EFFECTS OF AMMONIUM SULFATE AND AMMONIUM CARBONATE AS CONTAMINATED AMMONIA IN FLY ASH ON PROPERTIES OF MORTARS

BY

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ABSTRACT

Post-coal combustion process with SCR or SNCR technologies is widely used to reduce NO_x gas in coal power plants. This is done by NH_3 injection to convert NO_x gas to N_2. Some unreacted ammonia left in the process can cause ammonia-contaminated fly ash which are mostly found in forms of ammonium sulfate ($(NH_4)_2SO_4$) and ammonium carbonate ($(NH_4)_2CO_3$). The objective of this study is to investigate the effects of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in fly ash on the properties of mortars with varied ammonia concentrations in the ammonium salts which are 0, 100, 200, 600, and 1000 ppm. As the ammonia contaminated fly ash does not contain only a single type of ammonium salt, this study also investigates the blended ammonium salts of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$. The varied ratios of $(NH_4)_2SO_4$ to $(NH_4)_2CO_3$ are 0, 0.25, 0.5, 0.75, and 1 at the total ammonia concentration in the ammonium salt of 200 ppm. The types of fly ash which are used in the tests are fly ashes having low CaO (FAR), high CaO (FAA), and high CaO with high free lime (FAB) contents at the total ammonia concentration of 200 ppm. The high free lime fly ashes which contain total free lime contents of 5% and 10% are also investigated at the total ammonia concentration of 200 ppm. Mortar specimens with 30% replacement of fly ash and w/b of 0.5 were prepared. The ammonia contamination was prepared by dissolving ammonium salts in water. The test results show that the workability of fresh mortars containing ammonium salts was improved. Setting times of cement pastes containing ammonium salts were delayed. Compressive strength of mortars containing $(NH_4)_2SO_4$ decreased when compared to that of mortars with no ammonium salts. On the other hand, the compressive strength of mortars containing $(NH_4)_2CO_3$ increased. Total shrinkage of mortars containing $(NH_4)_2SO_4$ increased when compared to that of mortars with no ammonium salts. On the other hand, total shrinkage of mortars with $(NH_4)_2CO_3$ decreased. The test results of properties of mortars containing both ammonium salts with different ratios of $(NH_4)_2SO_4$ to $(NH_4)_2CO_3$ were in between the properties of the mortars containing $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ separately. For the test results of properties of mortars containing different types of fly ash, the effects of ammonium salts show the same tendency as in the above explanation. Quantitively, the differences of results come from the differences in chemical compositions of the fly ashes. For properties of mortars containing high contents of free lime, the results show that the workability of fresh mortars containing fly ash with high free lime content decreased while the compressive strength of mortars containing fly ash with high free lime content increased when compared to mortars containing low free lime fly ash.

Keywords: Fly ash, Contaminated ammonia , Ammonium sulfate, Ammonium carbonate, Low CaO fly ash, High CaO fly ash, High free lime fly ash, Mortar

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Ms. Shayapa Roongruangsarn

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LIST OF SYMBOLS/ABBREVIATIONS

Symbols/Abbreviations	**Terms**
NSO	Ammonium sulfate
NCO	Ammonium carbonate
FAR	Low CaO fly ash
FAA	High CaO fly ash
FAB	High CaO and high SO_3 fly ash
FAC5%	FAA fly ash with the 5% of total free lime content
FAC10%	FAA fly ash with the 10% of total free lime content
H_2O	Water
N_2	Nitrogen gas
O_2	Oxygen gas
NH_3	Ammonia gas
NO_x	Nitrogen oxides
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction

CHAPTER 1

INTRODUCTION

1.1 Effects of Ammonia Contaminated Fly ash on Properties of Mortar

Thailand has been using coals, especially lignite and bituminous coals, which are local and imported, respectively, to generate electric power for many decades. Majority of the by-products from the power generation process is fly ash (Burnard & Bhattacharya, 2011; Iea Etsap, 2010).

Fly ash is also known as the pozzolanic material (Al-chaar, Alkadi, & Asteris, 2013) which is effectively used to replace cement to reduce the cost and to improve properties of concrete (Thomas, 2007). The coal combustion process produces not only fly ash, but also generates and releases toxics gases like NO_x which affects human health and environment. Due to environmental impacts, the electric power plant manages to reduce NO_x by installing NO_x control technologies such as Selective Catalytic Reduction (SCR) or Selective non-Catalytic Reduction (SNCR) at the power plant. In both SCR and SNCR technologies, ammonia is injected into the flue gas stream to convert NO_x gas into nitrogen gas (N_2) and water (H_2O), as shown in the following equations (Bittner, Gasiorowski, & Hrach, 2001; G.F. Brendel, J.E. Bonetti, R.F. Rathbone, and R.N. Frey, 2000; Nahavandi, 2015; Xuan, Yue, Li, & Yao, 2003):

$$6NO+4NH_3 \rightarrow 5N_2+6H_2O \tag{1.1}$$

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

The unreacted ammonia residue from the process of removing NO_x from the fly ash is usually defined as “ammonia slip” typically represents less than 2% of the total ammonia injection. Around 70% of the ammonia slips are adsorbed on the surface of fly ash in various forms such as ammonia gas or ammonium salts (Wang, Ban, Golden, & Ladwig, 2002). Ammonium salts can be formed by the reaction between NH_3 and flue gas such as ammonium sulfate ($(NH_4)_2SO_4$) and ammonium bi-sulfate (NH_4HSO_4). Moreover, ammonium carbonate ($(NH_4)_2CO_3$) is also produced from the reaction between NH_3 and CO_2 existing in the exhaust gases. Equations (1.3-1.5) show the reactions between ammonia and the flue gases to generate ammonium salts.

$$2NH_3+SO_3+H_2O\rightarrow(NH_4)_2SO_4 \tag{1.3}$$

$$NH_3+SO_3+H_2O\rightarrow NH_4HSO_4 \tag{1.4}$$

$$2NH_3+CO_2+H_2O\rightarrow(NH_4)_2CO_3 \tag{1.5}$$

According to the industry recommendation (Larrimore, 2002), the limit of ammonia in the ammonia-contaminated fly ash (ACFA) should not be over 200 ppm for use in concrete. This is because the high content of ammonia in ACFA may possibly cause adverse effects on the properties of concrete as well as the health of workers.

Kim et al. conducted an experiment using ammonia contaminated fly ash (ACFA) with ammonia concentrations of 0-620 ppm. The results show that setting times delay when increasing ammonia concentration. Compressive strength of both mortar and concrete specimens decrease due to the aggressive impacts of ammonium ions and sulfate ions dissolved from ACFA in the concrete mixtures (Kim, Cho, Lee, & Kim, 2007).

Ling Qin et al. (2019) conducted an experiment using coal fly ash containing ammonium bisulfate (NH_4HSO_4) at 3.0-6.0% by fly ash weight and ammonium sulfate ($(NH_4)_2SO_4$) at 1.5-3.0% by fly ash weight. The results show that setting times delay when increasing ammonium salts because sulfate ions lower the hydration reaction rate. Compressive strength of cement paste specimens decreases because the release of NH_3 gases increases the formation of coarse pores with high diameter and a decreasing of hydration reaction rate (Qin, Gao, & Li, 2019).

As mentioned earlier, many researchers have paid attention to the effects of ACFA on properties of concrete from the formation of ammonium sulfate ($(NH_4)_2SO_4$) and ammonium bi-sulfate salt (NH_4HSO_4). However, not only ammonium sulfate ($(NH_4)_2SO_4$) and ammonium bi-sulfate salt (NH_4HSO_4), but ammonium carbonate

($(NH_4)_2CO_3$) may be another product from the combustion process installed with NO_x removing process (SCR or SNCR technologies). Studies on the effects of $(NH_4)_2CO_3$ are scarcely found. Therefore, this study aims to investigate the effects of ACFA on the properties of mortars. In this study, to be able to vary the concentration of the ammonium salts in the fly ash by maintain other fly ash properties, two compounds of ammonium salt were added in the fly ash mortar mixtures, instead of using the real ACFA. Tests on mortar properties include flow test, setting time, compressive strength, autogenous shrinkage, and total shrinkage.

1.2 Statement of problem

In Thailand, fly ash from power plants has been popularly utilized as a pozzolanic material. Thailand has recently installed SCR technology in power plant. SCR technology uses ammonia to change NO_x to N_2 which is more environmental friendly. But not all the injected ammonia would react with NO_x. There are some ammonia left in the system and cause contamination in fly ash. The problem is there has been no ammonia-contaminated fly ash in Thailand before. So, it is not known that there are any problems or effects on properties of concrete that incorporates ammonia-contaminated fly ash. Therefore, this research focuses on studying the effects of ammonia-contaminated fly ash on properties of mortars.

1.3 Objectives of research

This study is aimed to investigate the effects of ammonia-contaminated fly ash on mortars by mixing the fly ash with ammonium sulfate ($(NH_4)_2SO_4$) and ammonium carbonate ($(NH_4)_2CO_3$) instead of using real ammonia-contaminated fly ash. Fly ash samples without ammonium contamination were collected from Mae Moh power plant, Lampang province, and BLCP Power plant, from Rayong province.

The main objectives of this study include:

1. To investigate the properties of mortars containing ammonia-contaminated fly ash as a pozzolanic material
   1.1 Effects of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in fly ash on properties of mortars

    1.2 Effects of blended $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in fly ash on properties of mortars
    1.3 Effects of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in different types of fly ash (high CaO and low CaO fly ashes) on properties of mortars
    1.4 Effects of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in high free lime content in fly ash on properties of mortars
2. To investigate mechanisms of effects of ammonia-contaminated fly ash on properties of mortars

1.4 Scope of study

The scope of this study includes:

1. Materials
    - 1.1 Ordinary Portland cement (OPC type I)
    - 1.2 Fly ash
        - 1.2.1 Mae Moh fly ash
            - 1.2.1.1. FAA – high CaO content
            - 1.2.1.2. FAB – high CaO content and high free lime content
        - 1.2.2 BLCP fly ash
            - 1.2.2.1. FAR – Low CaO content
    - 1.3 Ammonium salts
        - 1.3.1 Ammonium sulfate
        - 1.3.2 Ammonium carbonate
    - 1.4 Ammonia concentrations in the ammonium salt are 0 to 1000 ppm
2. Water to binder ratio is 0.5
3. Fly ash to binder ratio is 0.3
4. Test items
    - 4.1 Flow ability
    - 4.2 Setting times
    - 4.3 Compressive strength
    - 4.4 Shrinkage
        - 4.4.1 Autogenous shrinkage

4.4.2 Total shrinkage

4.5 Porosity

CHAPTER 2

LITERATURE REVIEW

2.1 General information of NO_x removal process

Fly ash is a by-product from coal combustion process in an electricity generation plant. In Thailand, the amount of fly ash produced is approximately 3 million tons per year during the past 10 years. Mae Moh power plant is the largest coal power plant that produces about 90% of the country's total fly ash production, as shown in Figure 2.1;

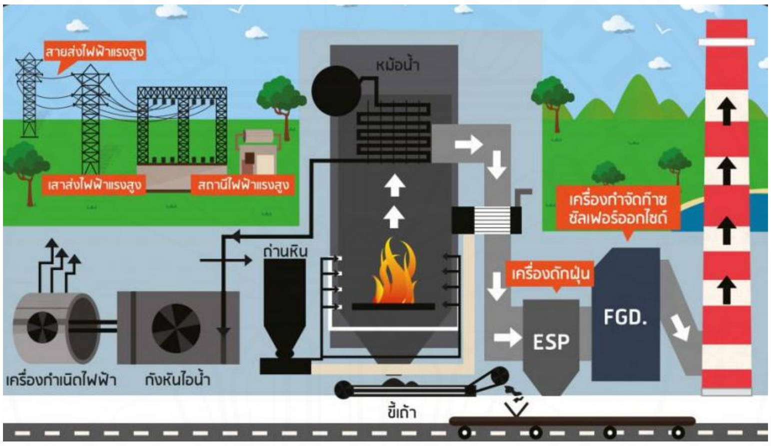


Figure 2.1 Coal power plant (Suvisisarsa & Ninkanha, 2020)

Coal combustion process does not only produce fly ash as a by-product but also releases gases such as CO_2, NO_x, and SO_2. NO_x and SO_2 cannot be too much released to the environment as they cause environment and human health problems. In the past, only SO_2 removal process which is fuel-gas desulfurization (FGD) had been installed, but not NO_x removal facilities.

2.2 NO_x removing technology

Nowadays, there are many new technologies for NO_x removal process such as Selective Catalytic Reduction (SCR) and Selective non-Catalytic Reduction (SNCR). In both SCR and SNCR processes, NH_3 is injected into the exhaust gas to convert NO_x into nitrogen gas (N_2) and water (H_2O), as shown in Figure 2.2 and Figure 2.3

with the reactions shown in equations (2.1) and (2.2), which are more environment friendly (Iea Etsap, 2010), (Larrimore, 2002).

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

$$2NO_2+4NH_3+O_2 \rightarrow 3N_2+6H_2O \tag{2.2}$$

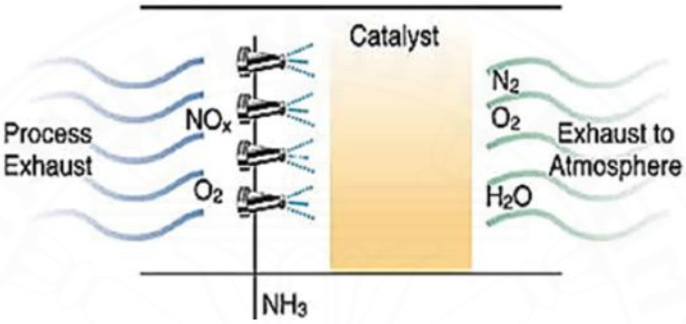


Figure 2.2 SCR (Selective Catalytic reduction) Process (Iea Etsap, 2010)

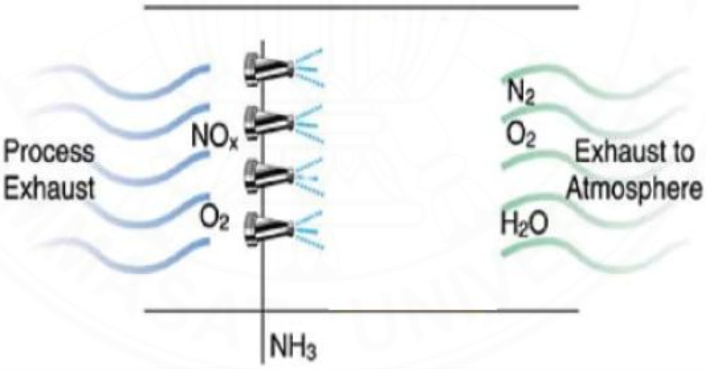


Figure 2.3 SNCR (Selective Non-Catalytic Reduction) process

The efficiency of NO_x removal process by SCR is around 60-90% while that of SNCR is around 40-75%. Since the catalyst is used to reduce the activation energy, the formation of N_2 and H_2O are faster. Then, the amount of NH_3 slip from SCR process is about 2-5 ppm, but that from the SNCR process is around 5-20 ppm with the initial ammonia concentration of 200 and 1000 ppm. So, SCR process, as shown in Figure 2.4, is very commonly used in many countries.

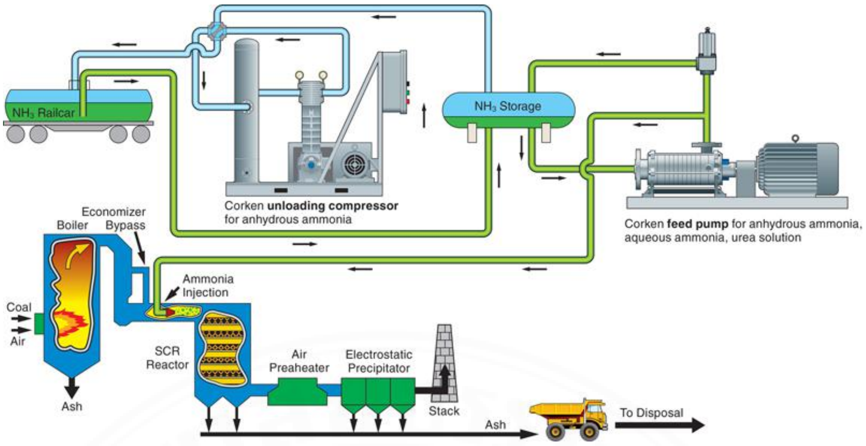


Figure 2.4 Coal combustion process with NOx removal process (Iea Etsap, 2010)

2.3 Selective Catalytic Reduction (SCR)

SCR is the process of removing NO_x by injecting ammonia into the exhaust gas from the boiler, and then convert NOx into nitrogen (N_2) and water (H_2O). This process has been developed for industrial stationary applications such as natural gas, crude oil, light or heavy oil and pulverized coal (Technologies, 2008.).

SCR involves a metal-based catalyst with activated sites to increase the formation rate of Nitrogen and water (Mussatti, Daniel C, Dr. Ravi Srivastava, 2002). The usually used catalyst for SCR is Vanadium Oxide/Titanium Dioxide (V_2O_5/TiO_2) or Vanadium Oxide-Tungsten Trioxide/Titanium Dioxide (V_2O_5-WO_3/TiO_2).

2.3.1 Reducing agent and Catalytic reactions

SCR process is used as the reducing agent of NO_x. There are various forms of ammonia used in SCR system

- **Pure anhydrous ammonia**

  It is a toxic chemical substance. This type of ammonia needs thick-shell, pressurized storage tanks and piping due to its high pressure.

- **Aqueous ammonia ($NH_3 \cdot H_2O$)**

  It is less hazardous and easier to handle than pure anhydrous ammonia. The amount of ammonia injected into SCR process has to be enough to convert NO_x gas. But it should not be over-supplied because the ammonia will cause problems to the system and fly ash after finishing the combustion process. The amount of injection should follow the stoichiometric ratio from the chemical reaction.

2.3.2 Chemical reactions

The chemical reactions occur in the SCR process are to convert the NO_x gas to nitrogen (N_2) and water (H_2O). There are many reactions depending on the concentration of NO_x gas and ammonia and some reactions may involve with oxygen (O_2) (Theotoki, 2015), (G.F. Brendel, J.E. Bonetti, R.F. Rathbone, and R.N. Frey, 2000).

$$6NO+4NH_3 \rightarrow 5N_2+6H_2O \tag{2.3}$$

$$4NO+4NH_3+O_2 \rightarrow 4N_2+6H_2O \tag{2.4}$$

$$6NO_2+8NH_3 \rightarrow 7N_2+12H_2O \tag{2.5}$$

$$2NO_2+4NH_3+O_2 \rightarrow 3N_2+6H_2O \tag{2.6}$$

$$NO+NO_2+2NH_3 \rightarrow 2N_2+3H_2O \tag{2.7}$$

In addition, ammonia can also react with NO_x gas and form ammonium nitrate (NH_4NO_3), which is an explosive substance.

$$2NH_3+2NO_2+H_2O \rightarrow NH_4NO_3+NH_4NO_2 \tag{2.8}$$

Equation (2.8) can occur when the temperature is around 100-200 °C.

NH_4NO_2 can be solid or liquid forms of catalyst in the pores and cause deactivation of catalyst.

When the flue gas contains CO_2, the ammonia can react with CO_2 to form ammonium carbonate $(NH_4)_2CO_3$ and ammonium bi-carbonate $(NH_4)HCO_3$.

$$2NH_3+CO_2+H_2O \rightarrow (NH_4)_2CO_3 \quad (2.9)$$

$$NH_3+CO_2+H_2O \rightarrow (NH_4)HCO_3 \quad (2.10)$$

When the flue gas contains sulfur, sulfur dioxide (SO_2) can be oxidized to sulfur tri-oxide (SO_3). SO_3 reacts with ammonia to form $(NH_4)_2SO_4$ and $(NH_4)HSO_4$. These two ammonium salts can deposit on the catalyst, piping and equipment when the temperature is below 250 °C (Fernando, 2003), (James T. Murphy, 2007).

$$NH_3+SO_3+H_2O \rightarrow NH_4HSO_4 \quad (2.11)$$

$$2NH_3+SO_3+H_2O \rightarrow (NH_4)_2SO_4 \quad (2.12)$$

The SCR process requires the control injection rate of ammonia. The rate should be precisely not too high to cause undesirable ammonia left to the environment. The ammonia slip (ammonia emissions to environment) will increase if the ratio of NH_3 to NO_x is increased.

2.3.3 Catalysts

2.3.3.1 V-based SCR Catalysts (V_2O_5/TiO_2) or (V_2O_5-WO_3/TiO_2)

Vanadia-based SCR catalyst are Vanadium pent-oxide (V_2O_5) which is the first commercial catalyst for NO_x emission reduction. In the process, Vanadium oxide (V_2O_5) is the active catalyst but it needs the support catalyst which is Titanium dioxide (TiO_2) and sometime it needs Tungsten Trioxide (WO_3) to work as chemical and physical promoter for Vanadium oxide and Titanium dioxide.

Commercial Vanadia-based catalyst has a high activity for NO_x reduction with the range of temperature between 300-450 °C. It also has high resistance to sulfur, hydrocarbon, and lubricant poisoning. When the catalyst was deactivated and get low activity, the release of volatile vanadium should be in concern because of its toxic nature.

2.3.3.2 Zeolite SCR Catalysts

Zeolites are a hydrated crystalline aluminosilicate with micro-porous structure. Due to the micro-porous structure, zeolite allows only small molecules to pass through and trap larger molecules.

