A STUDY ON ASR EXPANSION MITIGATION BY MINERAL ADMIXTURES AND LiOH・H2O

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鉱物質混和材および $LiOH \cdot H_2O$ による ASR 膨張の抑制に関する研究

MOHD ISNEINI

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A DISSERTATION

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By

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ABSTRACT

Nowadays, concrete deterioration has become a major problem throughout the world. One of the actors that contribute to the deterioration of concrete is Alkali-silica reaction (ASR). ASR will occur when these components such as reactive silica, alkalis, and sufficient moisture are present in concrete (ACI 221.1R-98).

Several ways have been applied to control or even stop ASR in concrete: such as utilization blended cement, cement with low alkali content, innocuous aggregate, control of total alkali in concrete. Currently, it is generally accepted that supplementary cementitious materials (SCMs) such as fly ash (FA), silica fume (SF), blast furnast slag (BFS), are typical SCMs used in concrete. SCMs have been used spreadly and successfully to mitigate ASR. This experimental program was carried out in the laboratory to investigate the effectiveness of mineral and chemical admixtures in order to reduce expansion. The production of mortars and concrete are included in this study. The pessimum proportion of aggregate is determined when reactive and non reactive aggregates were mixed with the ratio of 30:70. Concrete prisms were made according to RILEM AAR-3, and mortar prism were made based on JIS A 1146. Concrete specimens were cured under 40^{o} C, and R.H. 100% for expansion test. Meanwhile, mortar specimens were also treated under 40^{o} C, and R.H. 100% for expansion measurement.

It is interesting to conduct research in real life. However, It is difficult to conduct and predict mineral and chemical admixtures effectivity in suppressing the expansion due to ASR in a real environment. Duration of the observation in a long time period and patience are needed in order to evaluate and observe the concrete in real environments.. So that, testing in a real environment is not a good choice to be conducted. Based on these reasons, research in the laboratory is selected. One of the advantages of research in laboratory, strictly controlled conditions can be arranged.

This dissertation consists of seven chapters.

In **Chapter 1**, research background, objectives of the research and thesis arrangement are explained.

In **Chapter 2**, brief introduction and theoretical background are explained. As well as, aggregates and methodology. Description about supplementary cementitious materials (SCMs) such as SF, FA, EPP, and chemical admixtures such as $LiOH^{\cdot}$ H_2O are also explained.

In **Chapter** 3, there are three kinds of experiments in this chapter. First, SF was used in the level of 10% and 15%. SF was also used in different of w/b: 0.5, 0.4 and 0.3 in concrete. The results showed that SF at level 10% is enough in reducing expansion when reactive and non

reactive aggregates were mixed with the ratio of 30:70. Some researchers used SF in concrete and mortar with different types of portland cement such as high alkalis, and low content of SiO_2. However, in this study, SF has high content of SiO_2 and no content of alkalis. Second, The effectiveness of FA and SF have been shown by some researchers that the both of them are beneficial in order to suppress expansion due to ASR. However, incorporation of them to reduce expansion are very rare. As a result, it is interesting to combine them. The results showed that incorporation of FA and SF are lower than FA itself (FA10SF5 and FA15SF10) in reducing expansion. So, it can be used in mitigating ASR. The third, The combination of two minerals is also shown in reducing expansion due to ASR. The incorporation of FA and expanded perlite powder (EPP) is also conducted. The effectiveness of them is also lower than FA itself (FA15EPP10) in order to reduce expansion due to ASR.

In **Chapter 4**, the reasons why some minerals such as FA, SF, and EPP can reduce expansion are described.

In **Chapter 5**, previous research showed that when 4M of $LiOH{\cdot}H_2O$ solution was used to immerse reactive aggregate to create passivated aggregates greatly reduced expansion in accelerated mortar bar tests compared to non passivated aggregates. In this study, 4M of $LiOH{\cdot}H_2O$ is used not only in mortar but also concrete. The results show that after 4M of $LiOH{\cdot}H_2O$ solution was used to treat reactive aggregates in 80°C for 5 days , solution is enough to reduce expansion of andesite contain crystobalite. Then, when reactive aggregates are treatment at 80°C for 10 days, the expansion is greatly decrease for andesite contain opal. Furthermore, when reactive aggregates are covered with cement paste contained $LiOH{\cdot}H_2O$ solution, then immersed in $LiOH{\cdot}H_2O$ solution, the expansion is also decreased.

In **Chapter 6**, when FA at level 10% and 15% do not enough to reduce expansion. Then reactive aggregates can be treated by immersing with 2M and 3M of $LiOH{\cdot}H_2O$ in order to reduce expansion in mortar.

In **Chapter 7**, conclusions, recommendations and future works are presented.

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TERMINOLOGY

ASR (alkali silica reaction) is a reaction which occurs in concrete between the highly alkaline from cement or other sources and silica found in aggregates, given sufficient moisture.

Expansion: the process of increasing of something in size. Determination of Length change due to ASR can be determined through standard such as: ASTM C 1260, JIS A 1146, RILEM AAR-3, RILEM AAR-4, etc.

RILEM (Reunion Internationale des Laboratoires D'essais et de Recherches sur les Materiaux et les Constructions), with headquarters in Paris, is The International Union of Testing and Research Laboratories for Materials and Structures. **RILEM AAR-3**: Method of test for Alkali-silica reactivity of aggregates by concrete prisms method.

JIS: Japanese Industrial Standards. **JIS A 1146**: Method of test for Alkali-silica reactivity of aggregates by mortar-bar method.

Compressive strength: the capacity of a material to withstand loads.The compressive strength is obtained experimentally by means of a compressive test. Compressive strength is measured on a universal testing machine (UTM).

Ultrasonic pulse velocity test: This test is conducted to assess the quality of concrete or material. Quality of concrete is assessed by measuring the velocity of an ultrasonic pulse passing through a concrete. Higher velocities indicate good quality and continuity of the concrete.

Porosity: is one of important characteristics of pore system, the other is: pore size distribution. Pore system can be determined through mercury intrusion porosimetry (MIP). The pore system in cement-based materials consists of some types of pores: gel pores, capillary pores, macropores.

Mineral admixtures: additional substance act as a filler, to improve physical structure by occupying the spaces between the cement particles, and as a "pozzolan," to react chemically for greater strength and durability.

Fly Ash (FA) is a by-product of the combustion of pulverized coal in electric power plants.

Silica Fume (SF) is a by-product of the smelting process in the silicon and ferrosilicon industry that is used as a pozzolan.

Perlite is also a pozzolan due to its glassy structure and high SiO_2 and Al_2O_3 contents.

CHAPTER 1. GENERAL INTRODUCTION

1.1 Research Background

Nowadays, concrete deterioration has become a major problem. One of the factors that contribute to the deterioration of concrete is alkali silica reaction (ASR). ASR is a reaction between alkali in the cement pastes and reactive silica in the aggregates(1.1), (1.2). To control total alkali in concrete is one of the effective ways to mitigate ASR(1.2). When these components such as alkali, water (moisture content) and reactive aggregates are present, then ASR will occur in concrete(1.3). Some ways to reduce ASR have been applied e.g. use of non-reactive aggregates, use of cement with low alkalies, and use of pozzolans or mineral admixture(1.4). Due to the lack of river gravel, the usage of reactive mountain gravel or crushed stones are commonly used in some countries such as Japan. Cement with low alkalies sometimes is not enough to decrease expansion due to ASR, because alkalies can be supplied from other external sources.

Adding the supplementary cementitious material (SCMs) as cement replacement is one of effective ways to improve the durability of concrete. Durability is defined as the ability of concrete to resist weathering action, chemical attack, abrasion, and other service conditions(1.5). The usage of mineral admixtures as replacement portion of cement could reduce expansion due to ASR in concrete(1.6), (1.7). The most general admixtures are used for reducing ASR: fly ash, silica fume, and slag blast-furnace. Further, the individual usage of mineral admixture is also commonly used in concrete. The effectiveness of mineral admixtures in mitigating ASR depends on some factors, such as: the replacement level, the fineness of the mineral admixtures, and the composition of the admixtures(1.8). In future time, the source of mineral admixtures will be changed. It might that the availability of the minerals has reduced. As a result, the combination of minerals is important to be conducted, and the usage of chemical admixture for suppressing ASR is also important to find other effective ways.

1.2 Research Objectives

The purpose of this research is to study on mitigating ASR when aggregates were used in pessimum proportion. The main objective of this research: firstly, to determine the suitable level of silica fume in suppressing ASR. Secondly, to evaluate the effectiveness of combination between fly ash with silica fume. Thirdly, to evaluate the effectiveness of combination between fly ash with expanded perlite powder. Finally, to study the effectiveness of $LiOH \cdot H_2O$ in reducing expansion by treating reactive aggregates in $LiOH \cdot H_2O$ solution.

1.3 Dissertation Arrangement

The dissertation outline is summarized in Fig. 1.1 which composes of seven chapters as described as follows:

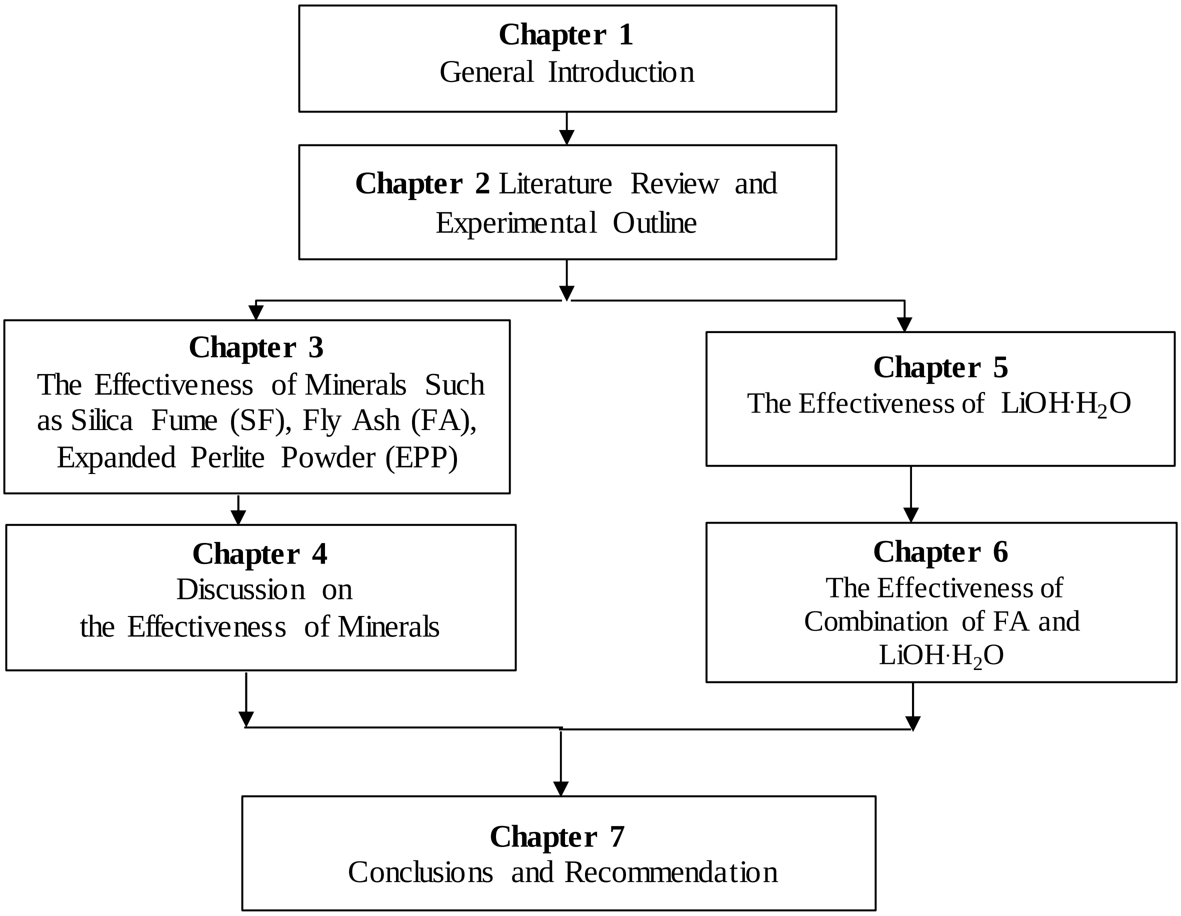

Fig. 1.1 Organization of each chapter

Chapter 1 describes the research background and the purpose of this study.

Chapter 2 describes the previous studies related to mitigating ASR, theoretical background, methodology and testing method.

In **Chapter 3,** first experiment is conducted to determine the suitable level of SF in mitigating ASR with some various water binder ratio. Second experiment is conducted to describe the effectiveness of mineral combinations of fly ash (FA) with silica fume (SF). First step, experiment was conducted with FA at level 15% and 25%. Second step, SF at level 5% and 10% were also conducted. Third step, to combine FA and SF. Third experiment, the effectiveness of two mineral combinations, between FA and EPP are also investigated. First step, experiment was conducted with FA at level 15% and 25%. Second step, EPP at level 10%, 15% and 20% were also conducted. Third step, to combine FA and EPP.

Chapter 4 is about discussion on the effectiveness of minerals in mitigating ASR. The discussion is mainly described based on silicon dioxide content in minerals.

In **Chapter 5,** reactive aggregates were treated by using $LiOH{\cdot}H_2O$. The treatments are : reactive aggregates were immersed in $LiOH{\cdot}H_2O$ solution, reactive aggregates were covered with cement paste contained $LiOH{\cdot}H_2O$, reactive aggregates were covered with cement paste contained $LiOH{\cdot}H_2O$ and then immersed in $LiOH{\cdot}H_2O$ solution.

Chapter 6 first step, experiment was conducted with fly ash at level 10% and 15%. Second step, $LiOH{\cdot}H_2O$ was used at dosage 2M, 3M per liter to immerse reactive aggregates. The last, to combine FA with $LiOH{\cdot}H_2O$. When FA at level 10% and 15% do not enough to reduce expansion then reactive aggregates can be treated by immersing in 2M or 3M of $LiOH{\cdot}H_2O$ solution in order to reduce expansion.

Chapter 7 concludes the results of the study and describes recommendations and future research.

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CHAPTER 2. LITERATURE REVIEW AND EXPERIMENTAL OUTLINE

2.1 Literature review

2.1.1 Introduction

Some ways of mitigating and test methods are continuously developed to find more effective ways to suppress expansion. Some ways of countermeasures against alkali silica reaction (ASR) can be conducted by limiting of alkali under 3.0 kg/m^3, using blended cement and innocuous aggregates(2.1), (2.2). In Japan, the usage of FA at the level 15% to 25% are considered sufficient in reducing concrete expansion(2.2). Cement partially replaced with mineral admixtures such as FA, ground granulated blast-furnace slag (GGBFS) and SF. In addition, the usage of FA, or GGBFS and combination of minerals is also suggested(2.3). The levels of cement replacement between 15 and 25% by several pozzolans are effective in controlling expansion due to ASR(2.4),(2.5). Furthermore, there are some studies on the utilization of minerals to inhibit ASR: Rasheeduzzafar et al. showed that in most cases of medium-to-high alkali cements, 10% cement replacement by microsilica is adequate for ASR control(2.6). They used SF with Na_2O_{eq}: 0.9% and quartz glass as aggregate for mortar under the condition of 70°C. Zhang et al. showed that when the content of SF was less than 10%, SF did not influence the expansion of ASR, when the content was 15-20%, SF only may delay the expansion(2.7). Bektas et al. showed that both expanded and natural perlite powder (NPP) were potential to suppress expansion when incorporated into mortar bars, and mortar containing expanded perlite to replacement level of 16% performed better than mortar bars containing natural perlite(2.8).

D. S. Lane et al. said that in the ternary slag concretes, 2.5% and 5% SF greatly improved the ASR resistance. In his studies, the performance of combinations of FA and SF, combinations of SF and BB were evaluated. He concluded that incorporating small amounts of SF with OPC and FA or BB in ternary systems can be used to counterbalance the negative effect of high FA or BB replacement level on early strength and low replacement level on durability(2.9). Shehata et al. said that high-alkali (4.14%) FA was not as effective as the low-alkali (1.41%) FA in mitigating the expansion. When FA was used with 5% SF; a higher level of SF (say 7%) may be required to put such an FA to work more effectively. In his studies, the performance of combinations of SF and FA was evaluated(2.10). Tanaka, Y. et al. concluded that expansive strain was reduced when silicate fine powder (FA or SF) and blast furnace slag (BB) were used simultaneously. Then, Tanaka, Y., et al. said that the preventive effect of multiple use of additives can be estimated by summing up the preventive effect of single additive. In his studies, the performance of combinations of FA and BB, SF and BB (FA30BB40, SF20BB40) were evaluated. The expansion reduction due to combination of FA and BB, SF and BB were smaller than 2000 μ after 26 weeks(2.11). Furthermore, Craig W., Hargis et al. made an effort to limit ASR in: aggregate passivation. A lithium silicate layer was created on reactive natural siliceous aggregate surfaces by treating the aggregates in a lithium hydroxide solution prior to use(2.12). Lu et al. investigated that the formation of lithium silicate and lithium carbonate were observed on the aggregate surfaces, after soaking the aggregates in 1.8 M LiOH at 150 °C for 150 hours(2.13). However, the usage of lithium hydroxide in concrete is not clarified well.

2.1.2 Mineral admixtures

Nowadays, it is well known that supplementary cementitious materials (SCMs) such as fly ash (FA), silica fume (SF), blast furnace slags (BFS), metakaolin, and perlite have a significant effect to control ASR. FA, which is produced as an industrial by-product, is one of SCMs utilized in concrete. When FA is used, some improvements are achieved, such as increase of long-term strength and decrease of heat of hydration. Further, it is well known that appropriate usage of FA can suppress the alkali-silica reaction (ASR). This statement is supported by laboratory research and field experience(2.1), (2.4), (2.7), (2.14), (2.15), (2.16), (2.17). Furthermore, FA contain high alkali or less calcium are effective in suppressing expansion due to ASR. So, the high replacement level is needed to prevent expansion.

Silica Fume is defined by the American Concrete Institute (ACI) as a "very fine non-crystalline silica produced in electric arc furnaces as a by-product of production of elemental silicon or alloys containing silicon". SF, also referred to as condensed silica fume or micro silica that is used as a pozzolan. Its color, usually gray, powder somewhat similar to portland cement or FA. Fundamental performance properties of SF are pozzolanic reaction and micro filler effect, and they lead to improve durability of concrete. Moreover, perlite is also known as pozzolan due to its glassy structure and high SiO_2 and Al_2O_3 contents(2.8), (2.18), (2.19), (2.20), (2.21). In the construction industry, perlite is used as lightweight aggregate.

2.1.3 Chemical admixtures

This study is also made in efforts to reduce alkali-silica reaction focuses on the use of lithium hydroxide monohydrate ($LiOH \cdot H_2O$) as a chemical admixture in concrete. Lithium is a soft, silver-white metal and belongs in the Alkali Metal Group together with sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr). Pegmatite rocks are the most common sources of lithium.

Lithium is denoted by the chemical symbol "Li". It has atomic number 3 and its atomic mass is 6.941 grams (g), and lithium position is at the third lightest element after hydrogen (H) and helium (He). The Lithium main application for the construction industry is in the formulation of chemical admixtures for concrete. There are some various of lithium compounds such as Li_2CO_3, LiOH, Li_2SO_4.

Mc Coy and Caldwell reported the usage of lithium compounds to control ASR for the first time(2.22). A comprehensive investigation was conducted by using potential chemical admixtures to prevent ASR at that time. They used more than 100 different compounds in their studies such as metallic salts, acids, oils, organic chemicals, proteins and proprietary admixtures.

2.1.4 ASR mechanism

It is widely known that alkali-aggregate reactions (AAR) is a chemical reaction in concrete, between cement hydroxides and minerals in the aggregates. AAR was identified for the first time by Stanton more than 70 years ago in California. Since then, AAR has been recognized in many countries all over the world.

Two types of alkali-aggregate reaction are well known. The first is alkali-silica reaction (ASR) and the second is alkali-carbonate reaction (ACR). The differences between ASR and ACR are in mineral phases and mechanism. Many researchers agree that : ASR is a deleterious reaction between alkali hydroxide and mineral usually silica present in the aggregates that occurs in concrete. Meanwhile, ACR is a reaction between alkali hydroxides in the pore water of concrete and dolomitic aggregates. ACR case was reported for the first time in the late of 1950s. However, the cases of ACR are very rare.

Some theories about ASR mechanism were proposed by researchers. However, there are still on debates about the theories. Here is step by step theories about ASR mechanism which is summarized and explained by a certain theory, described as follows (George J.Z.Xu et al., E.G. Aydin et al.)(2.24):

(1) The reactive aggregates were attacked by hydroxyl ion and stops its dissolution.

(2) Alkali-silica gels were formed when alkalis (Na^+ or K^+) reacted with dissolved silica.

(3) Then, concrete expansion occurred due to osmotic pressure generated by alkali silica(te) gels (Hansen) (2.25).

(4) Cracks and widening of cracks due to mechanical pressure triggered the further expansion (Gowan and Vivian)(2.26). Moreover, concrete expansion depends on the type of reaction products. When the swelling alkali-silica gel is formed, then expansion will occur(2.26).

In his studies, George J.Z. Xu et al. said that: ASR expansion was reduced by mineral admixtures by two reactions: pozzolanic reaction and alkali silica reaction. Furthermore, The permeability of concrete was reduced by pozzolanic reaction between mineral admixtures and cement hydrates, then some fraction of the alkali ions were entrapped. Moreover, many researchers agreed that pozzolanic reaction could be written as follow :

$$SiO_2\,(s) + Ca^{++}\,(aq) + 2\,OH^-\,(aq) \rightarrow xCaO.SiO_2.yH_2O\ (CSH) \qquad \ldots\ldots\ldots.(2.1)$$

In his paper, George J.Z. Xu et al. added explanations that the availability of alkali ions were consumed by alkali silica reaction. Therefore, prevents the reaction between alkalis and aggregate. As written in his study, the expression of alkali-silica reaction was expressed as follows:

$$SiO_2 + 2\,Na^+ (K^+) + 2\,OH^- \rightarrow Na_2.(K_2)\,SiO_3.H_2O \qquad \ldots\ldots\ldots(2.2)$$

George J.Z. Xu et al. also explained that both reactions show similarities, there was a possibility in first reaction, some alkali metal ions were incorporated into secondary CSH hydrates, lime-alkali-silica gel might also formed in second reaction when Ca^{++} ions were incorporated. Then, the properties of concrete were improved by secondary CSH hydrates, if produced in large quantity while expansive alkali-silica gel would damage the concrete. Under alkali environment, and the presence of mineral admixtures, both reactions can concurrently take place. Alkali-silica reaction occurred not only between alkali and aggregate, but also between alkali and minerals because of the presence of mineral admixtures. Hence, the gel produced could be accommodated by concrete and distributed within the concrete (George J.Z. Xu et al.). Consequently, alkali content in concrete would be reduced by pozzolanic reaction and alkali-silica reaction. Moreover, permeability of concrete would also be reduced and also reduced alkali ions free movement. So that, potential reaction between alkalis and aggregate would be prevented or reduced. Lastly, George J.Z. Xu et al. concluded that both pozzolanic reaction and alkali silica reaction could take place at the same time and consume alkali ions, then reduced the permeability of concrete.

McCoy and Caldwell firstly reported the use of lithium compounds for controlling expansion due to ASR. They used a lot of chemicals to prevent or minimize expansion due to ASR. They used mortar test method based on ASTM C 277. Their results showed that lithium compounds were chemicals admixture that have good prospects in reducing ASR expansion in future time. After a couple of years, in 1956, and especially in 1985 's many studies were begun to report on the usage of lithium compounds. Here are, some researchers that report their study by using lithium compounds, such as: Chatterji(2.27), Sakaguchi et. al.(2.28), Kurtis et al. in 1998 and 2000, Stark, Diamond and Ong(2.34). With increasing a number of research, the expansion reduction mechanisms based on the use of lithium were proposed by the researchers(2.35), (2.36).

The **first theory**: Lithium might alter the composition of ASR products, resulting in products that are less expansive.

Lawrence and Vivian suggested: LiOH complex produced silica that could form a surface layer, thus protecting silica from other alkali attacks. Still in same years, they added explanation that with the increasing concentration of LiOH, thus silica gel tends to be less reactive with NaOH. Moreover, Stark, Diamond and Ong in 1992 concluded almost the same thing. They concluded that sufficient concentration of lithium or lithium increases the amount of expansion would decline.

The **second theory**: Silica dissolution was suppressed by Lithium

Lawrence and Vivian showed that lithium could reduce the rate of dissolution, not the solubility of silica. Furthermore, Sakaguchi`s studies in 1989, He suggested that lithium reaction with silica gel or ASR was preferential for the reaction with sodium and potassium cations, so as to reduce the level of dissolution, effectively reducing the rate of formation of large gels. Meanwhile, Collins summed up the results of his studies in 2002, he showed that dose was important.

The **third theory**: Repolymerization was decreased by Lithium

Lier in 1956 postulated that highly hydrated lithium ions adsorbed not as close to the surface of the silicate as a cation, which has a smaller radius hydrated, such as sodium or potassium. Then in a couple of years, Sakaguchi showed that the adsorption of $Li+$ was favored over $Na+$ and $K+$ adsorption, physical mechanism to prevent repolymerization gel might exist. Further, Kurtis et al. in 1998 and 2000 seemed support Sakaguchi. Kurtis et al. suggested that reducing the level of silica dissolution, the lithium could limit repolymerization species of silica dissolved into a gel, thus effectively reducing the potential for expansion. He proposed the theory that when lithium was present in sufficient concentrations, becomes gel potentially repolymerization expansive not happen.

The **last theory**: Lithium might reduce repulsive forces between colloidal ASR gel particles.

So far, There are not so many researchers who propose this theory:

Prezzi et al. proposed that the usage of an electric double layer (EDL) theory to explain the expansion of alkali-silica reaction gel, and extended the theory to describe the proposed mechanism by which chemical additives, including lithium salt can inhibit expansion. Then, he added that the reduction in surface charge density effectively reduced pressure generated by the expansion of ASR gel. Furthermore, Rodrigues et al. showed that in systems with both sodium and lithium ions, the surface charged density opal and alkali-silica gel (obtained from dam-ASR affected) decreased in the presence of LiCl, compared with sodium chloride (NaCl). Then he also added that the decrease in repulsive forces between colloidal particles ASR gel in the presence of lithium would reduce the pressure generated by the extensive swelling gel.

Then, in the next a couple of years, D.S. Lane said: ”Lithium was believed to incorporate into alkali-silica gels, resulting in an insoluble lithium silicate with little or no potential for absorbing water and swelling”. Lithium compound’s mechanism in inhibiting ASR was not clear yet. As stated in ACI 221.1R-98, expansion would happen if the important factors exist. Three most important components for ASR to occur, were: Alkali, moisture content and reactive silica. ASR will occur when these components were present in concrete.

2.1.5 Sufficient alkali

OPC is very important binder in concrete, and OPC is alkali main contributor. Alkali in concrete, predominantly sodium (Na^+) and potassium (K^+). The other sources of alkali are: supplementary cementing materials (such as, fly ash, silica fume, slag), chemical admixtures, aggregates, external sources (sea water and deicing salts). The quantity of alkali is usually expressed in:

$$Na_2O_{eq} = Na_2O + 0.658K_2O \qquad \text{…………..(2.3)}$$

Where:
Na_2O_e = Total sodium oxide equivalent (%),
Na_2O = sodium oxide content (%),
K_2O = potassium oxide content (%).

The bulk of the alkalies resides in the pore solution of concrete, and it is associated with hydroxyl (OH^-) concentration that produces high pH in the pore solution (i.e., 13.2 to 14.0).

2.1.6 Reactive silica

In some countries such as Japan, and some ares in Indonesia, etc, aggregates are taken from rocks in volcanic mountain. The rocks in these areas are usually reactive. The reactivity of aggregate depends on some factors: aggregate mineralogy, degree of crystallinity, and solubility (of the silica in pore solution). Even, aggregates have been confirmed as reactive aggregates based on mineral types. Some tests are still needed to be conducted. To determine aggregate reactivity is not as simple as classifying rock or mineral type. Aggregate reactivity has to be determined by experimental procedure, such as ASTM C 1260, JIS A 1146 (Mortar bar Method) standard test method for determining length change due to ASR.

The lists of rocks and reactive minerals can be seen in **Table 2.1** (Folliard et al. 2005, Kosmatka 2005) (2.35), (2.36), (2.37).

Table 2.1 Table of rock types and possible reactive minerals

Rock Types		**Reactive Minerals and Glass**
Andesite	Hornfels	Cristobalite
Arenite	Quartz-arenite	Cryptocrystalline (or microcrystalline)
Argillite	Quartzite	quartz Opal
Arkose	Rhyolite	Strained quartz Tridymite
Basalt	Sandstone	Volcanic glass
Chert	Shale	
Flint	Silicified	
Gneiss	carbonate	
Granite	Siltstone	
Greywacke	Tuff	

Damaged in concrete will occur if rock types contain sufficient reactive silica, and the reactivity of silica in concrete depends on the crystal structure of the silica. For example: quartz has a well-ordered crystal structure and stable in concrete at normal temperature. On the other hand, opal has a poorly ordered crystal aggregate of silica (cristobalite and/or tridymite) and reactive in concrete (2.35), (2.36).

2.1.7 Sufficient moisture

Moisture is very important factor when considering damage due to ASR. It is generally accepted that minimum relative humidity of 80 percent is required to cause significant expansion due to ASR. Pedneault in 1996 said: concrete that was maintained in an environment with less than 80% R.H. did not undergo significant expansion (e.g., expansion was less than 0.04 percent after 2 years)(2.35), (2.36).

2.2 Summary of literature review

Some literature review can be summarized as follows:

- Rasheeduzzafar et al. showed that in most cases of medium-to-high alkali cements, 10% cement replacement by microsilica is adequate for ASR control. Zhang et al. showed that when the content of SF is less than 10%, SF does not influence the expansion of ASR. **However, their studies do not use pessimum ratio between reactive to non reactive aggregates.**
- The levels of cement replacement between 15 and 25% by several pozzolans are effective in controlling expansion due to ASR (L.J. Malvar et al, Foroughi, M. et al.). In Japan, the use of FA at the level 15% to 25% are also considered sufficient in reducing concrete expansion (Y. Kawabata et al.). **Based on these reasons, my studies used FA at level 15% and 25% to be combined with FA and EPP.**
- Bektas et al. showed that both expanded and natural perlite powder (NPP) were potential to suppress expansion when incorporated into mortar bars, and mortar containing expanded perlite to replacement level 16% performed better than mortar bars containing natural perlite. **Based on this reason, it is interesting to use different levels of EPP in mortar**

and concrete and use pessimum ratio. Moreover, perlite is not common mineral in Indonesia, that is why I was interested in using it in order to reduce expansion.

