO_3 conditions. The results show that sulfate expansion of low CaO fly ash mortars increases when the free lime content is increased in normal, medium, and high SO_3 conditions. When the SO_3 content is increased, sulfate expansion of low CaO fly ash mortars increases. The mortars containing low CaO fly ash that is contaminated by ammonia with varied free lime and SO_3 contents have lower sulfate expansion compared to the OPC-only mortars at 36 weeks.



(a) 0.28% SO_3 content



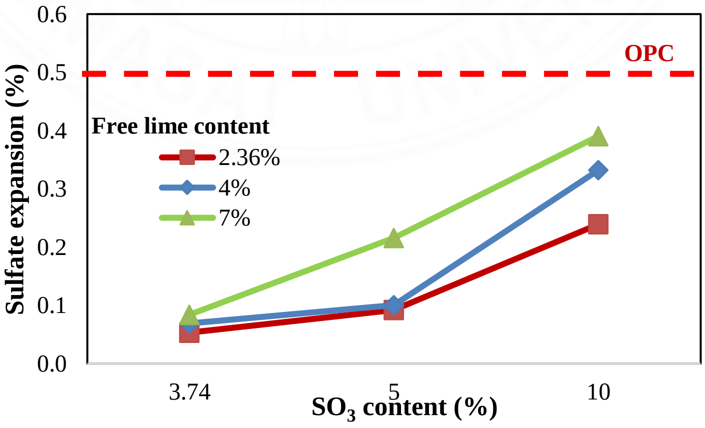
(b) 5% SO_3 content



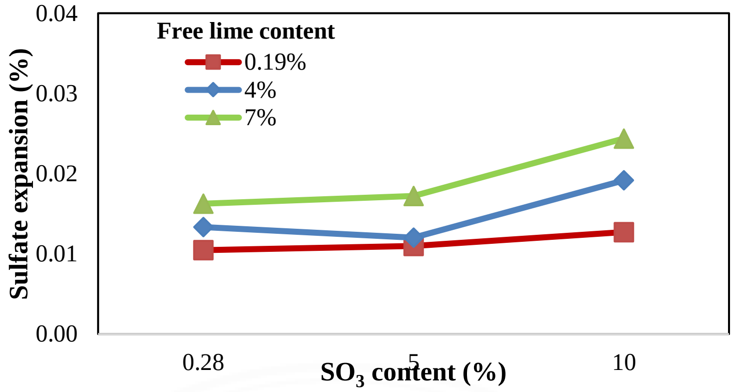
(c) 10% SO_3 content

Figure 7.34 Sulfate expansion of low CaO fly ash mortars with varied free lime and SO_3 contents

Figures 7.35(a) and 7.35(b) show that the non-ammonia mortars containing high CaO and low CaO fly ash with low, medium, and high free lime contents lead to an increase in the sulfate expansion of mortars when SO_3 content increases. All mixtures show that sulfate expansion increases when SO_3 content increases. Figures 7.36(a) and 7.36(b) show that ACFA mortars containing high CaO and low CaO fly ash with medium and high free lime contents lead to an increase in the sulfate expansion of mortars when SO_3 content increases.