Zeolite can be operated at lower temperature than commercial vanadium-based catalyst. It is more preferable than commercial vanadium-based catalyst due to the following characteristics:

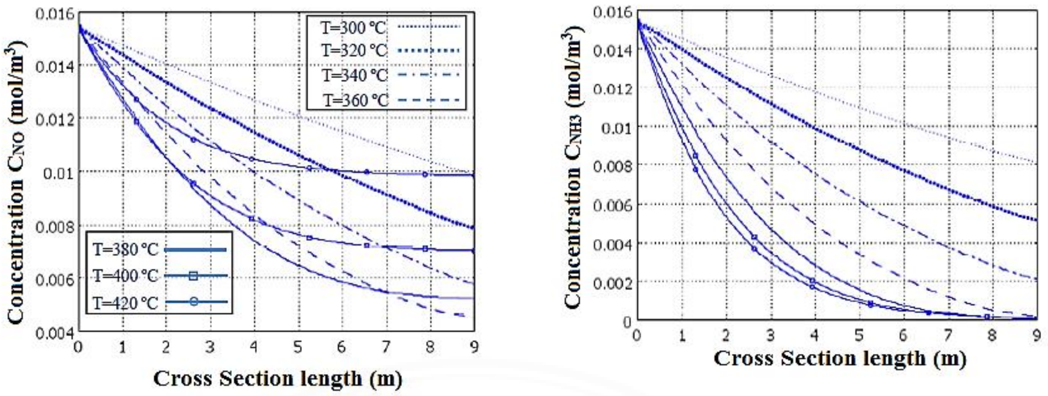
- Low price
- Non-toxicity
- High SCR activity and selectivity to N_2
- Good performance at low temperature
- High thermal durability at high temperature

However, it has the problem that it needs to avoid the reheating of the exhaust gases at the required temperature which is unlike commercial vanadium-based catalyst (Hemelsoet, Wispelaere, & Mynsbrugge, 2014), (Izquierdo et al., 2004).

2.3.4 Effects of temperature

The ammonia slip decreases with the increase of temperature but the conversion of NO_x depends on temperature. The rate of NO_x conversion can be ignored when the temperature is lower than 400 °C according to simulation which is based on a knowledge of SCR kinetics for prediction of NO conversion over a V_2O_5/TiO_2 catalyst (Xuan et al., 2003).

From Figure 2.5, the temperature at 360 °C results in maximum conversion.



(a) NO (b) NH_3

Figure 2.5 Effects of temperature on NO_x conversion (Xuan et al., 2003)

2.3.5 Effects of Gas Velocity

The conversion of NO_x and NH_3 depends on gas velocity. This variation can be expressed as a parameter which is Gas Hourly Space Velocity (GHSV). This parameter can change residence time and conversions. Normally, reducing the residence time by increasing the gas velocity, decreases the conversion (Xuan et al., 2003).

2.3.6 Effects of Inlet Concentration

The process may have some outlet ammonia gas. The amount of outlet ammonia also depends on the process temperature and the inlet of ammonia (Xuan et al., 2003).

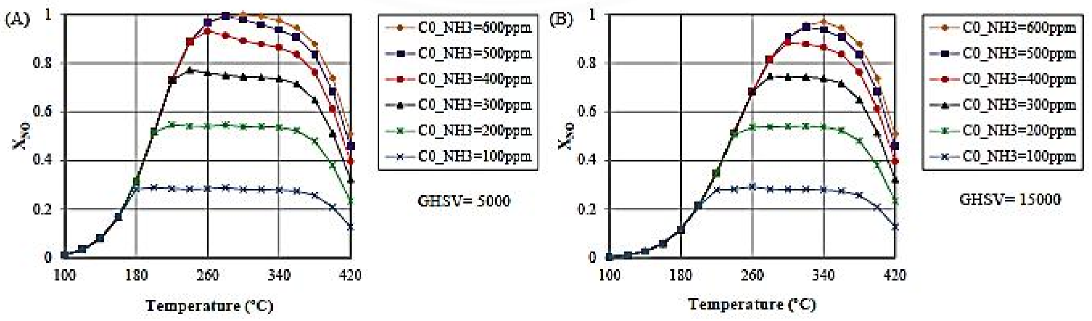


Figure 2.6 Effects of NH_3 inlet concentration on NOx conversion at different temperatures and initial concentration of NOx of 350ppm (Xuan, Yue, Li, & Yao, 2003).

From Figure 2.6, at different values of Gas Hourly Space Velocity (GHSV) with the same initial concentration of ammonia, there is insignificant difference in the conversion. As for the different initial concentration of ammonia with the same temperature, the conversion is different with the higher initial concentration of ammonia, causing high conversion rate. When the temperature is too high, the rate of conversion drops. So, the temperature is a significant parameter that affect the rate of conversion of NO_x.

2.4 Ammonia slip

The ammonia that is injected into the SCR process to reduce NO_x may have some unreacted ammonia left in the process which is called "ammonia slips". The amount of ammonia slips is very small when compared to the amount at initial injection. According to many researches, the amount of ammonia can be divided into 5 parts; (Larrimore, 2002), (Lockert, 2009)

1. Around 99% of ammonia converts NO_x to N_2 and water. So, the ammonia slip will be around 1% of the total:
2. Ammonia gas slip is adsorbed by the fly ash.
3. Ammonia gas slip reacts with exhaust gases such as SO_2, NO_x, and CO_2 to form ammonia salt (Theotoki, 2015) such as

- Ammonium sulfate, $(NH_4)_2SO_4$
- Ammonium bi-sulfate, $(NH_4)HSO_4$
- Ammonium carbonate, $(NH_4)_2CO_3$
- Ammonium bi-carbonate, $(NH_4)HCO_3$
- Ammonium nitrate, $(NH_4)NO_3$

3.1 70% of ammonia salts is attached to the surface of fly ash
3.2 5% of ammonia salts goes to air heater and burns out as gases
3.3 The left over may stay in the equipment.

But the ammonium salts that are mostly found in this process are ammonium sulfate, ($(NH_4)_2SO_4$) and ammonium bi-sulfate, (NH_4HSO_4). It is because the temperature of process is quite favorable to form ammonia sulfate and ammonia bi-sulfate (G.F. Brendel, J.E. Bonetti, R.F. Rathbone, and R.N. Frey, 2000).

4. Around 20% of ammonia slip goes to air heater.
5. Less than 1% of ammonia slip goes to stack and release to environment.

2.5 Reaction between cement substances and ammonium salts

The reaction of ammonium salts in concrete has been recognized as potentially aggressive reaction that can change the properties of mortar and concrete. The most aggressive ammonium salts that can deteriorate the mortar and concrete structure are ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate ($(NH_4)_2NO_3$). The process that involved in the deterioration of mortar and concrete in the presence of ammonium compounds involves the reaction between the portlandite (Calcium hydroxide, $Ca(OH)_2$), C-S-H, and the ammonium salts (Ravindra K. Dhir, Michael John McCarthy, 2002).

- Ammonium sulfate: (Star & Committee, 2013), (Kumar & Kameswara Rao, 1994)
  - ➢ The reaction with calcium hydroxide

$$(NH)_4SO_4+Ca(OH)_2 \rightarrow \underbrace{CaSO_4 \cdot 2H_2O}_{\text{Gypsum}}+2NH_{3(g)} \tag{2.13}$$

  - ➢ The reaction at C-S-H phase

$$CaO \cdot SiO_2 \cdot H_2O+(NH_4)_2SO_4 \rightarrow \underbrace{CaSO_4 \cdot 2H_2O}_{\text{Gypsum}}+2NH_{3(g)}+SiO_{2(aq)} \tag{2.14}$$

  - ➢ The reaction at AFm phase

$$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O+(NH_4)_2SO_4+Ca(OH)_2+20H_2O \\ \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O+NH_3+H_2O \tag{2.15}$$

- Ammonium bi-sulfate:

$$NH_4HSO_4+Ca(OH)_2 \rightarrow \underbrace{CaSO_4 \cdot 2H_2O}_{\text{Gypsum}}+NH_{3(g)} \qquad (2.16)$$

Gypsum can react with Calcium-Aluminate-Hydrate (C-A-H) and form the compound which called “Ettringite” which has higher volume than the initial substances of the reaction. So, the formation of the Gypsum and Ettringite causes expansion and may be cracks in the mortar and concrete (Bassuoni & Nehdi, 2012). Some of the ammonia will be released as the ammonia gas to the environment and some will be trapped in the capillary pore (Robert Cerny, 2002) of the mortar and concrete causing the mortar and concrete to have high porosity which affects the properties of mortar and concrete.

- Ammonium nitrate: (Star & Committee, 2013), (Arafa, Alqedra, & Shubair, 2015)
    - ➢ The reaction with calcium hydroxide

$$2NH_4NO_3+Ca(OH)_2 \rightarrow CaNO_3+2H_2O+NH_{3(g)} \qquad (2.17)$$

$$CaNO_3+(H\text{-}C\text{-}A) \rightarrow \underbrace{C\_N\_S}_{Leaching\ process} \qquad (2.18)$$

➢ The reaction at C-S-H phase

$$2w(NH_4NO_3)+(CaO)_x(SiO_2)_y(H_2O)_z \rightarrow (CaO)_{x-w}(SiO_2)_y(H_2O)_{2-w} +wCa^{2+}2wCO_3^-+2w(NH_3 \cdot H_2O) \qquad (2.19)$$

➢ The reaction at AFm phase

$$3CaO \cdot 3CaSO_4 \cdot Al_2O_3 \cdot 12H_2O+12NH_4NO_3 \rightarrow 4Ca^{2+}+SO_4^{2-} +2Al^{2+}+12(NO_3^-)+12(NH_3 \cdot H_2O)+6H_2O \qquad (2.20)$$

- The reaction at AFt phase

$3CaO \cdot 3CaSO_4 \cdot Al_2O_3 \cdot 32H_2O + 12NH_4NO_3 \rightarrow 6Ca^{2+} + 3SO_4^{2-} + 2Al^{2+} + 12(NO_3^-) + 12(NH_3 \cdot H_2O) + 26H_2O$ (2.21)

- Ammonium carbonate: (Matschei, Lothenbach, & Glasser, 2007)
  - The reaction with Calcium hydroxide

$(NH_4)_2CO_3 + Ca(OH)_2 \rightarrow \underbrace{CaCO_3}_{Carbonation} + 2H_2O + 2NH_{3(g)}$ (2.22)

- The reaction at AFm phase

$3CaCO_3 + C_3A + 32H_2O \rightarrow C_3A \cdot 3CaCO_3 \cdot 32H_2O$ (Calcium carbo alumminate) (2.23)

The product from the carbonation reaction which is calcium carbonate can improve the workability of fresh concrete both with and without the pozzolanic materials. Calcium carbonate also increases compressive strength at the early age of the mortar (Antoni, Chandra, & Hardjito, 2015). Not only to improve the early age compressive strength, it still reduces the porosity as well (Gambhir, 2004).

- Ammonium chloride: (Yilmaz, Dehri, & Erbil, 2002)

$NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O + 2NH_{3(g)}$ (2.24)

Ammonia gases, which are produced from all the reactions, work as air bubbles in the fresh mortar and concrete. They also improve the workability such as flow-ability and cohesiveness of fresh mortar and concrete. It also increases porosity inside the fresh mortar and concrete which affects the other properties of mortar and concrete.

2.6 Adsorption of ammonia on fly ash

The adsorption of ammonia on fly ash depends on many parameters which are related to each other; (Yun-long et al., 2015)

- Fly Ash composition.
- Unburned carbon content.
- Surface area of fly ash.
- Porosity of fly ash.
- Pressure.

2.6.1 Fly Ash composition

The ammonia adsorption, influenced by heating temperature, is also influenced by composition of coal ashes burned at different temperatures. According to the study of silica-alumina zeolite molecular sieve, the change of solid surface acidity depends on the alumina content, and the total acidity would decrease as the Si/Al ratio increases (Shirazi, Jamshidi, & Ghasemi, 2008). It means that the higher Si/Al ratio, less ammonia gas can be adsorbed by fly ash because ammonia gas has the property as acid (Zecchina, Lamberti, & Bordiga, 1998), (Barthomeuf, 1991).

2.6.2 Unburned carbon content

When coal contains moisture and volatile matter, dehydration and de-volatilization would contribute to the formation of pores and small pathways in carbon particles when the coal is burned and allow the oxygen to diffuse into carbon particles.

When the burning process of coal is finished, it has the bond between carbon and oxygen on the surface of fly ash (C-O) and (C=O) where the ammonia is adsorbed, mainly, at these acid sites when ashes contain carbon.

The unburned carbon can be measured by using SEM. The result of ammonia adsorption with different of unburned carbon content is shown in Figure 2.7.

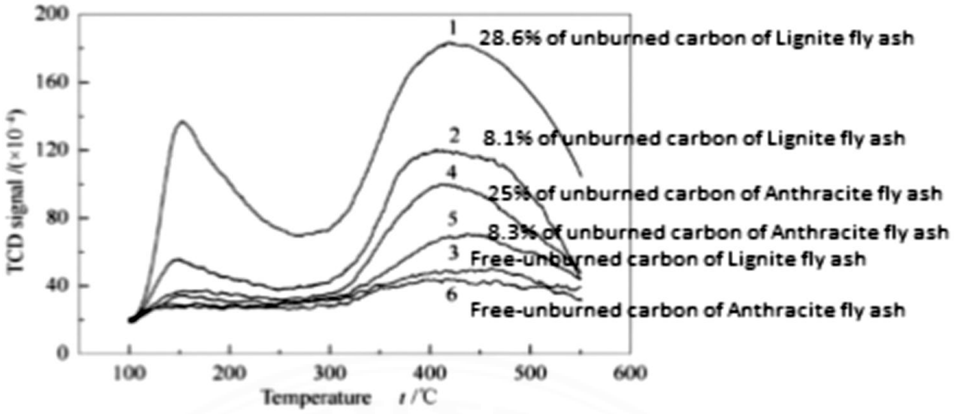


Figure 2.7 TCD graph of fly ash with different amount for unburned carbon (Yun-long et al., 2015)

2.6.3 Surface area of fly ash

Calculating the surface area can be done using the Brunauer, Emmet and Teller (BET) theory. From the experiment, higher surface area means more adsorption of ammonia gas (Schure, Soitys, Natusch, & Mauneys, 1985)

2.6.4 Porosity of fly ash

Calculating the porosity can be done using Dubinin-Radushkevich (DR) theory. Fly ash has three types of porosity based on IUPAC classification: (Schure et al., 1985), (Rajwar, Inder, & Pandey, 2014)

- Micro-pores – pore size smaller than 20A
- Meso-pores – pore size between 20 and 500A
- Macro-pores – pore size larger than 500A

The porosity can also be determined as the surface area, which means more porosity can lead to more adsorption of ammonia gas.

2.6.5 Pressure

The high pressure of gas injection increases the adsorption of ammonia. This experiment is conducted to observe the behavior of adsorption of fly ash with the relative pressure of ammonia. P_0 is the saturation vapor of ammonia at the temperature of experiment of 273 K. Figure 2.8 shows that the LOI and pressure are related to each other (Yun-long et al., 2015).

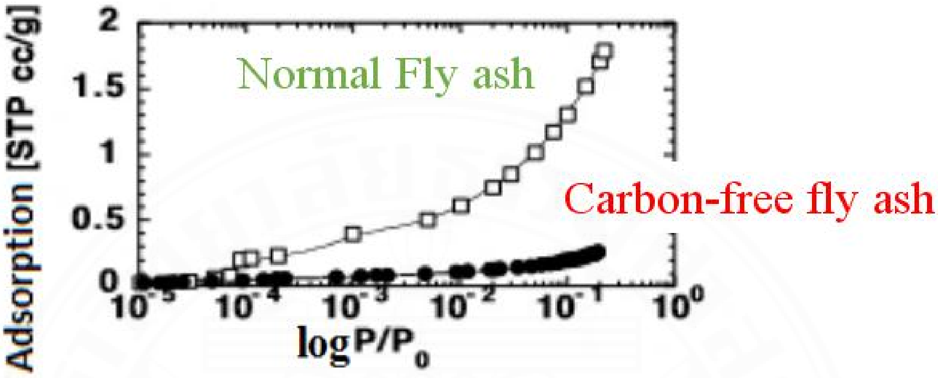


Figure 2.8 Ammonia adsorption isotherms on logarithmic relative pressure scale

2.6.6 Effects of ammonia on utilization application

For ammonia under high pH conditions in mortar, the result shows that the evolution rate is slower than expectation after 500 hours of experiment. The initial ammonia is still present in the samples. The recommendation for work in unvented area is limited at 100 ppmw of ammonia. For the good ventilation area, the limit is at 200 ppmw ammonia. Figure 2.9 shows the acceptable levels of ammonia on ash for products (Larrimore, 2002).

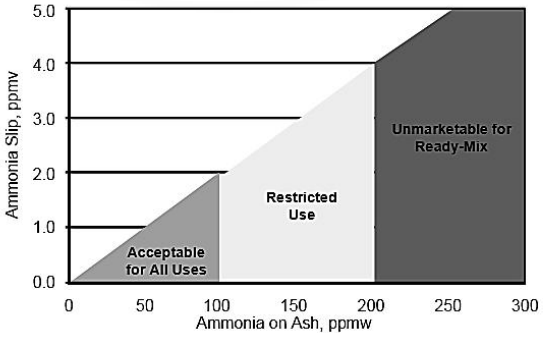


Figure 2.9 Acceptable levels of ammonia on ash from industry opinions

2.6.7 Effects on ash handling and disposal

For evolution ammonia in gas phase, the pH is very important. At a pH lower than 11, it is easily dissolved into water and causes environment problem.

2.7 Effects of ammonia contaminated fly ash on properties of mortar and concrete

Fly ash is a pozzolanic material. It is used as the replacement of cement to reduce the cost and improve various properties of concrete and mortar. There are problems when the fly ash is contaminated with ammonia. These are some properties that are expected to be affected by the ammonia contamination in fly ash (Kim et al., 2007).

- Setting times
- Deterioration and expansion
- Compressive strength
- Resistance to the freezing and thawing cycle

2.7.1 Setting times

The replacement of normal fly ash increases the initial setting time and final setting time. When the fly ash is contaminated with ammonia, setting times will be longer than normal fly ash concrete because the presence of ammonium ion and sulfate II ions may interfere the change in solubility of cement paste cation (calcium II ion, Ca^{2+}) and anions (aluminates and silicates). So setting times are longer when the concentration of ammonia is increased (Kumar & Kameswara Rao, 1994), (Yijin, Shiqiong, Jian, & Yingli, 2004), (Webster, Xiaozheng, & Aisha, 2015).

Table 2.1 Setting times of mortars with different fly ash replacement and different ammonia contamination

Fly ash replacement (%)	Ammonia concentration (ppm)	Initial setting time	Final setting time
-	0	3hr 15min	6hr 5min
10	0	3hr 40min	6hr 25min
	6	3hr 40min	6hr 30min
	56	3hr 50min	6hr 30min
	115	3hr 55min	6hr 35min
	620	3hr 55min	6hr 30min
15	0	3hr 45min	6hr 35min
	6	3hr 45min	6hr 40min
	56	4hr	6hr 45min
	115	4hr	6hr 50min
	620	4hr 5min	6hr 40min

2.7.2 Deterioration and expansion

Deterioration comes from the reaction between calcium hydroxide ($Ca(OH)_2$) and ammonia sulfate salts ($(NH_4)_2SO_4$/ NH_4HSO_4). This reaction forms gypsum ($CaSO_4 \cdot 2H_2O$) and ammonium hydroxide (NH_4OH) which has the acidity property that can deteriorate the concrete and mortar (Kumar & Kameswara Rao, 1994), (Cwalina, 2008), (Suleiman, 2014).

$$Ca(OH)_2+(NH_4)_2SO_4 \rightarrow \underbrace{CaSO_4 \cdot 2H_2O}_{\text{Gypsum}}+\underbrace{2NH_4OH}_{\text{Weak base}} \qquad (2.25)$$

Expansion comes from the reaction of the product of C_3A and gypsum from deterioration, forming ettringite as product with high molecular weight which leads to expansion of the concrete and mortar (Winter, 2005).

$$C_3A+6H_2O \rightarrow 4CaO\cdot Al_2O_3\cdot xH_2O \qquad (2.26)$$

$$\underbrace{4CaO\cdot Al_2O_3\cdot xH_2O}_{\text{C-A-H}}+3(CaSO_4\cdot 2H_2O)+H_2O \rightarrow \qquad (2.27)$$
$$\underbrace{3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot xH_2O}_{\text{Ettringite}}+Ca(OH)_2$$

2.7.3 Compressive Strength

Due to the deterioration of concrete and mortar, compressive strength is also affected. Due to the presence of ammonia in ammonia-contaminated fly ash, the formation of hydration products in cement mortar is suppressed.