- D.S. Lane et al. said that in the ternary slag concretes, 2.5% and 5% SF greatly improved the ASR resistance. Tanaka, Y. et al. said the preventive effect of multiple use of additives can be estimated by summing up the preventive effect of single. **In his studies, D.S. Lane et al. used SF only at level 5%, that is why it is interesting to use SF at level 10% in my studies.**
- Shehata et al. said that high-alkali (4.14%) FA was not as effective as the low-alkali (1.41%) FA in mitigating the expansion when used with 5% SF; a higher level of SF (say 7%) may be required to put such an FA to work more effectively. Shehata et al. used FA level mostly quite large, 20% and 30%. **That is why the expansion reduction due to usage large level of FA are effective. It is interesting to use SF at level 10% in my studies. However, combination minerals are not clarified well.**
- Craig W. Hargis et al. made an effort to limit ASR in: aggregate passivation. A lithium silicate layer was created on reactive natural siliceous aggregate surfaces by treating the aggregates in a lithium hydroxide solution prior to use. Lu et al. investigated that on the aggregate surfaces, the formation of lithium silicate and lithium carbonate were observed after soaking the aggregates in 1.8 M LiOH at 150 °C for 150 hours. **However, the usage of lithium hydroxide in concrete do not clarified well. Based on this reason, it is interesting to study in mortar and concrete then use pessimum ratio.**
- Uchimura showed that maximum expansion was happening when aggregate was used in the ratio 30:70 between reactive and non reactive aggregates. **Based on this reason, all of the mixture proportion in my studies used pessimum ratio 30:70 between reactive to non reactive aggregates.**

Moreover, there are still a lot of paddy fields in Indonesia. After harvesting, there will be waste such as rice husk ashes (RHA) that easy to find. In addition, RHA does not only as low cost material but also categorized as eco material. RHA can be proposed to use it as mineral admixture in reducing expansion in Indonesia. RHA has good chemical content such as SiO_2. The values SiO_2 content of RHA can be as high as SF's . That is why, SF is used in this studies, before I use RHA in Indonesia.

2.3 Experimental outline

2.3.1 Materials

Four types of binder were used in this study, namely: Ordinary Portland Cement (OPC), Fly ash (FA), Silica fume (SF), and expanded perlite powder (EPP). OPC, FA and SF meet the requirements of JIS R 5202, JIS A 6201, and JIS A 6207, respectively. Fineness of FA is one of the most important physical properties affecting pozzolanic activity. The content of CaO (calcium oxide or lime) has been shown to have the greatest effect on the efficiency of the ash in mitigating ASR (Malvar et al). Chemical composition of OPC, FA, SF, and EPP are depicted in **Table 2.2.**

Table 2.2 Chemical compositions of OPC, FA, SF, and EPP

Constituents	**OPC**	**FA**	**SF**	**EPP**
MgO, %	0.92	1.30	0.56	0.14
SiO_2, %	20.89	54.96	95.5	65.85
SO_3, %	2.02	0.49	0.18	-
Na_2O, %	0.35	1.07	-	4.68
K_2O, %	0.36	1.30	-	4.07
Al_2O_3, %	-	-	-	9.96
CaO, %	64.25	3.18	0.00	0.75
LoI, %	1.87	2.37	1.22	-

ASTM Class F fly ash, which is characterized by relatively low calcium contents (i.e. <10% CaO). Alkalis (Na_2O and K_2O), sodium and potassium oxides have historically been grouped together and their content limited, both in the cement and the fly ash. When reactive aggregates are used, it is recommended to use low-alkali cement ≤0.6% (content per ASTM C 150 (1997)), and for fly ash, the available alkalis are sometimes limited to 1.5% (Malvar et al.). Magnesium oxide (MgO), AASHTO M 295 (similar to ASTM C 618 and CSA A23.5) used to require a 5% MgO limit in the fly ash. Sulfur trioxide (SO_3) is limited to a maximum of 5% in ASTM C 618 for both Class C and F ashes. All of minerals that usage in this study contained SO_3 less than 5%. Silicon dioxide (SiO_2) shows pozzolanic activity, that is, forms a cementitious product by reaction with calcium hydroxide (Mehta 1986)(2.38). To increased contents of SiO_2 have proven to increase the ash effectiveness and lower the expansion. Meanwhile, Uchimura showed that maximum expansion was happening when aggregate was used in the ratio 30:70 between reactive and non reactive aggregates(2.39). The results can be seen in **Fig. 2.1**

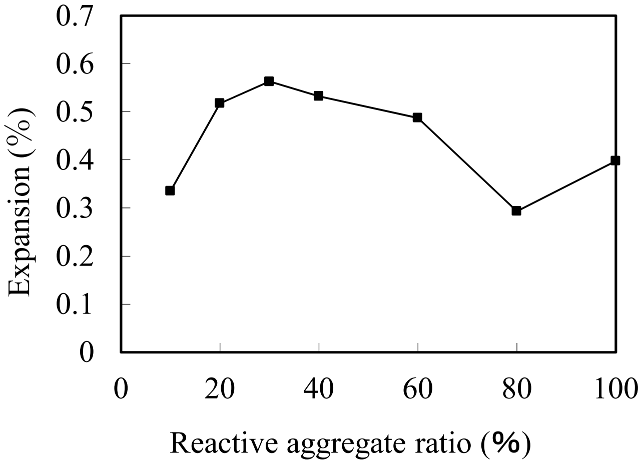

Fig. 2.1 Expansion at 6 months of mortar bars with different reactive aggregate ratio (Uchimura 2012)

Two aggregates were used in this experiment: one was classified as alkali silica reactive (andesite) and the other was classified as non-reactive (limestone). In this study, the aggregates combination (in the ratio 30:70) between reactive and non-reactive were prepared in concrete and mortar for all mixtures. This study will be carried out by making concrete cylinder, concrete prism specimens, mortar bar specimens. Specimens will be cast based on concrete mix design and mortar design with varying levels of mineral admixtures, and combination of minerals. Chemical admixtures will also be used to suppress ASR. Therefore, a study on ASR is continually needed to be conducted and has not clarified well. Plotted data of chemical tests of aggregate can be seen in **Fig. 2.2**. Sc value of andesite is larger than Rc. As a result, andesite-1 is confirmed reactive aggregate (based on JIS A 1145, if Sc > Rc, the aggregate is judged as potential harmful).

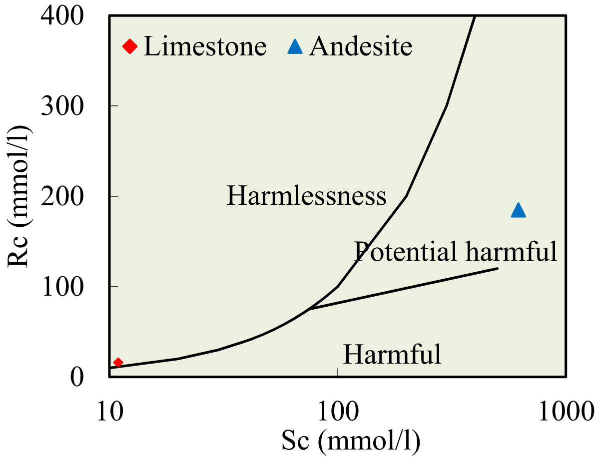

Fig. 2.2. Chemical test results of aggregate

Meanwhile, the physical properties of material are presented in **Table 2.3**.

Table 2.3 Physical properties of material

Material	**Description**
Cement, OPC	Density = 3.16 g/cm^3, Specific Surface Area = 3330 cm^2/g
Fly ash,(Type II)	Density = 2.26g/cm^3, Specific Surface Area = 3970 cm^2/g
Silica fume	Density = 2.35 g/cm^3, Specific Surface Area = 18 m^2/g
EPP	Pass sieve No. 200 (0.075 mm), Density = 2.58 g/cm^3
Fine aggregate (Limestone)	Density (SSD) = 2.70 g/cm^3, Water absorption = 0.61%, Rc = 8 mmol/l, Sc = 1 mmol/l
Coarse aggregate (1): (Andesite-1)	Density (SSD) = 2.60 g/cm^3, Water absorption = 2.75%, Rc = 185 mmol/l, Sc = 620 mmol/l
Coarse aggregates (2): (Andesite-2)	Density (SSD) = 2.68 g/cm^3, Water absorption = 2.75%, Rc = - mmol/l, Sc = - mmol/l
Coarse aggregate (3): (Limestone)	Density (SSD) = 2.70 g/cm^3, Water absorption = 0.55%, Rc = 8 mmol/l, Sc = 1 mmol/l

After sieving, a number of EPP passed sieve No. 200 (0.075 mm) were taken (about 40 gr). Then, particles distribution of EPP were checked by using machine SALD-3101 (Laser Diffraction Particle Size Analyzer). Particles distribution of perlite can be seen in **Fig. 2.3**.

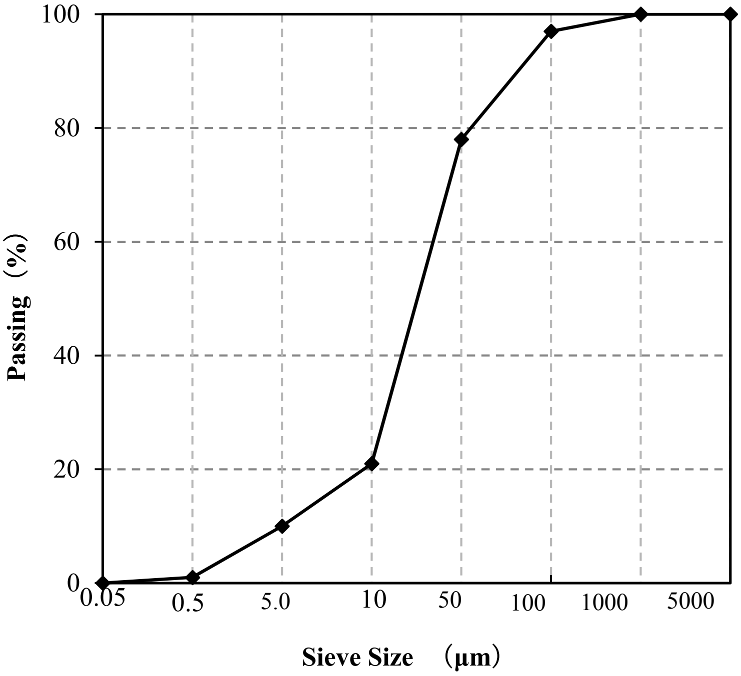

Fig. 2.3. Perlite particle distribution

Pictures of aggregate can be seen in **Photo 2.1,** and **Photo 2.2** and **Photo 2.3**. Andesite-1 contain crystobalite and andesite-2 contain opal.

Photo 2.1 Limestone aggregate

Photo 2.2 Andesite-1 aggregates

Photo 2.3 Andesite-2 aggregates

2.3.2 Methodology and testing method

In this study, the effect of mineral, combination of minerals and treatment of reactive aggregates with $LiOH{\cdot}H_2O$ were investigated in order to reduce expansion. As a result, some concrete prisms and mortar bars were made. Concrete prisms were made based on RILEM AAR-3, and mortar bars were made based on JIS A 1146. Concrete specimens were stored in controlled room with 40°C, and R.H. 100%, except compressive strength specimens were cured in controlled room with 20°C, R.H. 60%. Meanwhile, mortar specimens for expansion measurement were also treated under 40°C, and R.H. 100% of controlled room.

1) Compressive strength and elastic modulus tests

Concrete cylinders were demoulded after 24 hours of casting, wrapped with wet cloth and plastic sheet in, then cured in a room maintained at 20°C and 60% R.H. Furthermore, tests were conducted after 28 days of curing in accordance with JIS A 1108 and JIS A 1149. The average values of compressive and elastic modulus were determined from three specimens for each concrete mixture.

2) Porosity test

Concrete cylinder specimens were cut into 5mm-thick slices samples after curing for 28 up to 365 days at 20°C and 60% R.H. Then, acetone was used for washing and immersing the fragments for 15 minutes to stop cement hydration. Then, the sliced samples were kept for two days in freeze drying to remove all remaining water in the pores. Micromeritics auto pore III (Pore analyzer) was used to test the porosity or total pore volume of concrete specimens. The range of the measured radius of pore size distributions are: 6.6-20nm, 20-50nm, 50-100nm, 100-200nm, 200-10μm, and more than 10μm. The pore system in cement-based materials consists of: gel pores (micro pores, size 0.5-10 nm), capillary pores (mesopores, 5-5000 nm), macro pores due to deliberately entrained air and macro pores due to inadequate compaction. The gel pores and pore with diameter less than 0.029 μm do not influence the permeability and the strength of concrete(2.40), (2.41). Picture of porosity test can be seen in **Photo 2.4**.

(a) Preparation (b) Vaccuming (c) Pore analyzer

Photo 2.4 Porosity testing procedure

3) Ultrasonic pulse velocity (UPV) test

UPV test was used to determine the concrete quality. The basic principle of this test: measuring the time of travel of an ultrasonic pulse passing through the concrete was being tested. It is possible to determine average pulse velocity, if the distance is known. Higher velocity was obtained when concrete quality was good in terms of density, uniformity, homogeneity etc. Pictures of velocity test can be seen in **Photo 2.5**.

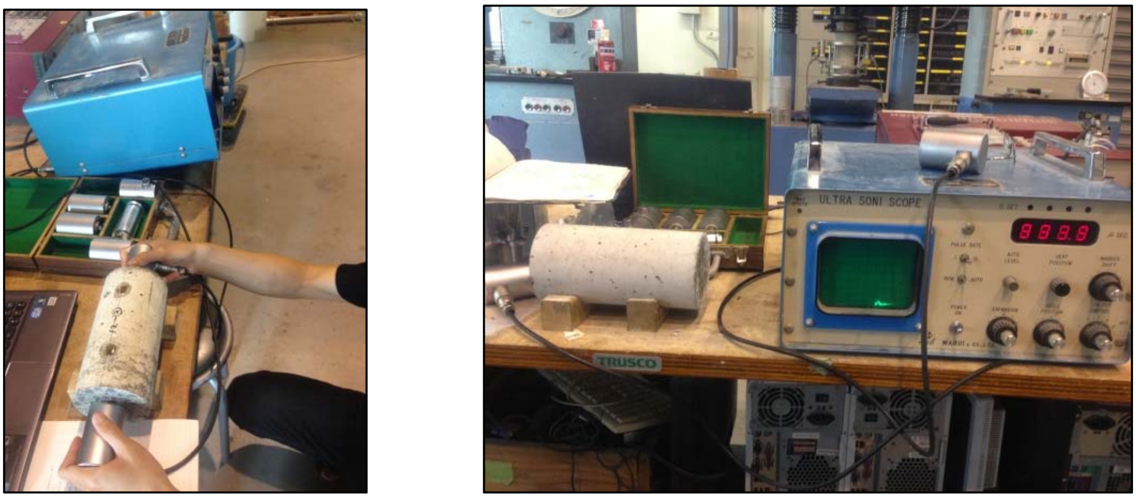

Photo 2.5 Ultra pulse velocity testing

Pulse velocity can be calculated as follows:

$$V=L/T \qquad \text{…………..(2.4)}$$

Where :
V = pulse velocity, m/s,
L = distance between centers of transducer faces, m, and
T = transit time, s.

4) Expansion test

Mortar test

The size of the mortar was 40x40x160 mm. Samples were wrapped with wet paper and placed vertically in stainless container, then stored in a 40ºC and 100% R.H. controlled room. Pictures of mortar inside container with water in the bottom and the water was adjusted to a constant level can be seen in **Photo. 2.6**.

Photo 2.6 Wrapped mortar inside stainless container

Measuring was conducted to observe expansion behavior of mortar, at day 1, 2 weeks, 4 weeks, 8 weeks, 12 weeks and 24 weeks. Picture of mortar measurement is shown in **Photo 2.7**.

Photo 2.7 Length measurement of mortar

Interpret test results of expansion:

JIS A 1146

If the expansion ratio for 3 months is over 0.05% or for 6 months is over 0.1% indicates as: deleterious.

Concrete test

The size of the specimen was 75x75x250 mm. Prism specimens were wrapped with wet paper and thin plastic sheet. Then, specimens were placed in a polyethylene container with water in the bottom and the water was adjusted to a constant level. After completing the measurement, specimens were maintained in controlled room. Moisture control is an important issue for concrete prisms. One piece of wet unwoven paper (KimTex, size: 355 x 425 mm) was used to wrap a specimen. Then, it was covered with thin plastic sheet. Picture of the specimen after wrapping can be seen in **Photo 2.8**.

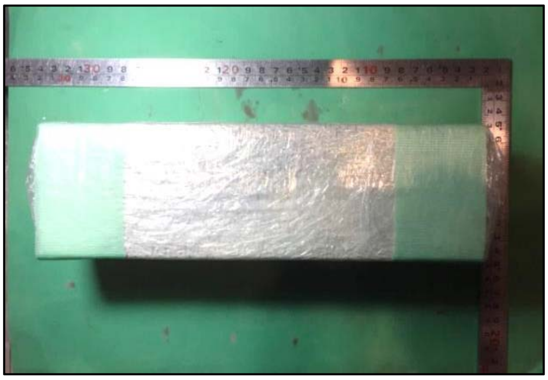

Photo 2.8 Completion of wrapping

Further, specimens for each experiment were placed vertically in a polyethylene container and were stored in a 40ºC of controlled room. The specimens were maintained in controlled room can be seen in **Photo 2.9**.

(a) Polyethylene container (b) Controlled room

Photo 2.9 Specimen condition in container and controlled room

The length of concrete was measured periodically for every two weeks. Before measuring, container was moved to 20^oC room to cool specimens for 24 hours. Picture of concrete measurement can be seen in **Photo 2.10**.

Photo 2.10 Length measurement of concrete

Interpret test results of expansion :

RILEM AAR-3

1. Expansions of less than 0.05% after 1 year, indicate that the aggregate can be regarded as **non reactive.**
2. Expansions of more than 0.10% after 1 year, indicate that the aggregate can be regarded as **reactive**.
3. Expansions between 0.05% - 0.1% after 1 year, are known to be **potentially alkali-reactive**.

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CHAPTER 3. THE EFFECTIVENESS OF MINERALS ADMIXTURES SUCH AS SILICA FUME (SF), FLY ASH (FA) AND EXPANDED PERLITE POWDER (EPP)

3.1 Introduction

Concrete damage due to alkali silica reaction (ASR) was a phenomenon that recognized around 75 years ago in the U.S.A., and damages have been observed in many countries. Crack was caused by ASR occurred during the service life of structures, and gave early warnings of damage(3.1). L.J Malvar et al. summarized some mitigation techniques in the united states, various countries, and international organizations. One of their recommendations is related to the usage of FA: Class F fly ash or Class N Pozzolan can be used at level 25% to 40% by weight(3.2). The usage of supplementary cementitious materials (SCMs) in construction industry have many advantages, such as reduce environmental pollution, reduce the cost, and the most important one enhances the concrete durability.

Here are some SCMs that can be used to reduce expansion due to ASR, such as silica fume (SF), fly ash (FA), blast furnace slag (BFS), Perlite, etc. SF is by-product material which is used as a pozzolan. SF is produced by the reduction of high-purity quartz with coal in an electric arc furnace in the manufacture of elemental silicon or alloys containing silicon. Fundamental performances of SF are pozzolanic reaction and micro filler effect, and lead to improve durability of concrete. Furthermore, SF is a reactive pozzolanic material because of its high SiO_2 content and extreme fineness particles. An additional binder material called calcium silicate hydrate (C-S-H) was created when SF reacts with calcium hydroxide. Additional binder is very similar to C-S-H formed by Portland cement that gives concrete with SF improved its properties. Mechanism of concrete with SF basically based on these roles(3.3):

1. Refinement of pore-size and matrix densification:

   Due to its fineness, SF acts as filler and fits into the spaces between grains in concrete, and SF can cause a reduction in the volume of pores at all ages.

2. Reaction with Free-lime (cement hydration):

   SF reacts with the calcium hydrate (CH), thus CH content decrease.

3. Interfacial refinement of cement paste-aggregate:

   Improvement of mechanical properties and durability due to enhancement in interfacial or bond strength.

A number of studies have proven that SF quite effective to suppress expansion. There were some studies relate to ASR: Touma et al. reported that 10% of cement replacement by SF can reduce expansion and close to a level 20% of FA Class F(3.4). Concrete strength was also increased, and lower concrete permeability. Touma et al. also reported that 10% of SF in replace of cement seems effective for moderately reactive aggregate(3.5). The influence of SF on mortars made with high-alkali cement was studied by Hooton(3.6). Hooton concluded that 10, 15, and 20 % SF met the ASTM limit of expansion 0.02%, at the age of 14 days. The significant effect of SF at 10% of cement replacement was shown by E.G. Aydin and H. Yildirim(3.7). **So, one of the objective of this study** was intended to determine the amount of SF level required to reduce expansion. Then, the effectiveness of SF was investigated in some various of water binder ratio toward expansion when the pessimum proportion is used.

FA is a by-product of the combustion of pulverized coal in electric power plants. In Japan, the use of FA at the level of 15% to 25% are considered to be sufficient in mitigating concrete expansion(3.8), (3.9), (3.10). Based on this reason, this study is also focus on FA at levels 15% and 25%. These FA levels are determined to combine with other minerals such as SF and EPP. Even SF has a lot of advantages such as: high content of SiO_2 and extreme fineness particles but its price quite expensive than other minerals. The other SCMs is perlite. Perlite is a pozzolan due to its glassy structure and high SiO_2 and Al_2O_3 contents. In the most parts of the world, such as Turkey, perlite is easy to acces. Two thirds of perlite deposits are in this country. Perlite can be denoted to natural or expanded perlite. Expanded perlite is used as lightweight aggregate in the construction industry due to its lightness, thermal, and acoustic properties (Demirboga 2001, Bektas 2005)(3.11), (3.12).

Bektas et al. showed that as a cement replacement expanded perlite powder (EPP) could be used in small quantities due to its high water absorption capacity. Bektas et al. also showed that when perlite powder incorporated into mortar bars, perlite powder was potential to suppress expansion induced by ASR. As a results, further investigation was needed to determine the adequate replacement level of EPP to suppress expansion and the effectiveness combination of FA with EPP. In this study, EPP has high value of alkali compare to SF. That is why it was interesting to combine EPP with FA.

Moreover, the combinations of these minerals were also compared to mixtures with FA itself. So, **The other aim of this study** was also to investigate the combination effect of FA with SF and FA with EPP at level 15% and 25% of FA when aggregates were used in pessimum proportion (ratio 30:70) between reactive to non-reactive aggregates. Mortar bars were made based on JIS A 1146 and mortar specimens for expansion measurement were treated at temperature 40°C, and R.H. 100%. Meanwhile, concrete prisms were made based on RILEM AAR-3, and concrete specimens were stored at 40°C, and R.H. 100%, except compressive strength specimens were cured at 20°C, R.H. 60%.

3.2 Material and mixture proportions

3.2.1 Materials

Four types of binder were used in this study, namely: Ordinary Portland Cement (OPC), silica fume (SF), fly ash (FA) and expanded perlite powder (EPP). Chemical composition of OPC, SF, FA and EPP were depicted in **Table 3.1**. It can be seen in **Table 3.1** that there are no content of Na_2O and K_2O in SF. Then, the content of Na_2O and K_2O in EPP was very high. The content of amorphous silicon dioxide of SF was very high, more than 90%. The particles of SF are extremely small. SF has more than 95% of the particles less than 1μm. OPC, FA and SF met the requirements of JIS R 5202 and JIS A 6201, and JIS A 6207, respectively.

Table 3.1 Chemical compositions of OPC, SF, FA, and EPP

Constituents	**OPC**	**SF**	**FA**	**EPP**
SiO_2, %	20.89	95.5	54.96	65.85
SO_3, %	2.02	0.18	0.49	-
MgO, %	0.92	0.56	1.30	0.14
Na_2O, %	0.35	-	1.07	4.68
K_2O, %	0.36	-	1.30	4.07
CaO, %	64.25	0.00	3.18	0.75
LoI, %	1.87	1.22	2.37	-

Pictures of the binders can be seen in **Photo 3.1**, **Photo 3.2**, **Photo 3.3**, and **Photo 3.4**.

Photo 3.1. OPC

Photo 3.2. Silica fume

Photo 3.3 Fly ash

Photo 3.4 Expanded perlite powder

Meanwhile, physical properties of material were presented in **Table 3.2.** Two aggregates were used in this experiment; one was classified as alkali silica reactive (andesite) and the other classified as non-reactive (limestone).

Table 3.2 Physical properties of materials

Material	Description
Cement, OPC	Density = 3.16 g/cm^3, Specific Surface Area = 3330 cm^2/g
SF	Density = 2.35 g/cm^3,Specific Surface Area = 18000 cm^2/g
FA (Type II)	Density = 2.26g/cm^3, Specific Surface Area = 3970 cm^2/g
EPP	Pass sieve No. 200 (0.075 mm), Density = 2.58 g/cm^3
Fine aggregates (Limestone)	Density (SSD) = 2.70 g/cm^3, Water absorption = 0.61%, Rc = 8 mmol/l. Sc = 1 mmol/l.
Coarse aggregates (Andesite-1)	Density (SSD) = 2.60 g/cm^3, Water absorption = 2.75%, Rc = 185 mmol/l. Sc = 620 mmol/l.
Coarse aggregates (Limestone)	Density (SSD) = 2.70 g/cm^3, Water absorption =0.55%, Rc = 8 mmol/l. Sc = 1 mmol/l.

3.2.2 Mixture proportions of SF with various w/b

Some concrete and mortar mixtures were prepared based on the same level of SF. Mortar bars were made based on JIS A 1146. Andesite coarse aggregate was crushed into fine aggregate that meet the requirement of particle size distribution in JIS A 1146. Water to cement ratio of mortar was adjusted to 0.50 and alkali content was set such that Na_2Oeq of cement 1.2% of weight by adding NaOH solution to the mixing water. Mixture proportions of mortar are shown in **Table 3.3**.

Table 3.3 Mixture proportions of mortar

No.	Description	w/c (%)	Water+ NaOH (g)	Cementitious material (g)		Aggregates (g)	NaOH (ml)
				OPC	SF		
1.	Mix 1 (Control)	0.5	300	600	-	1350	120
2.	Mix 2 (SF5)	0.5	300	570	30	1350	114
3.	Mix 3 (SF10)	0.5	300	540	60	1350	108
4.	Mix 4 (SF15)	0.5	300	510	90	1350	102

Meanwhile, concrete prisms were made based on RILEM AAR-3. Mixture proportions of concrete were shown in **Table 3.4**. These mixtures were designed according to the Japan Society of Civil Engineers Standards. Some concrete mixtures with water binder ratio 0.3, 0.4, and 0.5 were prepared, by using tap water. Mixture 1 was made for control (w/b=0.5); Mixture 2, 3 and 4 used SF at a level 5%, 10% and 15%. Mixture 5 was made for control (w/b=0.4); Mixture 6 and 7 used SF at a level 10% and 15%. Mixture 8 was made for control (w/b=0.3); Mixture 9 and 10 used SF at a level 10% and 15%. Furthermore, test results of expansion were evaluated to investigate the suitability replacement level and effectiveness of SF in mitigating ASR. Total alkali in concrete was 6 kg/m^3. By enlarging alkali content up to 6 kg/m^3 in concrete, it will be easy to observe the expansion line.

Table 3.4 Mixture proportions of concrete

Mix	**w/b (%)**	**s/a (%)**	**kg/m^3**						**g/m^3**			**Temp °C**	**Slump mm**	**Air Content (%)**
			Water	**OPC**	**SF**	**Sand**	**Gravel**	**NaOH**	**WR+ AE**	**SP**	**AE**			
1	50	45	160	320	-	843	992	5.347	1000	-	12.8	19	80	5.0
2				304	16	841	990	5.467	1000	-	12.8	22	70	3.8
3				288	32	838	987	5.587	1000	-	12.8	21	60	3.5
4				272	48	836	984	5.706	1400	-	17.6	22	30	3.0
5	40	45	160	400	-	812	956	4.748	-	2000	9.6	18	105	4.3
6				360	40	806	949	5.048	-	4400	19.2	18	80	5.0
7				340	60	804	945	5.197	-	4400	19.2	18	30	3.0
8	30	45	160	533	-	761	895	3.751	-	4797	9.6	19	45	2.5
9				480	53	753	887	4.149	-	10670	19.2	18	120	5.0
10				453	80	749	882	4.349	-	10670	19.2	18	55	3.0

(WR+AE) = water reducing and air entraining agent, AE = air entraining agent, SP = Superplasticizer

3.2.3 Mixture proportions of combination FA with SF

This study presents an experimental study carried out on concrete and mortar mixtures. Mortar bars were made based on JIS A 1146. Andesite coarse aggregate was crushed into fine aggregate that matches requirement of particle size distribution in JIS A 1146. Aggregate combination (in the ratio 30:70) between reactive and non-reactive were prepared in mortar and concrete. Previous studies showed maximum expansion was happening when aggregate was used in this ratio (Uchimura, 2012). Water to cement ratio of mortar was adjusted to 0.50 and alkali content was set such that Na_2Oeq of cement 1.2% of weight by adding NaOH solution to the mixing water. Mixture proportions of mortar were shown in **Table 3.5**.

Table 3.5 Mixture proportions of mortar

No.	**Description**	**w/c (%)**	**Water+ NaOH (g)**	**Cementitious material (g)**			**Aggregates (g)**	**NaOH (ml)**
				OPC	**FA**	**SF**		
1	Mix 1 (Control)	0.5	300	600	-	-	1350	120
2	Mix 2 (FA15)	0.5	300	510	90	-	1350	102
3	Mix 3 (FA25)	0.5	300	450	150	-	1350	90
4	Mix 4 (SF5)	0.5	300	570	-	30	1350	114
5	Mix 5 (SF10)	0.5	300	540	-	60	1350	108
6	Mix 6 (FA10SF5)	0.5	300	510	60	30	1350	102
7	Mix 7 (FA15SF10)	0.5	300	450	90	60	1350	90

Meanwhile, concrete prisms were made based on RILEM AAR-3. Mixture 1 was made for control; Mixture 2 and 3 used FA at level 15% and 25%. Mixture 4 and 5 used SF at a level 5% and 10%.

Furthermore, to investigate the incorporation effect of FA with SF, Mixture 6 (FA10%, SF5%) and Mixture 7 (FA15%, SF10%) were made. Seven concrete mixtures with water binder ratio 0.5 were prepared, by using tap water and total alkali in concrete was 6 kg/m^3. In the author's view, by enlarging alkali content in concrete up to 6 kg/m^3, the expansion will also be high. So, it will be easy to observe and study the expansion behavior. Mixture proportions of concrete are shown in **Table 3.6**.