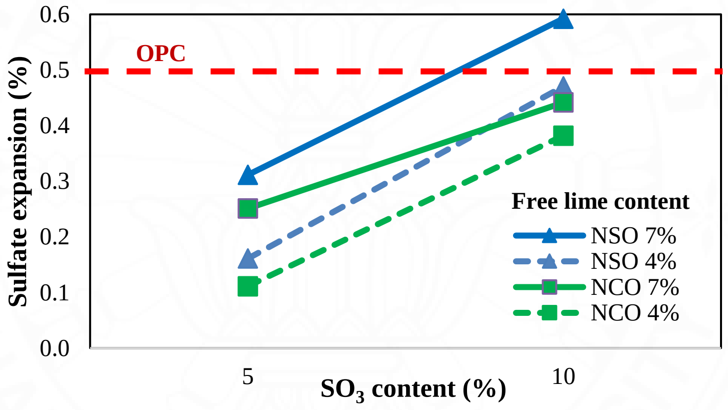


(a) High CaO fly ash

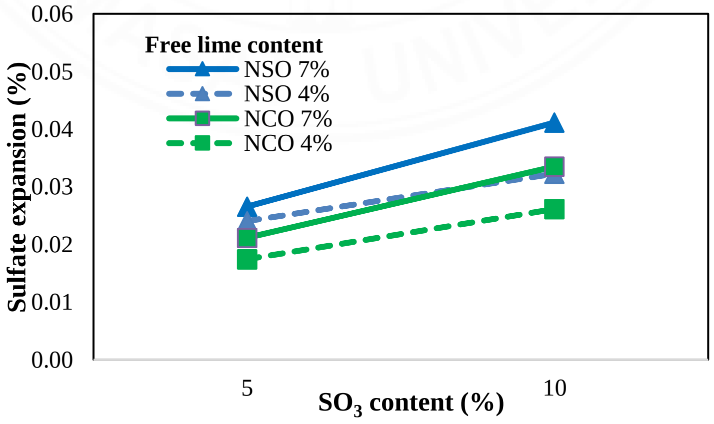


(b) Low CaO fly ash

Figure 7.35 Sulfate expansion of non-ammonia fly ash mortars with varied free lime and SO$_3$ contents



(a) High CaO fly ash



(b) Low CaO fly ash

Figure 7.36 Sulfate expansion of ammonia-contaminated fly ash mortars with varied free lime and SO$_3$ contents

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

8.1 Conclusions

1) Effects of different types and concentrations of ammonium salts on the properties of pastes and mortars

The evaluation of the effects of ammonia-contaminated fly ash on the properties of mortars was conducted by applying ammonia concentrations in the range of 0-1000 ppm, with 20-30% fly ash replacement. Two types of fly ash, high CaO and low CaO fly ashes were used in this study. Two forms of ammonium salts are $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$. The fly ash mortars containing ammonium salts show different results in their properties. The summary of all test results from this study and previous studies is demonstrated in Tables 8.1 and 8.2.

Table 8.1. Performances of fly ash pastes and mortars with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ when compared to mixtures containing fly ash without ammonium salts

Properties	Fly ash mortars containing $(NH_4)_2SO_4$		Fly ash mortars containing $(NH_4)_2CO_3$	
	High CaO	Low CaO	High CaO	Low CaO
Normal consistency	Better	Better	Better	Better
Workability	Better	NA	Better	NA
Autoclave expansion	*Worse	Slightly Worse	*Worse	Slightly Worse
Sulfate expansion	**Worse	**Worse	Slightly Worse	Slightly Worse
Early compressive strength	Slightly Worse	Slightly Worse	Better	Better
Long-term compressive strength	Slightly Worse	Slightly Worse	Better	Better
Autogenous shrinkage	Better	Better	Better	Better
Total shrinkage	**Worse	**Worse	Better	Better

Note: * = Still below the limit, ** = Still better than OPC, NA = Not available

Table 8.2. Performances of fly ash pastes and mortars with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ when compared to mixtures containing OPC-only

Properties	**Fly ash mortars containing $(NH_4)_2SO_4$**		**Fly ash mortars containing $(NH_4)_2CO_3$**	
	High CaO	**Low CaO**	**High CaO**	**Low CaO**
Normal consistency	Better	*Worse	Better	*Worse
Workability	Better	NA	Better	NA
Autoclave expansion	*Slightly Worse	Better	*Slightly Worse	Better
Sulfate expansion	Better	Better	Better	Better
Early compressive strength	*Worse	*Worse	*Worse	*Worse
Long-term compressive strength	*Worse	*Worse	Better	Better
Autogenous shrinkage	Better	Better	Better	Better
Total shrinkage	Better	Better	Better	Better

Note: * = worse due to the effects of fly ash types, NA = Not available

In Tables 8.1 and 8.2, the test results from this study are normal consistency, autoclave expansion, sulfate expansion, early-age compressive strength, long-term compressive strength, and autogenous shrinkage. Workability and total shrinkage were obtained from a study reported by Krerkchaiwan (2017). Table 8.1 shows the performances of fly ash pastes and mortars with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ when compared to mixtures containing fly ash without ammonium salts. Table 8.2 shows the performances of high CaO and low CaO fly ash pastes and mortars with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ when compared to mixtures with OPC-only. From Tables 8.1 and 8.2, the change in properties of pastes and mortars depends on the types and concentrations of ammonium compounds, as follows.