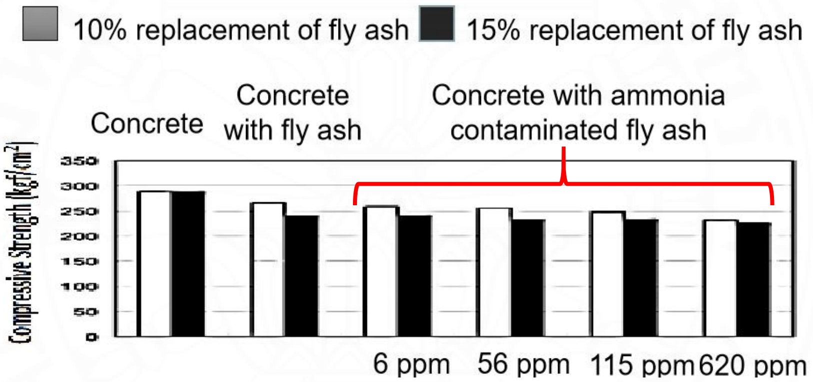


Figure 2.10 Compressive strength at 28 days of concrete with and without replacement of ammonia contaminated fly ash (Kim et al., 2007)

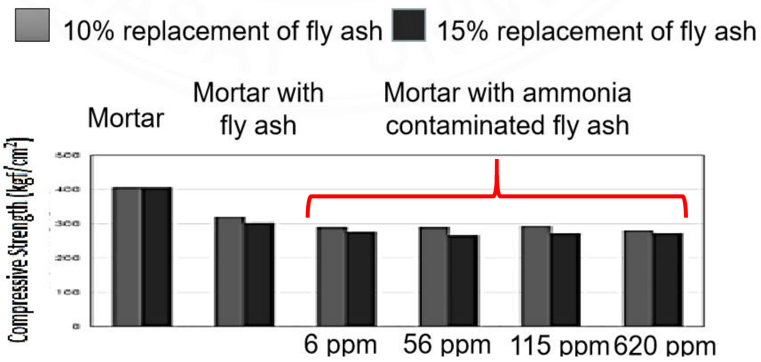


Figure 2.11 Compressive strength at 28 days of mortar with and without replacement of ammonia contaminated fly ash (Kim et al., 2007)

From Figure 2.10 and Figure 2.11, the compressive strength decreases with the increase of ammonia contamination. Even with the same percentage of fly ash replacement but different in ammonia contamination, the compressive strength decreases.

2.7.4 Resistance to freezing and thawing cycle

Ammonia concentration affects dynamic modulus of elasticity of concrete and mortar.

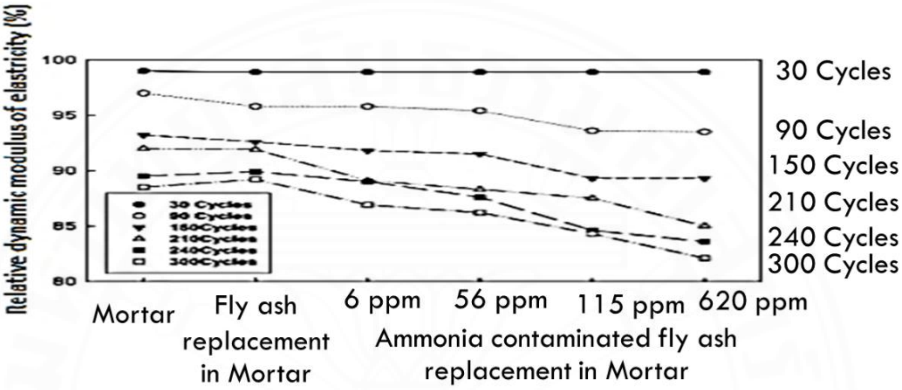


Figure 2.12 Relative dynamic modulus of elasticity of mortar mixtures blended with ammonia contaminated fly ash (Kim et al., 2007)

From Figure 2.12, the higher concentration of ammonia in fly ash with more freezing and thawing cycles decreases the relative dynamic modulus of elasticity of concrete. But in Thailand, this case is not significant.

2.8 Ammonia gas released from fly ash in concrete (Shou et al., 2014)

From the physical and chemical condition of concrete, ammonia released from concrete can be divided into 3 periods:

1. Mixing period
2. Initial setting period
3. Curing period

The characteristic of released ammonia in each period is different depending on the physical and chemical condition in that period.

According to laboratory experiment with 5 sets of ammonia contaminated fly ash in which concentrations of the ammonia are 65, 500, 862, 1,378, and 3,211 ppm, with the water to binder ratio equals to 0.53 and the replacement of fly ash is equal to 0.50.

Figures 2.13 and 2.14 show the experimental setup to observe the behavior of ammonia released from concrete. The amount of released ammonia was measured by using 2 real-time ammonia gas monitors. The first one of the ammonia gas monitors is located 2-3 cm above the concrete's surface for measuring ammonia concentration near concrete interface and the second one is for ambient ammonia concentration of the chamber. And before release the air from the chamber to environment, the ammonia will be trapped by sulfuric acid solution and then analyzed by Ion chromatography.

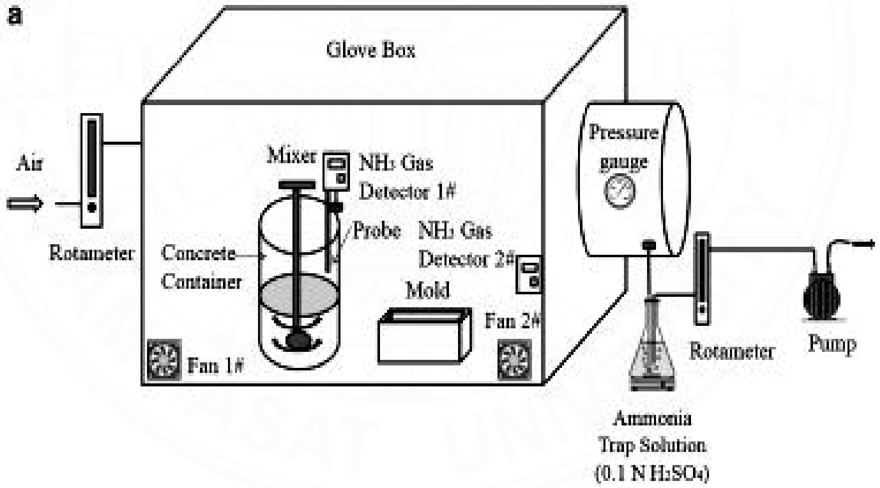


Figure 2.13 Experimental setup for mixing and initial period (Shou et al., 2014)

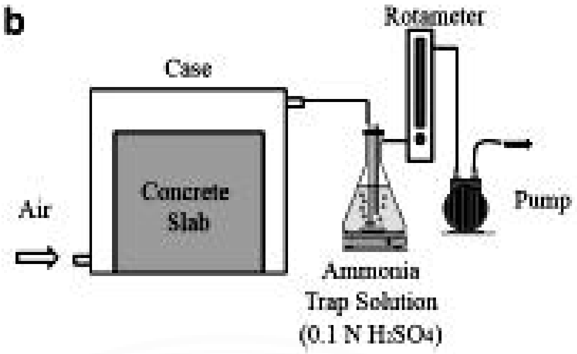


Figure 2.14 Experimental setup for curing period (Shou et al., 2014)

The ammonia concentration at the surface of concrete was always higher than that in the ambient air in the chamber. It tells that the ammonia release rate is continuous.

For mixing period, the observation was around 20 minutes after the experiment started. Released ammonia gas increased by stirring which can be explained by convective mass transfer on the liquid-air interphase with large diffusivity.

For initial setting period, the observation was started after mixing period up until 8 hours. In this period, there is no stirring so ammonia was released from the liquid-air interface with constant diffusivity.

For curing period, ammonia release occurs on the interface between “bleed water” on the surface of concrete and air. It can be explained by convective mass transfer with diffusion that is controlled by the solid-phase mass transfer. The evaporated water was the way to release the ammonia from the concrete.

The amount of ammonia gas released between mixing and initial setting period, measured by real-time monitor, is shown in Figure 2.15 and that during curing period is shown in Figure 2.15.

After the ammonia gas release until non-detectable levels (around 80% was emitted from mixing and initial setting period), there was still around 20% to 70% of ammonia retained in the concrete as ammonium salts.

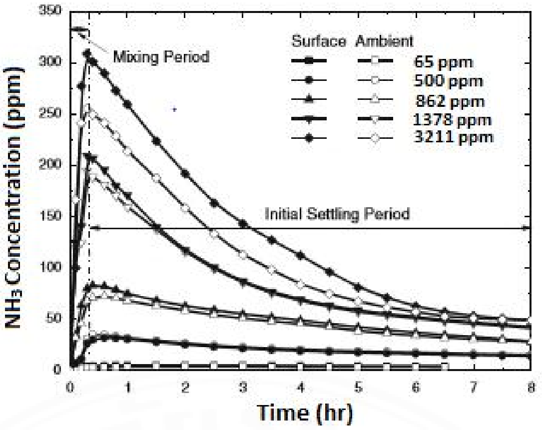


Figure 2.15 Ammonia concentration measured by real-time monitoring during the mixing and initial setting period of concrete specimens (Shou et al., 2014)

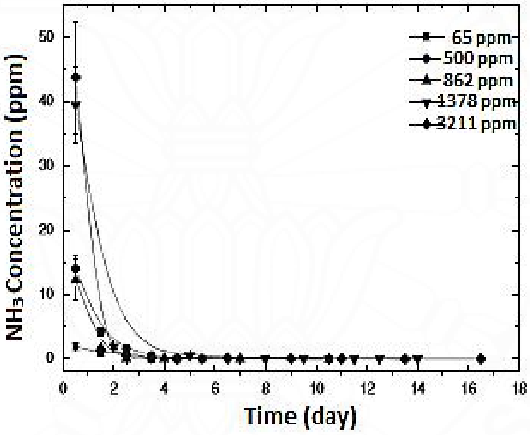


Figure 2.16 Ammonia concentration measured by real-time monitoring during the curing period of concrete specimens (Shou et al., 2014)

2.9 Measurement of ammonia gas (Sear & Guest, 2012)

1. Optical Absorption Spectroscopy.

The method uses a laser and a spectrograph, and may use visible, ultra violet or infrared light to do wavelength analysis.

2. Differential Optical Absorption Spectroscopy (DOAS)

The method is used to determine trace gases by measuring the specific narrow band adsorption structures in the UV and visible spectral region.

3. Tunable Diode Laser Absorption Spectroscopy (TDLAS)

Very narrow bandwidth in the IR region is scanned. More absorption of the IR region means more target gas concentration.

4. Photo-acoustic IR Spectroscopy (PAS)

Absorb gases with infrared that can be detected by sensitive microphones. This is accurate only at 0.5 ppm or 1ppb.

5. Radar Detection

Detection is done by using radar signals. This method is good for high pressure systems.

6. Thermo-gravimetric analyzer/Mass Spectrometer (TGA/MS)

The technique is used for analyzing gas and it is capable of measuring the ammonia gas inside the specimen. Even if it has a very small amount left. This equipment is composed of two main parts which are the thermo-gravimetric analyzer and mass spectrometer.

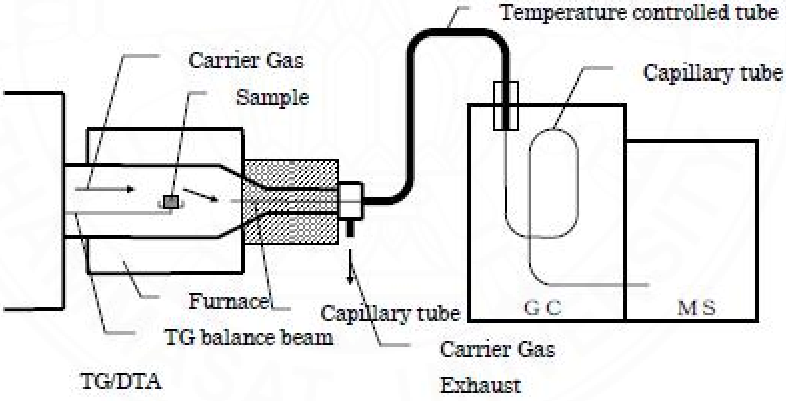


Figure 2.17 TGA-MS structure (Sear & Guest, 2012)

Thermo-gravimetric analyzer (TGA) utilizes the technique called thermo-gravimetric analysis which can measure the change in the mass of the sample as a function of temperature under a controlled atmosphere. This technique can be operated up until 1000°C (Martin, 2010) Not only measuring the change in the mass, it also measures the filler contents in polymers, moisture and solvent content, and the percentage of composition of the component of a compound (PhotoMetrics, 2011). Unfortunately, this technique does not show the information of the products that are lost from the sample. So, in order to measure the ammonia gas loss from the sample, the mass spectrometer will be coupling with the Thermo-gravimetric analyzer.

The mass spectrometer is the technique to analyze and quantify the known materials by identifying the unknown compounds of sample, and explain the structure and chemical properties of molecules. This technique will convert the sample into the gaseous ions and determine by characterizing as their mass to charge ratios (m/z). There are 4 stages in order to complete mass spectrometer analysis:(Budzikiewicz & Wilson, 1963), (Hoffmann & Stroobant, 2007), (Woodford, 2021), (Biosoft, 2011), (Anant, 2014)

1. Ionization

The atom or molecule is ionized by giving up one electron and become positive ion or radical cation. Most of mass spectrometer usually works with the positive ions. For the negative ions, it needs another ionization technique (Clark, 2000), (Gross, 2015).

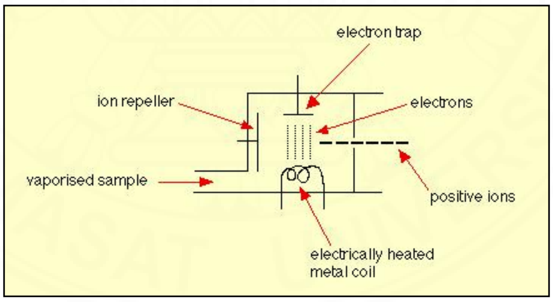


Figure 2.18 Ionization chamber (Franklin Institute, 1964)

2. Acceleration

The positive ions that shoot out from the vacuum chamber will be accelerated by an electric field (the region that develops between two metal plates that charged to high voltages) so the ions will have the same kinetic energy (Gross, 2015).

3. Deflection

After get accelerated, the positive ions move to magnetic field (the invisible magnetically active area between the poles of magnet) to be deflected which depends on

- The mass of ion (the lighter weight ions deflect more than the heavier ones)
- The charge of ion (More positive ions charge, more deflection)

Then, the ions will split into a different spectrum according to its mass and its electrical charge.

4. Detection

In this stage, using the computer to record the spectrum from the electrical detector to show how many ions arrive, depending on the mass to charge ratios which is used to identify the atoms or molecules in the sample.

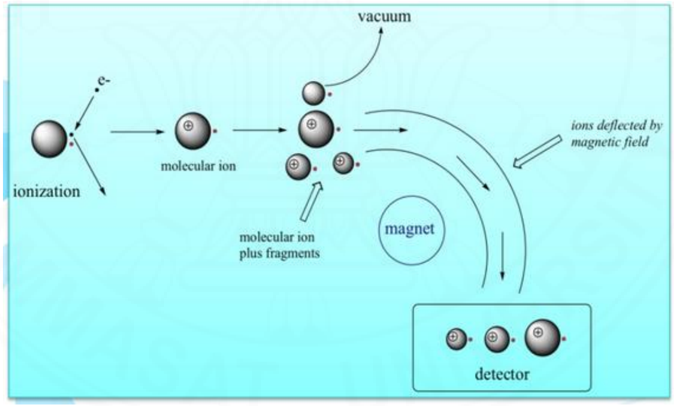


Figure 2.19 Simple mass spectrometry (Dearnaley, 1958)

6. Gas sensors

6.1. Metal Oxide Gas sensors

Measured by absorbing and de-absorbing the gas by alternating the temperature of the sensor and change in electrical conductivity. They are accurate to 5 ppm.

6.2. Catalyst Bead ammonia sensors

Also known as Wheatstone Bridge LEL sensors. Use a palladium gate material and it has the detection limit around 1 ppm. At the high concentration, the catalyst life-time may be limited to minutes and hours.

6.3. Conducting polymer gas detectors

Using polymer that can react with ammonia. But the polymers cannot be easily regenerated. The lower limit from this method is 1 ppm.

6.4. Photo Ionization potential (PID)

Measure the ammonia up to 10000 ppm (Sear & Guest, 2012).

2.10 Exposure limits of ammonia

Ammonia gas (Steven Issley, MD, FRCPC Attending Physician, Department of Emergency Medicine, University Health Center, Toronto, 2019) is a toxic gas for human and it affects to human health depending on the amount of exposure. So, it is necessary that the people or workers who have to work or involve with ammonia should have the limits of exposure during the working hours. There are 3 standards that recommend the exposure limits to ammonia gas (National Institute for Occupational Saftey and Health (NIOSH), 1994; Occupational Safety and Health, 1992), (Bo, 1996), (Zone, At, & Gas, 2017), (Of, Effects, Route, & Exposure, 2008).

1. The Occupational Safety and Health Administration (OSHA) permissible exposure limit (Canadian Centre for Occupational Health and Safety, 2013)

Their recommendation has two limits which are not more than 35 ppm or 27 mg/m^3 as 15 minutes short term which should not exceed during the workday and 50 ppm as 8 hours for working time.

2. The National Institute for Occupational Safety and Health (NIOSH) (CDC, 2019)

Their recommendation has 2 types of limits which are 35 ppm or 24 mg/m^3 as a 15 minutes short term and 25 ppm or 17 mg/m^3 as 8 hours of working time.

3. The American Conference of Governmental Industrial Hygienists (AGGIH)

Their recommendation has 2 types of limits which are 35 ppm or 24 mg/m^3 as a 15 minutes short term and 25 ppm or 17 mg/m^3 as 8 hours' work day and 40 hours' work week.

The first two standards are normally used in the situation when ammonia gas happens to leak out and the last one is used for the worker who work with the ammonia.

Even through there are the limits for the exposure, but sometime the situation of ammonia leakage cannot be controlled. Table 2.2 summerizes the sign and symptom (Steven Issley, MD, FRCPC Attending Physician, Department of Emergency Medicine, University Health Center, Toronto, 2019) for human that exposes to ammonia in many concentration (Murphy, 2007), (ACADEMIES, 2008).

Table 2.2 Summary of toxic effects following acute exposure to ammonia by inhalation

Exposure		Signs and symptoms
mg/m^3	ppm	
35	50	Irritation to eyes, nose and throat (2 hours' exposure)
70	100	Rapid eye and respiratory tract irritation
174	250	Tolerable by most people (30-6- minutes' exposure)
488	700	Immediately irritating to eyes and throat
>1,045	>1,500	Pulmonary oedema, coughing, laryngospasm
1,740-3,134	2,500-4,500	Fatal (30 minutes' exposure)
3,480-6,965	5,000-10,000	Rapidly fatal due to airway obstruction, may also cause skin damage
Values in mg/m^3 are approximate calculations from ppm, where mg/m^3 = ppm x gran molecular weight/24.45 (molar volume of air at standard temperature and pressure)		

2.11 Ammonia removal process

The ammonia removal process can be divided into 2 main types: (EPRI, 2007), (Ammonia & Mitigation, 2005)

2.11.1 Thermal removal process

It is the process that rely on heat to separate ammonia compounds or to remove physically adsorbed ammonia from the fly ash surface. The result is to volatilize the ammonia from solid phase to gas phase, or to thermally decompose ammonia molecules. But the destroyed ammonia may create the nitrogen oxide $\left(NO_x\right)$ emission. The time and temperature in this process is dependent and it is possible to use chemical reagent to improve the potential of process. But in some cases, this process is used to decrease the moisture or carbon content to reduce the ammonia adsorption of fly ash.

The followings are the examples of thermal removal process (Fisher & Antonio, 2004).

1. Carbon Burn-Out (Laura, Jardim, Silvestre-albero, & Rodríguez-reinoso, 2011), (Cochran et al., 2010), (Frady & Hay, 1999.; Kirkconnell, President, & Manager, 2006)

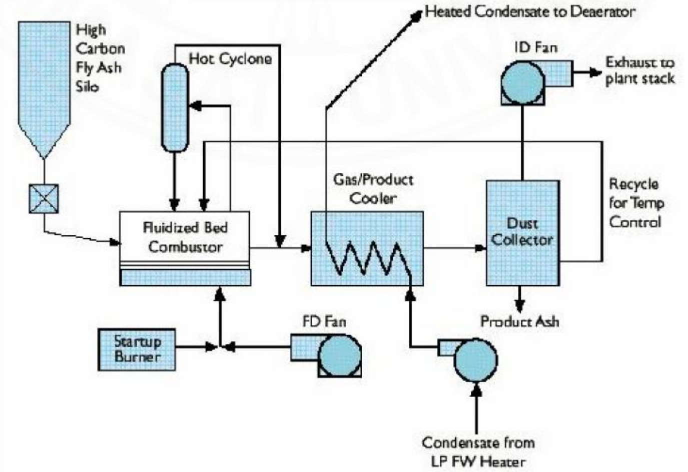


Figure 2.20 Carbon burn out ammonia removal process flow diagram (Amit Kumar Vishwakarma1, 2014)

Burning the fly ash that has high LOI value, before passing the fly ash to post-combustion process. This process is very commercial process for industry. It is producing a very consistent, low carbon, and high quality pozzolanic material.

2. Re-Use Technology Ammonia Removal Process

   Recycling the ammonia from the fly ash to use it again for (NO_x) reduction process.

3. Semi-Dry Ammonia Removal Processes (Brugghen, Berg, Ash, Methods, & Berg, 2000; Gao et al., 2002)

   Using water mist or a flowing warm humid air stream, which is ozone or with other co-oxidants such as hydrogen peroxide, to remove ammonia from the fly ash.

4. Re-burning in a dedicated FBC Unit (Report, 2016)

   Using fluidized bed combustion to burn the fly ash.

5. Re-burning in an Ash Fuel System (Arachchilage & Madumal, 2014), (Piekos, 1999)

   Re-burning the fly ash by burning the carbon again to reduce the change of adsorption of ammonia.

2.11.2 Chemical removal process

It is a process that rely on chemicals to convert ammonia into other chemicals, or to combine with ammonia for volatilization, or to force ammonia releasing from the surface of fly ash. The problems of this process are the operating cost and it may change the properties of fly ash.