Table 3.6 Mixture proportions of concrete

Mix	w/b (%)	s/a (%)	kg/m^3							g/m^3		Temp °C	Slump mm	Air Content (%)
			Water	OPC	FA	SF	Sand	Gravel	NaOH	WR+ AE	AE			
1	50	45	160	320		-	843	992	5.347	1000	12.8	19	80	5.0
2	50	45	160	272	48	-	836	984	5.706	1000	9.6	23	150	4.0
3	50	45	160	240	80	-	831	978	5.946	1000	16.0	22	180	2.8
4	50	45	160	304	-	16	841	990	5.467	1000	12.8	22	70	3.8
5	50	45	160	288	-	32	838	987	5.587	1000	12.8	21	60	3.5
6	50	45	160	272	32	16	824	970	5.706	880	12.8	21	125	4.5
7	50	45	160	240	48	32	813	957	5.946	880	12.8	21	125	3.1

(WR+AE)= water reducing and air entraining agent, AE=air entraining agent

3.2.4 Mixture proportion of combination FA with EPP

This study presents an experimental study carried out on concrete and mortar mixtures. Mortar bars were made based on JIS A 1146. Andesite coarse aggregates was crushed into fine aggregates that matches requirement of particle size distribution in JIS A 1146. Aggregates combination (in the ratio 30:70) between reactive and non-reactive were prepared in mortar and concrete. Water to cement ratio of mortar was adjusted to 0.50 and alkali content was set such that Na_2Oeq of cement 1.2% of weight by adding NaOH solution to the mixing water. Mixture proportions of mortar are shown in **Table 3.7**.

Table 3.7 Mixture proportions of mortar

No.	Description	w/c (%)	Water+ NaOH (g)	Cementitious material (g)			Aggregates (g)	NaOH (ml)
				OPC	FA	EPP		
1	Mix 1 (Control)	0.5	300	600	-	-	1350	120
2	Mix 2 (FA15)	0.5	300	510	90	-	1350	102
3	Mix 3 (FA25)	0.5	300	450	150	-	1350	90
4	Mix 4 (EPP10)	0.5	300	540	-	60	1350	108
5	Mix 5 (EPP15)	0.5	300	510	-	90	1350	102
6	Mix 6 (EPP20)	0.5	300	480	-	120	1350	96
7	Mix 7 (FA10EPP5)	0.5	300	510	60	30	1350	102
8	Mix 8 (FA15EPP10)	0.5	300	450	90	60	1350	90

Furthermore, eight concrete mixtures with water binder ratio 0.5 were prepared, by using tap water. Mix 1 until Mix 3, total alkali are 6 kg/m^3. Then Mix 4 until Mix 8 are: 6.4 kg/m^3, 6.6 kg/m^3, 6.8 kg/m^3, 6. 1 kg/m^3, 6.4 kg/m^3, successively. Mixture 1 was made for control; Mixture 2 and 3 used FA at level 15% and 25%. Mixture 4, 5 and 6 used EPP at level 10%, 15% and 20%. Furthermore, to investigate the incorporation effect of FA with EPP, Mixture 7 (FA10%, EPP5%) and Mixture 8 (FA15%, EPP10%) were made. Mixture proportions of concrete were shown in **Table 3.8**.

Table 3.8 Mixture proportions of concrete

Mix	w/b (%)	s/a (%)	kg/m^3							g/m^3		Temp °C	Slump (mm)	Air Content (%)
			Water	OPC	FA	EPP	Sand	Gravel	NaOH	WR+ AE	AE			
1	50	45	160	320		-	843	992	5.347	1000	12.8	19	80	5.0
2	50	45	160	272	48	-	836	984	5.706	1000	9.6	23	150	4.0
3	50	45	160	240	80	-	831	978	5.946	1000	16.0	22	180	2.8
4	50	45	160	288	-	32	838	987	5.587	1400	17.6	24	57	4.0
5	50	45	160	272	-	48	836	984	6.496	1400	17.6	25	65	2.9
6	50	45	160	256	-	64	833	981	6.878	1400	17.6	22	55	3.9
7	50	45	160	272	32	16	824	970	5.772	880	12.8	20	100	3.3
8	50	45	160	240	48	32	813	957	6.472	880	12.8	20	90	2.9

(WR+AE)= water reducing and air entraining agent, AE=air entraining agent

3.3 Results and discussion of SF with various w/b

3.3.1 Expansion test

The expansion behavior of mortar is shown in **Fig. 3.1**. In the case of mortar without SF, expansion increased slowly until 56 days, then increased quickly until the end of the observation. It can be seen that there was expansion reduction due to the beneficial usage of SF. The expansion rate of mortar with SF at level 5% was lower compared to mortar expansion without SF. Meanwhile, the expansion rate of mortar with SF at level 10% was lower than mortar with SF5%, and then the usage of SF at the level of 15% showed the lowest expansion.

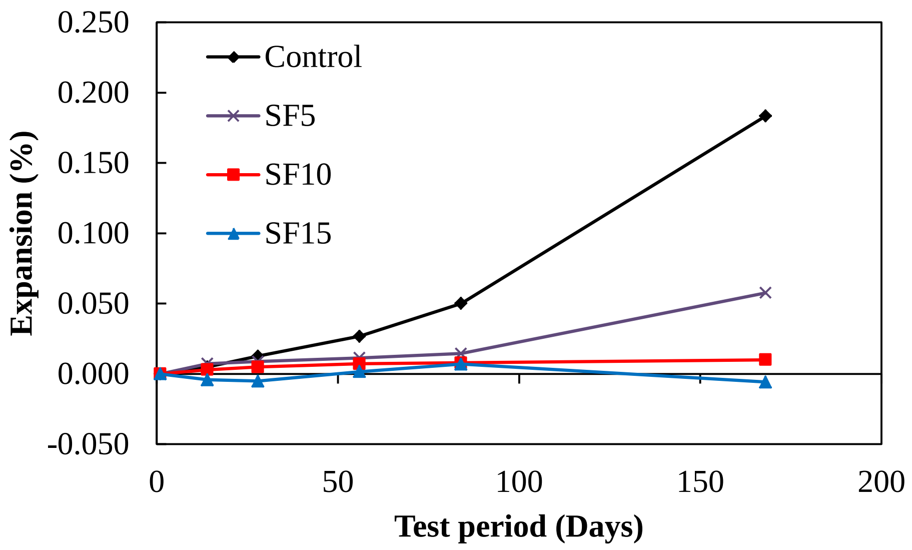


Fig. 3.1 Mortar expansion (JIS A 1146)

Expansion reduction of mortar by SF are under 0.1% that classified as innocuous. Furthermore, **Fig. 3.2**, **Fig. 3.3**, **Fig. 3.4**, show the expansion behavior of concrete. In the **Fig. 3.2**, concrete with w/b=0.5, in the case of concrete without SF, its expansion increased slowly up to 56 days, then suddenly enlarged and fast until the end of this period.

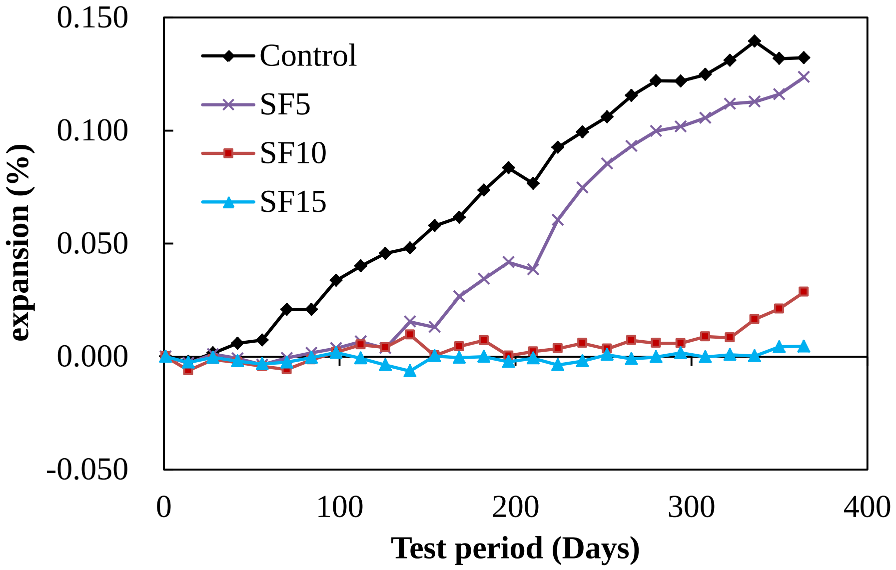


Fig. 3.2 Concrete expansion for w/b=0.5

It can be seen that expansion was reduced due to usage of SF. Concrete expansion by using SF at the level of 5% showed expansion reduction compared to concrete expansion without SF. The expansion rate of concrete by using SF at the level of 5% was moderate whereas concrete with SF at the level of 10% was lower and concrete with level of 15% was the lowest. Expansion reduction by using SF at level 10% and level 15% are under 0.05%, that classified as non-reactive.

Furthermore, concrete expansion graphs with w/b=0.4 can be seen in **Fig. 3.3**. In the case of normal concrete or concrete without mineral admixtures, its expansion was slow until 60 days then increased very fast and large until the end of period. There was an expansion reduction because of the beneficial usage of SF. The expansion rate of concrete with SF15% was lower compared to concrete with SF at level 10%.

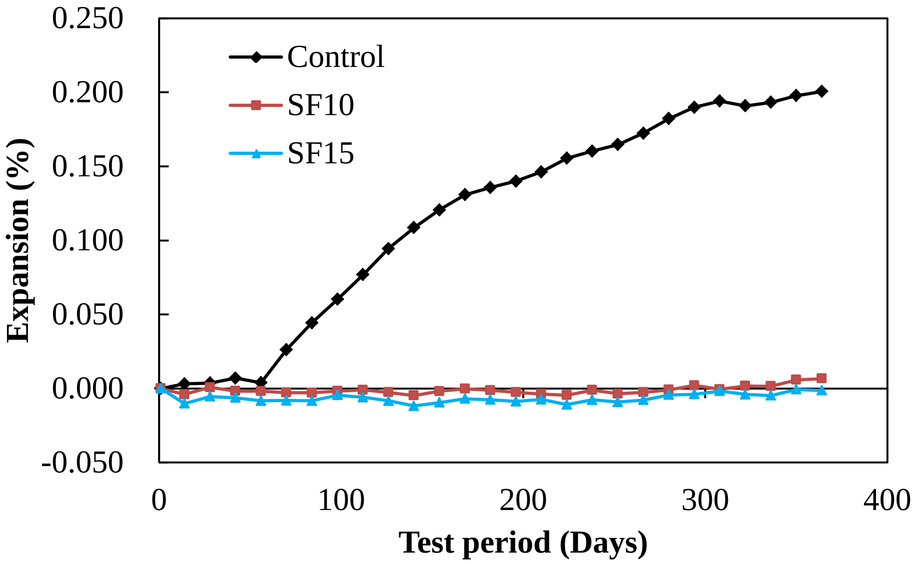


Fig. 3.3 Concrete expansion for w/b=0.4

The pattern of concrete expansion for concrete with w/b=0.3 was almost same with the concrete with w/b=0.4 and w/b=0.5. Concrete expansion behavior can be seen in **Fig. 3.4**.

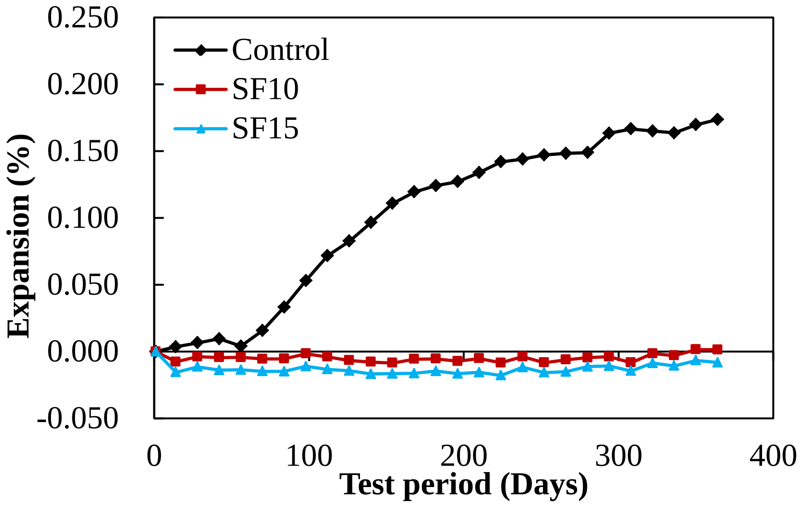
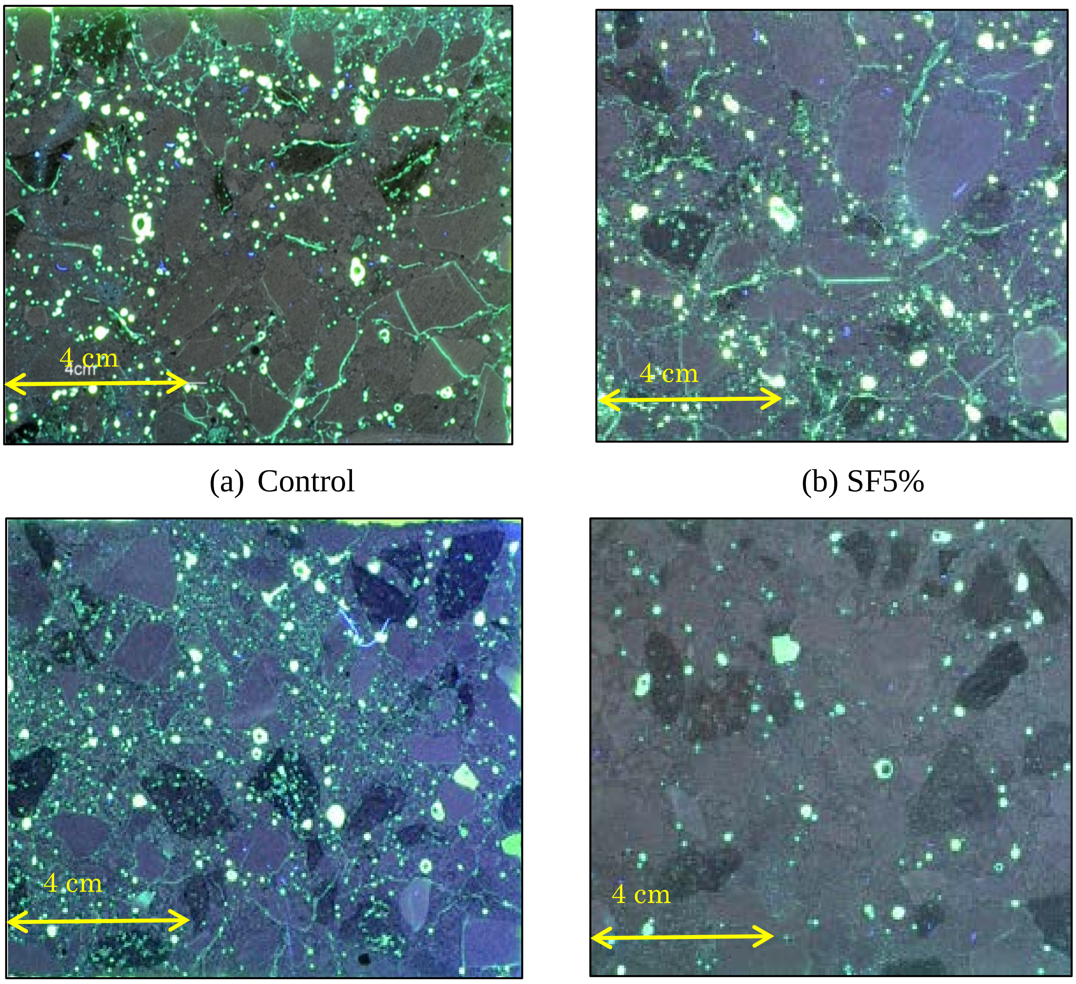


Fig. 3.4 Concrete expansion for w/b=0.3

For the control concrete, its expansion was slow until 60 days then increased quickly and large until the end of this period. The expansion rate of concrete with SF15% was lower compared to concrete with SF10%. Further, pictures of inner cracked of specimens are shown in **Photo 3.5**.



(a) Control

(b) SF5%

(c) SF10%

(d) SF15%

Photo. 3.5 Inner crack of concrete with SF

It can be seen that there are a lot of cacks line in control crack. However, crack lines are decreased when SF is used in concrete.

3.3.2 Discussion on the SF effectiveness

It was reported by Shah et al. that the low porosity and the presence of mineral admixtures in high performance concrete (HPC) would protect HPC from deterioration due to ASR by the lack of water and by the beneficial influence of mineral admixtures(3.13). Chiara F. Ferraris et al. mentioned that: the higher air content results in lower expansion, because of gel expanding into the available capillary pores or void without stressing the structure of the cement matrix. Chiara F. Ferraris et al. also mentioned that: the influence of the w/b on expansion was not clear-cut, higher w/c leads to either higher or lower expansion depending on the factors such as age and aggregate size. The higher w/c generally results in higher expansion (Chiara F. Ferraris et al.)(3.14). In this study, the higher w/b results in a higher expansion too, especially for concrete with SF. It can be observed that for all w/b there was expansion reduction due to usage of SF. Concrete with SF showed expansion reduction compared to control concrete. The expansion rate of concrete with SF15% was the lowest.

SF is a reactive pozzolanic material because of its fineness and high amorphous silicon dioxide content. Finer pozzolans is also sufficient in mitigating ASR (Tenoutasse N et al.)(3.15). SF with particle size of approximately 0.1 μm is also very effective in preventing ASR. SF reacts with calcium hydroxide ($Ca(OH)_2$) to form additional Calcium Silica Hydrate (C-S-H), which is similar to the calcium hydrate formed from the Portland cement. The product of the pozzolanic reaction (secondary C-S-H) can incorporate alkali metal ions into their structure and reduce the alkalinity of the pore solution. At the same time, the secondary C-S-H hydrates fill the adjacent pores and reduce the permeability of concrete, consequently, reducing the free movement of alkali ions (George J. Z et al.)(3.16).

3.3.3 Compressive strength and elastic modulus

The results of compressive strength at 28 days are shown in **Fig. 3.5**.

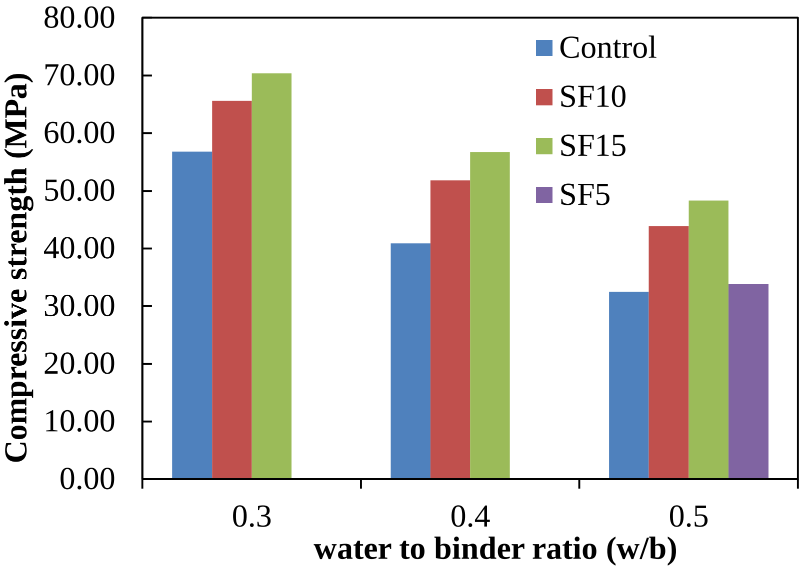


Fig. 3.5 Compressive strength of concrete at 28 days

It could be noticed that the usage of SF would influence the compressive strength values. The larger the water per binder ratio the lower the compressive strength. Furthermore, the larger the content of SF the larger the compressive strength results. The compressive strength of concrete with SF 5%, 10% and 15% are larger than the strength of control concrete. SF increased compressive strength of the concrete. The highest strength is achieved in concrete with SF15% and w/b= 0.3. The relationship between compressive strength and elastic modulus at 28 days are shown in **Fig. 3.6**. Most of the relation between compressive strength (*f'c*) and modulus elasticity (E_c) are above JSCE standard line. A good linear correlation between compressive strength and elastic modulus is acquired.

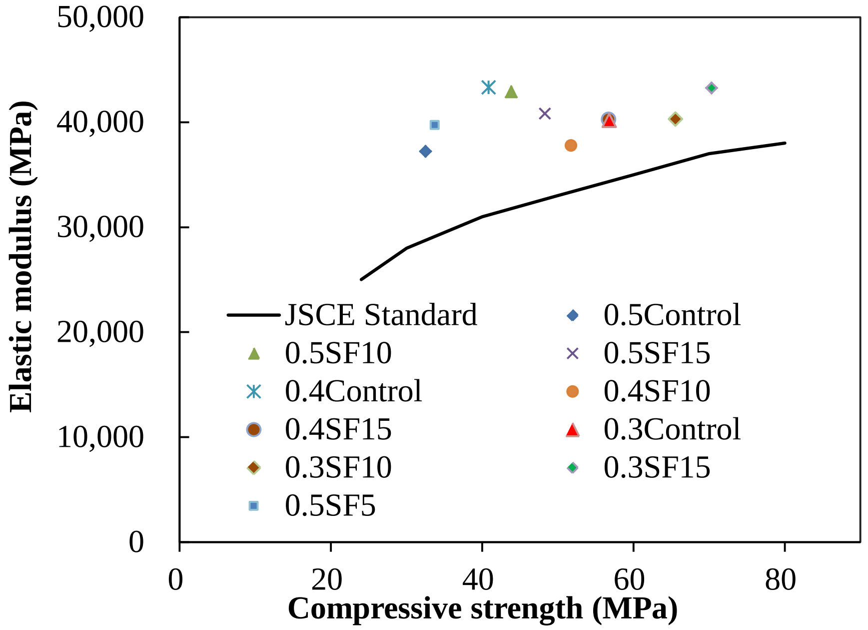


Fig. 3.6 Relationship between compressive strength and elastic modulus

3.3.4 Porosity test

Porosity or total pore volume is usually expressed in percent. Porosity is a measure of the proportion of the total volume of concrete occupied by pores (A.M.Neville) (3.17). In the cement paste there are two different pore systems. Capillary pore, with diameter larger than 0.01 µm and gel pore with diameter smaller than 0.01 µm are considered to affect on permeability (Lu Cui et al.) (3.18).

The rate of fluid flow into a porous material is governed by permeability. The pore of the structure of this material is complex. So some assumptions are made such as: the pores are interconnected and distribution size is not affected by the loss of water upon drying. Porosity or total pore volume and distribution of pore size can be measured by mercury intrusion. Mercury intrusion test results of concrete at the age of 28 up to 365 days are depicted in **Fig. 3.7.** Then, **Fig. 3.8** until **Fig. 3.17** show the pore size distribution. Porosity results are in the range of 8.26% to 18.73%. It can be seen that the water per binder ratio could influence to reduce porosity. The lower w/b show the reduction of porosity. For w/b=0.3 and w/b=0.4, porosity of concrete with SF at level 10% and 15% are larger than control concrete.

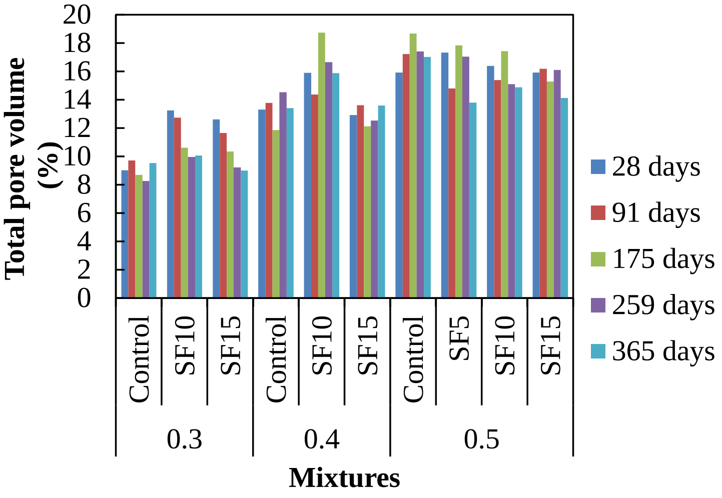


Fig. 3.7 Total pore volume at 28 up to 1 year

However, porosity of concrete with SF 15% is lower than concrete porosity with SF10%. For w/b=0.5, it can be seen that the trends of porosity with SF at level 5%, 10%, 15% are lower compared to control concrete. Porosity values show decrease with time, from 28 days to 365 days (for w/b=0.3 and w/b=0.4, concrete with SF at level 10% and 15%; for w/b=0.5, concrete with SF at level 10% and 15%), but the others show up and down.

For each water per binder ratio, the effect of SF can not be observed clearly in reducing the total porosity. It might be the effect of ASR deterioration due to crack on concrete. Although mineral admixtres reduced the crack, crack still occurred. As a result, the porosity values fluctuate. The usage of SF as cement replacement seem more effective to refine the pore size distribution. It can be observed in **Fig. 3.8** until Fig. **3.17**, for all w/b, the pore size distribution of concrete with SF show well-ordered compare with control concrete, especially for concrete with SF at level 15%. The study of pozzolanic activity of SF blended cement showed the beneficial influence of SF in reducing the porosity, and hence the permeability of the cement pastes (Tenoutasse N et al.)(3.15). Smaller particles will fill in the spaces between cement grains when SF is added into concrete mixture. This micro filling greatly reduces permeability and improves the paste to aggregate bond.

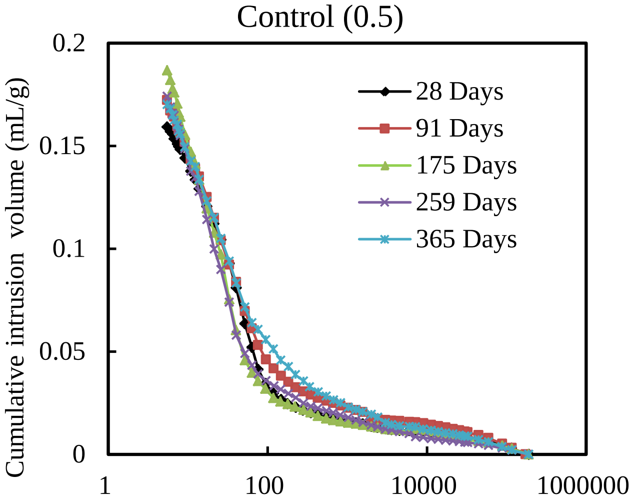


Fig. 3.8 Pore size distribution of control concrete (w/b=0.5)

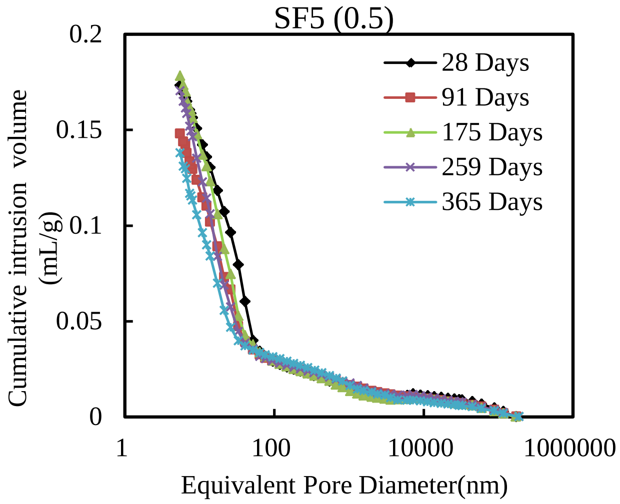


Fig. 3.9 Pore size distribution of concrete SF5 (w/b=0.5)

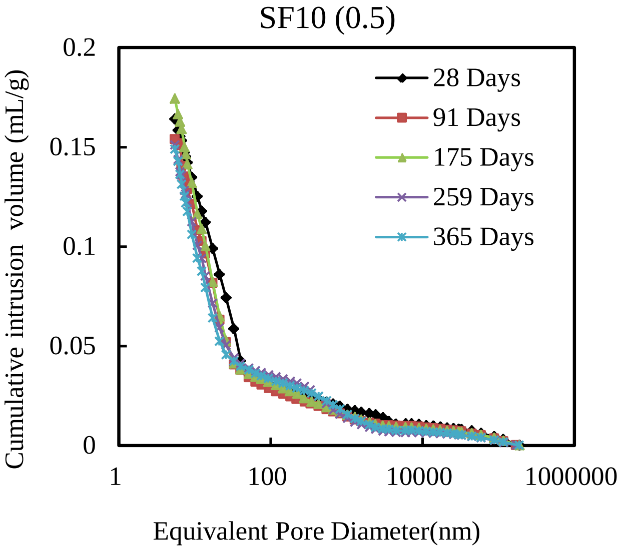


Fig. 3.10 Pore size distribution of concrete SF10 (w/b=0.5)

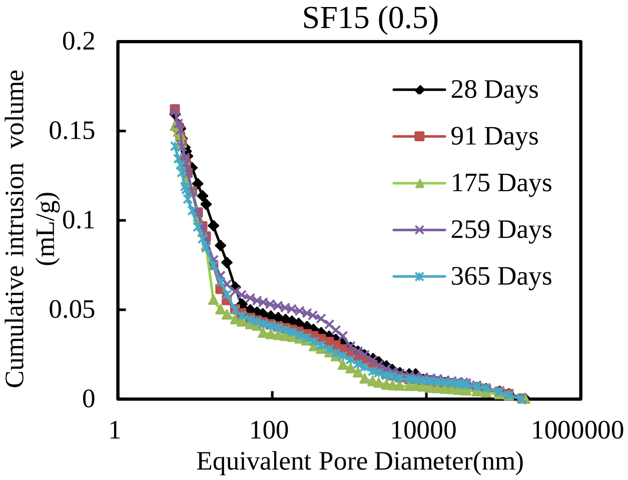


Fig. 3.11 Pore size distribution of concrete SF15 (w/b=0.5)

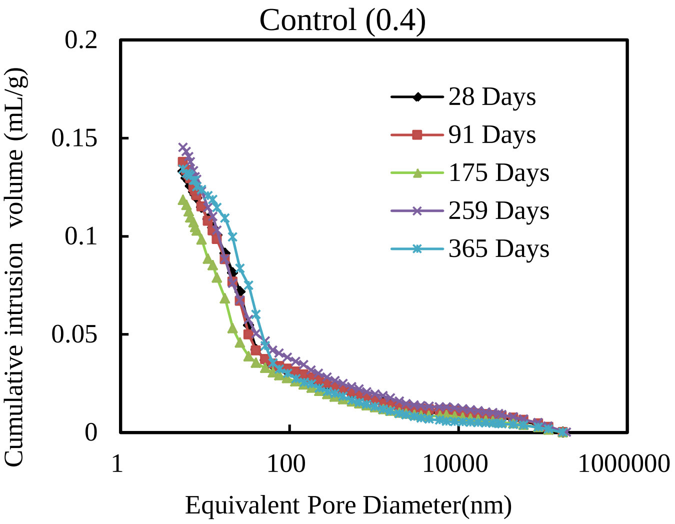


Fig. 3.12 Pore size distribution of control concrete (w/b=0.4)