For normal consistency, the pastes containing either $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ show improvement in normal consistency by reducing the normal consistency values. Autoclave expansion and sulfate expansion results show the same tendency. $(NH_4)_2SO_4$ leads to higher expansion of pastes and mortars because of the formation of ettringite and gypsum that resulted from $(NH_4)_2SO_4$ reaction. $(NH_4)_2CO_3$ leads to the higher expansion of pastes and mortars, but the mechanism is still under investigation.

For early-age compressive strength, the behavior of fly ash mortars with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ follows the behavior of the fly ash mixtures that is, lower compressive strength at an early age when the fly ash is incorporated into the mixtures. From long-term compressive strength results, in the case of $(NH_4)_2SO_4$ salt, the existence of expansive products such as gypsum and ettringite leads to a reduction of compressive strength of mortars due to the micro-cracking. In contrast, the compressive strength of the mortars with $(NH_4)_2CO_3$ is improved because of the formation of $CaCO_3$.

Both $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ improve flowability, and consequently, the setting times tend to delay due to the dissolving of ammonium ions. For shrinkage, both $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ increase autogenous shrinkage of the tested mortars. The total shrinkage of the mortars with $(NH_4)_2CO_3$ contaminated fly ash decreases compared to the non-ammonia fly ash mortars due to the generation of $CaCO_3$.

Autogenous shrinkage results show that the existence of expansive products such as gypsum and ettringite leads to a reduction of the mortar shrinkage, in the case of $(NH_4)_2SO_4$ salt. Similarly, $(NH_4)_2CO_3$ leads to a reduction of shrinkage compared to non-ammonia fly ash mortars, but the mechanism for the latter is still under investigation.

From the performances of high CaO and low CaO fly ash pastes and mortars with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ when compared to mixtures with OPC only, it can be concluded that the ammonia-contaminated fly ash can be used as a cement replacing material. The change of mortar properties depends on type of fly ash, type of ammonium salt, and concentrations of ammonium compounds to generate products in the cement matrix.

2) Effects of blended ammonium salts on properties of pastes and mortars.

The results of normal consistency, autoclave expansion, and sodium sulfate expansion of the mixtures containing fly ash with blended ammonium sulfate and ammonium carbonate with 20-30% fly ash replacement are in between those of the mixtures containing single ammonium salt (pure ammonium sulfate and pure ammonium carbonate).

3) **Effects of ammonium salts with different fly ash types on properties of pastes and mortars.**

The results of ammonia-contaminated low CaO and high CaO fly ash pastes and mortars with 20-30% fly ash replacement have the same trend. The results follow the characteristics of each type of fly ash. The effects of fly ash properties in the pastes and mortars have the same trend as the mixtures containing non-ammonia contaminated fly ash.

4) **Effects of ammonium salts in fly ash with different free lime and SO_3 contents on properties of pastes and mortars.**

The results of the pastes and mortars using fly ash containing different free lime and SO_3 contents with ammonium salts and using 20-30% fly ash replacement show a similar tendency to the pastes and mortars using fly ash containing different free lime and SO_3 contents without ammonium salts.

8.2 Recommendations for future studies

According to the results of this study, the test of real ammonia-contaminated fly ash cannot be conducted. The recommendations for future studies are in the following list.

1. Properties of mixtures using real ammonia-contaminated fly ash from the power plant should be studied.
2. The mechanisms of autoclave and sulfate expansion due to ammonium carbonate cannot be clearly concluded. More intensive studies should be conducted.
3. Shrinkage properties of mixtures containing ammonium salt contaminated fly ash with different free lime and SO_3 contents should be investigated.
4. Ammonia-contaminated fly ash using very high CaO fly ash is needed to be investigated.

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