1. Shallow Trench Isolation (STI) Process (Prince, 2003) (Bittner et al., 2001)

It is a process that uses alkali to react with ammonium salts ($(NH_4)_2SO_4$ or

$(NH_4)HSO_4$) and release the ammonia as a gas from fly ash. The cheapest source of alkali is calcium oxide (CaO).

$$(NH_4)_2SO_{4(s)}+CaO_{(S)}\rightarrow 2NH_{3(g)}+CaSO_{4(s)}+H_2O_{(g)} \tag{2.28}$$

$$(NH_4)_2SO_{4(aq)}\rightarrow 2NH^{+}_{4(aq)}+SO^{2-}_{4(aq)} \tag{2.29}$$

But this process has to be careful about the moisture that has to be removed to the level well below the limit in the ASTM C 618 standard. Because it will produce highly unstable alkali or hydrated lime, in this case is calcium hydroxide.

$$CaO_{(s)}+H_2O\rightarrow Ca(OH)_{2(s)} \tag{2.30}$$

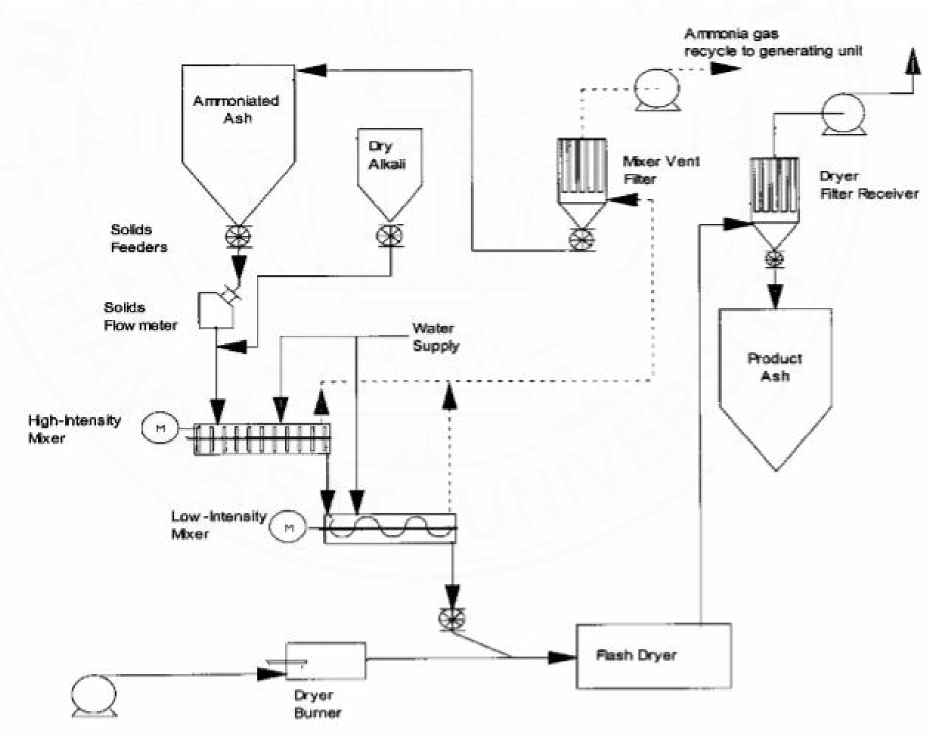


Figure 2.21 STI ammonia removal process flow diagram (Bittner et al., 2001)

2. Ozone Treatment (Investigators & Description, 2005)(Altman, Alto, Examiner, & Phasge, 2002), (X. Chen, 2003)

Unburned carbon of fly ash has been treated or deactivated by ozone. So, the ammonia cannot attach on the surface of fly ash.

3. Using Hypo-chlorites as chemical treatment reagents (Ammonia & Mitigation, 2005)

Mostly using Calcium Hypochlorite which is strong oxidizers and also can be added in as dry or liquid form to the ammonia-contaminated fly ash. The reaction may be more immediate, but the high efficiency mixing to disperse the chemical would be required. The rate of ammonia reduction depends on pH, temperature, time, initial dosage, and presence of competing reducing agents, as shown in Table 2.3. Theoretically, a stoichiometric molar ratio between hypochlorite and ammonia, (Cl: N), of 1.5:1, according to chemical reaction as shown below, is sufficient to convert ammonia to nitrogen gas.

$$2NH_3+3OCl^{-}\rightarrow N_2+3Cl^{-}+3H_2O \tag{2.30}$$

But the ratio between hypochlorite and ammonia will be required to compensate for higher carbon contents or having pH less than the optimum point.

Table 2.3 Ammonia Removal Rate of fly ash with 600 ppm ammonia.

Reagent Dosage (Cl:N)	Required Chemical Addition (lb/ton)	Ash Moisture (%)	Ammonia Evolution as Determined by Headwaters (ppm)	Ammonia Reduction as Determined by Headwaters (%)
0.0:1.0	0	0	500	0
0.5:1.0	4	1	300	40
1.0:1.0	8	2	30	94
1.5:1.0	12	3	20	96
2.0:1.0	16	4	15	97

CHAPTER 3
METHODOLOGY

3.1 Introduction

At the time of this study, the real ammonia-contaminated fly ash was still not produced in Thailand. Therefore, in order to observe the effects of ammonia contaminated fly ash, ammonium salts were added into the normal fly ash. Mortars were prepared as representative of concrete to test the basic properties, shrinkage properties, and to investigate the mechanism of how ammonia-contamination affects the properties of mortars. The sources of fly ash are from Mae Moh and BLCP. The ammonium salts used in this study are ammonium salts which are ammonium sulfate ($(NH_4)_2SO_4$) and ammonium carbonate ($(NH_4)_2CO_3$).

3.2 Materials

3.2.1 Cement

Ordinary Portland cement type 1 (OPC) according to TIS 15 was used as a binder for all mixtures. The chemical compositions of the Ordinary Portland cement type 1 are shown in Table 3.1.

3.2.2 Fly ash

Fly ash was used to replace cement in percentage by weight of binder. Fly ash samples from Mae Moh power plant, one containing high CaO contents (FAA) and another containing high CaO contents and high SO_3 contents (FAB), and a sample from BLCP power plant which contained low CaO contents (FAR), were used in the study. According to TIS 2135, FAA and FAB were categorized as Class 2b (high CaO contents) and FAR was categorized as Class 2a (low CaO contents). The chemical compositions and physical properties of the Mae Moh fly ash and BLCP fly ash are shown in Table 3.1 and Table 3.2, respectively.

Table 3.1 Chemical compositions of OPC type 1, Mae Moh fly ash, and BLCP fly ash.

Chemical compositions (%)	**Cement (OPC type 1)**	**Mae Moh fly ash**		**BLCP fly ash**
		FAA	**FAB**	**FAR**
SiO_2	18.93	36.18	26.61	61.46
Al_2O_3	5.51	20.21	13.6	20.27
Fe_2O_3	3.31	13.89	18.34	5.56
CaO	65.53	18.74	24.97	1.73
MgO	1.24	2.69	2.33	0.96
Na_2O	0.15	1.14	1.75	0.73
K_2O	0.31	2.29	1.77	1.36
SO_3	2.88	3.74	8.53	0.38
LOI	-	0.25	0.53	5.38
Free lime	N.A.	0.58	3.93	0.03

Table 3.2 Physical properties of the tested cement and fly ashes

Physical properties	**OPC**	**FAR**	**FAA**	**FAB**
Specific gravity	3.13	2.17	2.21	2.57
Blaine fineness (cm^2/g)	3,660	2,723	2,867	2,820

3.2.3 Fine aggregate

River sand was used as the fine aggregate. The gradation of fine aggregate was in accordance with ASTM 33. The fine aggregate had a specific gravity of 2.61 g/cm^3 and an absorption of 1.19%.

3.2.4 Ammonium salts

Two forms of ammonium salts which are ammonium sulfate ($(NH_4)_2SO_4$) and ammonium carbonate ($(NH_4)_2CO_3$) were used in this study. The concentration of ammonia of 0-1000 ppm was varied for investigation.

3.3 Mixture proportions

The mixtures contained OPC type I with 30% of the total binder by weight replaced by fly ash. A water to binder ratio of 0.5 (w/b = 0.5) was used. Mortars with replacement of ammonia-contaminated fly ash were prepared by mixing ammonium salts solution. The solution of $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ were varied in the range of 0 and 1000 ppm (mg of ammonia per kg of fly ash). The tested mix proportions of mortar are in Table 3.3 to Table 3.6.

Table 3.3 Mixture proportions of the tested mortars with various ammonia concentrations

Mix	NH_3 (mg/kg fly ash; ppm) using ($(NH_4)_2SO_4$)	NH_3 (mg/kg fly ash; ppm) using ($(NH_4)_2CO_3$)	w/b	s/b	OPC type I (%)	Fly ash replacement (%)
1	0	-	0.5	2.75	70	30
2	100					
3	200					
4	600					
5	1000					
6	-	100				
7		200				
8		600				
9		1000				

Table 3.4 Mixture proportions of the tested mortars with various ratios of $(NH_4)_2SO_4$ to $(NH_4)_2CO_3$

Mix	%NSO ($(NH_4)_2SO_4$)	%NCO ($(NH_4)_2CO_3$)	NH_3 (ppm of fly ash)	w/b	s/b	f/b (%)
1	0	0	200	0.50	2.75	30
2	100	0				
3	25	75				
4	50	50				
5	75	25				
6	0	100				

Table 3.5 Mixture proportions of the tested mortars with different types of fly ash

Mix	**NH_3 (mg/kg fly ash; ppm) using (($NH_4)_2SO_4$)**	**NH_3 (mg/kg fly ash; ppm) using (($NH_4)_2CO_3$)**	**w/b**	**s/b**	**f/b (%)**
1	0	-	0.50	2.75	30
2	200				
3	-	200			

Table 3.6 Mixture proportions of the tested mortars with different free lime contents in fly ash

Mix	**Free lime content (%)**	**NH_3 (mg/kg fly ash; ppm) using (($NH_4)_2SO_4$)**	**NH_3 (mg/kg fly ash; ppm) using (($NH_4)_2CO_3$)**	**w/b**	**s/b**	**f/b (%)**
FAC 5%	5	0	-	0.50	2.75	30
		200				
		-	200			
FAC 10%	10	0	-			
		200				
		-	200			

3.4 Addition method of ammonium salts into fly ash

3.4.1 Dissolution method

The amount of ammonium sulfate and ammonium carbonate were dissolved in the water. The amount of ammonia in water can be calculated by using equation (3.1). The procedure of mortar mixing of this method is shown in Figure 3.1.

To calculate the concentration of ammonia in the mortars, equation (3.1) was used to calculate the amount of ammonium salts dissolved in the water.

$$NH_3 \text{ in water} \quad = \frac{NH_3 \ in \ Fly \ ash \times Fly \ ash}{Water} \tag{3.1}$$

By NH_3 in water = mass of ammonia dissolved in water (g)

NH_3 in fly ash = NH_3 concentrations in fly ash (mg of NH_3/ kg fly ash; ppm)

Fly ash = mass of fly ash in mortar (g)

Water = mass of water in mortars (g)

To calculate the mass of ammonium salt added to the water.

From chemical equation

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

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

Therefore,

$$n_{(NH_4)_2SO_4} = 2n_{NH_3}$$

$$\frac{W_{(NH_4)_2SO_4}}{M_{(NH_4)_2SO_4}} = 2\left(\frac{W_{NH_3}}{M_{NH_3}}\right)$$

$$W_{(NH_4)_2SO_4} = 2\left(\frac{W_{NH_3} \times 132}{17}\right)$$

$$\frac{W_{(NH_4)_2CO_3}}{M_{(NH_4)_2CO_3}} = 2\left(\frac{W_{NH_3}}{M_{NH_3}}\right)$$

$$W_{(NH_4)_2CO_3} = 2\left(\frac{W_{NH_3} \times 96}{17}\right)$$

Molecular weight of $(NH_4)_2SO_4$, $M_{(NH_4)_2SO_4}$ = 132

Molecular weight of $(NH_4)_2CO_3$, $M_{(NH_4)_2CO_3}$ = 96

Molecular weight of NH_3, M_{NH_3} = 17

$n_{(NH_4)_2SO_4}$ = Mole of $(NH_4)_2SO_4$

$n_{(NH_4)_2CO_3}$ = Mole of $(NH_4)_2CO_3$

n_{NH_3} = Mole of NH_3

$W_{(NH_4)_2SO_4}$ = grams of $(NH_4)_2SO_4$ (g)

$W_{(NH_4)_2CO_3}$ = grams of $(NH_4)_2CO_3$ (g)

W_{NH_3} = grams of NH_3 (g)

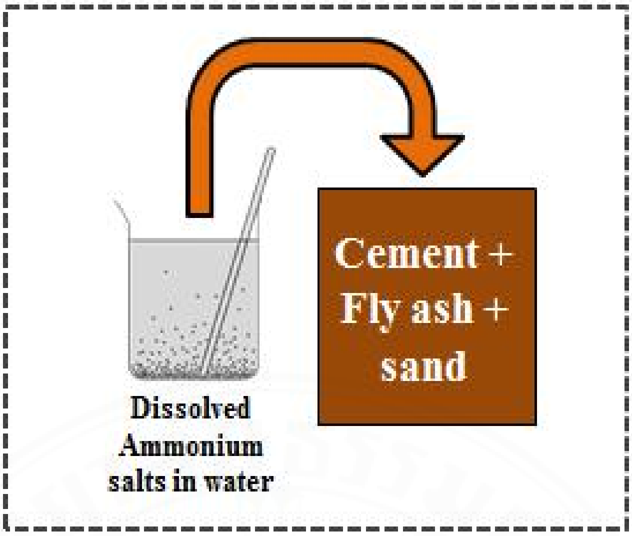


Figure 3.1 Method to add ammonia into mortar mixture by dissolved ammonium salt

3.5 Basic properties of mortar

3.5.1 Flow test and water requirement

According to ASTM C1437, the standard test method for flow of hydraulic-cement mortar, determines the flow when the mortar is unconfined and consolidated. Mortar mixture was placed in a 2 inches tall and 4 inches based conical brass mold. When the mold is removed, roll the holder 25 times in 15 seconds. The shape will change from conical shape to a “pancake” shape. The flow of mortar will be calculated as percentage based on the change in diameter from 4 inches to the diameter of pancake shape.

Water requirement was determined by varying amount of water added into the mixture to obtain flow equal to 110±5 %.

Figure 3.2 Flow table, flow cones, tamping rod, and Vernior caliper

3.5.1.1. Flow calculation

After getting the pancake shape, then measure the diameter of pancake shape 4 times.

$$\text{Flow (\%), in percentage} = \left(\frac{Average \quad of \quad flow - 100}{100} \right) \times 100 \qquad (3.2)$$

where average of flow is the average of 4 measured diameters of flow (millimeters).

3.5.2 Surface tension test (Contact angle measurement)

Surface tension test is used to explain the results of flow test and water requirement. The test measures the contact angle of ammonium sulfate and ammonium carbonate droplets on the same surface with different ammonium salt concentrations.

Contact angle measurement is used to determine the surface hydrophilic or hydrophobic properties and also the surface tension of solution. A liquid that has the ability to spread over the surface without forming the droplet is the liquid that has low surface tension. In contrast, the liquid that its surface does not allow the water to spread but creates the droplet is considered to be high in surface tension.

Contact angle measurement method

For a contact angle measurement method, the droplet of ammonium salt solution is dropped on the solid surface such as glass plate or plastic plate. The ammonium salt droplet was captured by a camera. Figure 3.3 shows different forms of contact angle of the liquid droplets. If θ>90°, it means the liquid has a high surface tension and forms bad wetting. On the other hand, θ<90° means the liquid has a low surface tension and forms good wetting.

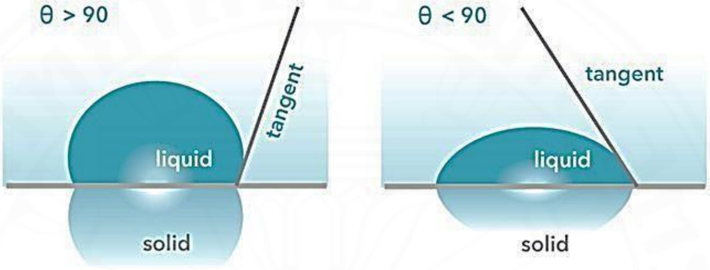


Figure 3.3 Different forms and contact angle of liquid droplets

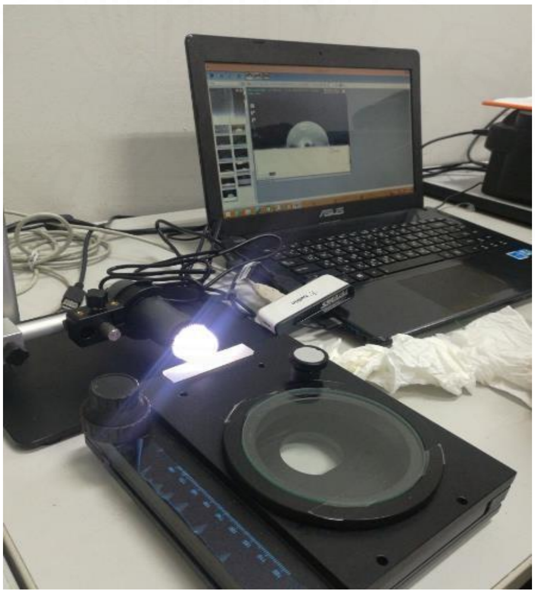


Figure 3.4 Contact angle measurement equipment

3.5.3 Normal consistency test

Normal consistency test method follows ASTM C187-89 which applies the Vicat's apparatus to find a quantity of water in order to get exactly 10 centimeters of penetration then continue to be testing for the initial and the final setting time.

3.5.4 Setting time test

This test was continued after getting the normal consistency value. The setting time test method follows ASTM C191. The setting time is divided into 2 types which are the initial setting time and the final setting time.

3.5.5 Preparation of mortar samples for compressive strength test

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

The mortar samples with sizes of 50x50x50 mm were prepared following the ASTM C109 and TIS 15. Samples were cured in high humidity for 24 hours and then cured by lime water after being removed from the molds for 3, 7, 28, and 91 days.

Figure 3.5 Compressive strength testing machine

3.6 Preparation of mortar samples for shrinkage test

The mortar samples with sizes of 25x25x285 mm were prepared. Each sample were cured in high humidity for 24 hours.

The shrinkage measurement will be conducted into 2 types.

- Autogenous shrinkage measurement

This test observes the macroscopic volume due to the chemical shrinkage that happens right after the final setting of mortar and the self-desiccation volume reduction due to water consumption by cement hydration reaction, using the water from capillary pores. After that self-equilibrating stresses are created by capillary tension in the capillary pore water and compression in the hydrated products.

According to ASTM C1698 standard, after specimens were removed from molds, the specimens were applied by paraffin wax, and then covered with plastic sheets and then covered again with aluminum foils to prevent the loss of moisture to the environment. The covered specimens were taken to the controlled environment with temperature of 28±2 °C and relative humidity of 70±5%. The length change and the weight lost were measured for 120 days by measuring every 2 days for the first 2 weeks and then every week for the rest.

Figure 3.6 Length comparator

Figure 3.7 Autogenous shrinkage specimens

- Total shrinkage measurement

This test observes the shrinkage due to loss of water to the environment.

According to ASTM C596 standard, specimens were prepared with the same size and procedure as those of the autogenous shrinkage test. After mold removal and 24 hours of curing, the samples were immediately taken for the initial reading and weighting. The specimens were cured in the water for 7 days after being removed from the mold and then curing was continued at the controlled environment with temperature of 28±2 ˚C and relative humidity of 70±5%. The length change and the weight loss were measured for 120 days by measuring every 2 days for the first 2 weeks and then every week for the rest.

Figure 3.8: Total shrinkage specimens

3.7 Preparation of mortar samples for Mercury Intrusion Porosimetry (MIP)

To measure the total porosity and average pore size of mortar specimens, Mercury Intrusion Porosimetry (MIP) analysis was conducted. In MIP test, the mortar specimens with sizes of 50×50×50 mm were prepared. At the age of 28 days, the hydration reaction of mortar specimens was stopped by immerging the specimens into acetone solution for 1 day. Then, put the specimens in the oven at 70˚C for 1 day. After that, the specimens were cut into sizes of 10×10×10 mm for MIP test (Abell, Willis, & Lange, 1999; BERODIER, BIZZOZERO, & MULLER, 2015; Ma, 2014)

CHAPTER 4

EFFECTS OF $(NH_4)_2SO_4$ AND $(NH_4)_2CO_3$ IN FLY ASH ON PROPERTIES OF MORTARS

4.1 General

This chapter shows the results and discussion on the effects of ammonium sulfate ($(NH_4)_2SO_4$) and ammonium carbonate ($(NH_4)_2CO_3$) in fly ash on properties of mortar. Both $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are products from NO_x controlling technologies which are contaminated in the fly ash. Each ammonium salt was dissolved in the water before added in the fly ash. The tested mortar properties consist of mortar flow, setting times, compressive strength, autogenous shrinkage, and total shrinkage.

4.2 Basic properties

4.2.1 Mortar flow

The results of flow percentage of mortar containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ with ammonia concentration from 0-1000 ppm are shown in Figure 4.1. The results show that the flows of fly ash mortars containing high concentration of ammonium salts increase when compared with that of non-ammonia fly ash mortar.