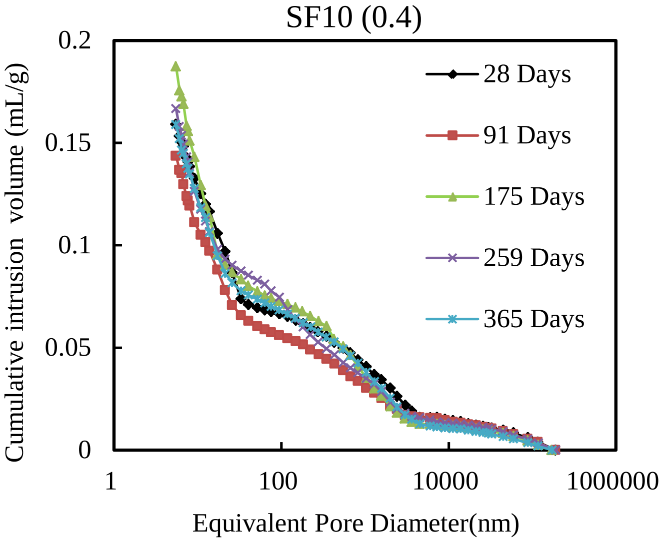


Fig. 3.13 Pore size distribution of concrete SF10 (w/b=0.4)

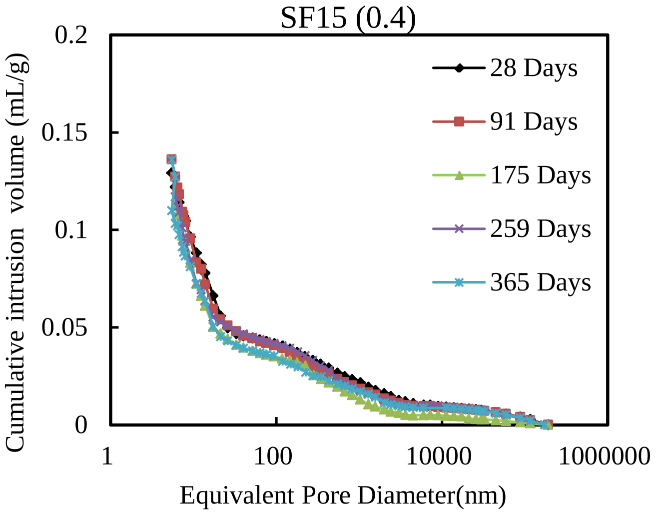


Fig. 3.14 Pore size distribution of concrete SF15 (w/b=0.4)

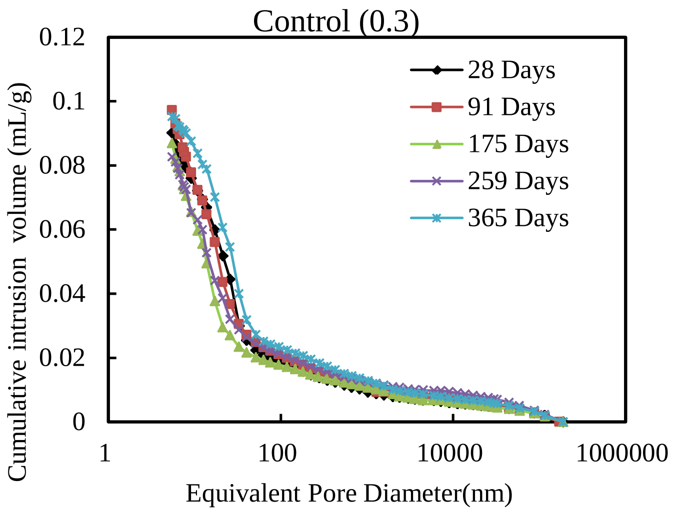


Fig. 3.15 Pore size distribution of control concrete (w/b=0.3)

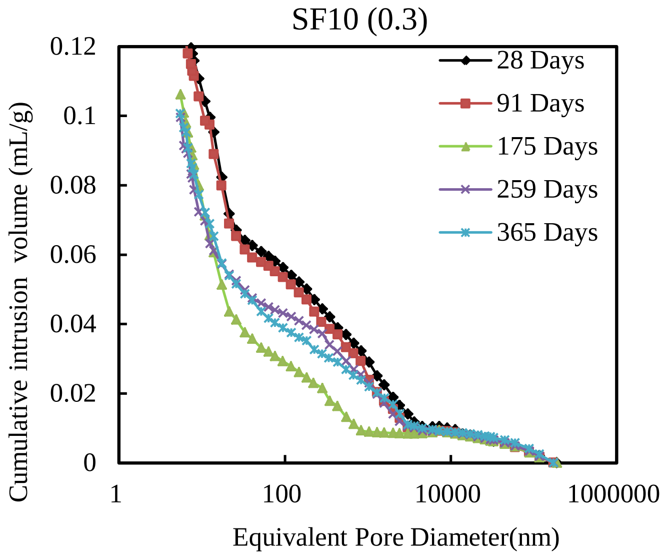


Fig. 3.16 Pore size distribution of concrete SF10 (w/b=0.3)

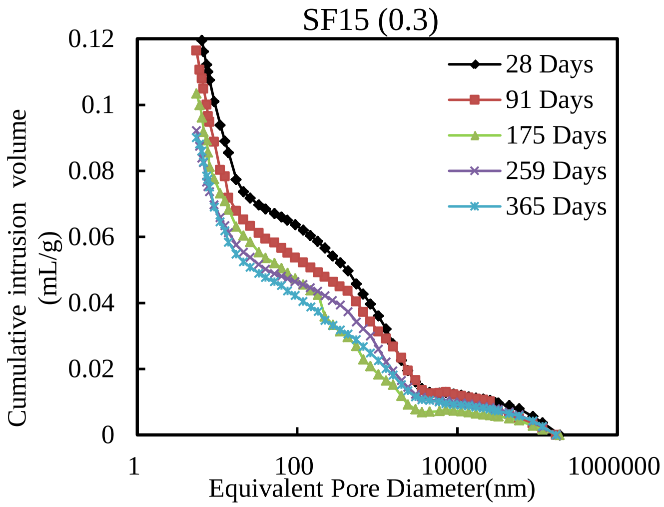


Fig. 3.17 Pore size distribution of concrete SF15 (w/b=0.3)

3.3.5 Ultrasonic pulse velocity (UPV) test

Test results of UPV at 28 up to 365 days are depicted in **Fig. 3.18**. Specimens were cured in 40°C and 100% R.H. controlled room. The values are in range of 3.83 km/s to 4.39 km/s. The results indicate that the concrete quality is good. All values mostly higher than 3.5 km/s (IS:13311-1-1992). It can be observed that for all w/b, the UPV values w/b=0.4 and w/b=0.3 do not have large differences, but UPV values at w/b=0.5 show a little low especially on control concrete.

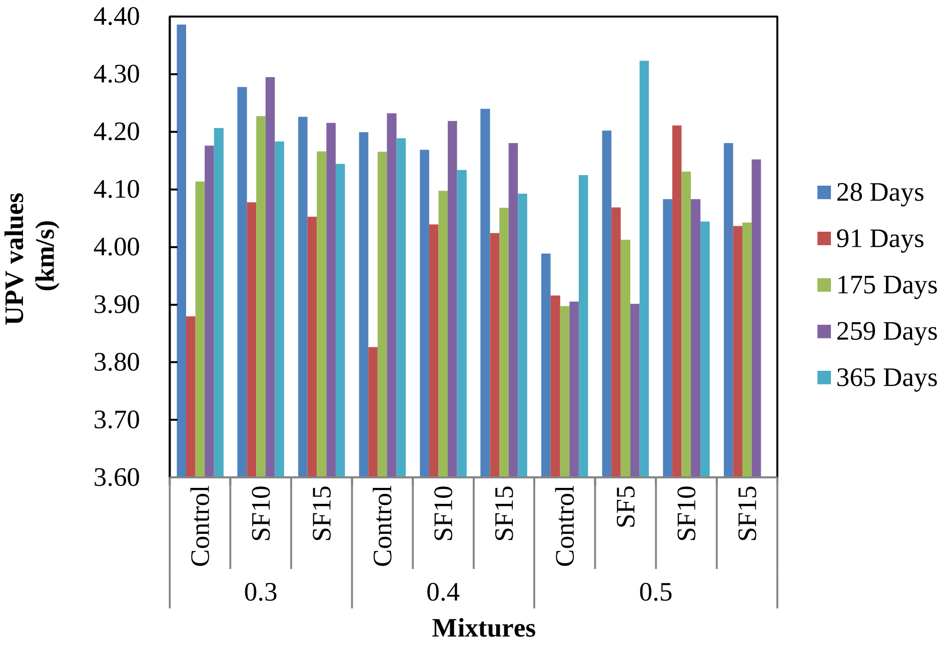


Fig. 3.18 UPV results of concrete at 28 up to 1 year

Further, for all w/b, UPV values of concrete with SF, mostly show a little higher than control concrete. It can be observed that most of UPV values showed decreased with the age. However, there are no significant differences in the UPV results for all ages, and at the same age, UPV values with low w/b are not higher than UPV values with high w/b. It looks relatively same. I. Lawson et al.(3.20) mentioned that UPV values increases with age, and at the same age UPV values with low w/c are higher than those with high w/c, but they used normal concrete on their study. The reasons might relate to the heterogeneity, etc. There is also another reason why the effect of SF toward UPV values are not stable. It may be caused by ASR deterioration. It may be due to crack on concrete. Although mineral admixtres reduced the crack, crack still occurred. As a result, the UPV values fluctuate. When we observe in **Fig. 3.7** and **Fig. 3.18**, it can be seen that on control concrete, porosity seems constant and UPV values do not decrease. However, ASR already occurred. It is very interesting. This phenomena can be explained on **Fig. 3.19**.

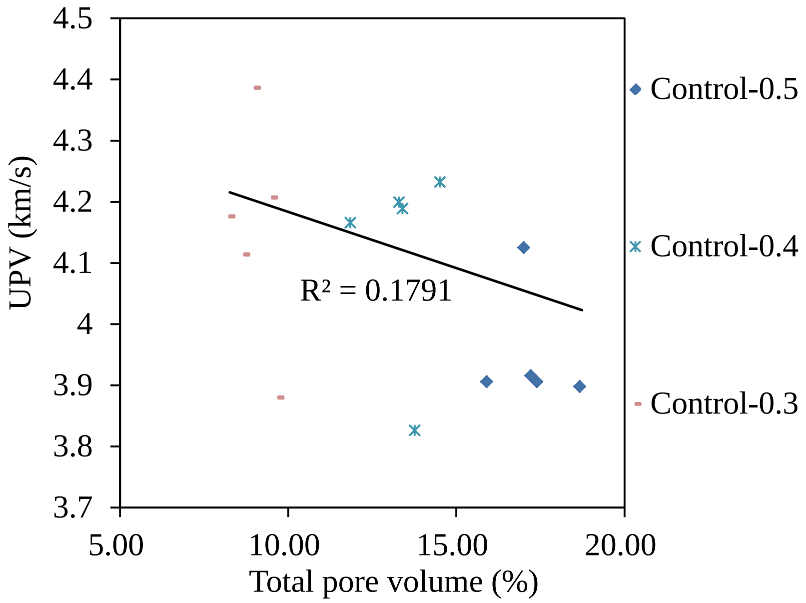


Fig. 3.19 Relationship between UPV and porosity of control concrete

It can be seen in **Fig. 3.19** that ultra pulse velocity decrease with porosity. An increase of porosity corresponds to reduction of UPV. Then, in **Photo. 3.5,** control concrete showed many crack lines compare to concrete with SF.

3.4 Results and discussions of combination FA with SF

3.4.1 Expansion test

The expansion behavior of mortar is shown in **Fig 3.20**. In the case of mortar without mineral admixtures, expansion was large and fast from the beginning until the end of test period. It can be observed that there was expansion reduction due to usage of FA and SF. The expansion rate of mortar with FA25% was lower compared to mortar expansion with FA15%. Mortar expansion by using SF showed expansion reduction compared to mortar expansion without mineral admixtures.The expansion rate of mortar to level SF5% was moderate whereas mortar with level SF10% was lower. Both mortar expansion reduction by using incorporation of FA and SF are under 0.1% that classified as innocuous.

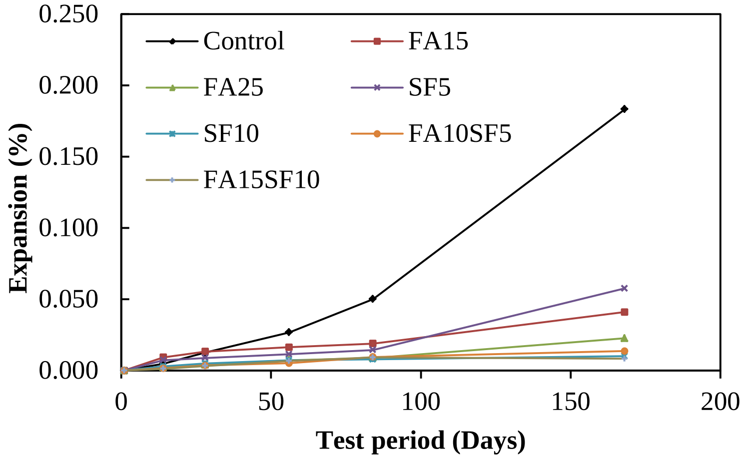


Fig. 3.20 Test results of mortar bar test (JIS A 1146)

Further, **Figure 3.21** shows expansion behavior of concrete by using limestone as fine aggregate and combines coarse aggregate between limestone and andesite.

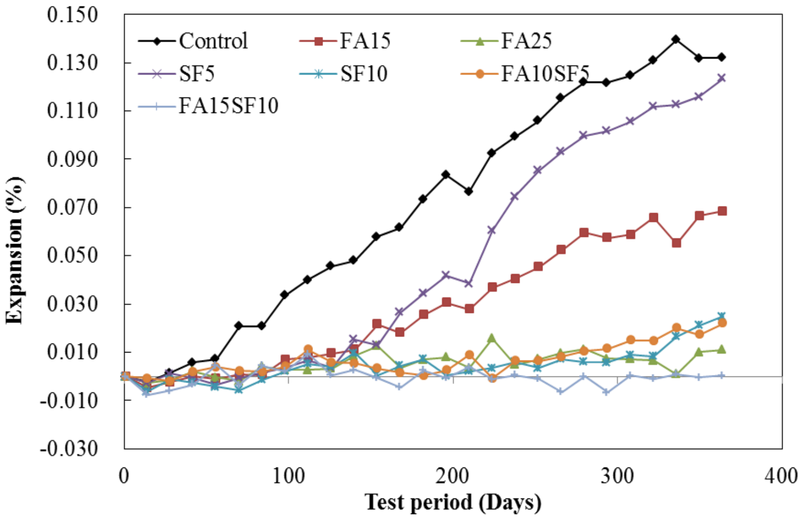


Fig. 3.21 Concrete expansion

In the case of concrete without mineral admixtures, expansion was large and fast from the beginning until the end of test period. It can be observed that there was expansion reduction due to usage of FA. The expansion rate of concrete with FA25% was lower compared to concrete with FA15%. The expansion rate of concrete with FA25% was lower compared to concrete with FA15%. Concrete expansion by using SF showed expansion reduction compared to concrete expansion without mineral admixtures. The expansion rate of concrete with level SF5% was moderate whereas concrete with level SF10% was lower.

Based on **Fig. 3.22** and **Fig. 3.23**, concrete expansion by using incorporation of FA and SF showed expansion reduction compared to concrete expansion without mineral admixtures. Expansion of concrete with incorporation of FA and SF was lower compared to concrete with FA. The effect of combination of FA with SF was larger than FA. Expansion reduction by using incorporation of FA and SF were under 0.05%. Then, it is classified as non-reactive.

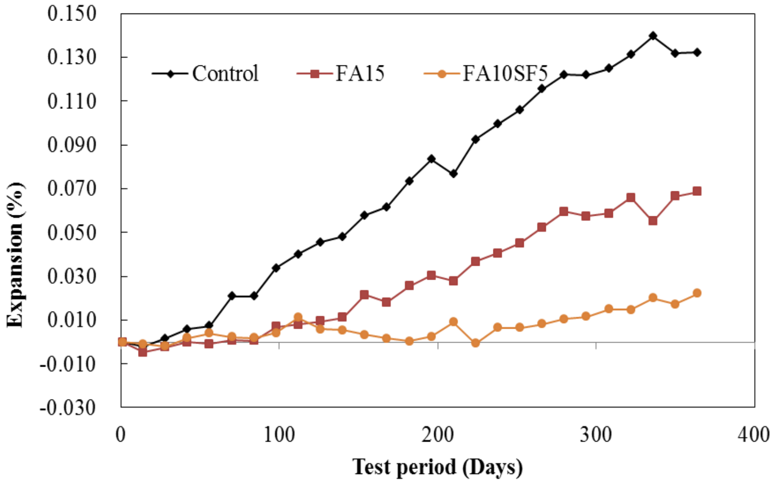


Fig. 3.22 Concrete expansion for control, FA15, and combination FA10SF5

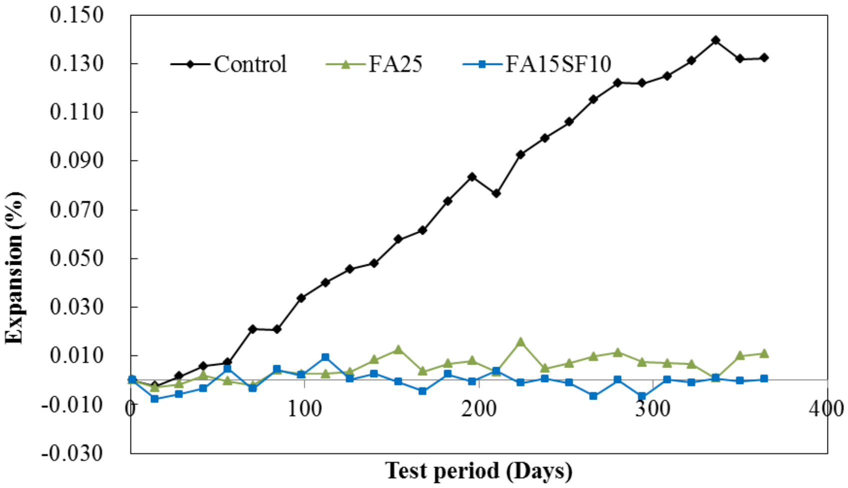


Fig. 3.23 Concrete expansion for control, FA25, and FA15SF10

3.4.2 Discussion on FA and SF effectiveness

FA reduces expansion by lowering alkali concentration and hydroxide ion in the pore solution. This is one of the mechanisms of mineral admixtures to suppress expansion. The addition of an appropriate amount of mineral admixture leads to the formation of C-S-H gel with low Ca/Si ratio, resulting in lower alkali concentrations and hydroxide ion (Y Kawabata et al., T Haruka et al.)(3.9), (3.10). FA combines with alkalis from cement that react with silica from aggregate, thereby preventing expansion.

The replacement of cement by FA leads to an increase in the total alkali content of blended cement. However, alkalis are not released from FA particles; alkalis seem to be kept in a hydrated product resulting from the pozzolanic reaction.N Tenoutasse'sconclusion mentioned that: FA have the ability to react chemically with the alkali hydroxide in Portland cement paste and absorbed alkalis, thus making them unavailable for reaction with silica in certain aggregates. Meanwhile, finer pozzolans are also sufficient in reducing ASR expansion, such as SF with particle size of approximately 0.1 μm is also very effective in preventing ASR (Tenoutasse et al.)(3.15). SF is a reactive pozzolanic material because of its finesses and high amorphous silicon dioxide content. SF reacts with calcium hydroxide ($Ca(OH)_2$) to form additional Calcium Silica Hydrate (C-S-H), which is similar to the calcium hydrate formed from the Portland cement. The product of pozzolanic reaction (secondary C-S-H) can incorporate alkali metal ions into their structure and reduce the alkalinity of the pore solution. At the same time, the secondary C-S-H hydrates fill the adjacent pores and reduce the permeability of concrete, consequently, reducing the free movement of alkali ions (George J.Z et al.)(3.16).

3.4.3 Compressive strength and elastic modulus

The test results of compressive strength at 28 days are shown in **Fig. 3.24**. It can be seen that the usage of minerals could influence the compressive strength values.

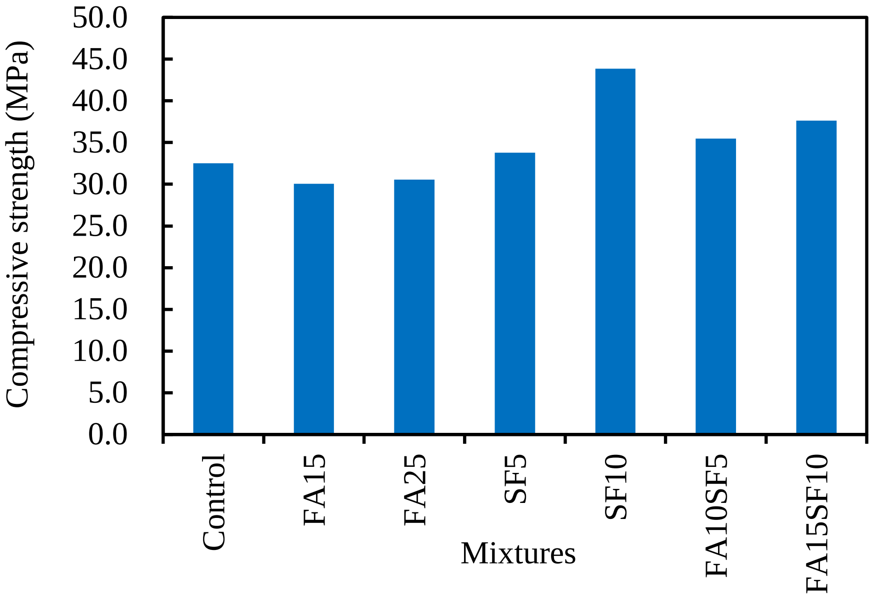


Fig. 3.24 Compressive Strength of concrete at 28 days (w/b=50%)

The compressive strengths of concrete with FA 15% and 25% are smaller than that of control concrete. FA reduced compressive strength of the concrete. The strength reduction because of the increasing of FA replacement level. The compressive strength reduction is related to the properties of FA that declines the heat of concrete hydration. As a result FA slow the rate of hardening and reduces the compressive strength (Ramazan D et al.)(3.21). On the other hand, the usage of SF and the combination of FA and SF enhance the compressive strength. The highest strength is achieved in concrete with SF 10%. A good linear correlation between compressive strength and elastic modulus is acquired. The relationship between compressive strength and elastic modulus at 28 days are shown in **Fig. 3.25**.

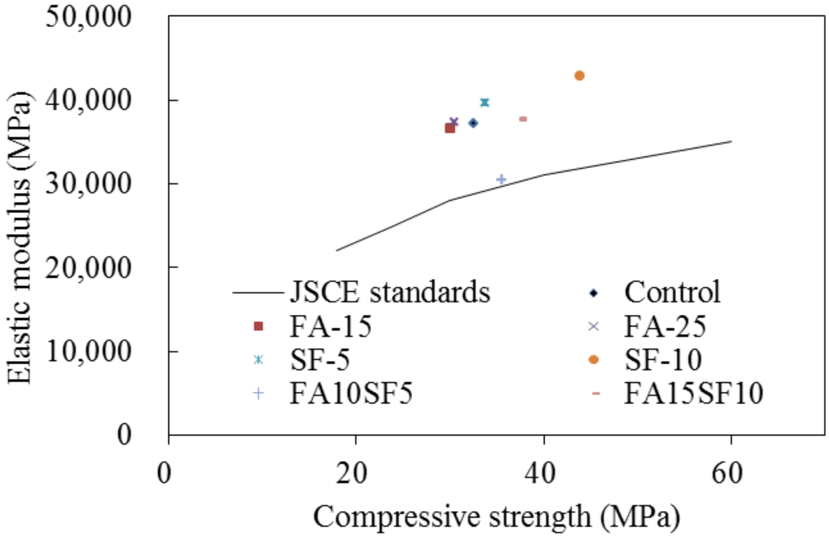


Fig. 3.25 Relationship between compressive strength and elastic modulus

It was observed that the higher compressive strength, the higher elastic modulus. Most of the relation between compressive strength (f'_c) and modulus elasticity (E_c) are above JSCE standard given by following equations.

E_c= (2.2+(f'c-18)/20) x 10^4 f'c < 30 N/mm^2 …………..(3.1)
E_c= (2.8+(f'c-30)/33) x 10^4 40≤f'c < 70 N/mm^2 ……………(3.2)
E_c= (3.1+(f'c-40)/50) x 10^4 40≤f'c < 70 N/mm^2 …………..(3.3)
E_c= (3.7+(f'c-70)/100) x 10^4 70≤f'c < 80 N/mm^2 …………..(3.4)

3.4.4 Porosity test

Porosity is a measure of the proportion of the total volume of concrete occupied by pores. The pore of the structure of this material is complex. So, some assumptions are made such as: the pores are interconnected and distribution size is not affected by the loss of water upon drying. Porosity or total pore volume can be measured by mercury intrusion. Porosity or total pore volume measurement is usually expressed in percent. Mercury intrusion test results of concrete are depicted in **Fig. 3.26**. Furthermore, **Fig. 3.27** until **Fig. 3.33** show pore size distribution.

In case of concrete with additional alkali, it seems that there are no significant effects of FA, and SF or incorporation of FA and SF towards porosity. Porosity values increase at control mixture, but not dramatically enlarge at FA15 and FA25 mixtures. Porosity results are in the range of 13.79% to 19.38%. The porosity of concrete with FA at level 15% is lower than control concrete. Further, the trends of porosity with SF at level 5%, 10% are also lower compared to control concrete. Meanwhile, porosity of concrete with FA at level 25%, combination of FA with SF are higher control concrete. Most of porosity values decrease with time from 28 days to 365 days such as: concrete with FA at level 15%, SF at level 10%, and combination of FA with SF. Meanwhile, the others do not show stable. The effect of FA, SF, and combination of FA with SF can not be observed clearly in reducing the total porosity. The usage of FA, SF, and combination of them seem very good at refining the pore size distribution. The pore size distribution of concrete with FA, SF, and combination of FA with SF show well-ordered compared with control concrete.

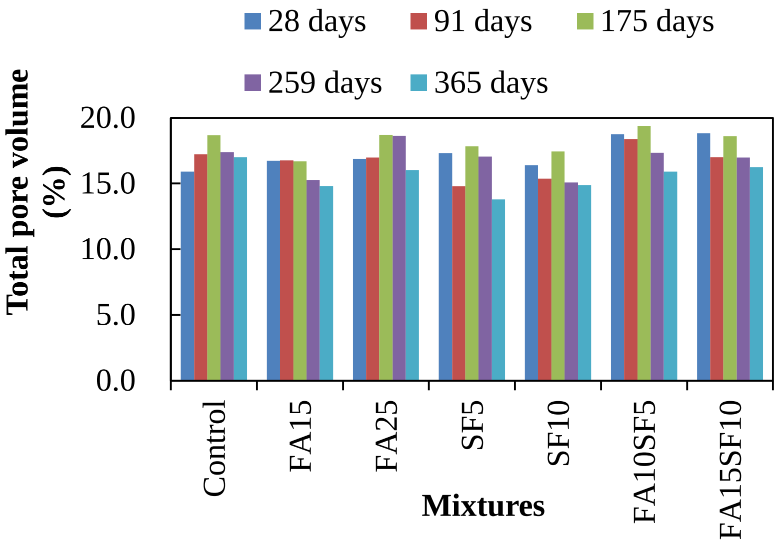


Fig. 3.26 Total pore volume at age of 28 up to 1 year (w/b=50%)

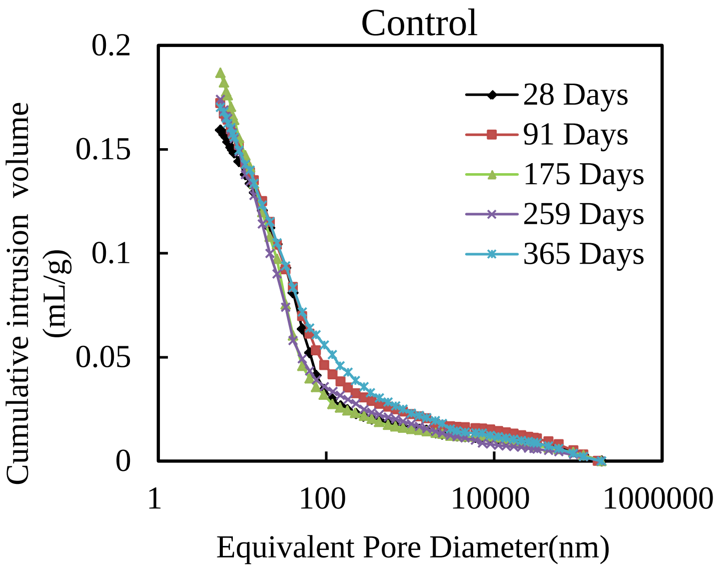


Fig. 3.27 Pore size distribution of control concrete (w/b=50%)

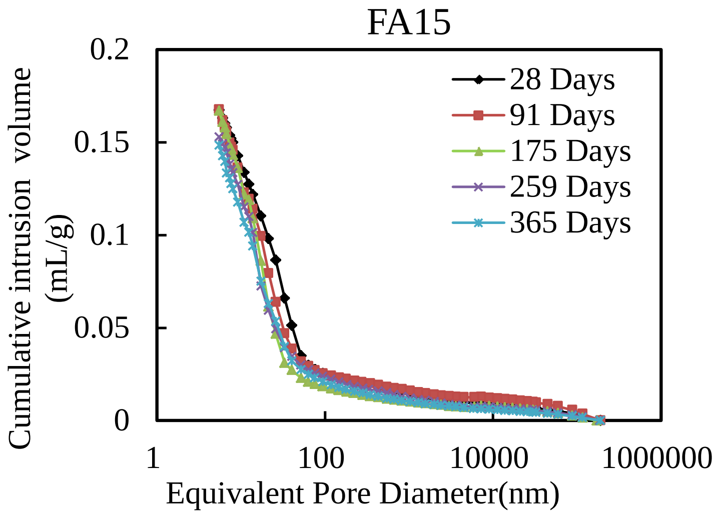


Fig. 3.28 Pore size distribution of concrete FA15 (w/b=50%)

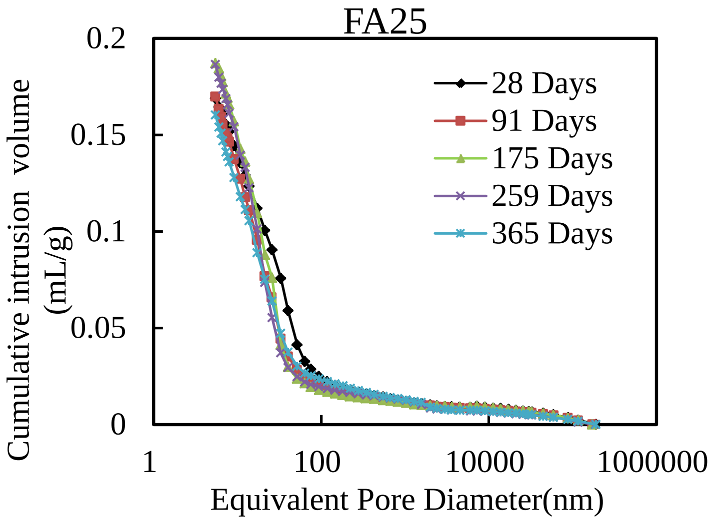


Fig. 3.29 Pore size distribution of concrete FA25 (w/b=50%)