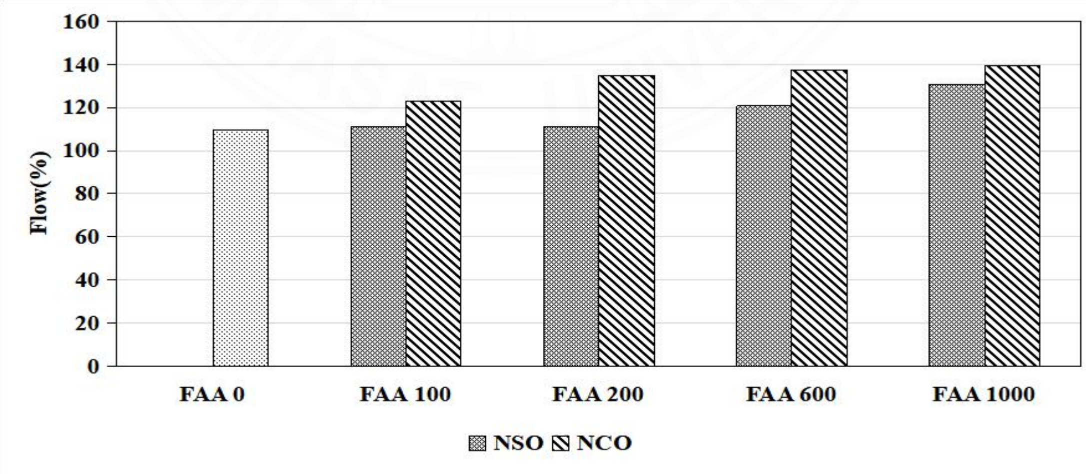


Figure 4.1 Flow percentages of fresh fly ash mortar with different ammonia concentration of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$

When comparing between flows of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ contaminated mixtures, the results show that flows of mortars containing $(NH_4)_2CO_3$ are higher than those of the mortars containing $(NH_4)_2SO_4$. It can be explained by using the results of contact angle measurement in the next section.

4.2.2 Surface tension test

Due to the addition of ammonium salts to fly ash mortars, the presence of ammonium ions (as shown in Eqs. (1.3) and (1.5)) from $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in water can interrupt the intermolecular attractive forces between the water molecule. This leads to a decrease of surface tension which can be observed by the contact angle measured on the water with the dissolved ammonium salts.

The surface tension can be observed by measuring the contact angle of the ammonium salt solutions. From the results of flow test, the flows of mortars containing higher ammonia concentration, $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, are higher. It can be explained that the reduction of surface tension of water due to the presence of ammonium ions in water can disturb the intermolecular attractive force between water molecules.

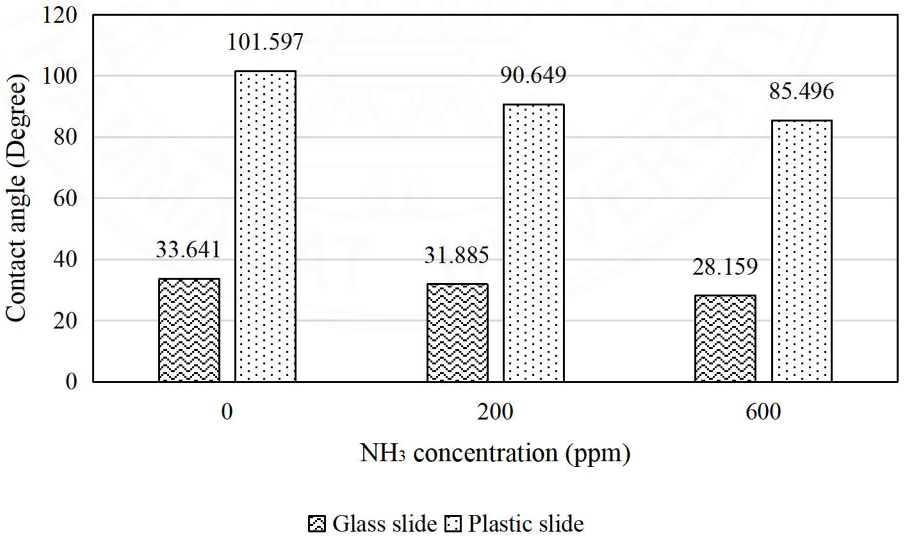


Figure 4.2 Contact angles of $(NH_4)_2SO_4$ solution on glass slide and plastic slide

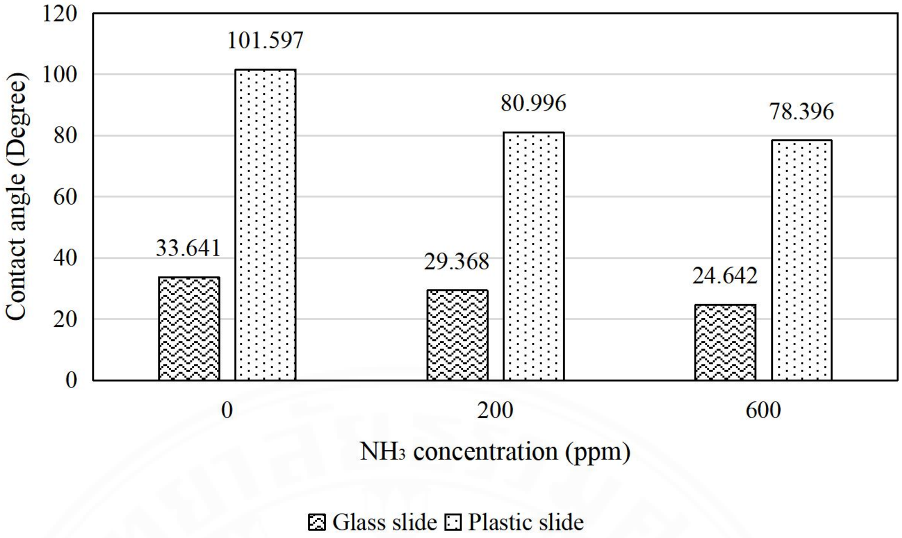
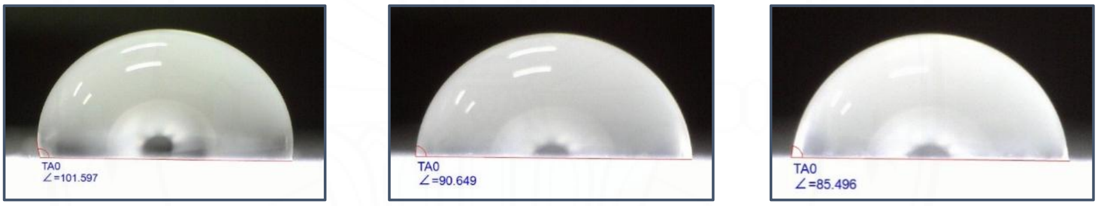
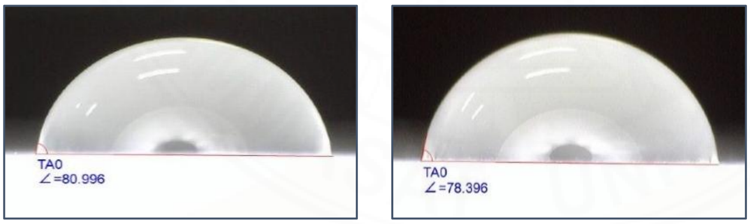


Figure 4.3 Contact angles of $(NH_4)_2CO_3$ solution on glass slide and plastic slide



(a) 0 ppm (b) 200 ppm of $(NH_4)_2SO_4$ (c) 600 ppm of $(NH_4)_2SO_4$



(d) 200 ppm of $(NH_4)_2CO_3$ (e) 600 ppm of $(NH_4)_2CO_3$

Figure 4.4 Contact angles of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ solutions on a plastic plate

Figure 4.2 shows the contact angles of $(NH_4)_2SO_4$ solution on glass slide and plastic slide. Figure 4.3 shows the contact angles of $(NH_4)_2CO_3$ solutions with ammonia concentrations of 0, 200, and 600 ppm on glass slide and plastic slide. The lower contact angle indicates the lower surface tension. The contact angles of $(NH_4)_2SO_4$ solutions at 200 and 600 ppm, which are 90.6˚ and 85.5˚, and the contact angles of $(NH_4)_2CO_3$ solutions at 200 and 600 ppm, which are 81.0° and 78.4°, are all lower than that of the pure water. Thus, the surface tension of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ solutions at 200 and 600 ppm concentrations are lower than that of the pure water. Increases of ammonium salt concentrations also decrease the contact angles which also means that they decrease the surface tension of the solutions. This leads to the increases of the flow percentages of the mortars containing the ammonium salts. Therefore, water lubricates cement particles better, which leads to decreasing the required flow force (Jiang, 2004)

4.2.3 Setting times

The plot between setting times (initial and final setting times) of pastes and concentration of ammonia in the forms of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are shown in Figure 4.5 and Figure 4.6. The ammonia concentrations at 0, 200, and 600 ppm were investigated. The results show that, for both fly ashes contaminated with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, initial and final setting times of the pastes increase with an increase of the ammonia concentration when compared to non-ammonia fly ash pastes. The setting times of pastes containing $(NH_4)_2CO_3$ contaminated fly ash seem to delay slightly more than that of the $(NH_4)_2SO_4$ contaminated fly ash pastes.

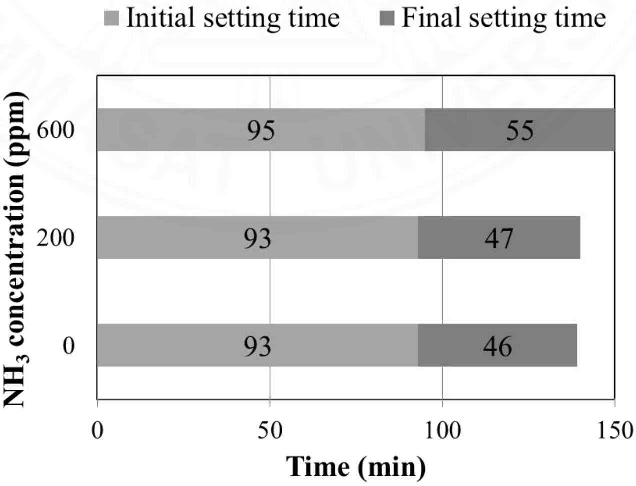


Figure 4.5 Setting times of pastes containing $(NH_4)_2SO_4$ contaminated fly ash (fly ash replacement = 30%)

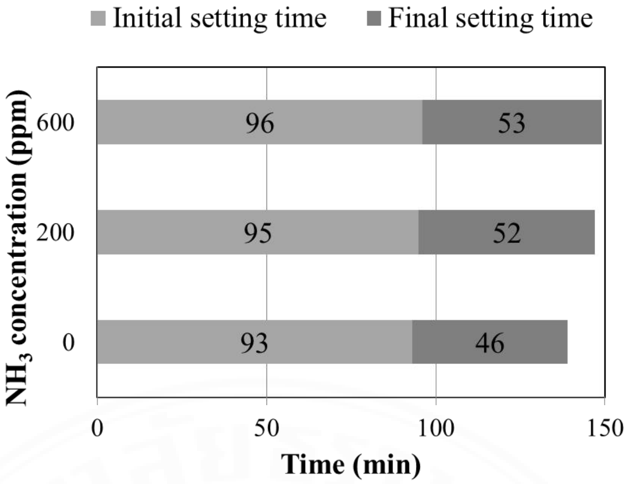


Figure 4.6 Setting times of pastes containing $(NH_4)_2CO_3$ contaminated fly ash (fly ash replacement = 30%)

In case of $(NH_4)_2SO_4$, the higher concentration of $(NH_4)_2SO_4$ induced the more prolonged induction period which resulted in delaying the early hydration reaction rate. This is possibly related to the high concentration of sulfate ions present which retards the early age hydration of cement (Qin et al., 2019).

As the addition of $(NH_4)_2SO_4$ was expected to affect alkalinity of the mixtures, the pH of the mortar mixes was measured by using litmus paper. The pH of $(NH_4)_2SO_4$ mixtures reduced from 13 to 12. The decrease of pH is beneficial for gypsum formation. Gypsum interrupts the hydration of C_3A and C_4AF and delay setting time (J. J. Chen, Thomas, Taylor, & Jennings, 2004; Liu, Deng, & Mo, 2015). In case of $(NH_4)_2CO_3$, the mortar flow increases due to the low surface tension of the solution of the mixing water by the presence of ammonium ions (NH_4^+). So, it results in delaying the setting times. However, more studies are needed to confirm this mechanism.

4.2.4 Compressive strength

The compressive strength of mortars containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ contaminated fly ash are shown in Figure 4.7 and Figure 4.8, respectively. The compressive strength at the ages of 3, 7, 28, and 91 days were measured.

The results show that the compressive strength of mortars containing

$(NH_4)_2CO_3$ contaminated fly ash increase while the compressive strength of mortars containing $(NH_4)_2SO_4$ contaminated fly ash decrease when compared to the compressive strength of non-ammonia fly ash mortars. The decrease of strength in the $(NH_4)_2SO_4$ mortars is because the mortars containing $(NH_4)_2SO_4$ release SO_4^{2-} that reacts with calcium hydroxide to form gypsum. Then, gypsum reacts further with alumina phase, like C_3A, to form ettringite, as shown in Eqs. (2.13) and (2.15). Also the addition of $(NH_4)_2SO_4$ retarded the hydration reaction. It is generally known that the amount of $Ca(OH)_2$ in a hydrated cement system can reflect the hydration degree of the cement system, and it was found that the amount of $Ca(OH)_2$ decreased. It can be the evidence that $(NH_4)_2SO_4$ produces a retarding effect on early age hydration (Qin et al., 2019). This reaction is promoted by the lower pH of the pore solution, from 13 to 12. Therefore, the decrease of the early age strength of the mortars occurs (Skalny, Marchand, & Odler, 2002).

On the other hand, the compressive strength of mortars containing $(NH_4)_2CO_3$ contaminated fly ash increases. Although, the addition of $(NH_4)_2CO_3$ retarded the hydration reaction, promoted by the lower pH of the pore solution, from 13 to 12, however, CO_3^{2-} reacts with calcium hydroxide ($Ca(OH)_2$) to form calcium carbonate ($CaCO_3$) as shown in Eq. (2.22). The calcium carbonate can fill pores and increases the denseness of the mortars, and so increases the strength of the mortars (Nakarai & Yoshida, 2015).

The denseness of mortar specimens at 28 days were observed by testing the Mercury Intrusion Porosimetry (MIP). To determine the porosity of the specimens, the specimens with the dimensions of 1×1×1 cm^3 were used. The results in Table 4.1 show that the total porosity of the non-ammonium salt mortar is 15.32%, the total porosity of the mortar containing $(NH_4)_2SO_4$ contaminated fly ash is 15.43%, and the total porosity of mortar containing $(NH_4)_2CO_3$ contaminated fly ash is 14.81%. The results show that the pore structure of $(NH_4)_2CO_3$ contaminated fly ash is denser than that of the non-ammonium salt fly ash mortar which is a reason of increase of compressive strength. But the pore structure of $(NH_4)_2SO_4$ contaminated fly ash is less denser than that of the non-ammonium salt mortar. In addition, the`average pore size of the mortar containing $(NH_4)_2CO_3$ contaminated fly ash is the smallest which is followed by the control mortar and mortar containing $(NH_4)_2SO_4$ contaminated fly ash.

All the above-mentioned results support that the mortar containing $(NH_4)_2CO_3$ contaminated fly ash gives the highest compressive strength and the mortar containing $(NH_4)_2SO_4$ contaminated fly ash has the lowest compressive strength when compared to other mortar specimens.

Table 4.1 Total porosity, average pore size, percentage of gel pore, and percentage of capillary pore of mortars with no ammonium salt, with 200 ppm of $(NH_4)_2SO_4$, and with 200 ppm of $(NH_4)_2CO_3$ at 28 days of age

Specimen	Total porosity (%)	Average pore size (nm)	Gel pore (10-2.5 nm) %	Capillary pore (Beyond 10µm-10nm) %
0	15.32	28.31	31.08	68.92
200 ppm of $(NH_4)_2SO_4$	15.43	33.99	30.69	69.31
200 ppm of $(NH_4)_2CO_3$	14.81	26.54	32.10	67.90

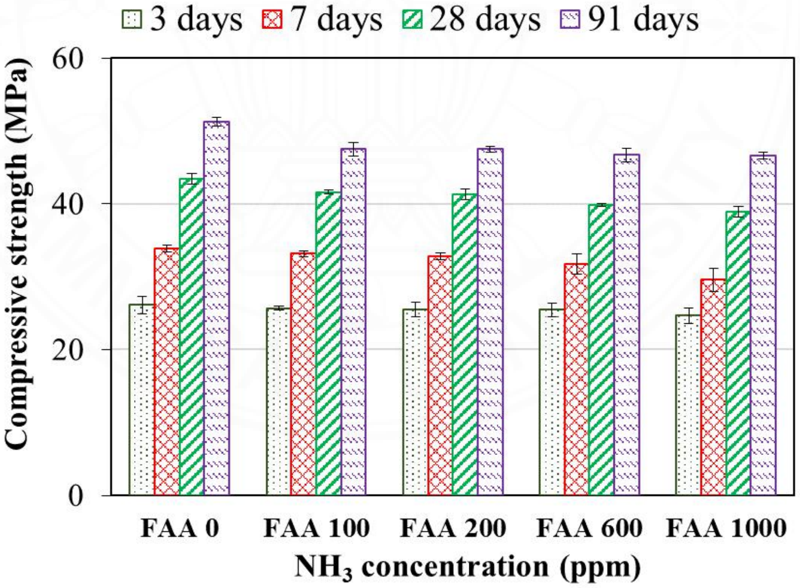


Figure 4.7 Compressive strength of mortars containing $(NH_4)_2SO_4$ contaminated fly ash (fly ash replacement = 30%)

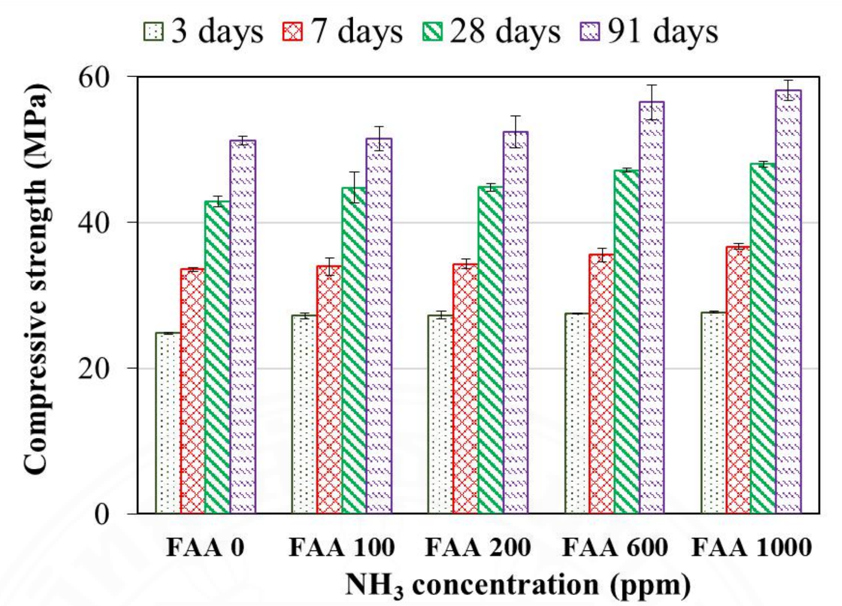


Figure 4.8 Compressive strength of mortars containing $(NH_4)_2CO_3$ contaminated fly ash (fly ash replacement = 30%)

4.3 Shrinkage

4.3.1 Autogenous shrinkage

Figure 4.9 and Figure 4.10 show the measured results of autogenous shrinkage in 56 days of mortars with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, respectively.

The results show that the mortars containing $(NH_4)_2SO_4$ demonstrate higher the autogenous shrinkage when increasing the ammonia concentration. For the physical effect of mortars containing $(NH_4)_2SO_4$, the formations of gypsum and ettringite, as shown in Eqs. (2.11) - (2.13), seem to decrease the stiffness of the specimens which cause an increase of autogenous shrinkage. However, more studies are needed to confirm this mechanism. For the mortar containing $(NH_4)_2CO_3$, the results show that the autogenous shrinkage is increased from that of the non-ammonia mortar. For the physical effect of mortars containing $(NH_4)_2CO_3$, calcium carbonate ($CaCO_3$) was produced, as shown in Eq. (2.20). The produced $CaCO_3$ can deposit inside the pores and densify the pore structure of the mortars which can be clarified by the lower total porosity and average pore size, as shown in Table 4.1. The lower porosity and pore size increases capillary pressure, causing larger autogenous shrinkage.

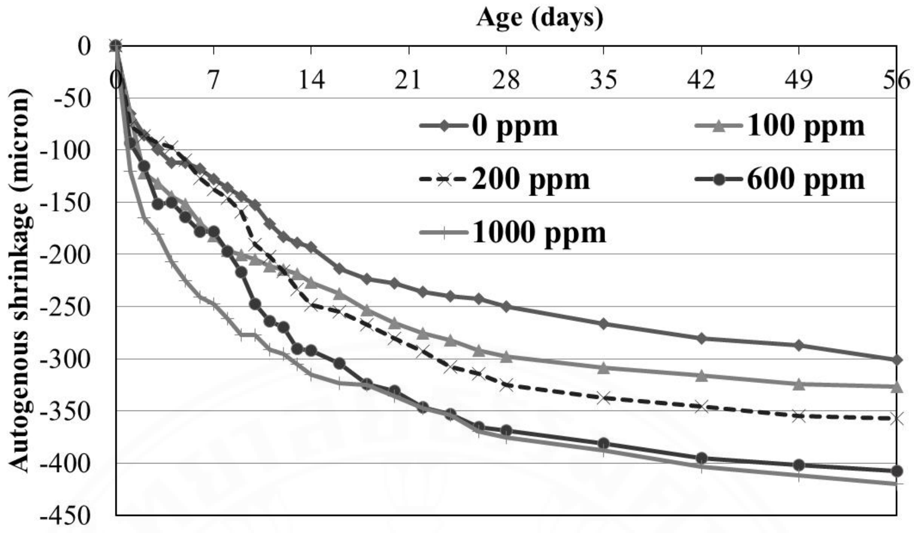


Figure 4.9 Autogenous shrinkage of mortars containing $(NH_4)_2SO_4$ contaminated fly ash (fly ash replacement = 30%)

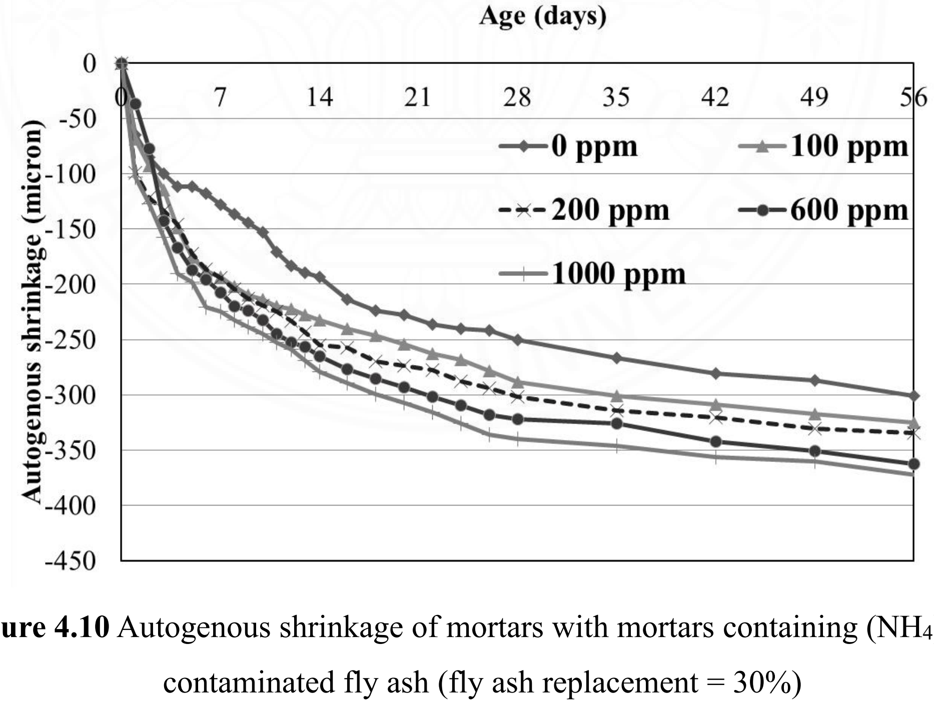


Figure 4.10 Autogenous shrinkage of mortars with mortars containing $(NH_4)_2CO_3$ contaminated fly ash (fly ash replacement = 30%)

4.3.2 Total shrinkage

Figure 4.11 and Figure 4.12 show the measured results of total shrinkage in 56 days of mortars with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, respectively.

For mortars containing $(NH_4)_2SO_4$, the results show that the total shrinkage increases when compared to the non-ammonium salt mortar. Due to high average pore size, high percentage of capillary pore, and high total porosity of the mortar containing $(NH_4)_2SO_4$, as shown in Table 4.1, the loss of free water to the environment is increased. Therefore, the drying shrinkage of the mortars containing $(NH_4)_2SO_4$ increases compared to the mortars with no ammonium salt.

For mortars containing $(NH_4)_2CO_3$, the results show that the total shrinkage decreases when compared to non-ammonium salt mortar. Due to the formation of calcium carbonate ($CaCO_3$), as shown in Eq. (2.20), the average pore size, the percentage of capillary pore, and the total porosity are lower as shown in Table 4.1. This reduces the evaporation of free water and also reduces the drying shrinkage (Qin et al., 2019).

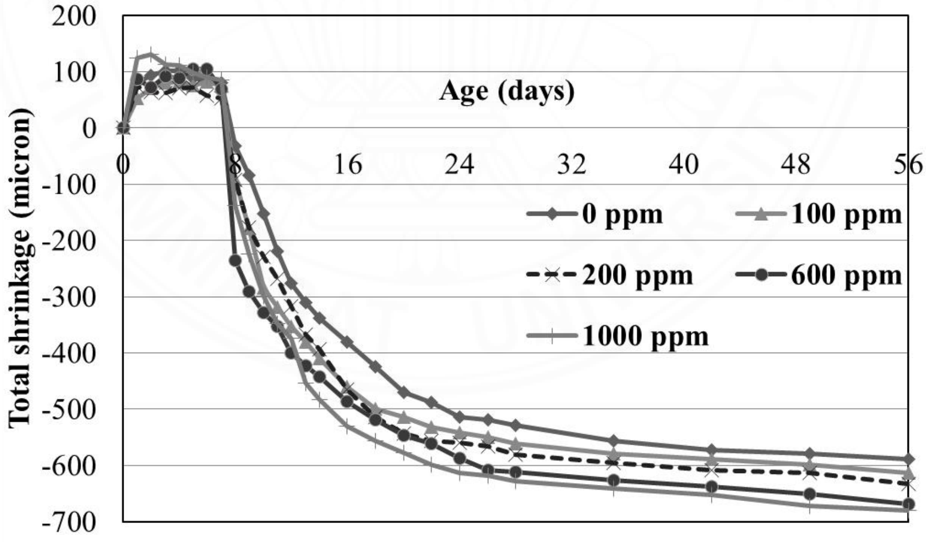


Figure 4.11 Total shrinkage of mortars with mortars containing $(NH_4)_2SO_4$ contaminated fly ash (fly ash replacement = 30%)

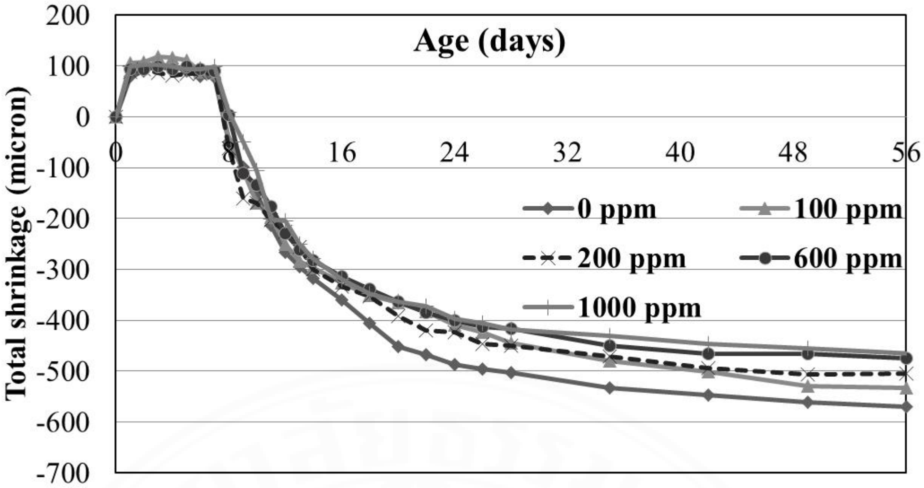


Figure 4.12 Total shrinkage of mortars with mortars containing $(NH_4)_2CO_3$ contaminated fly ash (fly ash replacement = 30%)

CHAPTER 5

EFFECTS OF BLENDED $(NH_4)_2SO_4$ AND $(NH_4)_2CO_3$ IN FLY ASH ON PROPERTIES OF MORTARS

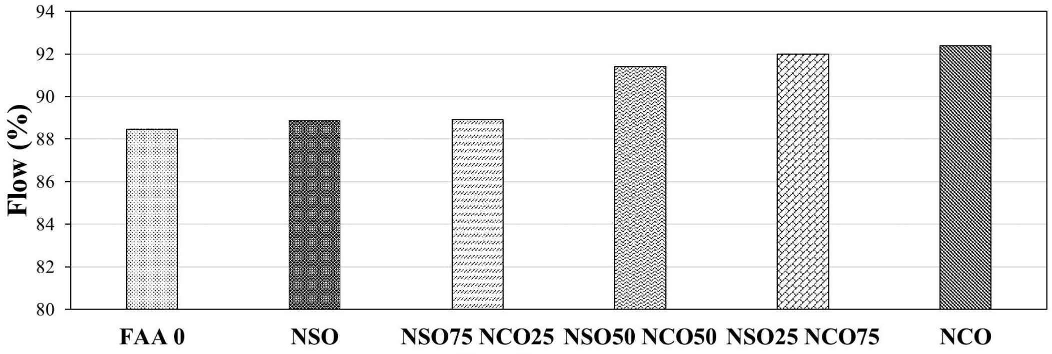
5.1 General

This chapter shows the results and discussion on the effects of blended ammonium sulfate ($(NH_4)_2SO_4$) and ammonium carbonate ($(NH_4)_2CO_3$) at an ammonia concentration of 200 ppm in fly ash on properties of mortars. Both $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are products from NO_x controlling technologies which contaminate the fly ash. In this test, the blended ammonium salts were prepared with different ratios of the two ammonium salts which are 0, 0.25, 0.5, and 1. Each ratio of the ammonium salts was mixed and dissolved in the water before added in the fly ash. The tested mortar properties consist of flow, compressive strength, autogenous shrinkage, and total shrinkage.

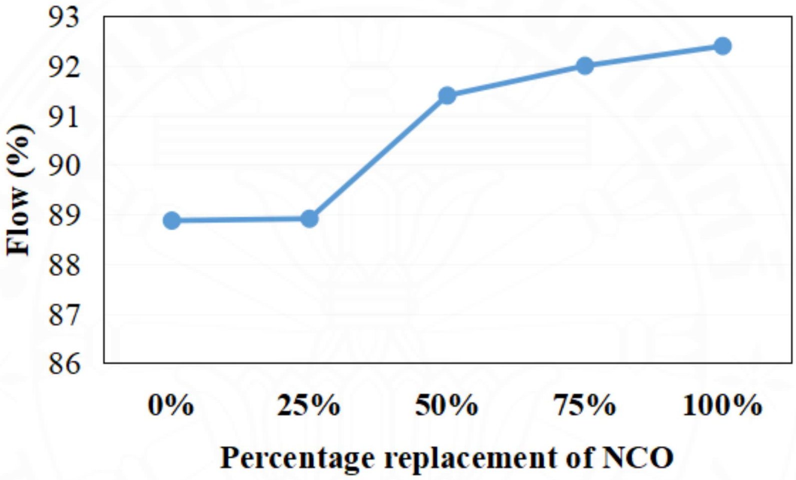
5.2 Basic properties

5.2.1 Mortar flow

The results of flows of mortars containing blended ammonium salts at an ammonia concentration of 200 ppm are shown in Figure 5.1. The results show that the flows of fly ash mortars containing more $(NH_4)_2CO_3$ portion are higher than those of fly ash mortars containing more $(NH_4)_2SO_4$ portion. Also, the results of flows of mixtures with blended ammonium salts are in between the flows of the mixtures with pure ammonium salt.



(a) Flows of fresh fly ash mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$



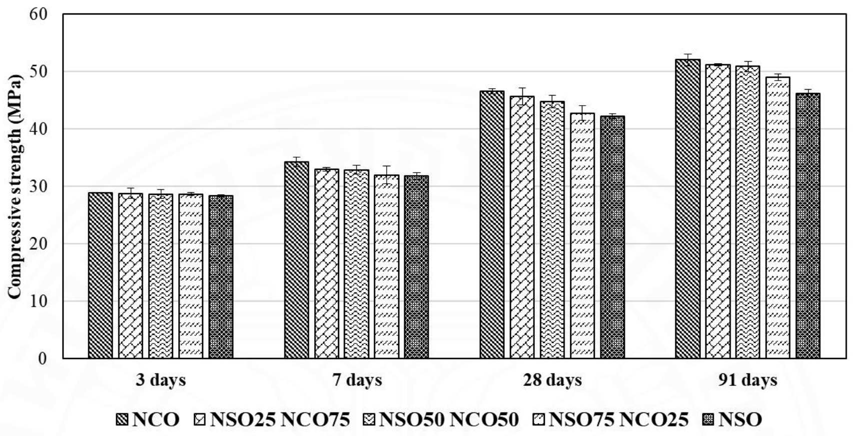
(b) Flows of fresh fly ash mortars with varied percentage replacements of $(NH_4)_2CO_3$

Figure 5.1 Flows of fresh fly ash mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at ammonia concentration of 200 ppm

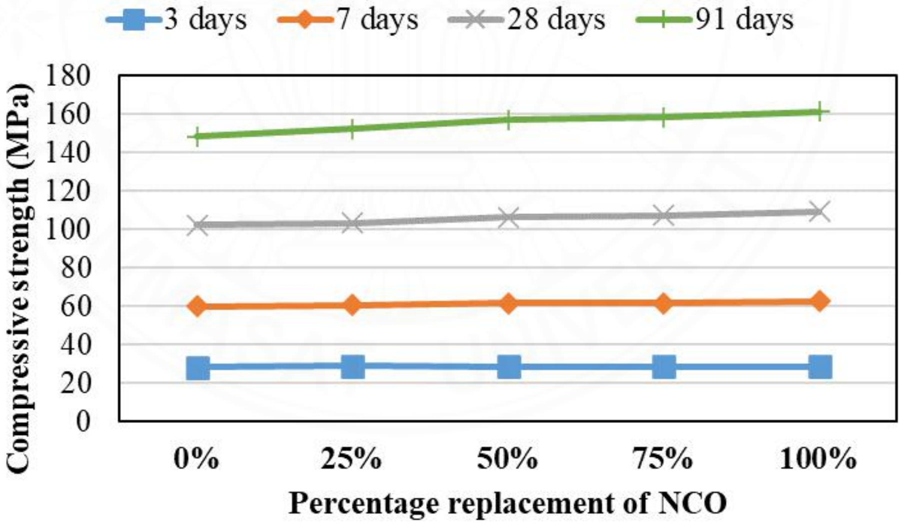
From the explanation of flow test and surface tension test in chapter 4, the contact angle of the $(NH_4)_2CO_3$ solution is lower than that of the $(NH_4)_2SO_4$ solution, as shown in Figure 4.2 and Figure 4.3. Thus, the flows of mortars containing $(NH_4)_2CO_3$ are higher than those of the mortars containing $(NH_4)_2SO_4$. Therefore, the flows of the mortars containing blended $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ are in between the flow percentages of the mortars with only $(NH_4)_2SO_4$ and mortars with only $(NH_4)_2CO_3$.

5.2.2 Compressive strength

Compressive strength of mortars with varied ratios of ammonium salts at an ammonia concentration at 200 ppm are shown in Figure 5.2. The compressive strength at the ages of 3, 7, 28, and 91 days were tested.



(a) Compressive strength of mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$



(b) Compressive strength of mortars with varied percentage replacements of $(NH_4)_2CO_3$

Figure 5.2 Compressive strength of mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at ammonia concentration of 200 ppm

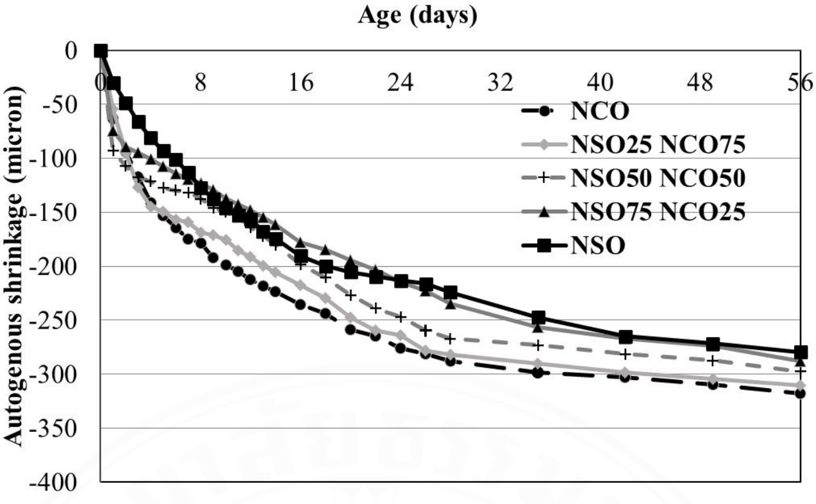
The results show that the compressive strength of mortars containing high portion of $(NH_4)_2CO_3$ are higher than those of mortars containing high portion of $(NH_4)_2SO_4$. From the explanation of compressive strength in chapter 4, the formation of $CaCO_3$ from $(NH_4)_2CO_3$ can fill pores and increase the denseness of the mortars, resulting in an increase of compressive strength. The formation of gypsum from $(NH_4)_2SO_4$ reacts with C_3A to form ettringite and retarded the hydration reaction of cement. Pore structure of mortar containing $(NH_4)_2SO_4$ contaminated fly ash is less dense than that of the non-ammonium salt fly ash mortar, as shown in Table 4.1. Both of them result in decreasing the compressive strength. Therefore, the compressive strength of the mortars with blended ammonium salts is in between those of the mortars with pure ammonium salt.

5.3 Shrinkage

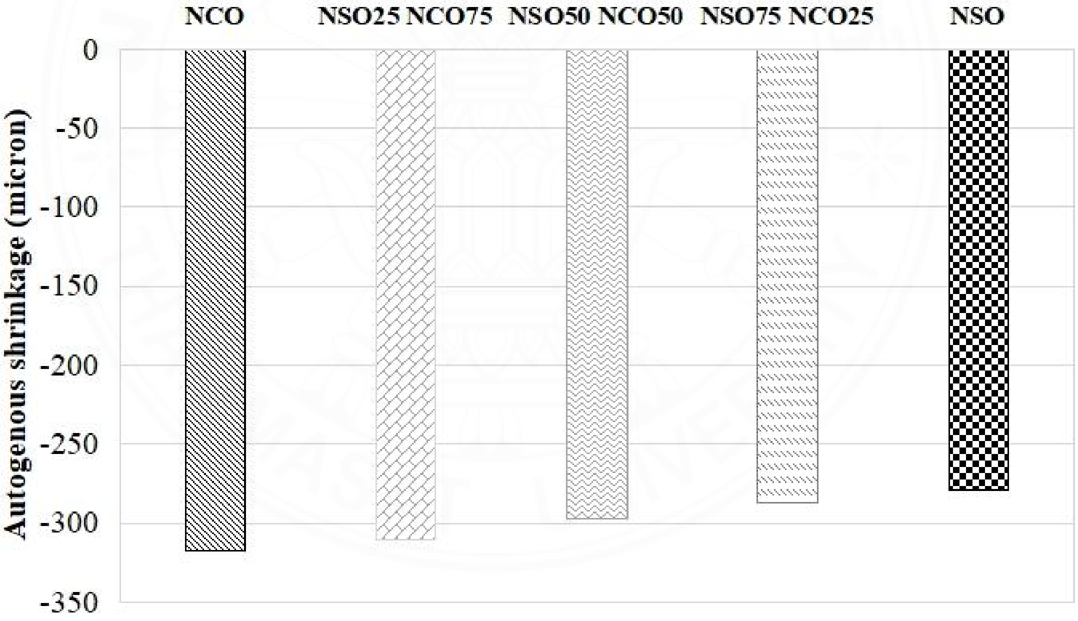
5.3.1 Autogenous shrinkage

The results of autogenous shrinkage in 56 days of mortars with varied ratios of blended ammonium salts at an ammonia concentration of 200 ppm are shown in Figure 5.3.

The results show that autogenous shrinkage of mortars containing varied ratios of blended ammonium salts are in between that of the mortars with pure ammonium salts. Both ammonium salts increase autogenous shrinkage. However, $(NH_4)_2CO_3$ tends to increase autogenous shrinkage more than $(NH_4)_2SO_4$. From the explanation of autogenous shrinkage in chapter 4, for mortars containing $(NH_4)_2SO_4$ contaminated fly ash, the formations of gypsum and ettringite, as shown in Eqs. (2.11) - (2.13), seem to decrease the stiffness of the specimens which cause an increase of autogenous shrinkage. For mortars containing $(NH_4)_2CO_3$ contaminated fly ash, the produced $CaCO_3$ can deposit inside the pores and densify the pore structure of the mortars which can be clarified by the lower total porosity and average pore size, as shown in Table 4.1. The increase of density increases capillary pressure, causing larger autogenous shrinkage. Therefore, autogenous shrinkage of mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ blends are in between those of the mortars with pure $(NH_4)_2SO_4$ and pure $(NH_4)_2CO_3$.