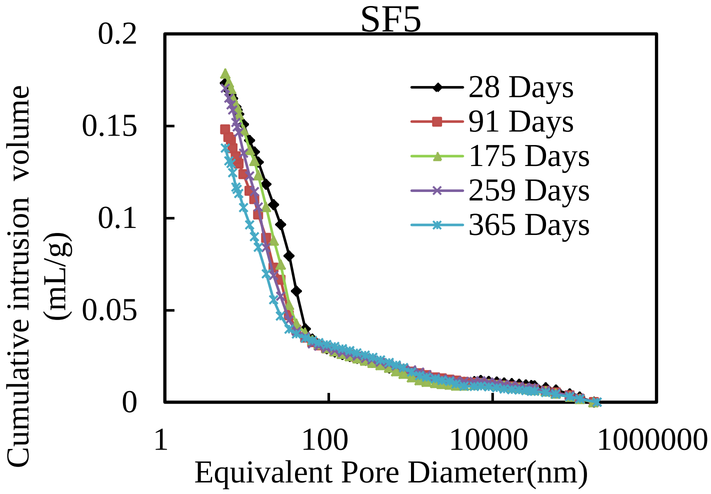


Fig. 3.30 Pore size distribution of concrete SF5 (w/b=50%)

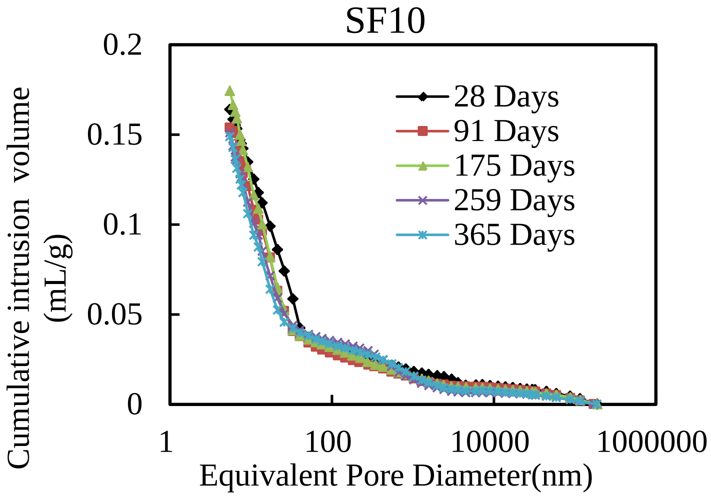


Fig. 3.31Pore size distribution of concrete SF10 (w/b=50%)

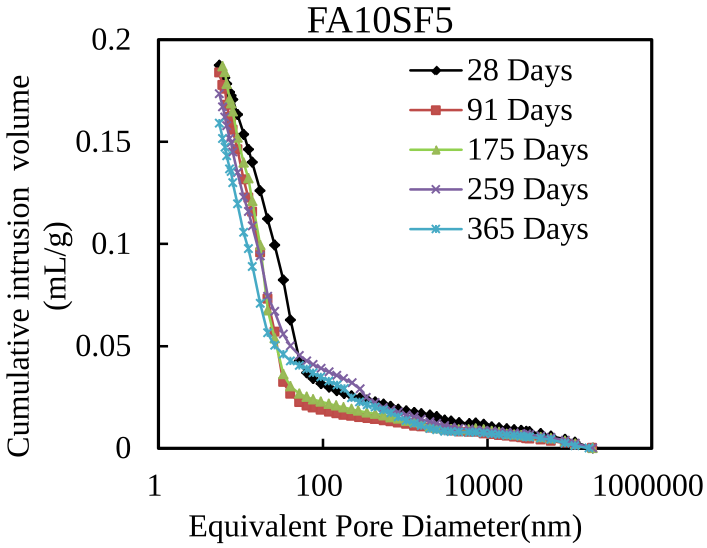


Fig. 3.32 Pore size distribution of concrete FA10SF5 (w/b=50%)

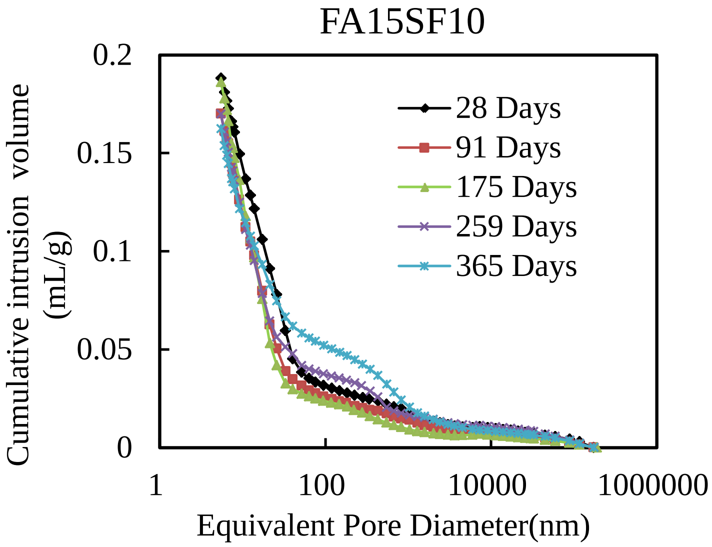


Fig. 3.33 Pore size distribution of concrete FA15SF10 (w/b=50%)

The study of pozzolanic activity of SF blended cement showed the beneficial influence of SF in reducing the porosity, and hence the permeability of the cement pastes (Tenoutasse N et al.)(3.15). Adding SF to concrete mixture would bring very small particles to fill in the spaces between cement grains. It would affect toward significant improvement of the concrete. Thus, this micro filling greatly reduces permeability and improves the paste to aggregate bond.

3.4.5 Ultrasonic pulse velocity (UPV) test

Test results of UPV at 28 up to 1 year days are depicted in **Fig. 3.34**. The values are in range of 3.90 km/s to 4.42 km/s. The results indicate that the concrete quality is good.

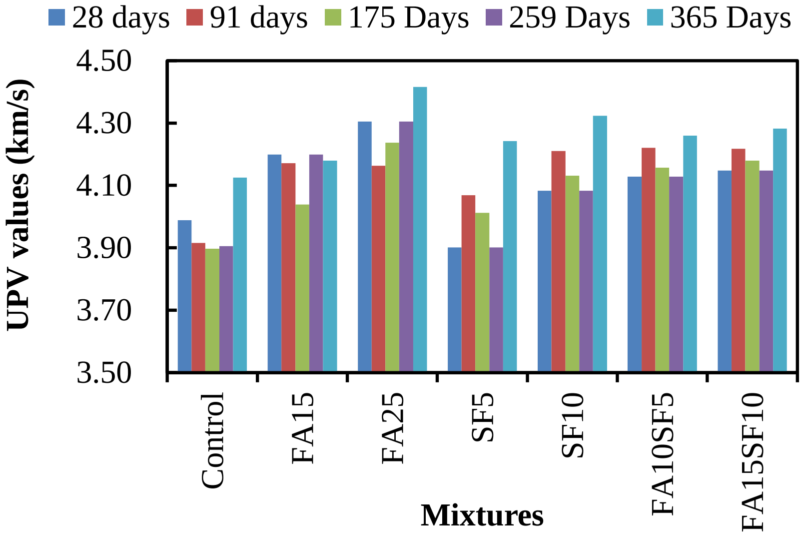


Fig. 3.34 UPV results of concrete at 28 up to 1 year

All values were higher than 3.7km/s (IS:13311-1-1992). Comparison of UPV results among concrete with mineral to concrete control, it seems that mineral admixture and also combination of FA and SF contribute to improve the concrete quality at all ages. It can be observed that upv values of concrete with FA at level 15%, FA at a level 25%, and SF at a level 10%, combination of FA with SF show higher than control concrete. UPV values of concrete with SF at level 5%, almost same with control concrete. There are fluctuation among the UPV results. However, it does not make significant differences in the UPV results for all ages.

3.5 Results and discussions of combination FA with EPP

3.5.1 Expansion test

Expansion behavior of mortar is shown in **Fig. 3.35**. In the case of control, expansion increased slowly until eight weeks, then enlarged until the end of the observation. Mortar expansion with EPP10 increased remarkably, but became lower than EPP0 at the end. However, when EPP level was increased, then there were expansion reduction. One of pozzolanic effect of EPP in suppressing the ASR was binding of alkalis into pozzolanic C-S-H (Bektas et al.)$^{(3.12)}$. Mortar bars containing 10%, 15% and 20% EPP showed expansion reduction. The expansion rate of mortar with FA25% was lower compared to mortar expansion with FA15%.

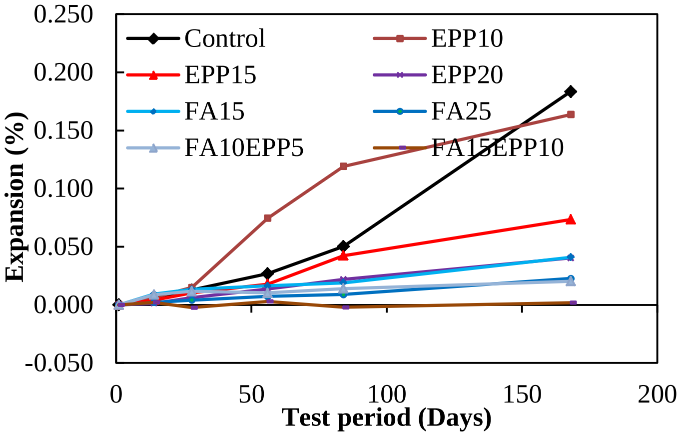


Fig. 3.35 Test results of mortar bar test JIS A 1146

It can be observed that there are expansion reduction due to usage of FA and EPP. Mortar expansion reduction by using incorporation of FA with EPP are under 0.1% that classified as innocuous. Furthermore, **Fig. 3.36** shows expansion behavior of concrete by using limestone as fine aggregate and combine coarse aggregate between limestone and andesite.

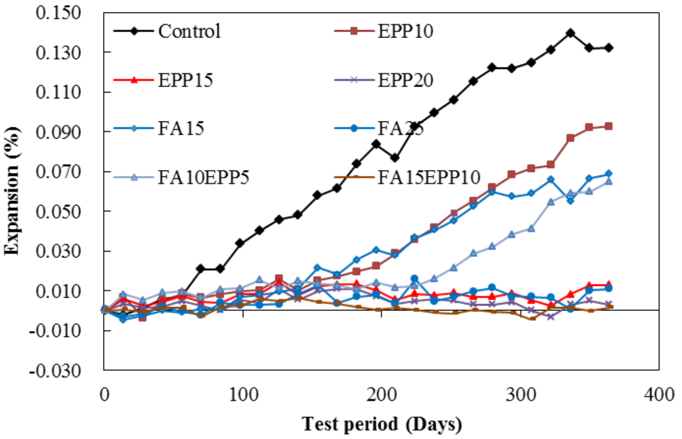


Fig. 3.36 Concrete expansion

In the case of concrete without mineral admixtures, expansion was large and fast from the beginning until end of this period. It can also be observed that there was expansion reduction due to usage of EPP. Concrete with EPP10 did little to inhibit expansion. However, increasing EPP levels decreased expansion. Concrete prisms containing 15% and 20% EPP showed expansion reduction. Expansion of concrete containing 15% EPP under 0.05% that classified as non-reactive.

The effectiveness of EPP in mitigating ASR can be attributed to pozzolanic activity possessed by the material. Pozzolanicity may be due to the binding of alkalis onto perlite (Bektas et al., 2002). It can be observed that there was expansion reduction due to usage of FA. The expansion line of concrete with FA25% was lower compared to concrete with FA15%. It can be observed that there are expansion reduction due to combination FA with EPP. Concrete expansion by using incorporation of FA and EPP can be seen clearly in **Fig. 3.37** and **Fig. 3.38**.

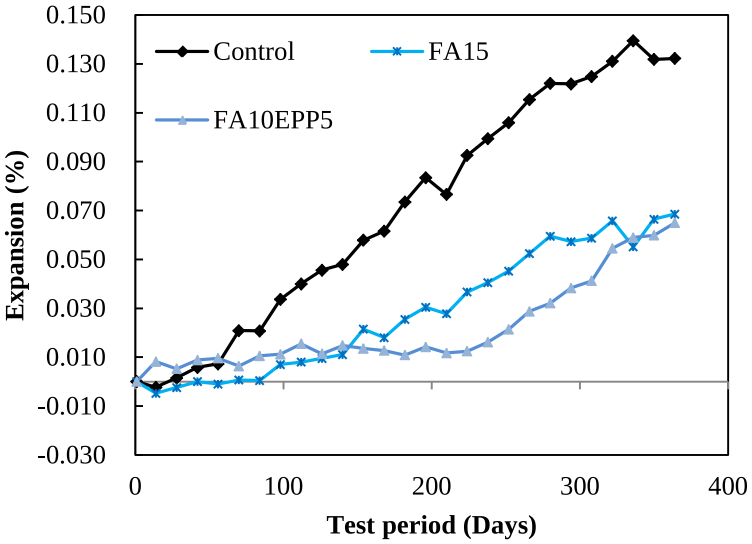


Fig. 3.37 Concrete expansion for control, FA15, and combination FA10EPP5

Combination minerals showed expansion reduction compared to concrete expansion without mineral admixtures. Concrete expansion by using combination of FA with EPP showed expansion reduction compared to concrete without mineral. The comparison of expansion between concrete with FA15 to concrete with FA10EPP5, and comparison of expansion between concrete with FA25 to concrete with FA15EPP10 show that concrete expansion with combination of FA with EPP (FA10EPP5) was lower compared to concrete with FA 15% and expansion with combination of FA with EPP (FA15EPP10) was lower than concrete with FA 25%. The effect of combination FA with EPP of Alkali-Silica Reaction were larger than FA itself. Expansion reduction by using incorporation of FA with EPP (FA15EPP10) was under 0.05% that classified as non-reactive.

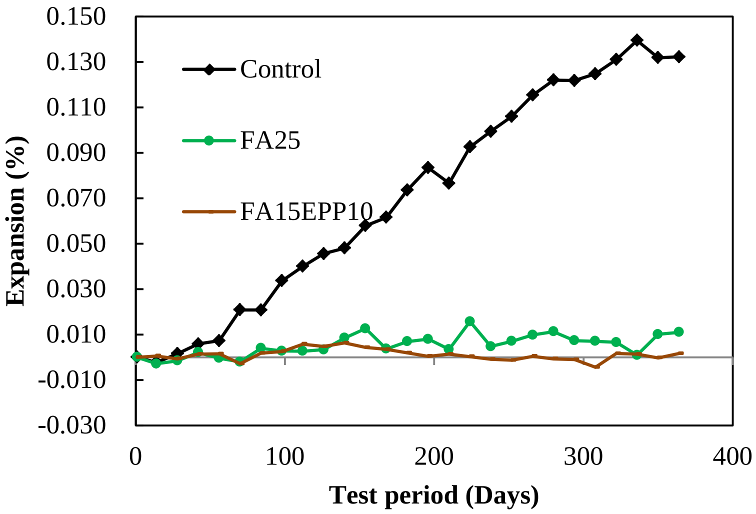


Fig. 3.38 Concrete expansion for control, FA25, and combination FA15EPP10

3.5.2 Discussion on FA and EPP effectiveness

FA reduces expansion by lowering alkali concentration and hydroxide ion in the pore solution; this is one of the mechanisms behind mineral admixtures to suppress expansion. The addition of an appropriate amount of mineral admixtures, lead to the formation of C-S-H gel with low Ca/Si ratio, resulting in lower alkali concentrations and hydroxide ion (Y Kawabata et al., T Haruka et al.)(3.8), (3.10). FA combines with alkalis from cement that react with silica from aggregate, thereby preventing expansion.

The replacement of cement by FA leads to an increase in the total alkali content of blended cement. However, alkalis are not released from FA particles; alkalis seem to be kept in a hydrated product resulting from the pozzolanic reaction. N Tenoutasse mentioned that FA has the ability to react chemically with the alkali hydroxide in portland cement paste and absorbed alkalis, thus making them unavailable for reaction with silica in certain aggregates(3.15). The effectiveness of EPP in mitigating ASR can be attributed to pozzolanic activity possessed by the material. Pozzolanicity may be due to the binding of alkalis onto perlite (Bektas et al.)(3.12). In suppressing expansion, the porous nature of EPP might play important role by providing a distributed air bubble system that accommodate expansive gel in concrete (Bektas et al.)(3.12).

3.5.3 Compressive strength and elastic modulus

The compressive strength of concrete at 28 days of age is presented in **Fig. 3.39**. The compressive strength of concrete with FA at level 15% and 25% are smaller than strength of control concrete (EPP0). FA reduced compressive strength of the concrete. Increasing level of FA replacement decreased the strength. The compressive strength reduction is related to the properties of FA that declines the heat of concrete hydration. As a result, FA slows the rate of hardening and reduces the compressive strength (Ramazan D et al.)(3.21).

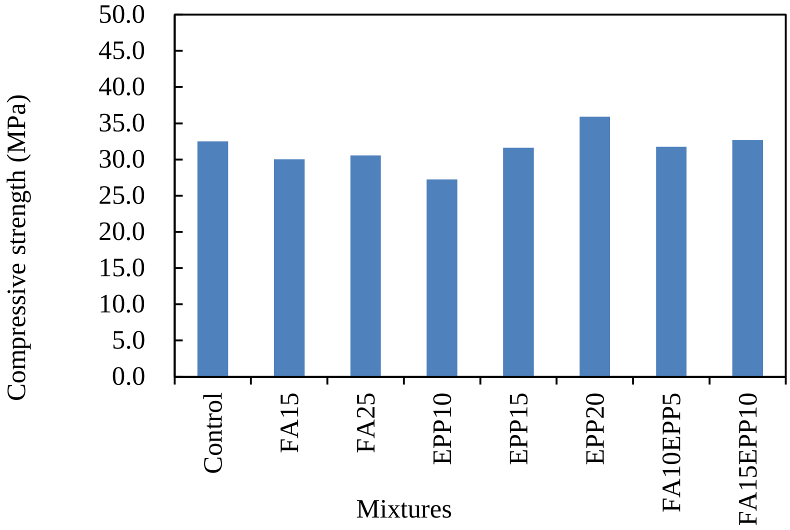


Fig. 3.39 Compressive Strength of concrete at 28 days (w/b=50%)

The strength of concrete with EPP at level 10% and 15% are smaller than compressive strength of control concrete. It could be noticed that the usage of EPP at the level 20% would influence to enhance the compressive strength values. Adding EPP to concrete mixture would bring small particles to fill in the spaces between cement grains. It would affect toward significant improvement of the concrete.

Finer pozzolans are also sufficient in increasing strength. Urhan in 1987 mentioned that the enhancement of bond strength between lightweight expanded perlite aggregate and cement matrix is due to pozzolanic activity of perlite$^{(3.33)}$. Demirbŏga et al. attributed the strength improvement of expanded perlite aggregate concrete to both the self-curing property and pozzolanic of perlite. The strength of combination between FA and EPP (FA15EPP10) show a little higher than control. The highest strength is achieved on concrete with EPP at level 20%. The relationship between compressive strength and elastic modulus at 28 days are shown in **Fig. 3.40**. It was observed that the higher compressive strength, the higher elastic modulus. All the relation between compressive strength (f'_c) and modulus elasticity (E_c) are above JSCE standard, a good relation is achieved.

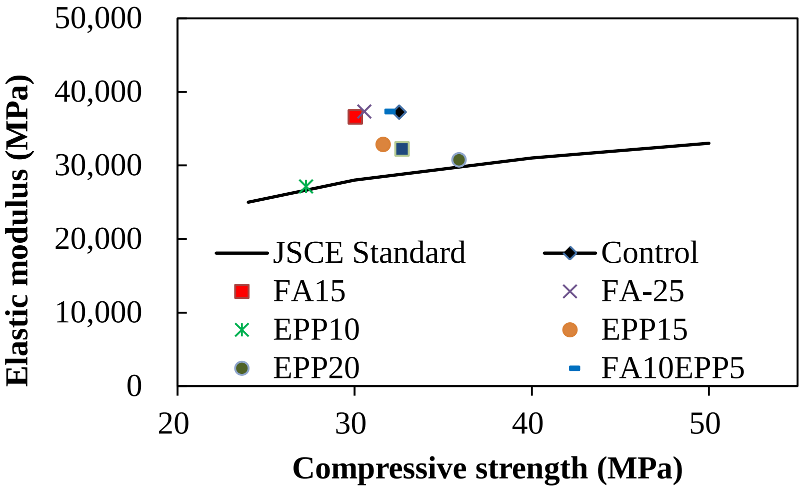


Fig. 3.40 Relationship between compressive strength and elastic modulus

Furthermore, the compressive strength and relationship between compressive strength and elastic modulus at 28 days at temperature 20°C and 40°C are presented in **Fig. 3.41** and **Fig. 3.42**. It could be noticed that the usage of EPP would influence to enhance the compressive strength values in 20°C and 40°C.

The compressive strength of concrete with EPP 15% and EPP 20% are greater than control (EPP0). The strength increase because of the increasing of EPP replacement level. It can be observed that when the expansion has just been started in the 40°C, the strength of EPP0 is low, and relation of elastic modulus to compressive srength of EPP0 is under of JSCE standar line. However, concrete with EPP 10%, EPP 15% and EPP 20% are above JSCE standar line, and good relation is achieved.

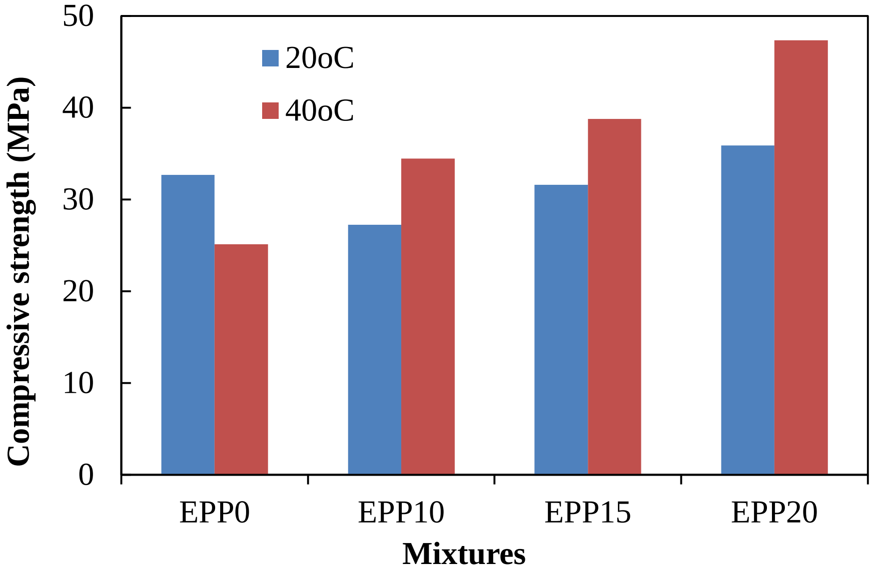


Fig. 3.41 Compressive Strength of concrete at 28 days with alkali

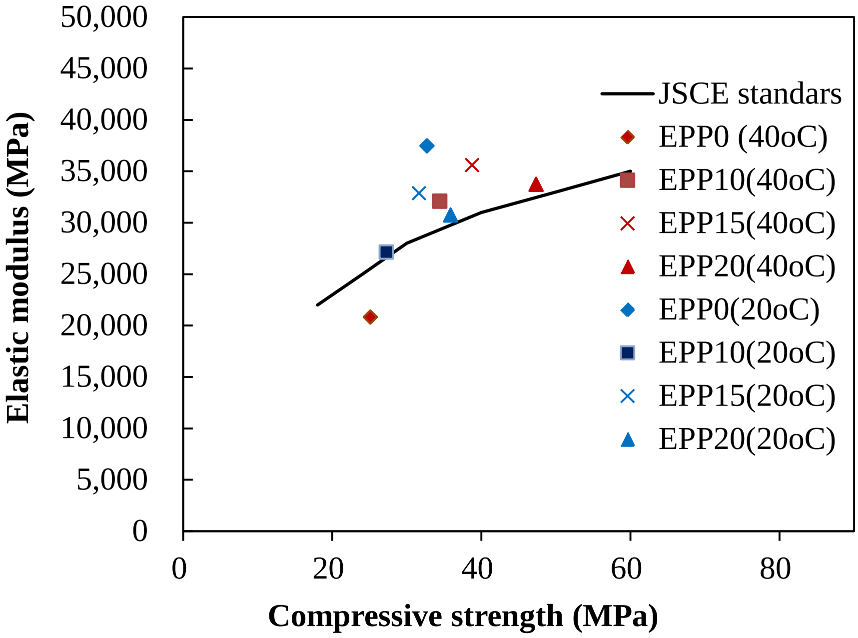


Fig. 3.42 Relationship between compressive strength and elastic modulus at temperature 20°C and 40°C

Then, **Fig. 3.43** and **Fig. 3.44** show the compressive strength and relationship between compressive strength and elastic modulus between concrete with alkali and concrete with no alkali.

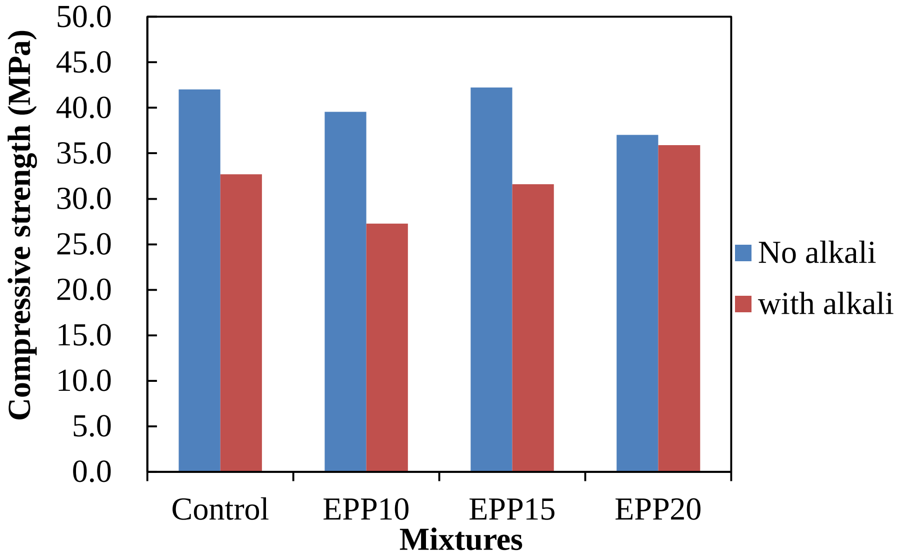


Fig. 3.43 Compressive Strength of concrete at 28 days at temperature 20°C

It can be observed that concrete with additional alkali has lower strength than concrete with no alkali. In concrete with no additional alkali, it can be looked that strength of concrete with EPP15 is little higher than EPP0. A good correlation is achieved between compressive strength and elastic modulus on concrete with and without additional alkali, as shown in **Fig. 3.44**.

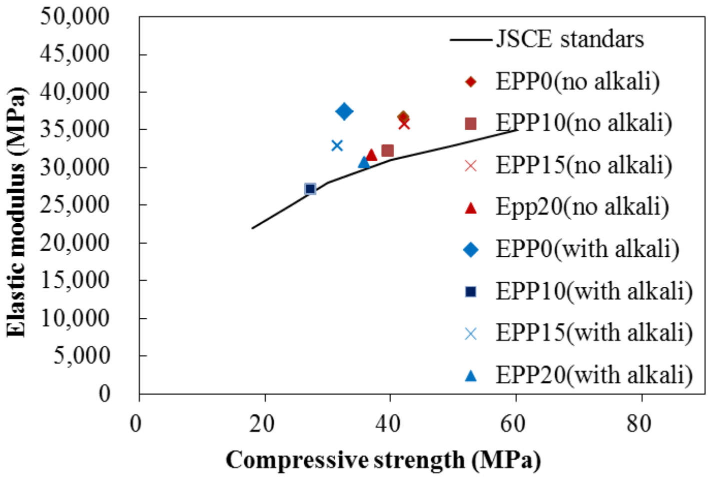


Fig. 3.44 Relationship between compressive strength and elastic modulus at temperature 20°C

3.5.4 Porosity test

Porosity is a measure of the proportion of the total volume of concrete occupied by pores. The pore of the structure of this material is complex. So some assumptions are made such as: the pores are interconnected and distribution size is not affected by the loss of water upon drying. Porosity or total pore volume can be measured by mercury intrusion. Porosity or total pore volume measurement is usually expressed in percent. Mercury intrusion test results of concrete are depicted in **Fig. 3.45**.

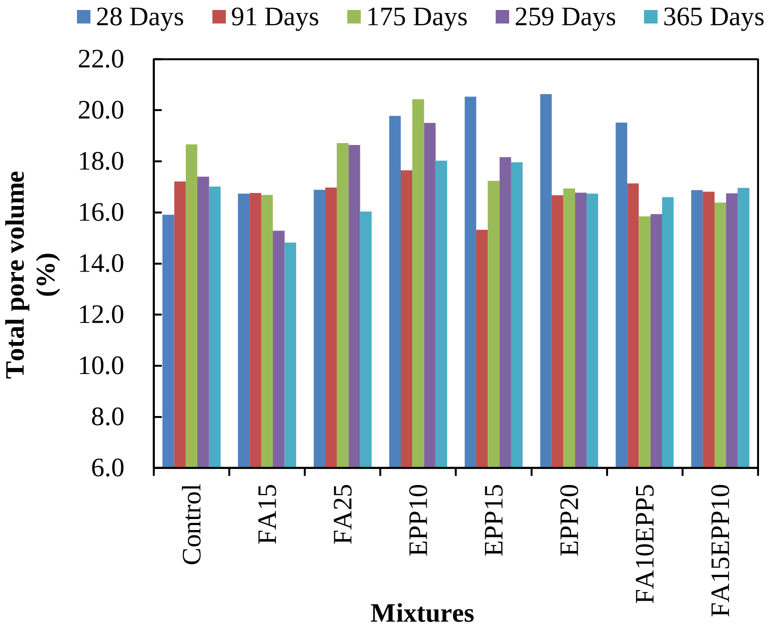


Fig. 3.45 Total pore volume at age 28 days until 1 year

In case of concrete with additional alkali, it seems that there are no significant effects of FA, and EPP or incorporation of FA with EPP towards porosity. Porosity results are in the range of 15.32% to 20.63%. Concrete porosity with FA at level 15% show little bit lower than control concrete. Concrete porosity with FA at level 25% show higher than porosity of FA at level 15%.

Porosity values increase with time at control mixture, and also enlarge at FA25, EPP10. Porosity of concrete with FA25, EPP10, and EPP15 show fluctuation. Porosity of concrete with Perlite at level 20% decrease after 28 days then look stable. Further, combination of FA with EPP (FA10EPP5) decrease with time, from 28 days to 175 days and increase until 365 days. Furthermore, combination of FA with EPP (FA15EPP10) show stable.

Adding EPP to concrete mixture would also bring small particles to fill in the spaces between cement grains. It would affect toward improvement of the concrete. Thus, this micro filling due to EPP greatly improves the paste to aggregate bond. The effect of FA, EPP, and combination of FA with EPP can not be observed clearly in reducing the total porosity. The usage of FA, EPP, and combination of them seem look good at refining the pore size distribution. The pore size distribution of concrete with FA, EPP, and combination of FA with EPP can be seen in **Fig. 3.46** until **Fig. 3.53** that show well-ordered than control concrete.

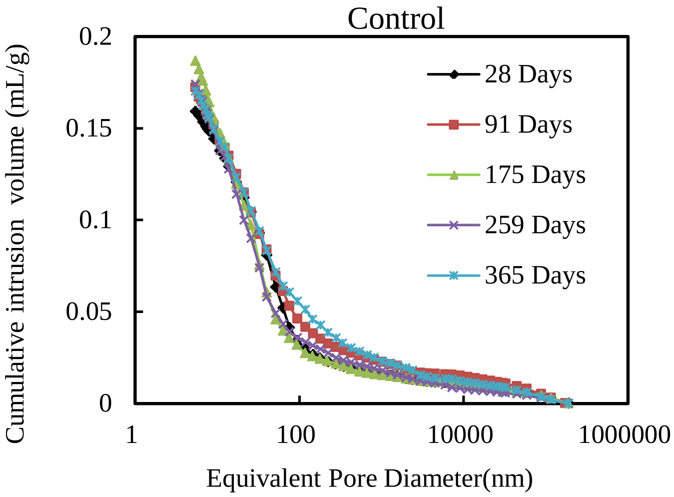


Fig. 3.46 Pore size distribution of control concrete

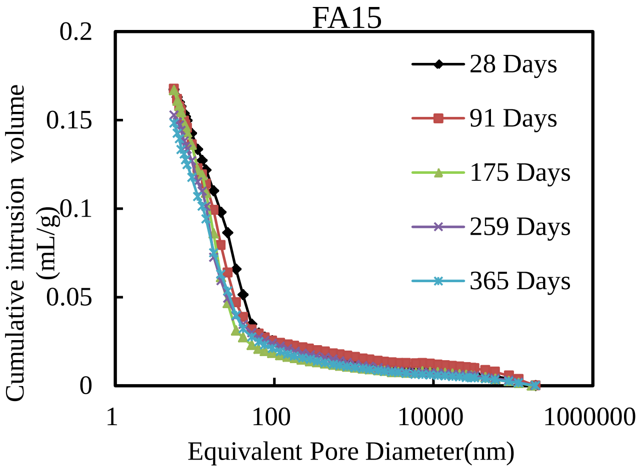


Fig. 3.47 Pore size distribution of concrete FA15

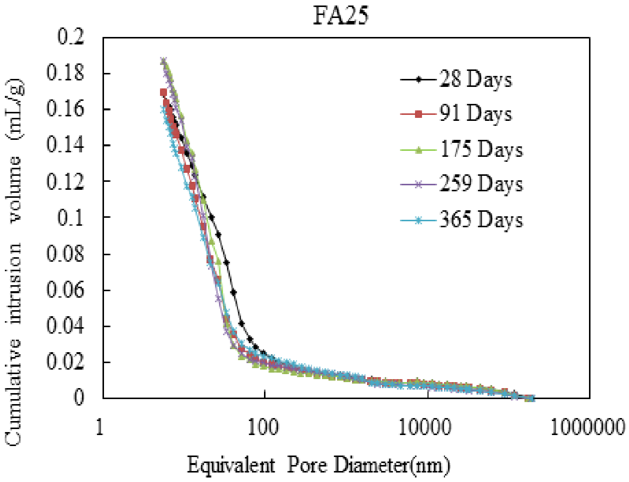


Fig. 3.48 Pore size distribution of concrete FA25

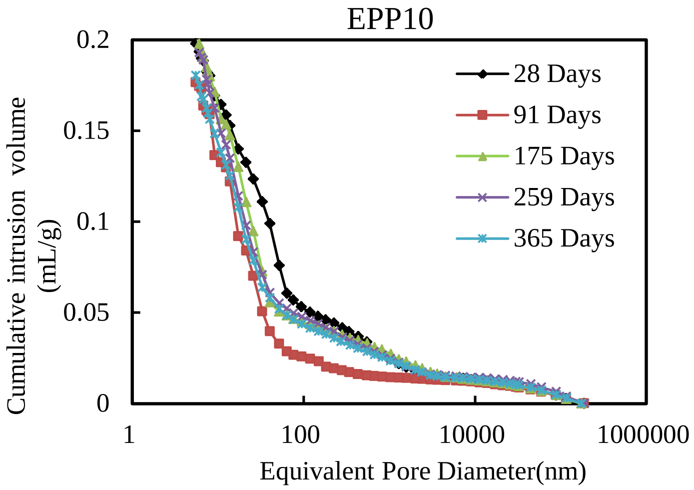


Fig. 3.49 Pore size distribution of concrete EPP10

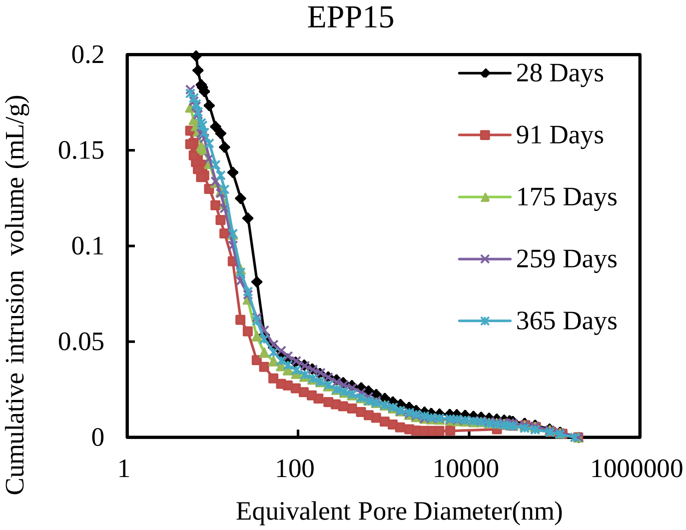


Fig. 3.50 Pore size distribution of concrete EPP15

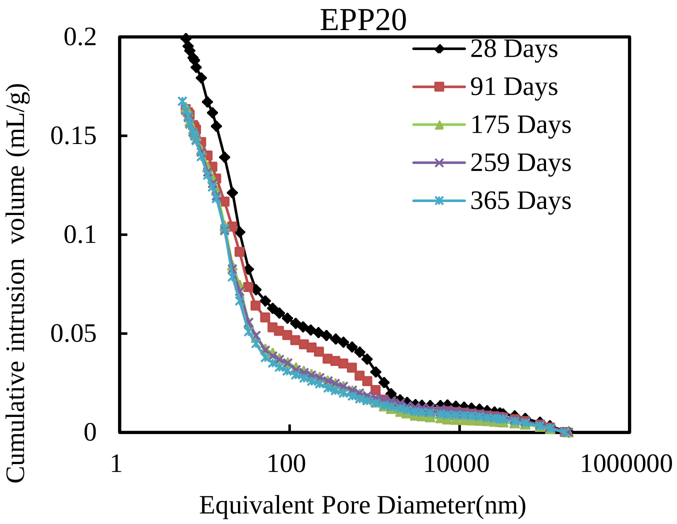


Fig. 3.51 Pore size distribution of concrete EPP20

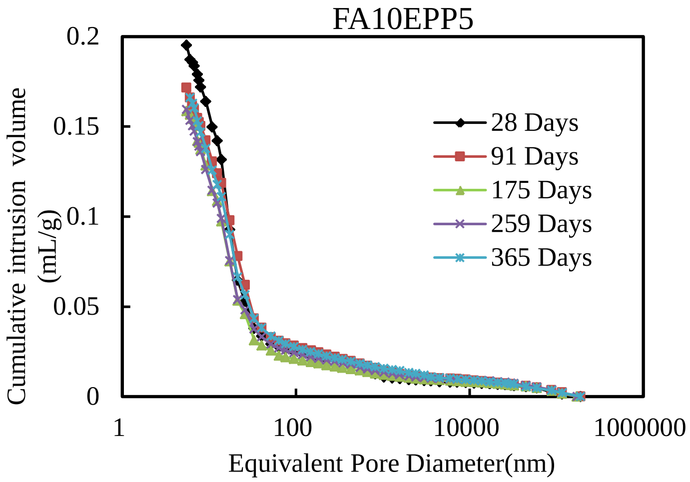


Fig. 3.52 Pore size distribution of concrete FA10EPP5

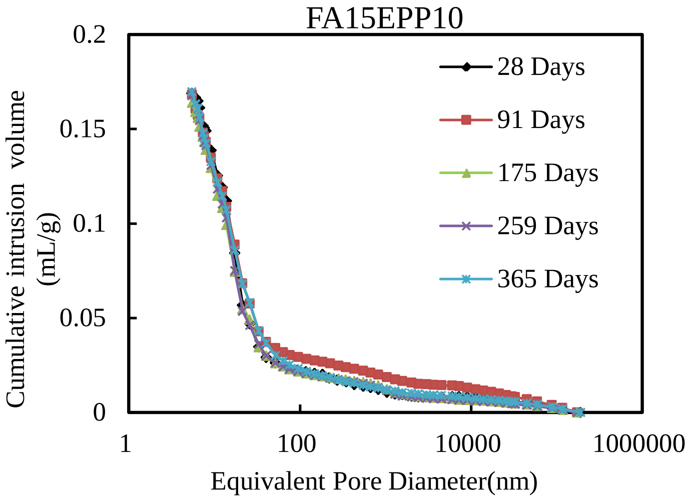


Fig. 3.53 Pore size distribution of concrete FA15EPP10

3.5.5 Ultrasonic pulse velocity (UPV) test

Test results of UPV are depicted in **Fig. 3.54**. The UPV values are in range of 3.9 km/s to 4.3 km/s. The UPV results indicate that the concrete quality is good.

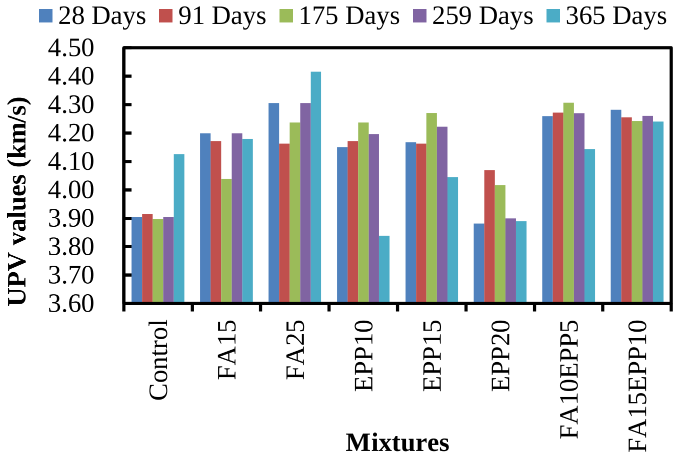


Fig. 3.54 UPV results of concrete at age 28 up to 1 year at temperature 40^{o}C

All values were higher than 3.5 km/s (IS:13311-1-1992). Comparison of UPV results among concrete with mineral to concrete control, it seems that FA, EPP, and combination of FA with EPP contribute to improve quality of concrete at all ages. There are UPV reduction of results compared to UPV of concrete with FA at level 15%, 25%, EPP at level 10%, and 15%, and combination of FA with EPP. It can be observed that UPV values of concrete with FA at level 15%, FA at level 25%, and EPP at level 10%, 15%, and combination of FA with EPP show higher than control concrete. UPV values of concrete with EPP at level 20% almost same with control concrete.

3.6 Summary

The results obtained are summarized as follows:

1. The effectiveness of SF at a level 10% could reduce expansion when aggregates are used in pessimum proportion.

2. The usage of SF at level 15% seems the most effective to refine the pore size distribution.

The following conclusions are obtained based on the results of combination of FA with SF:

3. The incorporation of FA and SF reduced expansion more effective compared to FA itself at the same levels of mineral investigated.

4. The effect of FA15% is lower compared to SF5%, meanwhile the effect of FA25% is same with the effect of SF10% to reduce expansion.

5. In the case of fresh concrete workmanship, degree of difficulty of concrete with SF is higher than concrete with a combination of SF with FA. Then concrete with FA is the easiest.

The following conclusions are obtained based on the results of combination of FA with EPP:

6. The effectiveness of EPP 10% could reduce expansion when aggregates are used in pessimum proportion.

7. Expansion reduction due to effect of FA10EPP5 lower than FA15%, and The effect of FA15EPP10 lower than FA25%

8. The usage of EPP seems effective to refine the pore size distribution.

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CHAPTER 4. DISCUSSION ON THE EFFECTIVENESS OF FA, SF, AND EPP

4.1 Introduction

Discussion on the effectiveness of minerals in mitigating ASR will be presented. The reasons why some minerals such as FA, SF, and EPP can reduce expansion are described. The discussion is mainly described based on silicon dioxide content in minerals.

4.2 Materials and mixture proportions

4.2.1 Materials

Four types of binder were used in this study, namely: Ordinary Portland Cement (OPC), FA, SF, and EPP. Chemical composition of OPC, Fly ash (FA), Silica fume (SF) and Expanded Perlite Powder (EPP) were shown in Chapter 2 in **Table 2.2**. There is no content of Na_2O and K_2O in SF compared to OPC. The content of Na_2O and K_2O in EPP is higher than OPC. OPC, FA. Furthermore, OPC, FA, and SF meet the requirements of JIS R 5202, JIS A 6201, and JIS A 6207, respectively. Perlite is a pozzolan due to its glassy structure and high SiO_2 and Al_2O_3 contents.

4.2.2 Mixture proportions

Mortar bars were made based on JIS A 1146 and mortar specimens for expansion measurement were treated under 40°C, and R.H. 100%. Meanwhile, concrete prisms were made based on RILEM AAR-3, and concrete specimens were stored under 40°C, and R.H. 100%. Mixture proportions of mortar and concrete are be shown in **Table 4.1** and **Table 4.2**.

Table 4.1 Mixture proportions of mortar

No	**Description**	**w/c (%)**	**Water+ NaOH (g)**	**Cementitious Materials (g)**				**Aggregates (g)**	**NaOH (ml)**
				OPC	**SF**	**FA**	EPP		
1	Mix 1 (Control)	0.5	300	600	-	-	-	1350	120
2	Mix 2 (FA15)	0.5	300	510	-	90	-	1350	102
3	Mix 3 (FA25)	0.5	300	450	-	150	-	1350	90
4	Mix 4 (SF5)	0.5	300	570	30	-	-	1350	114
5	Mix 5(SF10)	0.5	300	540	60	-	-	1350	108
6	Mix 6 (SF15)	0.5	300	510	90	-	-	1350	102
7	Mix 4 (EPP10)	0.5	300	540	-	-	60	1350	108
8	Mix 5 (EPP15)	0.5	300	510	-	-	90	1350	102
9	Mix 6 (EPP20)	0.5	300	480	-	-	120	1350	96
10	Mix 7 (FA10EPP5)	0.5	300	510		60	30	1350	102
11	Mix 8 (FA15EPP10)	0.5	300	450		90	60	1350	90
12	Mix 6 (FA10SF5)	0.5	300	510	60	30	-	1350	102
13	Mix 7 (FA15SF10)	0.5	300	450	90	60	-	1350	90

Table 4.2 Mixture proportions of concrete

Mix	w/b (%]	s/a (%)	(kg/m³)								(g/m³)		Temp, °C	Slump (mm)	Air Content (%)
			Water	OPC	FA	SF	EPP	Sand	Gravel	NaOH	WR +AE	AE			
Control	50	45	160	320		-	-	843	992	1.856	1000	12.8	19	80	5.0
FA15	50	45	160	272	48	-	-	836	984	2.499	1000	9.60	23	150	4.0
FA25	50	45	160	240	80	-	-	831	978	2.928	1000	16.0	22	180	2.8
SF5	50	45	160	304	-	16	-	841	990	2.070	1000	12.8	22	70	3.8
SF10	50	45	160	288	-	32	-	838	987	2.285	1000	12.8	21	60	3.5
SF15	50	45	160	272	-	48	-	836	984	2.499	1760	22.0	30	30	5.0
EPP10	50	45	160	288	-	-	32	838	987	3.613	1400	17.6	24	57	4.0
EPP15	50	45	160	272	-	-	48	836	984	4.491	1400	17.6	25	65	2.9
EPP20	50	45	160	256	-	-	64	833	981	5.370	1400	17.6	22	55	3.9
FA10 EPP5	50	45	160	272	32	-	16	824	970	5.706	880	12.8	21	125	4.5
FA15 EPP10	50	45	160	240	48	-	32	813	957	5.946	880	12.8	21	125	3.1
FA10 SF5	50	45	160	272	32	16	-	824	970	3.163	880	12.8	20	100	3.3
FA15 SF10	50	45	160	240	48	32	-	813	957	4.256	880	12.8	20	90	2.9

(WR+AE)= water reducing and air entraining agent, AE= air entraining agent

4.3 Expansion

4.3.1 Mortar bar

The expansion behavior of mortar with FA is shown in **Fig. 4.1**.

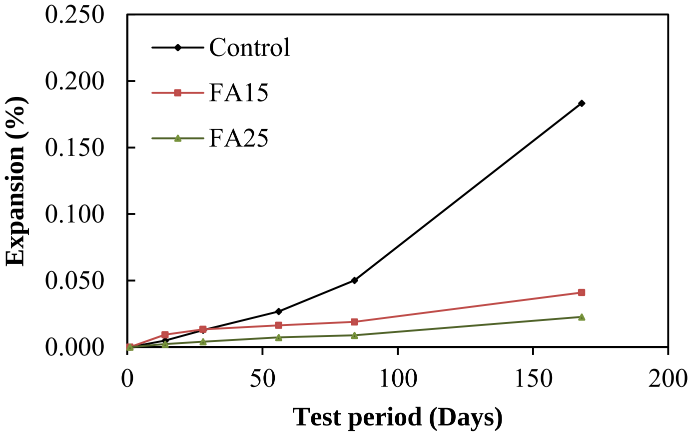


Fig. 4.1 Expansion of mortar with FA

In the case of mortar without mineral admixture, expansion increased slowly until eight weeks, then enlarge until the end of test period. It can be observed that there are expansion reduction due to usage of FA. The expansion rate of mortar with FA25% was lower than mortar expansion with FA15%.

Fig. 4.2 shows the expansion behavior of mortar with SF. Mortar expansion by using SF showed expansion reduction compared to mortar expansion without mineral admixtures. In the case of mortar without SF, expansion increased slowly until eight weeks, then dramatically increased until the end of the observation.

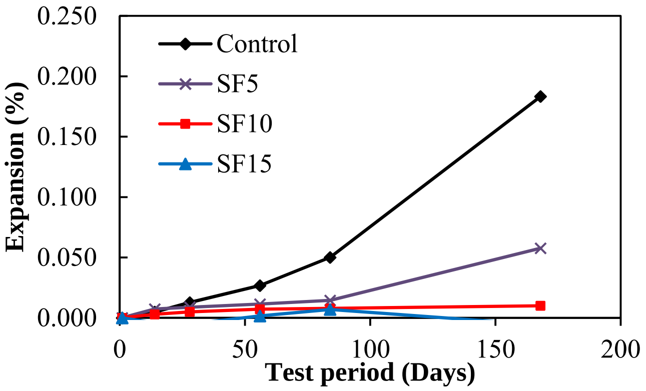


Fig. 4.2 Expansion of mortar with SF

An expansion graph of mortar with EPP is shown in **Fig. 4.3**. In the case of control, expansion increased slowly until eight weeks, then enlarged until the end of the observation.

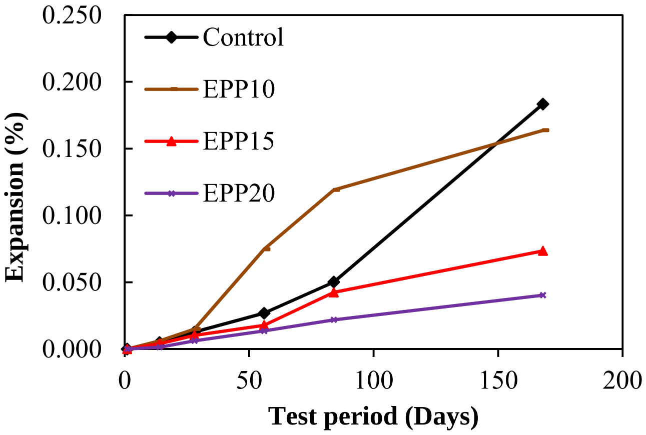


Fig. 4.3 Expansion of mortar with EPP

Expansion of mortar with EPP10 increased remarkably, but become lower than control at the end. Expansion of mortar with EPP15 increased gradually but became lower than expansion of mortar with EPP10 at the end. Mortar bars containing 10%, 15%, and 20% EPP show expansion reduction. The comparison of suppressing expansion by using all minerals are shown in **Fig. 4.4**. There are expansion reduction by using mineral incorporation of FA with SF. Mortar expansion with combination of FA with SF (FA10SF5) was lower than mortar with FA 15% and expansion of combination of FA with SF (FA15SF10) was lower than mortar with FA 25%. The combination effect of FA with SF reduce expansion due to ASR are larger than FA. Both expansion reduction by using incorporation of FA with EPP are under 0.01% that classified as non-reactive.

There are also expansion reduction by using mineral incorporation of FA with EPP. Mortar expansion of combination of FA with EPP (FA10EPP5) was lower than mortar with FA 15% and expansion of combination of FA with EPP (FA15EPP10) was lower than mortar with FA 25%. The effect of combination of FA with EPP in reducing expansion due to ASR are stronger than FA. Both expansion reduction by using incorporation of FA and EPP are under 0.01% that classified as non-reactive.

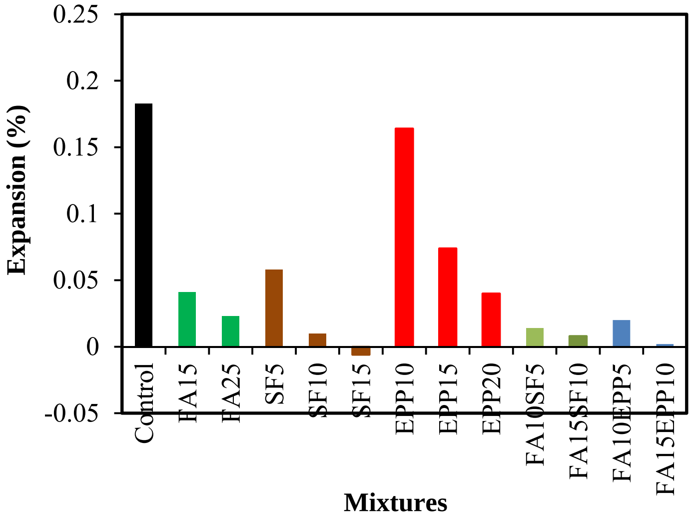


Fig. 4.4 Mortar expansion for FA, SF, and EPP at 24 weeks

4.3.2 Concrete prisms

Fig. 4.5 shows expansion behavior of concrete by using limestone as fine aggregate and combination coarse aggregate between limestone and andesite. In the case of concrete without mineral admixtures, expansion was large and fast from the beginning until the end of days of this period. It can be observed that there is expansion reduction due to usage of FA. The expansion line of concrete with FA25% was lower compared to concrete with FA15%.

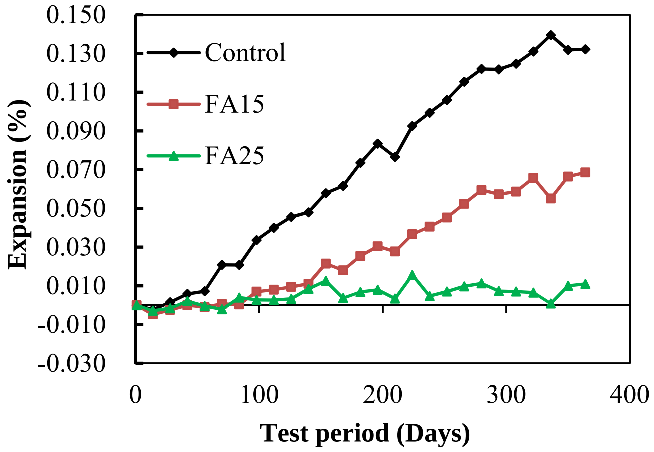


Fig. 4.5 Concrete expansion for FA

Concrete expansion by using silica fume is shown in **Fig. 4.6**. Concrete expansion by using SF showed expansion reduction compared to concrete without SF. The expansion rate of concrete with SF at level 10% was lower than concrete with SF at level 5%, whereas concrete with level 15% of SF was the lowest. Expansion reduction by using SF at level 10% and SF at level 15% are under 0.05% that classified as non-reactive.

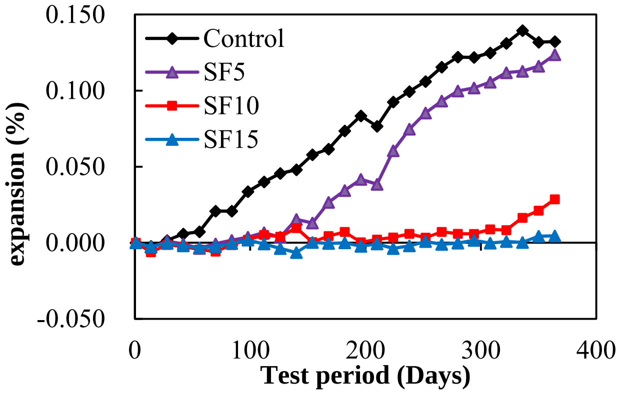


Fig. 4.6 Concrete expansion for SF

Furthermore, **Fig. 4.7** shows expansion behavior of concrete with expanded perlite powder (EPP).

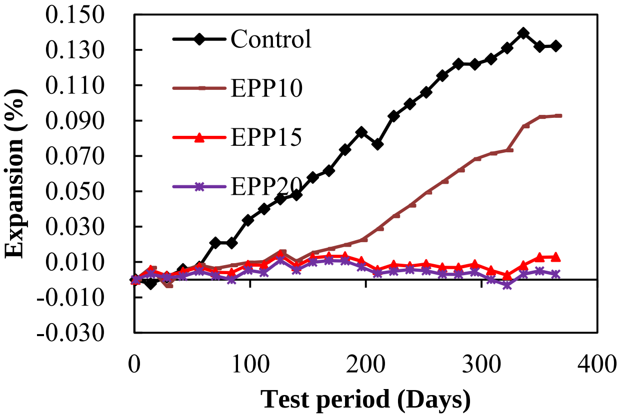


Fig. 4.7 Concrete expansion of Perlite

In case of concrete without EPP, its expansion was large and fast after 50 days. It can be observed that there is expansion reduction due to usage of EPP. Concrete prisms containing EPP at level of 15%, its expansion lower than concrete with EPP at level 10%. Concrete containing 10%, 15%, and 20% of EPP show expansion reduction. Expansion of concrete with EPP at level of 15% is under 0.05% that classified as non-reactive.The comparison of suppressing expansion by using all minerals used in this study can be seen in **Fig. 4.8**.

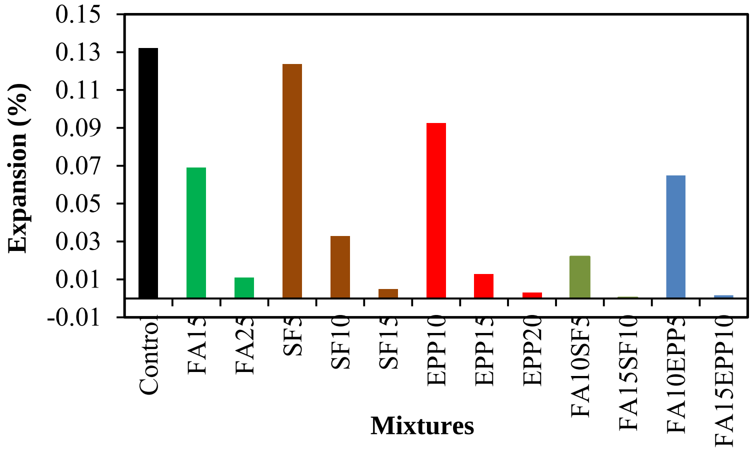


Fig. 4.8 Concrete expansion for FA, SF, and EPP at 1 year

Concrete expansion by using combination of FA with SF and FA with EPP showed expansion reduction compared to concrete with FA. Concrete expansion with combination FA with SF (FA10SF5) and FA with EPP (FA10EPP5) was lower compared to concrete with FA 15%. Then, concrete expansion of FA with SF (FA15SF10) and FA with EPP (FA15EPP10) was lower than concrete with FA 25%. The combination effect of FA with SF and FA with EPP reduce expansion due to alkali-silica reaction are larger than FA. Expansion reduction by using incorporation of FA with SF (FA10SF5, FA15SF10) and FA with EPP (FA10EPP5) are under 0.01% that classified as non-reactive.

4.4 Discussion on the effectiveness of FA, SF, and EPP in reducing expansion

Chemical compositions, such as oxide or lime (CaO), alkalis (Na_2O and K_2O), magnesium oxide (MgO), sulfur trioxide (SO_3), and silicon dioxide (SiO_2) also play an important role in contributing expansion reduction. The content of CaO (calcium oxide or lime) has been shown to have the greatest effect on the efficiency of the ash in mitigating ASR(4.1), (4.2), (4.3). Shehata et al. revealed that the expansion increases the alkali content or the calcium of fly ash increases or silica content of fly ash decreases(4.3).

Dunstan notes that CaO content may be a useful parameter to indicate the effectiveness of an ash to combat alkali silica reaction(4.4). Alkalis (Na_2O and K_2O), sodium and potassium oxides have been grouped together and their content limited, both in the cement and the fly ash. When reactive aggregates are used, it is recommended to use low-alkali cement (alkali content ≤0.6% based on ASTM C 150 (1997)). Alkalis in the cement is 0.587 %. AASHTO M 295 (similar to ASTM C 618 and CSA A23.5) require a 5% MgO limit in the fly ash. Sulfur trioxide (SO_3) is limited to a maximum of 5% in ASTM C 618 for both Class C and F ashes. Silicon dioxide (SiO_2), shows pozzolanic activity, that is, forms a cementitious product by reaction with calcium hydroxide(4.5). Increased contents of SiO_2 have proven to increase the ash effectiveness and lower the expansion.