(a) Autogenous shrinkage of mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$



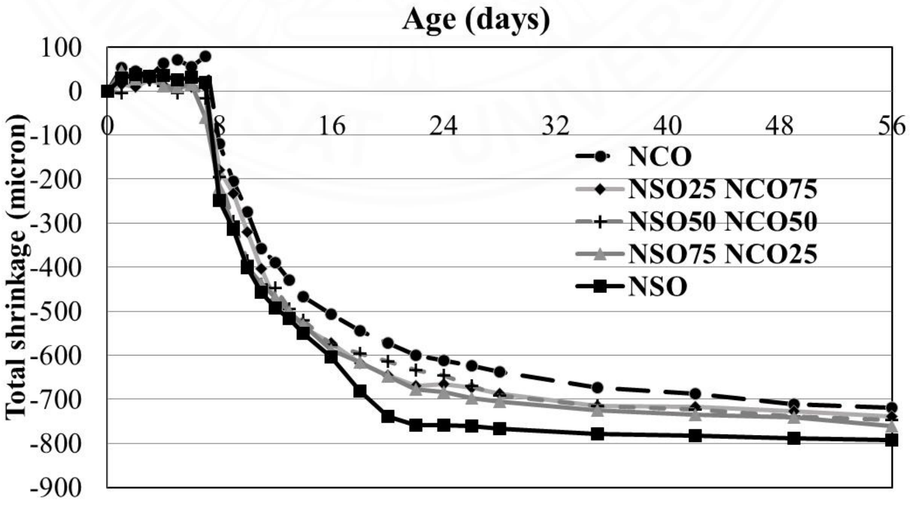
(b) Autogenous shrinkage of mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm at 56 days

Figure 5.3 Autogenous shrinkage of mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm

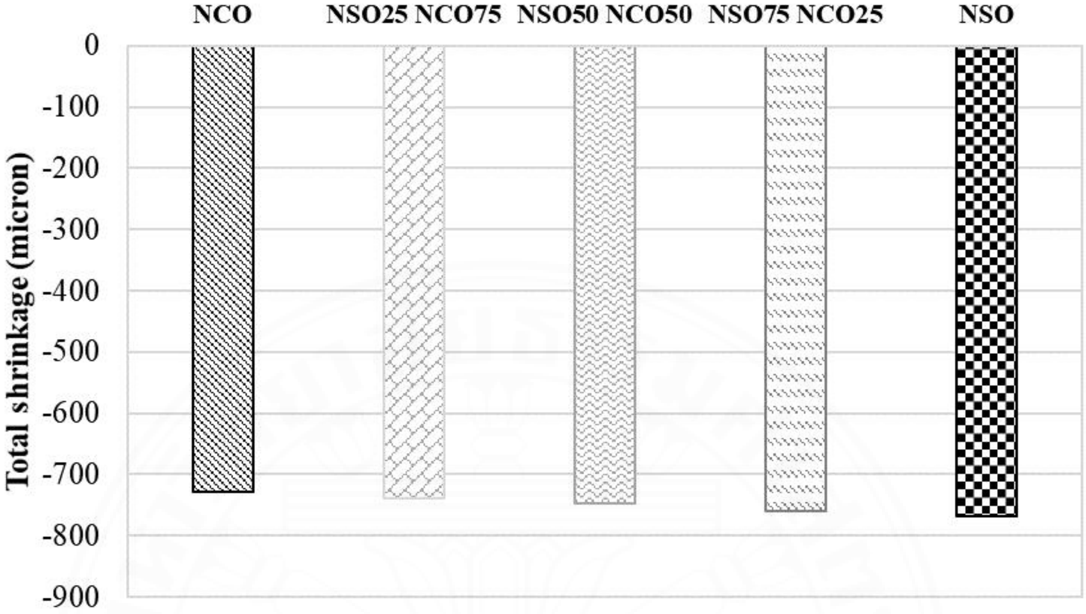
5.3.2 Total shrinkage

Total shrinkage in 56 days of mortars containing varied ratios of blended ammonium salts at an ammonia concentration of 200 ppm is shown in Figure 5.4.

The results show that the total shrinkage of mortars containing high portion of $(NH_4)_2CO_3$ are lower than that of the mortars containing high portion of $(NH_4)_2SO_4$. From the explanation of total shrinkage in chapter 4, for mortars containing $(NH_4)_2SO_4$, the results show that the total shrinkage increases when compared to the non-ammonium salt mortar. Due to high average pore size, high percentage of capillary pore, and high total porosity of the mortar containing $(NH_4)_2SO_4$, as shown in Table 4.1, the loss of free water to the environment is increased. Therefore, the drying shrinkage of the mortars containing $(NH_4)_2SO_4$ increases compared to the mortars with no ammonium salt. For mortars containing $(NH_4)_2CO_3$, the results show that the total shrinkage decreases when compared to non-ammonium salt mortar. Due to the formation of calcium carbonate ($CaCO_3$), as shown in Eq. (2.20), the average pore size, the percentage of capillary pore, and the total porosity are low as shown in Table 4.1. This reduces the evaporation of free water and also reduces the drying shrinkage. Therefore, the total shrinkage of mortars containing high portion of $(NH_4)_2CO_3$ is lower than that of the mortars containing high portion of $(NH_4)_2SO_4$.



a) Total shrinkage of mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$



b) Total shrinkage of mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm at 56 days

Figure 5.4 Total shrinkage of mortars with varied ratios of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm

CHAPTER 6

EFFECTS OF $(NH_4)_2SO_4$ AND $(NH_4)_2CO_3$ IN DIFEERENT TYPES OF FLY ASH ON PROPERTIES OF MORTARS

6.1 General

The two power plants in Thailand, which are Mae Moh power plant and BLCP power plant, use different types of coal to generate electricity. So, fly ashes produced from the two power plants have different chemical compositions. Therefore, the effects of the fly ashes on mortar properties are different. This chapter shows the results and discussion on the effects of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in different types of fly ash on properties of mortars at the ammonia concentrations of 0 and 200 ppm. In this chapter, the fly ashes are divided into 3 types which are low CaO content fly ash (FAR), high CaO content fly ash (FAA), and high CaO - high free lime content fly ash (FAB). The tested mortar properties consist of flow, setting times, compressive strength, autogenous shrinkage, and total shrinkage.

6.2 Basic properties

6.2.1 Mortar flow

The results of flows of mortars with different fly ashes containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm are shown in Figure 6.1.

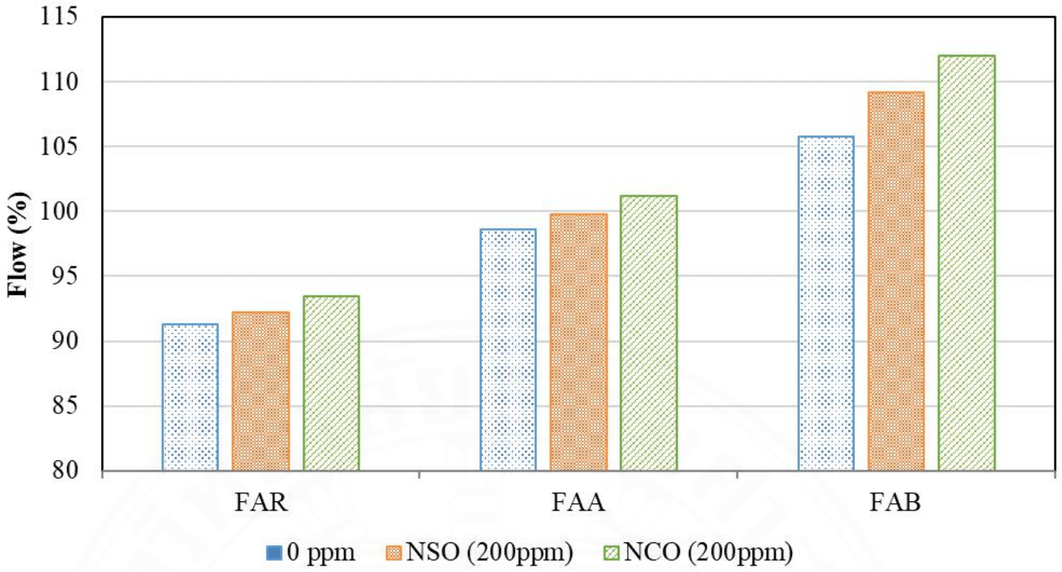


Figure 6.1 Flows of mortars with different types of fly ash containing $(NH4)_2SO_4$, and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm

The results show that even with different types of fly ash, the mortars containing $(NH_4)_2CO_3$ contaminated fly ash still have the highest flow when compared with the non-ammonia fly ash mortar and mortars containing $(NH_4)_2SO_4$ contaminated fly ash.

The affecting degrees of ammonium salts on each type of fly ash are different. Different flows of mortars containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at 0 ppm and 200 ppm obtained by Eq. (6.1) are shown in Figure 6.2.

$$\text{Flow difference (\%)} = \left(\frac{\mathrm{Fl}_{\mathrm{NH_4}} - \mathrm{Fl}_{\mathrm{no-NH_4}}}{\mathrm{Fl}_{\mathrm{no-NH_4}}}\right) \times 100 \qquad (6.1)$$

Where flow difference (%) is percentage of difference between flow of the mortar with $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ at 200 ppm and flow of mortar with no ammonium salt. $\mathrm{Fl}_{\mathrm{NH_4}}$ is flow of the mortar with $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$ at 200 ppm. $\mathrm{Fl}_{\mathrm{no-NH_4}}$ is flow of the mortar with no ammonium salt.

FAB is the most subjective to ammonium salts when compared with other two types of fly ash. From the chemical compositions of fly ashes in Table 3.1, FAB has the highest SO_3 content (8.53%), which is followed by FAA (4.26%) and FAR (0.28%). Additional SO_3 from the FAB may increase the flow percentage by reducing the surface tension of water in mortar mixture. Moreover, the Blaine fineness of FAB (2,820 cm^2/g) is lower than that of FAA (2,867 cm^2/g), which may result in a higher flow of FAB mixtures. However, the assumption needs future investigation.

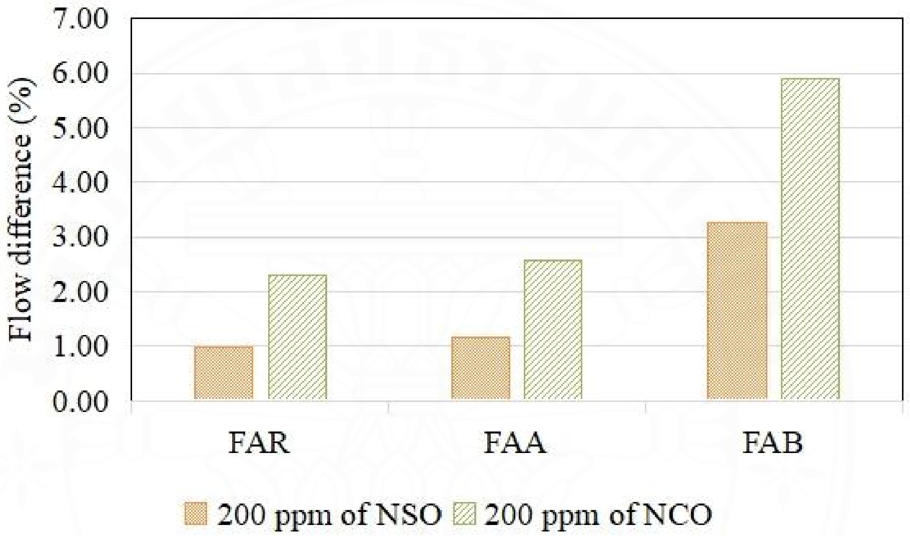


Figure 6.2 Percentage of difference of flow of mortars with different types of fly ash with ammonium salt at 200 ppm comparing to non-ammonium salt mortar

When comparing non-ammonia fly ashes, both $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, increase flows but the effects of $(NH_4)_2CO_3$ on fly ash is larger than that of $(NH_4)_2SO_4$ by resulting in higher flows, as explained in Chapter 4.

6.2.2 Setting times

The plots between setting times (initial and final setting times) of pastes with 0 and 200 ppm of ammonia concentration in the forms of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in different fly ashes (FAR, FAA and FAB) are shown in Figure 6.3.

When comparing among all 3 tested fly ashes, setting times of FAR when compared to FAA and FAB are the most delayed. According to the amount of free lime content in fly ash, FAR fly ash has the lowest free lime content, which is 0.03%, when compared to FAA (free lime =0.49%) and FAB (free lime =3.93%). The high amount of free lime accelerates the reactions of binders, resulting in decreasing the setting times. Also, FAR fly ash has the highest amount of LOI content, which are 5.38%, and has irregular shape, so it has higher water requirement as indicated by high normal consistency. Therefore, FAR fly ash results in longest setting times.

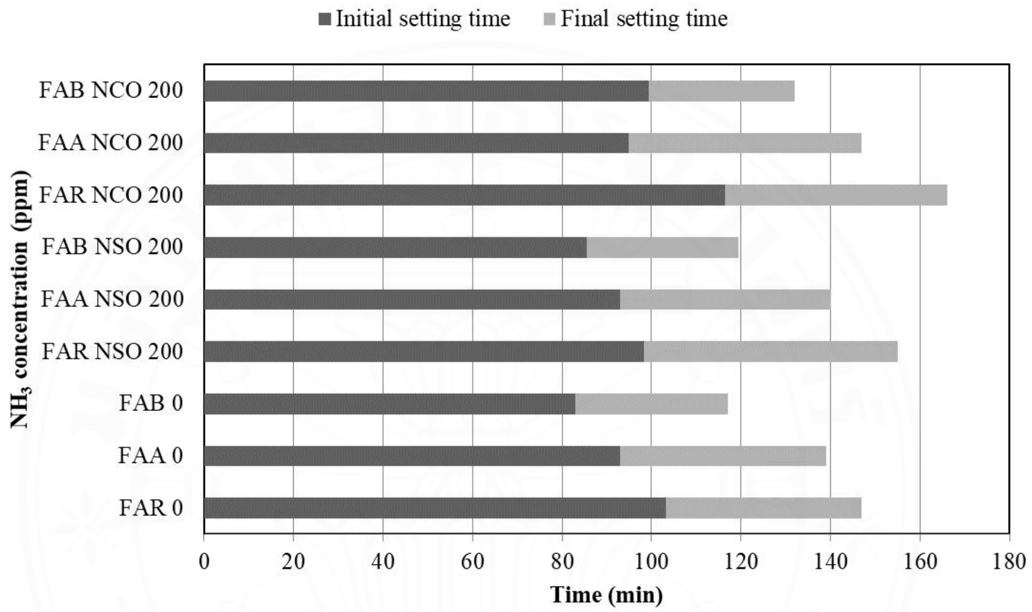
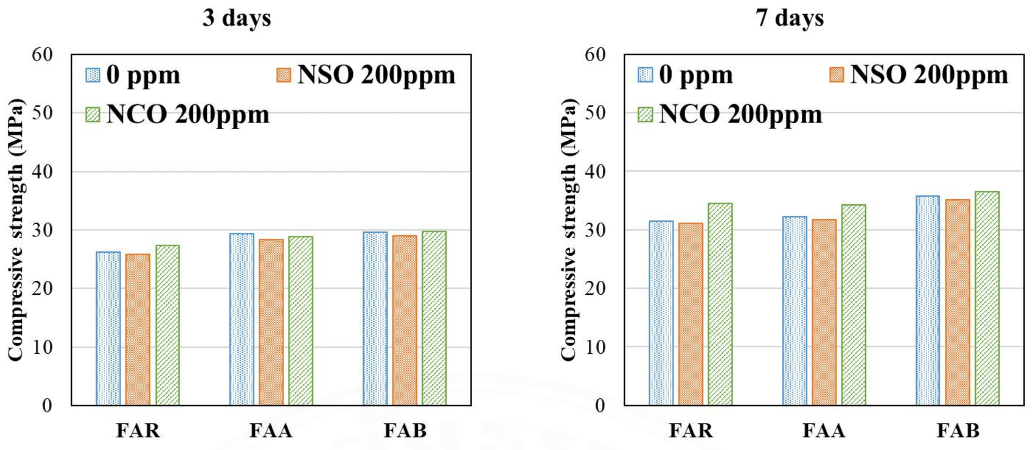


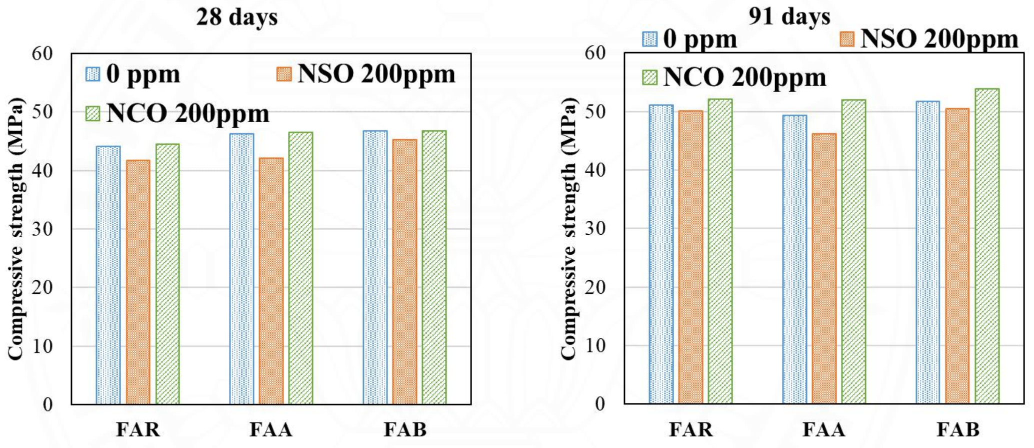
Figure 6.3 Setting times comparing between different types of fly ash

6.2.3 Compressive strength

The results of compressive strength of mortars with the 3 tested types of fly ashes (FAR, FAA and FAB) containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at 200 ppm are shown in Figure 6.4. The compressive strength at the ages of 3, 7, 28, and 91 days were tested.



(a) Compressive strength at 3 days (b) Compressive strength at 7 days



(c) Compressive strength at 28 days (d) Compressive strength at 91 days

Figure 6.4 Compressive strength of mortars with different types of fly ash containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at 200 ppm

The results show that the compressive strength of mortars containing $(NH_4)_2CO_3$ contaminated fly ash increase while the compressive strength of mortars containing $(NH_4)SO_4$ contaminated fly ash decrease, as described earlier.

For each types of fly ash, the results show that FAB has the highest compressive strength when compared with other types of fly ash at every age of test, as shown in Figure 6.4. At the early age, from the chemical compositions of fly ash, FAB and FAA contain higher CaO and higher free lime than FAR, thus, the binder reactions, which produce strength, are accelerated. But at 91 days, the strength of

FAR fly ash mortars increases beyond the strength of FAA fly ash mortars. It is due to the higher SiO_2 content of the FAR.

6.3 Shrinkage

6.3.1 Autogenous shrinkage

Figure 6.5, Figure 6.6, and Figure 6.7 show the measured results of autogenous shrinkage in 56 days of different types of fly ash (FAR, FAA, FAB) mortars with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, respectively.

All the results show that mortars containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ contaminated fly ash have larger autogenous shrinkage compared to non-ammonia mortar. Mixtures with $(NH_4)_2CO_3$ contaminated fly ash show larger autogenous shrinkage than the mixtures with $(NH_4)_2SO_4$ contaminated fly ash.

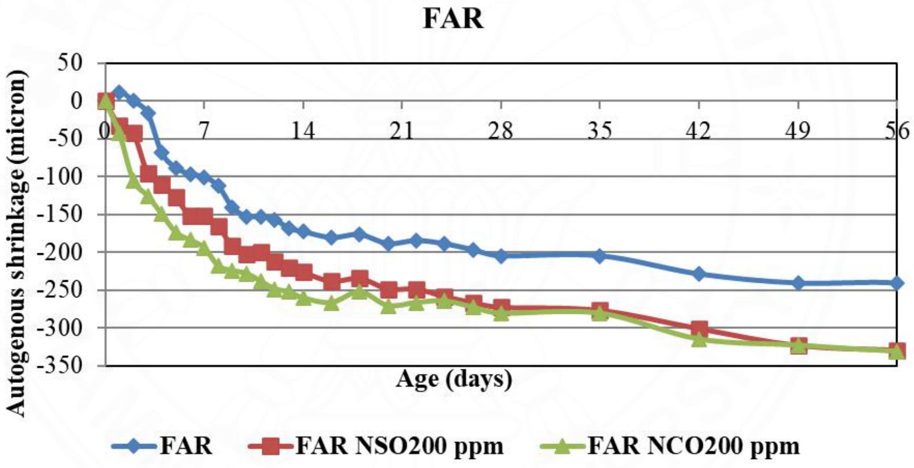


Figure 6.5 Autogenous shrinkage of FAR mortars containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm

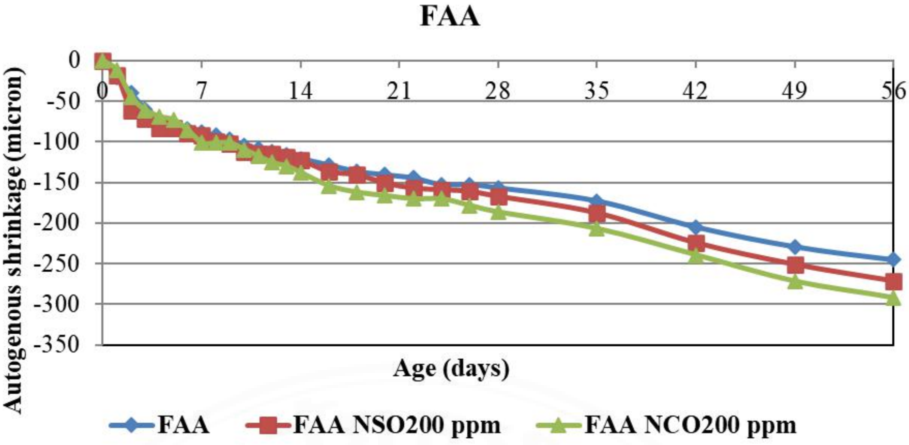


Figure 6.6 Autogenous shrinkage of FAA mortars containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm

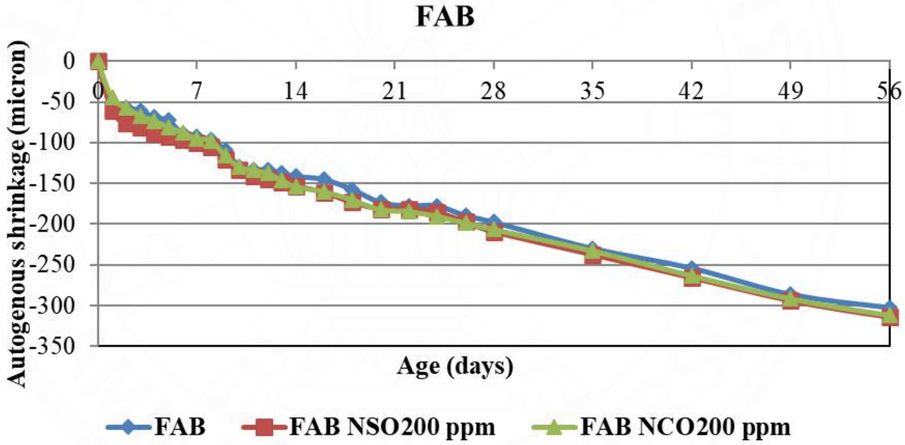


Figure 6.7 Autogenous shrinkage of FAB mortars containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm

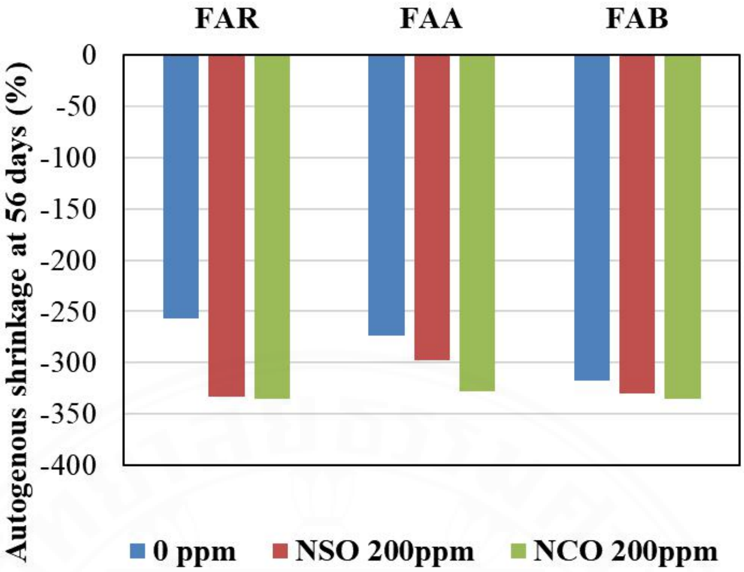


Figure 6.8 Autogenous shrinkage of different types of fly ash mortars with and without ammonium salt of 200 ppm at 56 days

From Figure 6.8, the results show that among the 3 tested types of fly ash, FAR fly ash seems to be the most subjective to ammonium salts in term of autogenous shrinkage.