Fly ash (FA)

It can be seen in Chapter 2 **Table 2.2**, FA has content of CaO = 3.18%. Alkalis content of FA=1.925%. MgO content of FA=1.30% < 5%. SO_3 content of FA=0.49% < 5%. SiO_2 content of FA=54.96%.

Silica fume (SF)

It is presented in Chapter 2 **Table 2.2,** SF has no content of CaO. Alkalis content of SF=0%. MgO content of SF=0.56% < 5%. SO_3 content of SF=0.18% < 5%. SiO_2 content of SF=95.5%.

Expanded Perlite powder (EPP)

It is shown in Chapter 2 **Table 2.2**, EPP has content of CaO=0.75%. Alkalis content of EPP=7.358%. MgO content of EPP=0.14% < 5%. SO_3 content of EPP=0. SiO_2 content of EPP=65.85%.

It can be summarized for all minerals: CaO content of SF=0 < EPP=0.75% < FA=3.18%). Alkalis in the cement is 0.587 %, (Alkalis content of SF=0 < FA=1.925% < EPP=7.358%). MgO content of EPP=0.14% < SF=0.56% < FA=1.30%). SO_3 content of EPP=0 <SF=0.18%

<FA=0.49%). All of minerals that used in this study contained SO_3 less than 5%. SiO_2 content of FA=54.96%< EPP=65.85% <SF=95.5%), SF has SiO_2 content largest of all. When cement is replaced by mineral, it means alkalis will be reduced. It is known that alkalis from cement will react with silica from aggregate. Further, Cement is replaced by FA at the level of 15%, 25%. FA has higher SiO_2 content and lower CaO content than OPC (SiO_2 Content of FA=54.96%<EPP=65.85%<SF=95.5%, and CaO content of SF=0<EPP=0.75%<FA=3.18%). In this study, FA at level 25% is enough to reduce expansion. Then, cement is replaced by SF at the level of 5%, 10%, 15%. SF has higher SiO_2 content and lower CaO content than OPC. In the experiment, SF at level 10% is enough to reduce expansion. Expansion of concrete with SF at level 10% is smaller than FA at level 25%. Furthermore, cement is replaced by EPP at the level of 10%, 15%, and 20%. EPP also has higher SiO_2 content and lower CaO content than OPC. In the experiment, EPP at level 15% is enough to reduce expansion. Expansion of concrete with EPP at level 15% is smaller than FA at level 25%, and EPP at level 15% is larger than SF at level 10%.

Furthermore, cement is replaced by FA in combination with SF (FA10SF5, FA15SF10) and EPP (FA10EPP5, FA15EPP10) at the level of 15%, 25%. It can be seen that when FA at level 15% and 25%, especially expansion line of FA at level 15% is quite large. However, when FA is replaced with 5%, 10% of SF and EPP, The expansion will decrease. It can be explained that additional SiO_2 content from SF and EPP will work in synergy with SiO_2 content from FA to increase ash effectiveness. Combination FA with SF show expansion reduction better than combination of FA with EPP. It might due to SiO_2 content of SF is higher than EPP. The contents of SiO_2 is important component to increase the ash effectiveness and lower the expansion not only in single mineral but also in mineral combination. Calculation SiO_2 ratio in mortar and concrete can be seen in **Table 4.3** and **Fig. 4.10**.

Table 4.3 Calculation SiO_2 ratio in binder in mortar and concrete

Mix	**SiO_2 (%)**				**SiO_2 Ratio in Binder(%)**
	OPC	**FA**	**SF**	**EPP**	
	20.89	54.96	95.5	65.85	
Control	20.89	0.00	0.00	0.00	20.89
FA15	17.76	8.24	0.00	0.00	26.00
FA25	15.67	13.74	0.00	0.00	29.41
SF5	19.85	0.00	4.78	0.00	24.62
SF10	18.80	0.00	9.55	0.00	28.35
SF15	17.76	0.00	14.33	0.00	32.08
EPP10	18.80	0.00	0.00	6.59	25.39
EPP15	17.76	0.00	0.00	9.88	27.63
EPP20	16.71	0.00	0.00	13.17	29.88
FA10SF5	17.76	5.50	4.78	0.00	28.03
FA15SF10	15.67	8.24	9.55	0.00	33.46
FA10EPP5	17.76	5.50	0.00	3.29	26.55
FA15EPP10	15.67	8.24	0.00	6.59	30.50

It can be observed in **Fig. 4.4**, **Fig. 4.8,** and **Fig. 4.9** that the larger the SiO_2 ratio the lower the expansion.

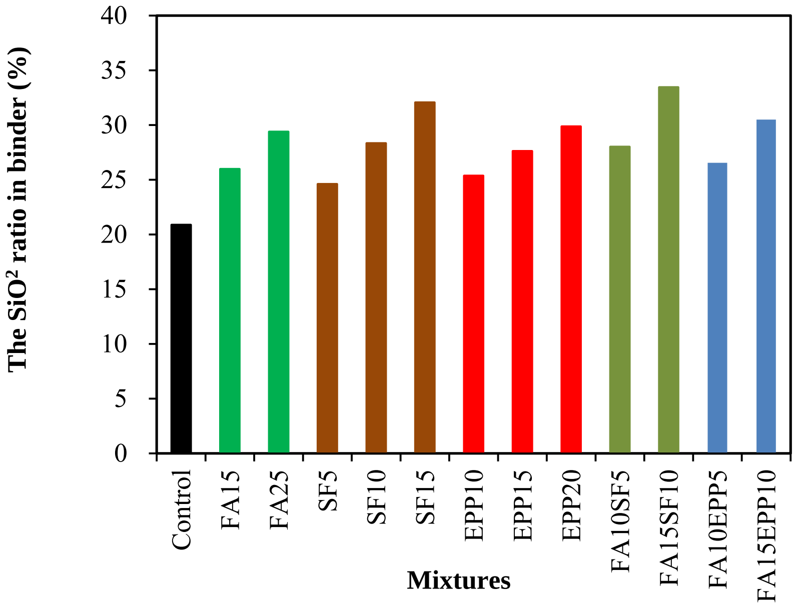


Fig. 4.9 SiO_2 ratio in binder in mortar or concrete

Furthermore, the relationship between SiO_2 ratio in binder and expansion will be shown in **Fig. 4.10** and **Fig. 4.11**. It can be seen that when the content SiO_2 ratio in binder increase, the expansion will decrease. A good correlation is achieved between SiO_2 ratio in binder and expansion in mortar and concrete.

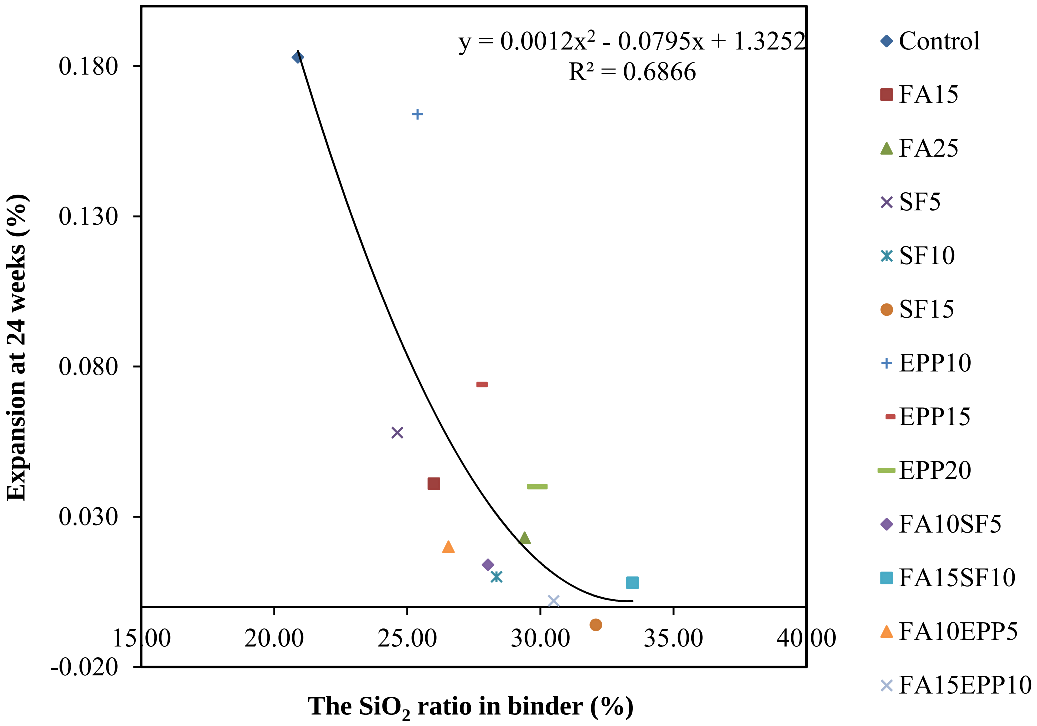


Fig. 4.10 The relationship between SiO_2 ratio in binder and expansion in mortar

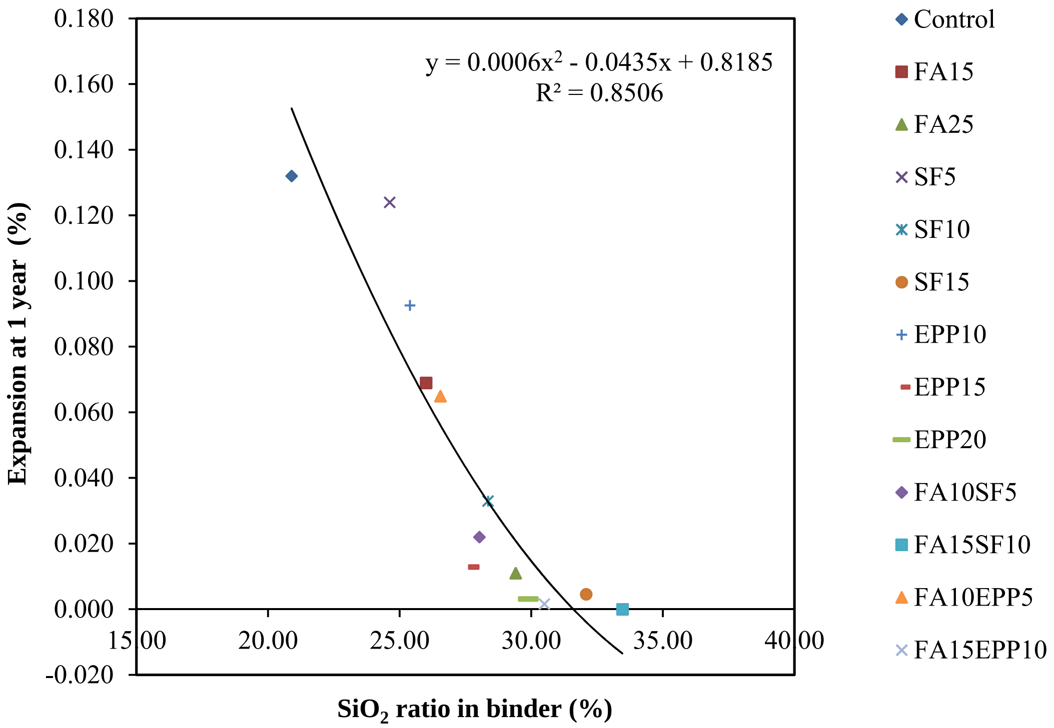


Fig. 4.11 The relationship between SiO_2 ratio in binder and expansion in concrete

Meanwhile, Calculation the amount of SiO_2 in mortar and concrete can be seen in **Table 4.4** and **Table 4.5**, and in **Fig. 4.12** and **Fig. 4.13.**

Table 4.4 Calculation the amount of SiO_2 in mortar

Mix	**Water**	**OPC**	**FA**	**SF**	**EPP**	**OPC**	**FA**	**SF**	**EPP**	**Total SiO_2 (g/l)**	**Expansion (%)**
	(g/l)					**20.89%**	**54.96%**	**95.50%**	**65.85%**		
Control	300	600	0	0	0	39.66	0.00	0.00	0.00	39.66	0.183
FA15	300	510	90	0	0	33.71	21.89	0.00	0.00	55.60	0.041
FA25	300	450	150	0	0	29.75	36.48	0.00	0.00	66.23	0.023
SF5	300	570	0	30	0	37.68	0.00	12.19	0.00	49.87	0.058
SF10	300	540	0	60	0	35.70	0.00	24.38	0.00	60.08	0.010
SF15	300	510	0	90	0	33.71	0.00	36.57	0.00	70.29	-0.006
EPP10	300	540	0	0	60	35.70	0.00	0.00	15.31	51.01	0.164
EPP15	300	510	0	0	90	33.71	0.00	0.00	22.97	56.69	0.074
EPP20	300	480	0	0	120	31.73	0.00	0.00	30.63	62.36	0.040
FA10SF5	300	510	60	30	0	33.71	14.59	12.19	0.00	60.50	0.014
FA15SF10	300	450	90	60	0	29.75	21.89	24.38	0.00	76.02	0.008
FA10EPP5	300	510	60	0	30	33.71	14.59	0.00	7.66	55.96	0.020
FA15EPP10	300	450	90	0	60	29.75	21.89	0.00	15.31	66.95	0.002

Table 4.5 Calculation the amount of SiO_2 in concrete

Mix	**Water**	**OPC**	**FA**	**SF**	**EPP**	**OPC**	**FA**	**SF**	**EPP**	**Total SiO_2** (kg/m³)	**Expansion** (%)
	(kg/**m³**)					20.89%	54.96%	95.50%	65.85%		
Control	160	320	0	0	0	66.85	0.00	0.00	0.00	66.85	0.132
FA15	160	272	48	0	0	56.82	26.38	0.00	0.00	83.20	0.069
FA25	160	240	80	0	0	50.14	43.97	0.00	0.00	94.10	0.011
SF5	160	304	0	16	0	63.51	0.00	15.28	0.00	78.79	0.124
SF10	160	288	0	32	0	60.16	0.00	30.56	0.00	90.72	0.033
SF15	160	272	0	48	0	56.82	0.00	45.84	0.00	102.66	0.005
EPP10	160	288	0	0	32	60.16	0.00	0.00	21.07	81.24	0.093
EPP15	160	272	0	0	48	56.82	0.00	0.00	31.61	88.43	0.013
EPP20	160	256	0	0	64	53.48	0.00	0.00	42.14	95.62	0.003
FA10SF5	160	272	32	16	0	56.82	17.59	15.28	0.00	89.69	0.022
FA15SF10	160	240	48	32	0	50.14	26.38	30.56	0.00	107.08	0.000
FA10EPP5	160	272	32	0	16	56.82	17.59	0.00	10.54	84.94	0.065
FA15EPP10	160	240	48	0	32	50.14	26.38	0.00	21.07	97.59	0.002

It can be observed in **Fig. 4.4, Fig. 4.8,** and **Fig. 4.12** then **Fig. 4.13** that the larger the amount of SiO_2 the lower the expansion.

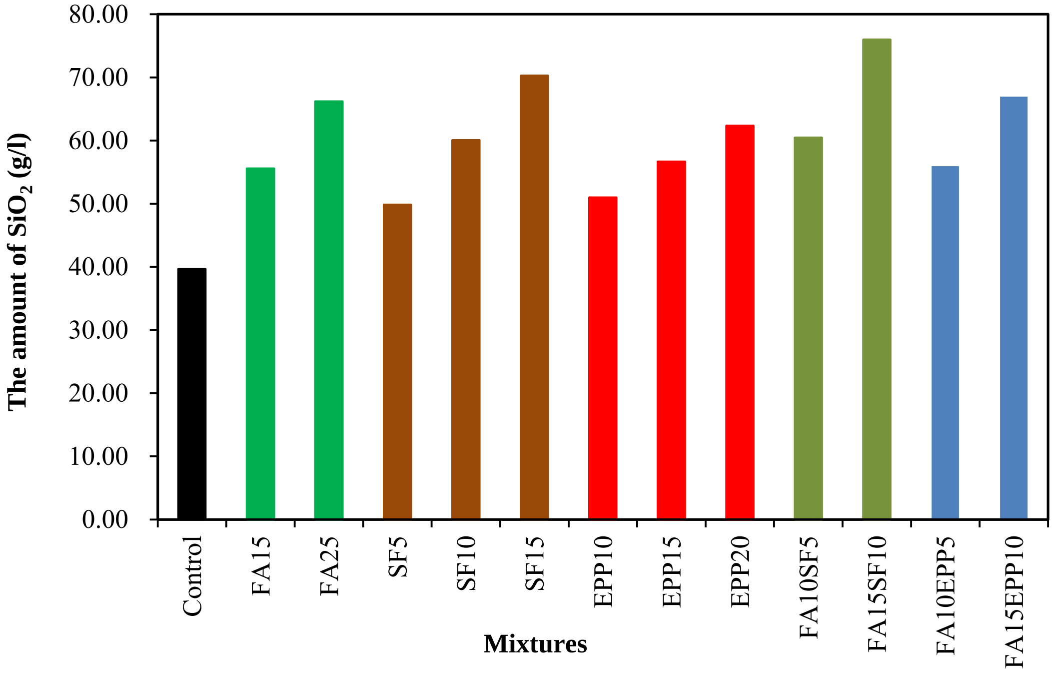


Fig. 4.12 The amount of SiO_2 in mortar

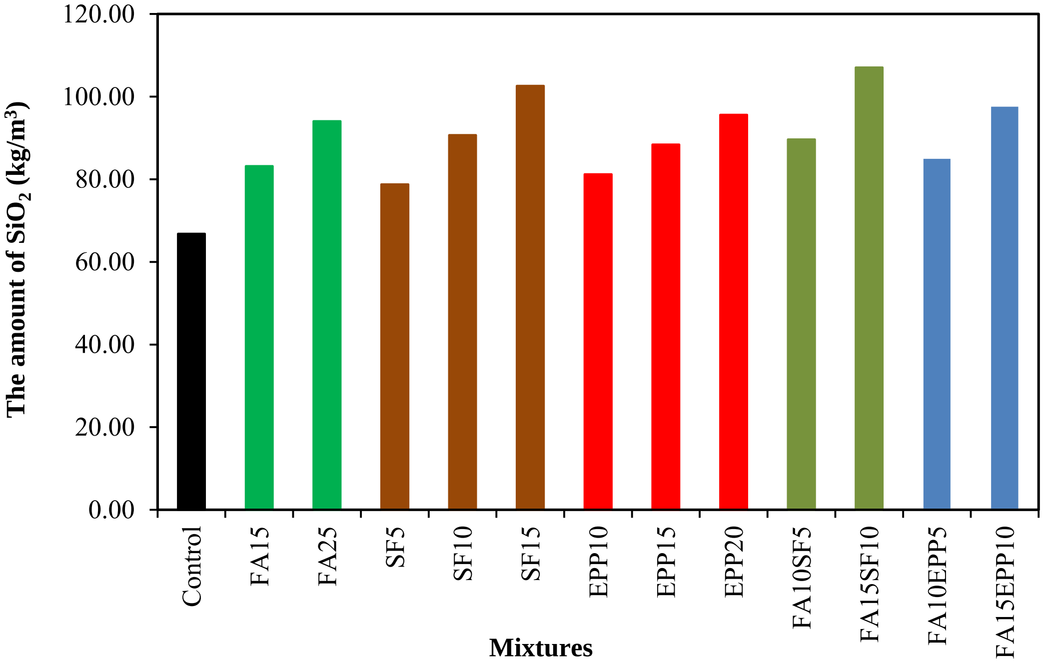


Fig. 4.13 The amount of SiO_2 in concrete

Furthermore, the relationship between the amount of SiO_2 and expansion will be shown in **Fig. 4.14** and **Fig. 4.15**. It can be seen that when the amount of SiO_2 increase, the expansion will decrease. A good correlation is achieved between the amount of SiO_2 and expansion in mortar and concrete.

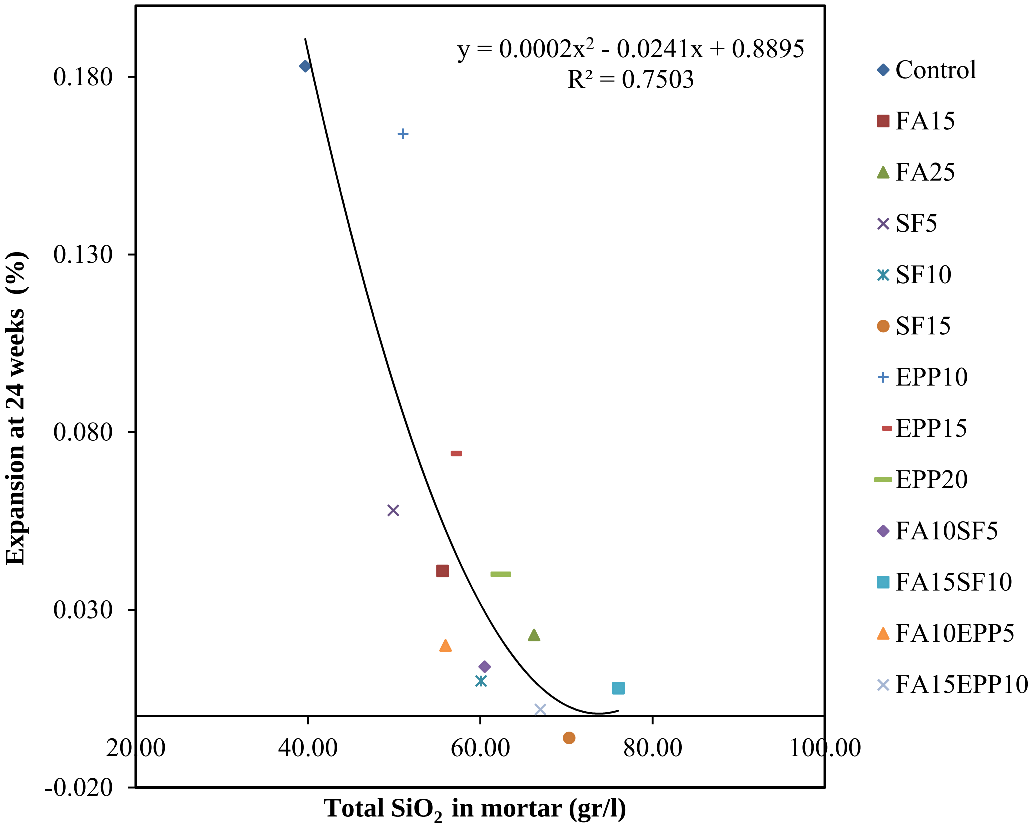


Fig. 4.14 The relationship between the amount of SiO_2 and expansion in mortar

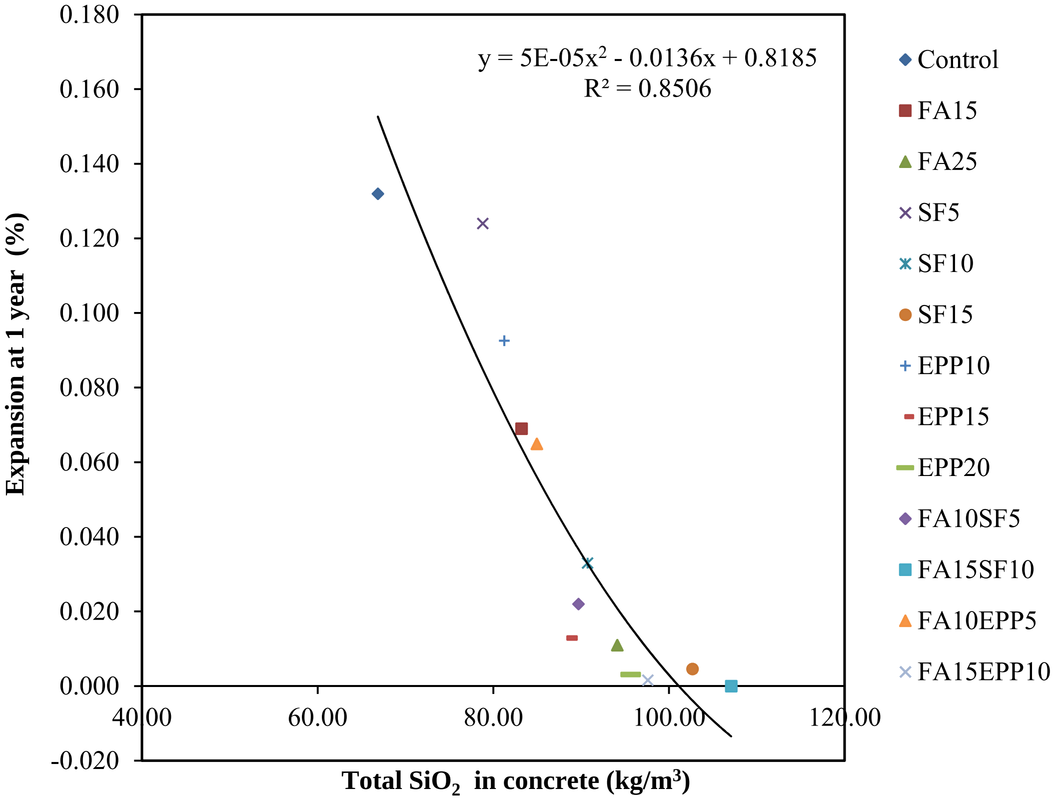


Fig. 4.15 The relationship between the amount of SiO_2 and expansion in concrete

Summary of expansion results for single and mineral combination can be seen in **Table 4.6** and **Table 4.7**.

Table 4.6 Expansion results for concrete FA with SF

Control	**FA (%)**		**SF (%)**			**FA10SF5**	**FA15SF10**
	15	**25**	**5**	**10**	**15**		
0.132	0.069	0.011	0.124	0.025	0.005	0.022	0.000

Table 4.7 Expansion results for concrete FA with EPP

Control	**FA (%)**		**EPP (%)**			**FA10EPP5**	**FA15EPP10**
	15	**25**	**10**	**15**	**20**		
0.132	0.069	0.011	0.919	0.013	0.005	0.055	0.002

The other researchers have mentioned the effectiveness of minerals in reducing expansion due to ASR, such as: J. Malvar et al. mentioned that finer pozzolans are efficient in mitigating ASR. Fineness of fly ash or minerals is one of the most important physical properties affecting pozzolanic activity(4.6). J. Malvar et al. mentioned that finer pozzolans are efficient in mitigating ASR. Particle size of SF is approximately 0.1 μm is also very effective in preventing ASR.

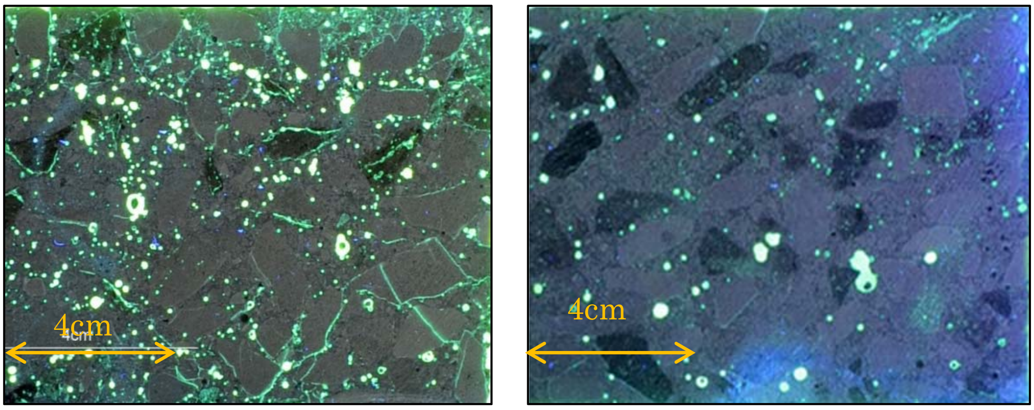
The mechanism of ASR by supplementary cementitious materials (SCMs) relates to the following factors: reduction in alkalinity of pore solution, consumption of calcium hydroxide, low permeability. The amount and composition of C-S-H gel were affected by SCM's type and amount. The additional of SCM lead to C-S-H gel formation with low Ca/Si ratio, result in lower alkali concentrations and hydroxide ion in the pore solution. Calcium hydroxide is consumed in SCMs reaction. The amount of C-(A)-S-H gel is increased by this reaction, result in low permeability due to cement paste densification. OPC replacement by SCMs reduced alkali and hydroxide ion. This mechanism is attributed to cement dilution, portlandite consumption and alkali sorption by C-S-H gel with low Ca/Si. One of the mechanisms of mineral admixtures, e.g. FA to suppress expansion by lowering alkali concentration and hydroxide ion in the pore solution. When an appropriate amount of mineral admixtures was added, lead to the formation of C-S-H gel with low Ca/Si ratio. As a result, alkali concentrations and hydroxide ion become low (4.7),(4.8). FA combines with alkalis from cement that react with silica from aggregate, thereby expansion is prevented. Total alkali content of blended cement is increased due to the replacement of cement by FA. However, FA particles do not release alkalis; alkalis apparently stored in a hydrated product resulting from the reaction of pozzolan. Furthermore, N Tenoutasse mentioned that: FA have had the ability to absorb alkalis when react chemically with the alkali hydroxide in Portland cement paste, thus making alkalis not available for reaction with silica in certain aggregates(4. 9).

A number of researchers have shown SF effectively by its high pozzolanic activity. Further, SF is a reactive pozzolanic material because of high amorphous silicon dioxide content and its fineness. One or a combination of these factors, such as consumption of calcium hydroxide, ionic mobility was reduced due to refined pore structure, and binding of alkalis into pozzolanic calcium silicate hydrates. These factors are pozzolanic effect in mitigating ASR. SF reacts with calcium hydroxide ($Ca(OH)_2$) to form additional Calcium Silica Hydrate (C-S-H), which is similar to the calcium hydrate formed from the Portland cement. The pozzolanic reaction product (secondary C-S-H) can incorporate alkali metal ions into their structure and alkalinity of the pore solution is reduced. At the same time, the adjacent pores are filled by secondary C-S-H hydrates and reduce the permeability of concrete, consequently, reducing the alkali ions free movement (George 1995)(4.10). Tanaka, Y., et al. concluded that the significant amount of both alkali and hydroxide ions were consumed by additives in ion analysis of pore fluid(4.11). Furthermore, the reduction in alkali concentration of pore fluid was the principal of minerals suppression mechanism(4.11). Shehata et al. also showed that pastes containing SF increased alkalinity at ages beyond 28 days, while pastes containing ternary blends maintained the low alkalinity of the pore solution throughout 3 years testing period. The presence of both FA and SF results in low pore solution alkalinity at early and late ages. SF is effective in reducing alkalinity at an early age, meanwhile FA become effective at later ages(4.12).