6.3.2 Total shrinkage

Figure 6.9, Figure 6.10, and Figure 6.11 show the measured results of total shrinkage in 56 days of mortars incorporating different types of fly ash (FAR, FAA, FAB) contaminated with $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$, respectively.

All the results show that mortars containing $(NH_4)_2CO_3$ contaminated fly ash have slightly lower total shrinkage (except for FAR mortars) while mortars containing $(NH_4)_2SO_4$ contaminated fly ash have slightly higher total shrinkage than the non-ammonia fly ash mortars. However, the differences are almost negligible.

From Figure 6.12, the results show that, FAB mortars have lowest total shrinkage and FAR mortars have the highest total shrinkage when compared to others. Due to higher content of CaO, SO_3, and free lime, the product from the hydration reaction of FAB is higher than other which can increase the denseness of specimens an also the formation of early ettringite causes an early expansion. So, the drying shrinkage is lower. Therefore, the total shrinkage of FAB mortars is lower than that of the FAA and FAR mortars.

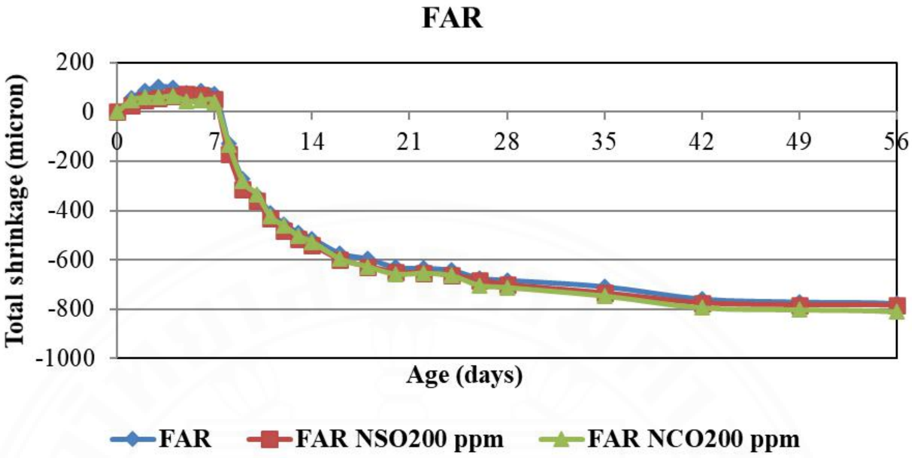


Figure 6.9 Total shrinkage of FAR mortars containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm

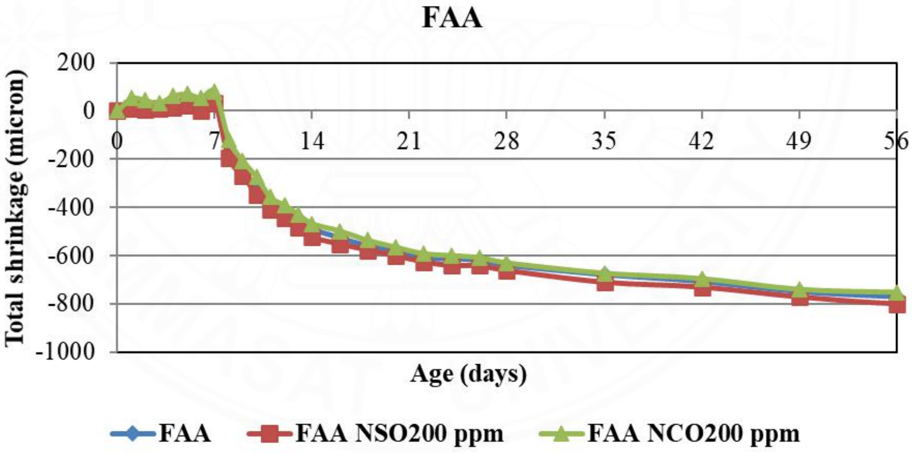


Figure 6.10 Total shrinkage of FAA mortars containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm

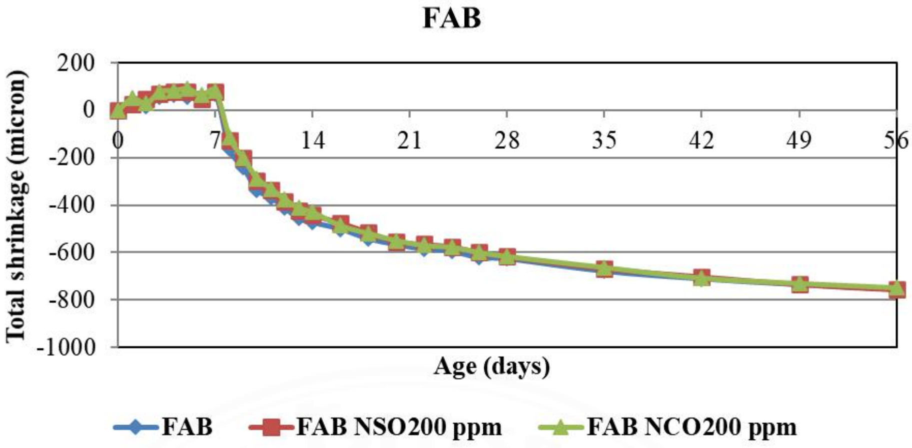


Figure 6.11 Total shrinkage of FAR mortars containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at an ammonia concentration of 200 ppm

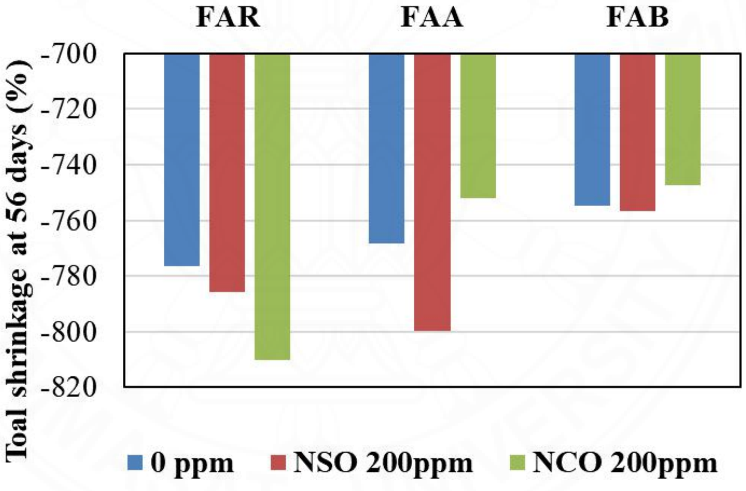


Figure 6.12 Total shrinkage of different types of fly ash mortars with and without ammonium salt of 200 ppm at 56 days

CHAPTER 7

EFFECTS OF $(NH_4)_2SO_4$ AND $(NH_4)_2CO_3$ IN HIGH FREE LIME FLY ASH ON PROPERTIES OF MORTARS

7.1 General

Many researches on fly ash that have been conducted in Thailand show that fly ash produced from Mae Moh power plant started to show signs of high free lime content. Therefore, this chapter shows the results and discussion on the effects of free lime content in fly ash on properties of mortars incorporating high free lime fly ash with an ammonia concentration of 200 ppm, using fly ash from Mae Moh as a base fly ash. High free lime fly ash was prepared by adding calcium oxide in the Mae Moh fly ash. Three free lime contents used in this study are originally free lime content in Mae Moh fly ash, 5% by weight of the fly ash, and 10% by weight of the fly ash. The tested mortar properties consist of flow and compressive strength. The original fly ash from Mae Moh is denoted as FAA while the Mae Moh fly ashes added with 5% and 10% by weight free lime are denoted as FAC5% and FAC10%, respectively.

7.2 Basic properties

7.2.1 Mortar flow

The results of flows of mortars with different fly ashes having different amounts of free lime and contaminated with ammonia concentration of 200 ppm are shown in Figure 7.1. The results show that flows of high free lime fly ash mortars decrease when compared to that of normal free lime fly ash mortars and the flows of high free lime fly ash mortars containing ammonia concentration of 200 ppm in the fly ash increase when compared to that of the non-ammonia high free lime fly ash mortars.

Due to high free lime content in fly ash, free lime (free CaO) adsorbed water into the pores and started the reaction to form calcium hydroxide ($Ca(OH)_2$). This consumption of water can lead to reduced fluidity of the mortars. Therefore, the flows of high free lime fly ash mortars decrease when compared to that of normal fly ash mortars.

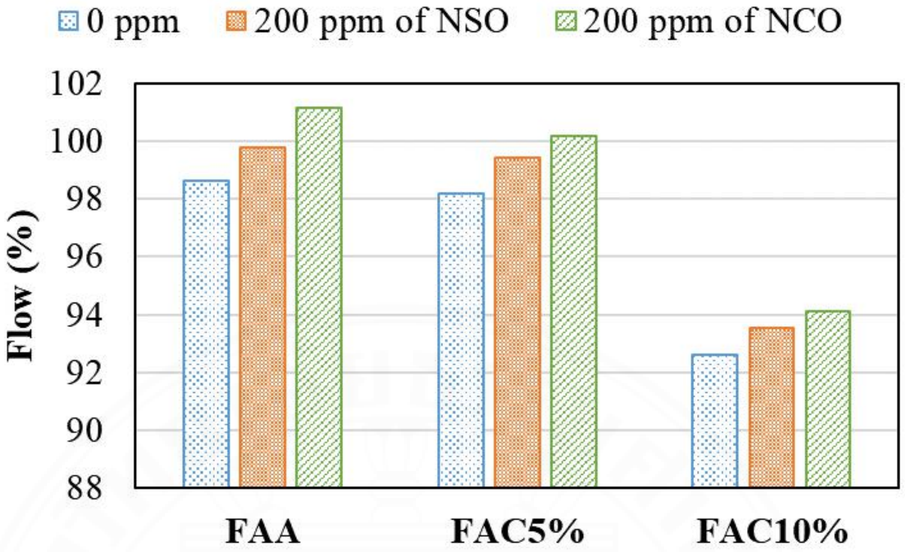
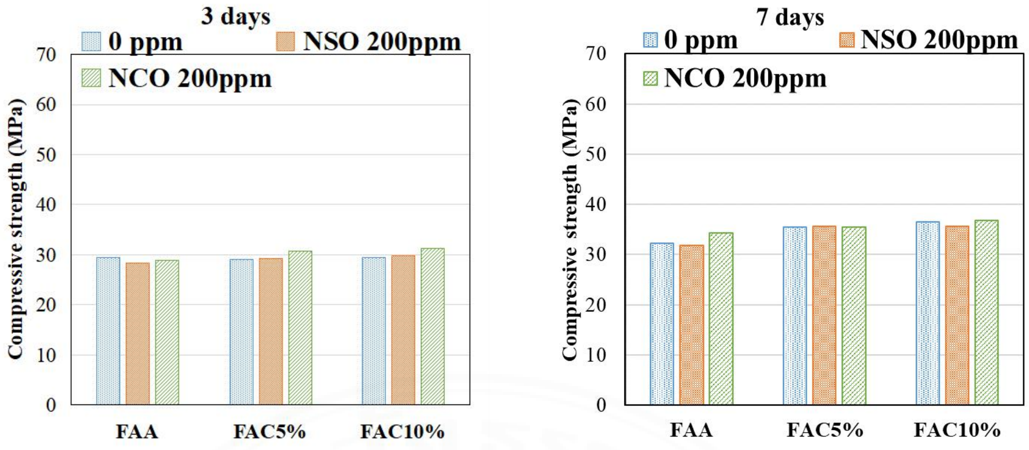


Figure 7.1 Flows of mortars with different amounts of free lime in fly ash containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at 200 ppm

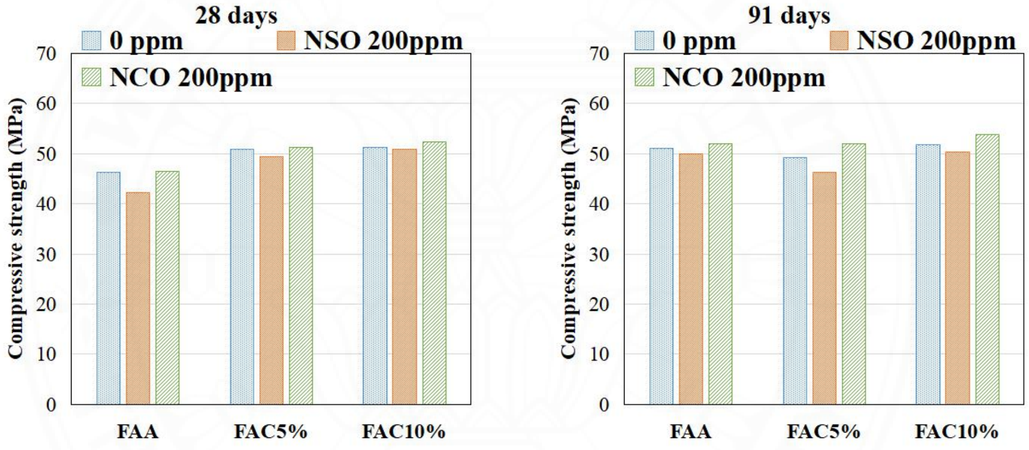
7.2.2 Compressive strength

The results of compressive strength of high free lime fly ash mortars with ammonia concentration of 200 ppm in fly ash are shown in Figure 7.2. The compressive strength at the ages of 3, 7, 28, and 91 days were tested.

The results show that the compressive strength of high free lime fly ash mortars containing $(NH_4)_2SO_4$ decreased while compressive strength of high free lime content fly ash mortars containing $(NH_4)_2CO_3$ increased, for both 5% and 10% total free lime contents, when compared to that of normal fly ash mortar. Due to high free lime content in fly ash, the hydration between free lime (free CaO) and water results in the formation of calcium hydroxide ($Ca(OH)_2$) and then produced CSH gel which contributed to compressive strength.



(a) Compressive strength at 3 days (b) Compressive strength at 7 days



(c) Compressive strength at 28 days (d) Compressive strength at 91 days

Figure 7.2 Compressive strength of mortars with different amounts of free lime contents in fly ash containing $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ at 200 ppm

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

8.1 Conclusions

8.1.1 Effects of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in fly ash on properties of mortars

The summary of all the results is shown in Table 8.1. The change in mortar properties depends on types and concentrations of ammonium compounds.

1) $(NH_4)_2SO_4$ reduces all tested properties except for the workability of mortars.

2) $(NH_4)_2CO_3$ contributes to improvement of the tested properties except for autogenous shrinkage.

3) Setting times are delayed in mixtures containing fly ash with $(NH_4)_2SO_4$ or $(NH_4)_2CO_3$.

Table 8.1 Summary of the tested properties of mortars containing ammonium sulfate and ammonium carbonate compared to non-ammonia mortar

Properties	**Fly ash with ammonium sulfate ($(NH_4)_2SO_4$)**		**Fly ash with ammonium carbonate ($(NH_4)_2CO_3$)**	
	Worse	**Better**	**Worse**	**Better**
Workability		**X**		**X**
Setting times	**Delayed**		**Delayed**	
Early Compressive strength	**X**			**X**
Long-term compressive strength	**X**			**X**
Autogenous shrinkage	**X**		**X**	
Total shrinkage	**X**			**X**

8.1.2 Effects of blended $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in fly ash on properties of mortars

The summary of all test results can be concluded that the change in mortar properties depended on both ammonium salts. The results of tested properties of mortars containing blended ammonium salts are in between the results of mortar containing pure ammonium salt depending on the ratio of each ammonium salt.

8.1.3 Effects of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in different types of fly ash on properties of mortars

The change in mortar properties depended on types of fly ash and types of ammonium compounds.

1) With and without ammonium salts, high CaO content and high free lime fly ash (FAB) resulted in highest flowability when compared to other fly ashes due to high SO_3 content.

2) Low CaO content FAR fly ash delayed the setting time the most when compared to other due to low free lime content, high LOI content, and irregular shape.

3) FAB fly ash leads to the highest compressive strength when compared with other types of fly ash at all tested ages.

4) Both FAB and FAR mixtures have higher autogenous shrinkage than the FAA mixture.

5) Mixtures containing the same type of fly ash with or without ammonium salts show insignificant differences in total shrinkage

8.1.4 Effects of $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ in high free lime fly ash on properties of mortars

The change of mortar properties come from difference of free lime content.

1) Both $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ increases the workability of mortars.

2) $(NH_4)_2SO_4$ decreases the compressive strength while $(NH_4)_2CO_3$ increases the compressive strength of mortars.

3) Flowability decreases when fly ash contains free lime. The higher the free lime content, the lower the flow of the mortar.

4) Compressive strength of mortars containing fly ash with high free lime content increases.

8.2 Recommendations for future studies

The recommendations for future studies are as follows.

1. More studies should be conducted for the clear mechanism on the results of autogenous shrinkage of mortars containing $(NH_4)_2SO_4$.
2. More studies should be conducted for the clear mechanism on the results of setting times of mortar containing $(NH_4)_2CO_3$.
3. It should be investigated more on why effects of ammonium salts in different types of fly ash, which are low CaO fly ash (FAR), high CaO fly ash (FAA), and high CaO and high free lime, are different except from the difference in chemical compositions of the fly ashes.
4. The other properties indicating the effects of free lime content in fly ash on properties of mortar with ammonia should be investigated.
5. Other durability properties such as sulfate resistance, chloride penetration, and carbonation should be investigated.
6. The effects of LOI on the ammonia contaminated fly ash should be investigated.
7. Tests using real ammonia contaminated fly ash should be conducted.
8. Methods of ammonia removal from fly ash should be studied.

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APPENDIX

AN EXAMPLE OF CALCULATION OF THE AMOUNT OF AMMONIUM SALTS

For example

Ammonia concentration in fly ash = 50 ppm = 50 mg/ 1kg of fly ash

Therefore, W_{NH_3} = 50 mg

For $(NH_4)_2SO_4$,

$$\frac{W_{(NH_4)_2SO_4}}{132} = 2\left(\frac{50\times10^{-3}}{17}\right)$$

$$W_{(NH_4)_2SO_4} = 0.78 \text{ g/ 1kg of fly ash}$$

Use fly ash = 150 g = 0.15 kg

Therefore, $W_{(NH_4)_2SO_4}$ for 150 g of fly ash = 0.78×0.15

= 0.11 g of $(NH_4)_2SO_4$

For $(NH_4)_2CO_3$,

$$\frac{W_{(NH_4)_2CO_3}}{96} = 2\left(\frac{50\times10^{-3}}{17}\right)$$

$$W_{(NH_4)_2CO_3} = 0.565 \text{ g/ 1kg of fly ash}$$

Use fly ash = 150 g = 0.15 kg

Therefore, $W_{(NH_4)_2CO_3}$ for 150 g of fly ash = 0.565×0.15

= 0.08 g of $(NH_4)_2CO_3$

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