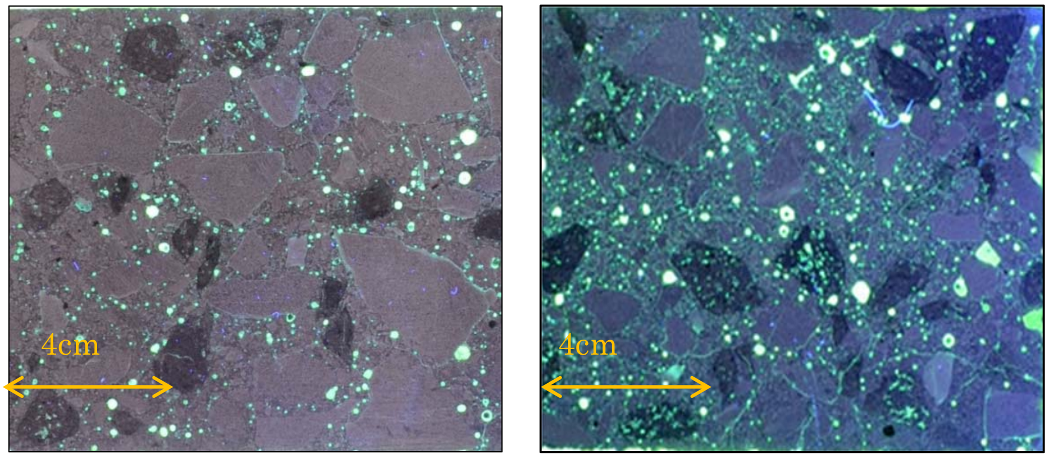
The effectiveness of EPP in mitigating ASR can be attributed to pozzolanic activity, possessed by the material(4.13), 4.14). Pozzolanic might be due to the binding of alkalis onto perlite. In suppressing expansion, the porous nature of EPP might play an important role by providing a distributed air bubble system that accommodates expansive gel in concrete(4.14). Bond strength enhancement between lightweight expanded perlite and cement matrix is due to perlite pozzolanic activity(4.15). Furthermore, G.E. Cristidis et al. reported that capable of sodium absorption or possess binding alkalis property are as a basis for pozzolanic activity of Perlite (4.16).

4.5 Inner Crack

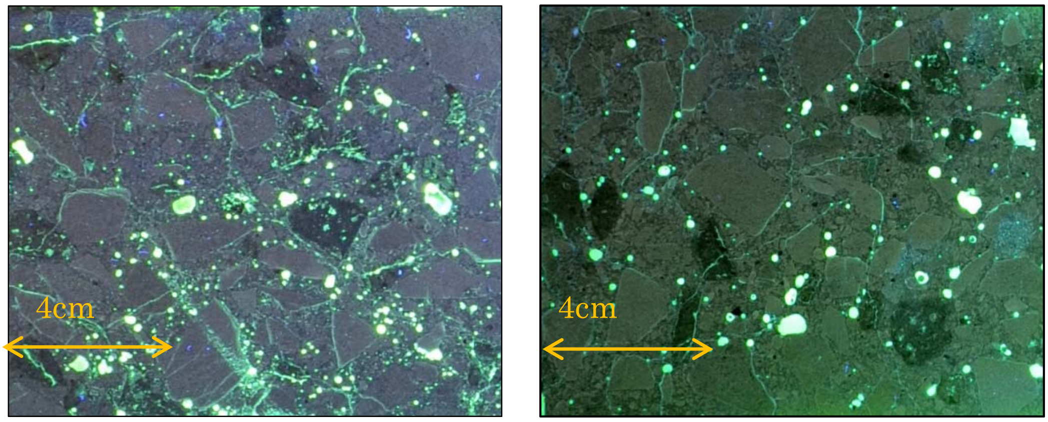
Inner crack was observed after completing the measurement. Pictures of inner crack can be seen in **Photo 4.1**. Prisms were sliced into two pieces in longitudinal direction after removing the plugs from both ends. Then, prisms were placed in vacuum box in order epoxy resin filled the voids and cracks. Then, let the specimen for a while in order the epoxy harden. Furthermore, the specimen was grinded to remove excessive hardened epoxy. Moreover, the photo can be taken.



(a) Control (b) FA25



(c) FA10SF5 (d) SF10



(e) EPP10 (f) FA10EPP5

Photo 4.1 Observion of inner crack of concrete after expansion test

It can be seen that there are a lot of cracks in control concrete. Cracks line can be observed easily. However, there is crack line reduction due to usage of minerals such as FA, SF, EPP and a combination of them. Cracks still occurred in concrete with SF at a level 10 %, EPP10 and cracks less occur on concrete with combination FA with SF, and FA with EPP.

4.6 Summary

1. The contents of SiO_2 is important component to increase the ash effectiveness and lower the expansion not only in single mineral but also in mineral combination.
2. Mixture proportions of concrete FA10SF5, FA15SF10, FA15EPP10 have a good performance in reducing expansion.
3. Mixture proportion of concrete FA10SF5 is more economical than mixture proportions of concretes FA15SF10, FA15EPP10 due to usage small amount of SF.

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CHAPTER 5. THE EFFECTIVENESS OF LITHIUM HYDROXIDE MONOHYDRATE ($LiOH^{.}H_2O$)

5.1 Introduction

Lithium compounds were used to reduce expansion for the first time by Mc Coy (5.1). In addition, a new method has been developed by Craig W. Hargis et al. that made an effort to limit ASR in: aggregate passivation(5.2). A lithium silicate layer was created on reactive natural siliceous aggregate surfaces by treating the aggregates in a lithium hydroxide solution prior to use. Their studies showed that the usage of passivated aggregates greatly reduced expansion in accelerated mortar bar tests compared to non-passivated aggregates. When aggregates were soaked, $LiOH^{.}H_2O$ solution reacted with the aggregates and retained in the pore of the aggregates (5.2). Furthermore, Lu et al. investigated that on the aggregate surfaces, the formation of lithium silicate and lithium carbonate were observed after soaking the aggregates in 1.8 M LiOH at 150 ^{o}C for 150 hours(5.3). However, the usage of lithium hydroxide in concrete is not clarified well. This study is intended to find out the effect of $LiOH^{.}H_2O$ as chemical admixtures, and this study is conducted in efforts to reduce alkali-silica reaction that focus on the usage of $LiOH^{.}H_2O$ in new concrete. The reactive aggregates will be treated by using this chemical solution. Firstly, $LiOH^{.}H_2O$ will be used to create a lithium silicate layer by immersing the coarse reactive aggregates in $LiOH^{.}H_2O$ solution prior to use. Secondly, coarse reactive aggregates is coated with cement paste (w/c=0.5) containing $LiOH^{.}H_2O$. Then, thirdly: combination step one and step two, the reactive aggregates were covered with cement paste (w/c=0.5) containing $LiOH^{.}H_2O$ then immersed in $LiOH^{.}H_2O$ solution. Futhermore, $LiOH^{.}H_2O$ is also used in mortar to create a lithium silicate layer by treating the fine reactive aggregates in a $LiOH^{.}H_2O$ solution prior to use.

The treatment of reactive aggregates will be combined with non reactive aggregates in pessimum ratio 30:70 between reactive and non-reactive. Previous study showed that maximum expansion was happened when aggregate ratio was used in this ratio(5.4). As a result, mortar bars and concrete prisms were made to investigate the effectiveness of $LiOH^{.}H_2O$. Mortar bars were made based on JIS A 1146 and concrete prisms were cast based on RILEM AAR-3. Mortar specimens for expansion measurement were treated at 40^{o}C, and R.H. 100% of controlled room. Meanwhile, concrete specimens were stored at 40^{o}C, and R.H. 100% of controlled room, except compressive strength specimens were cured at 20^{o}C, R.H. 60% of controlled room.

5.2 Material and mixture proportions

5.2.1 Material

In this study, ordinary Portland Cement (OPC) was used as a binder. OPC meet the requirements of JIS R 5202. Chemical compositions of cement were shown in **Table 5.1**.

Table 5.1 Chemical compositions of cement

Constituents	OPC
SiO_2, %	20.89
MgO, %	0.92
SO_3, %	2.02
Na_2O, %	0.35
K_2O, %	0.36
LoI,%	1.87

Meanwhile, the physical properties of materials are presented in **Table 5.2**. Two aggregates are used in this experiment; one is classified as alkali silica reactive (andesite) and the other is classified as non-reactive (limestone).

Table 5.2 Physical properties of materials

Material	Description
Cement, OPC	Density = 3.16 g/cm^3, Specific Surface Area = 3330 cm^2/g
Fine aggregates (Limestone)	Density (SSD) = 2.70 g/cm^3, Water absorption = 0.61%, Rc = 8 mmol/l. Sc = 1 mmol/l.
Coarse aggregates (Andesite-1)	Density (SSD) = 2.60 g/cm^3, Water absorption = 2.75%, Rc = 185 mmol/l. Sc = 620 mmol/l.
Coarse aggregates (Limestone)	Density (SSD) = 2.70 g/cm^3, Water absorption =0.55%, Rc = 8 mmol/l. Sc = 1 mmol/l.
Coarse aggregates (Andesite-2)	Density (SSD) = 2.68 g/cm^3, Water absorption = 2.75%, Rc = - mmol/l. Sc = - mmol/l.

5.2.2 Aggregates treatment

Treatment of reactive aggregates can be seen in **Table 5.3** and **Table 5.4**.

Table 5.3 Treatment for reactive aggregates

Mix	Treatment
L0	No treatment
L1	Immersed in $LiOH \cdot H_2O$ solution (3M or 4M)
L2	Coated by cement paste containing $LiOH \cdot H_2O$ (3M or 4M)
L3	Paste coated and immersed in $LiOH \cdot H_2O$ (3M or 4M)

Table 5.4 Summary of reactive aggregates treatment

Temperature in oven	Immerse (Days)	Andesite-1	Andesite-2	
		4M	3M	4M
80^oC	5	(L1,L2,L3)	-	-
	10	-	-	(L1-b,L2-b,L3-b)
40^oC	5	-	(L1-a,L2-a,L3-a)	-
	10	-	-	-

5.2.3 Mixture proportions

This study presents experimental results of mortar and concrete. Mortar bars were made based on JIS A 1146. Coarse aggregates were crushed into fine aggregates that matches requirement of particle size distribution in JIS A 1146. Crushed reactive aggregates were immersed in $LiOH^{\cdot}H_2O$ solution in sealed stainless container, and place them in oven. Before soaking the aggregates, 500 ml of $LiOH^{\cdot}H_2O$ solution was prepared for each 900 g of reactive aggregates.

Furthermore, aggregates and solution were allowed to cool to room temperature after removing from the oven. Then, aggregates were kept in a sealed plastic bucket in SSD condition. Water to cement ratio of mortar was adjusted to 0.50 and alkali content was set (Na_2Oeq of cement) to 1.2 wt% by adding NaOH solution to the mixing water. Mixture proportions of mortar are shown in **Table 5.5**.

Table 5.5 Mixture proportions of mortar

No.	Description	w/c (%)	Water+ NaOH (g)	OPC (g)	Aggregates (g)		NaOH (ml)
					Non reactive	reactive	
1	L0	50	300	600	945	405	120
2	L1	50	300	600	945	405	120
3	L0-a	50	300	600	945	405	120
4	L1-a	50	300	600	945	405	120
5	L1-b	50	300	600	945	405	120

Meanwhile, concrete prisms were cast based on RILEM AAR-3. Mixture proportions of concrete are shown in **Table 5.6**. Some concrete mixtures with water binder ratio 0.5 were prepared by using tap water. L0 was made for control. L1, reactive aggregates were immersed in 4M of $LiOH^{\cdot}H_2O$ solution in a sealed stainless container. Then, reactive aggregates were placed inside oven at temperature 80^oC for 5 days. Before soaking the aggregates, 500 ml of $LiOH^{\cdot}H_2O$ solution was prepared for each 900 g of reactive aggregates. Furthermore, aggregates and solution were allowed to cool to room temperature after removing from the oven. Then, aggregates were kept in a sealed plastic bucket in SSD condition. L2, reactive aggregates were covered with cement paste (w/c=0.5) containing 4M of $LiOH^{\cdot}H_2O$. Before covering aggregates with cement paste (w/c=0.5) containing 4M of $LiOH^{\cdot}H_2O$ solution, the aggregates were in dry condition. L3, reactive aggregates were treated by combining cement paste (w/c=0.5) containing 4M of $LiOH^{\cdot}H_2O$ and immersing in 4M of $LiOH^{\cdot}H_2O$ solution in a sealed stainless container. Then, reactive aggregates were placed inside oven at temperature 80^oC for 5 days. Mixtures L0 until L3 used andesite-1 contain crystobalite as reactive aggregates.

Table 5.6 Mixture proportions of concrete

Mix	w/b (%)	s/a (%)	kg/m^3					g/m^3		Temp. (^{o}C)	Slump (mm)	Air Content (%)
			Water	OPC	Sand	Gravel	NaOH	AE+WR	AE			
L0	50	45	160	320	843	992	5.347	1000	12.8	19.0	80	5.0
L1	50	45	160	320	843	992	5.347	1000	12.8	19.0	80	5.0
L2	50	45	160	320	843	992	5.347	1000	12.8	20.5	85	3.3
L3	50	45	160	320	843	992	5.347	1000	12.8	20.0	85	4.1
L0-a	50	45	160	320	843	1023	5.347	1200	12.8	19.5	70	4.0
L1-a	50	45	160	320	843	1023	5.347	1200	12.8	19.5	70	5.0
L2-a	50	45	160	320	843	1023	5.347	1200	12.8	20.5	75	3.3
L3-a	50	45	160	320	843	1023	5.347	1200	12.8	20.0	75	4.1
L0-b	50	45	160	320	843	1023	5.347	1200	12.8	19.5	70	4.0
L1-b	50	45	160	320	843	1023	5.347	1200	12.8	19.0	68	4.9
L2-b	50	45	160	320	843	1023	5.347	1200	12.8	20.0	69	3.1
L3-b	50	45	160	320	843	1023	5.347	1200	12.8	20.0	69	3.6

(WR+AE) = water reducing and air entraining agent, AE=air entrain agent

Pictures of reactive aggregates (andesite-1) can be seen in **Photo 5.1** and **Photo 5.2**.

Photo 5.1 Covering reactive aggregates with cement paste w/c= 0.5

Photo 5.2 Reactive aggregates were immersed in $LiOH^{\cdot}H_2O$ solution

The other mixtures (L0-a, L1-a, L2-a, L3-a, L0-b, L1-b, L2-b, L3-b) used andesite-2 as reactive coarse aggregates. These aggregates contain opal. For mixtures L0-a, L1-a, L2-a, and L3-a used 3M of $LiOH^{\cdot}H_2O$ and place in oven at temperature 40^{o}C for 5 days. L0-a was made for control, no treatment for reactive aggregates. (L1-a), reactive aggregates were immersed in

3M of $LiOH \cdot H_2O$ solution in a sealed stainless container. Then, reactive aggregates were placed inside oven at temperature 40^{o}C for 5 days. Before soaking the aggregates, 500 ml of $LiOH \cdot H_2O$ solution was prepared for each 900 g of reactive aggregates. Furthermore, aggregates and solution were allowed to cool to room temperature after removing from the oven. Then, aggregates were kept in a sealed plastic bucket in SSD condition. L2-a, reactive aggregates were covered with cement paste (w/c=0.5) containing 3M of $LiOH \cdot H_2O$. Before covering aggregates with cement paste (w/c=0.5) containing 3M of $LiOH \cdot H_2O$ solution, the aggregates were in dry condition. L3-a, reactive aggregates were treated by combining cement paste (w/c=0.5) containing 3M of $LiOH \cdot H_2O$ and immersing in 3M of $LiOH \cdot H_2O$ solution in a sealed stainless container. Then reactive aggregates were placed inside oven at temperature 40^{o}C for 5 days. Further, L1-b, L2-b, L3-b used 4M of $LiOH \cdot H_2O$ and cured in controlled room 80^{o}C for 10 days. These symbol L1, L1-a, L1-b, L2, L2-a, L2b, L3, L3-a, L3-b states same treatment for the reactive aggregates. Total alkali in concrete was 6 kg/m^3. By enlarging alkali content until 6 kg/m^3 in concrete, it would be easy to observe and study the expansion behavior because the expansion would be high.

5.2.4 Titration test procedure

Titration test was conducted to find out content of lithium in aggregates and solution during immersing, and to determine effective immersing period. Samples of fine aggregates: coarse aggregates were crushed and graded to have distribution as specified in JIS A 1146 (Mortar bar test). Samples of coarse aggregates: maximum size is: 2 cm. Pictures of titration test can be seen in **Photo 5.3**.

(a) Immersing in oven (b) aggregates filtering (c) Titration test

Photo 5.3 Procedure of titration test

Test procedure: 1) 45 g of aggregates and 25 ml of 3M & 4M of $LiOH \cdot H_2O$ solution (hereinafter, "LiOH") was placed and soaked in sealed HDPE bottle and place inside oven at 40^{O}C & 80^{O}C. 2) The bottle was removed from oven at day 1, 2, 3, 4, 5, 7, 10 days. After the removal, the aggregates and solution was allowed to cool to room temperature. 3) Then, the aggregates and solution are filtered under vacuum, and the filtrate collected. During the filtering process, deionized water was used to rinse the aggregates and HDPE bottle. 4) After filtrating, total solution was 200 ml (25 ml of $LiOH\cdot H_2O$ solution + rinse water), 5) Then, 0.8 ml solution was taken from step number 4. Further, deionized water was added to 0.8 ml up to 20 ml. Furthermore, the sample was ready to be titrated against potassium hydrogen phthalate (KHP) to determine the concentration of the $LiOH\cdot H_2O$ in the aggregates. 6) $LiOH\cdot H_2O$ solution was also examined (blank test). 7) Aggregates and solution were visually inspected.

5.3 Experimental results

5.3.1 Expansion test

The expansion behavior of mortar is shown in **Fig. 5.1** and **Fig. 5.2**. In the case of mortar without treating reactive aggregates with $LiOH\cdot H_2O$, expansion was large and fast from the beginning until the end of the period (L0 and L0-a). It can be observed that there was expansion reduction due to usage of $LiOH\cdot H_2O$. The expansion of mortar L1, L1-a, and L1-b was lower compared to mortar expansion for control. Mortar expansion reduction by immersing reactive aggregates with $LiOH\cdot H_2O$ was under 0.1%, that classified as innocuous.

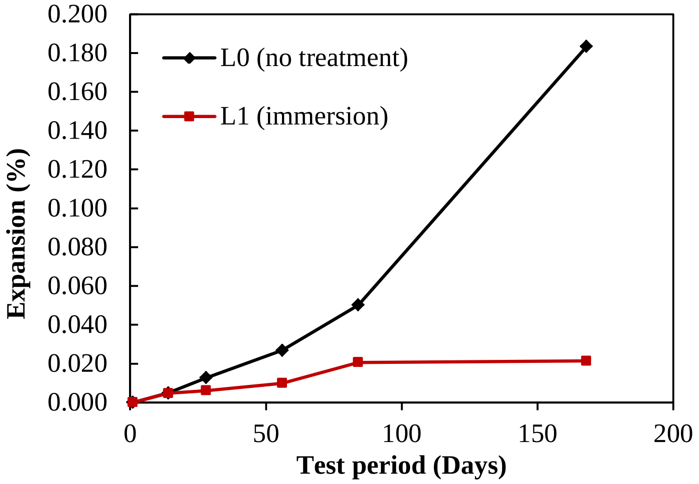

Fig. 5.1 Test results of mortar bar test (JIS A 1146) with Andesite-1

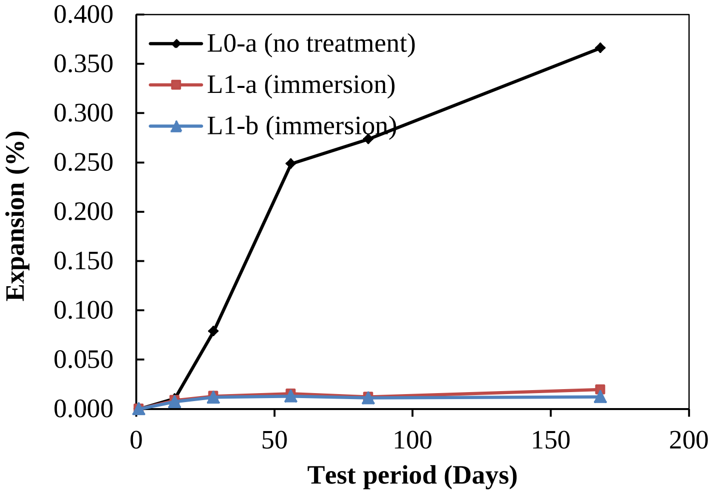

Fig. 5.2 Test results of mortar bar test (JIS A 1146) with Andesite-2

Furthermore, **Fig. 5.3** shows expansion behavior of concrete by using limestone as fine aggregates and combines coarse aggregates between limestone and andesite-1.

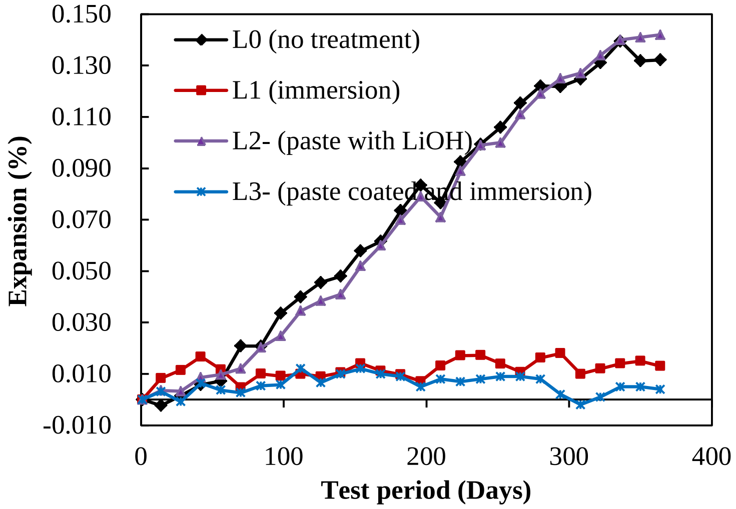

Fig. 5.3 Concrete expansion with Andesite-1

In case of concrete without treating reactive aggregates with $LiOH^{\cdot}H_2O$, expansion was large and fast from the beginning until the end of the period. Expansion of concrete L2 was almost same with control (L0). It seems that there was no effect of covering reactive aggregates with cement paste containing $LiOH^{\cdot}H_2O$. Covering reactive aggregates with cement paste can not avoid the silica in aggregate to react with alkali. It seems that $LiOH^{\cdot}H_2O$ in the cement paste can not decrease the amount of solubility silica.

However, It can be observed that there was expansion reduction due to usage of $LiOH^{\cdot}H_2O$, especially when reactive aggregates were immersed in $LiOH^{\cdot}H_2O$ solution (L1) and reactive aggregates were covered with cement paste and immersed in $LiOH^{\cdot}H_2O$ solution (L3). The expansion of concrete with L1 and L3 was lower than control concrete (L0) and concrete with L2. Expansion reduction of concrete L1 and L3 were under 0.05%, that classified as non-reactive. Further, **Figure 5.4** and **Figure 5.5** show expansion behavior of concrete by using limestone as fine aggregates and combines coarse aggregates between limestone and andesite-2.

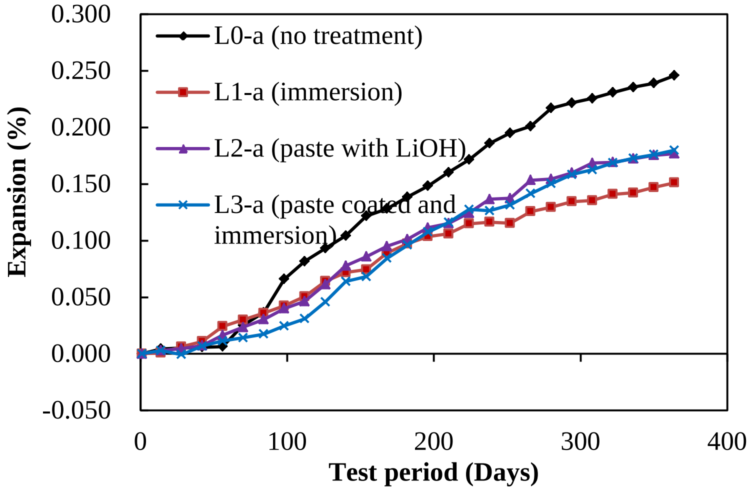

Fig. 5.4 Concrete expansion with Andesite-2 (3M,40°C, 5 days)

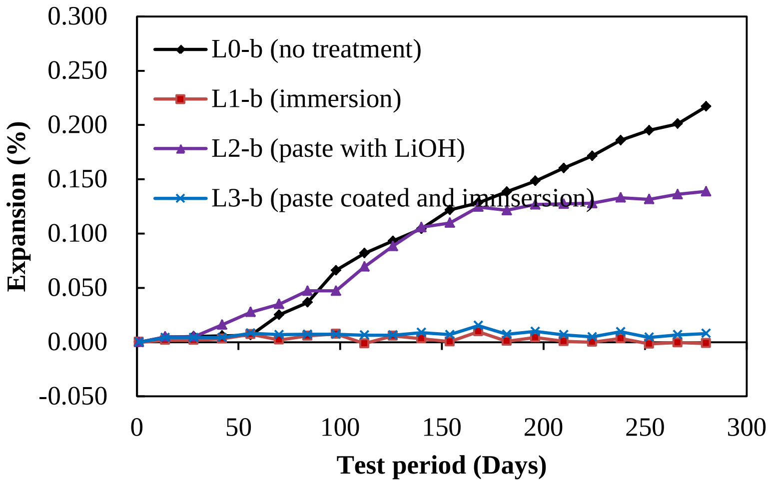

Fig. 5.5 Concrete expansion with Andesite-2 (4M, 80^{o}C, 10 days)

Expansion was large and fast from the beginning until end of the period for control concrete (L0-a). It can be observed that treatment of opal used 3M of $LiOH^{.}H_2O$, controlled room at 40^{o}C for 5 days, L1-a, L2-a, L3-a were not enough to reduce expansion. However, when opal were treated used 4M of $LiOH^{.}H_2O$, controlled room at 80^{o}C for 10 days. There were expansion reduction (L1-b, L2-b, L3-b).

5.3.2 Titration test

The results of titration test can be seen in **Fig. 5.6** to **Fig. 5.8**. Titration results of coarse and fine aggregates of andesite-1 can be seen in **Fig. 5.6**.

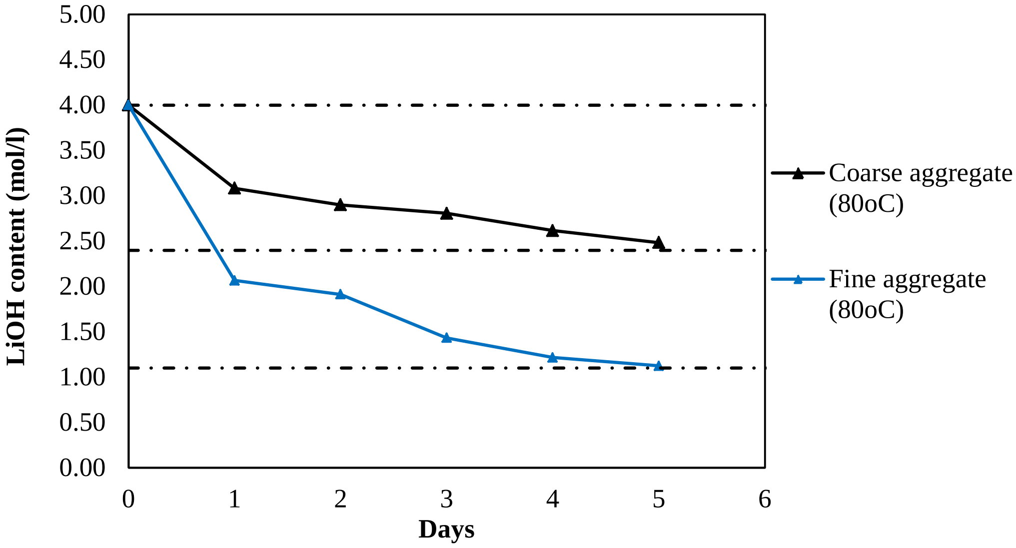

Fig. 5.6 Aggregates immersion in 4M of $LiOH^{.}H_2O$ (Andesite-1) for 5 days

Coarse aggregates absorbed $LiOH^{.}H_2O$ about 1.52 mol/l and Fine aggregates absorbed $LiOH^{.}H_2O$ about 2.87 mol/l. Fine aggregates absorbed $LiOH^{.}H_2O$ larger than coarse aggregate. Then, the results of titration test of andesite-2 immersed in 4M of $LiOH^{.}H_2O$ can be seen in **Fig. 5.7**.

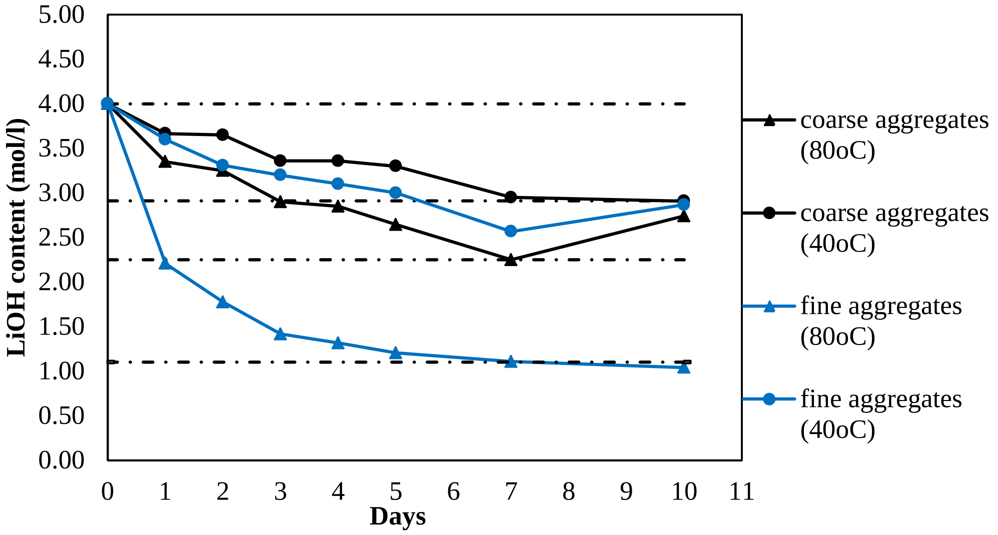

Fig. 5.7 Aggregates immersion in 4M of $LiOH^{\cdot}H_2O$ (Andesite-2) for 10 days

When aggregates were immsersed in 4M of $LiOH^{\cdot}H_2O$ solution, coarse aggregate absorbed $LiOH^{\cdot}H_2O$ about 1.75 mol/l at day 7 at 80^o C & absorbed about 1.09 mol/l at 40^o C. Meanwhile, fine aggregates absorbed $LiOH^{\cdot}H_2O$ about 2.89 mol/l at day 7 at 80^oC & absorbed about 1.43 mol/l at 40^o C. Furthermore, the results of titration test of andesite-2 immersed in 3M of $LiOH^{\cdot}H_2O$ can be seen in **Fig. 5.8**.

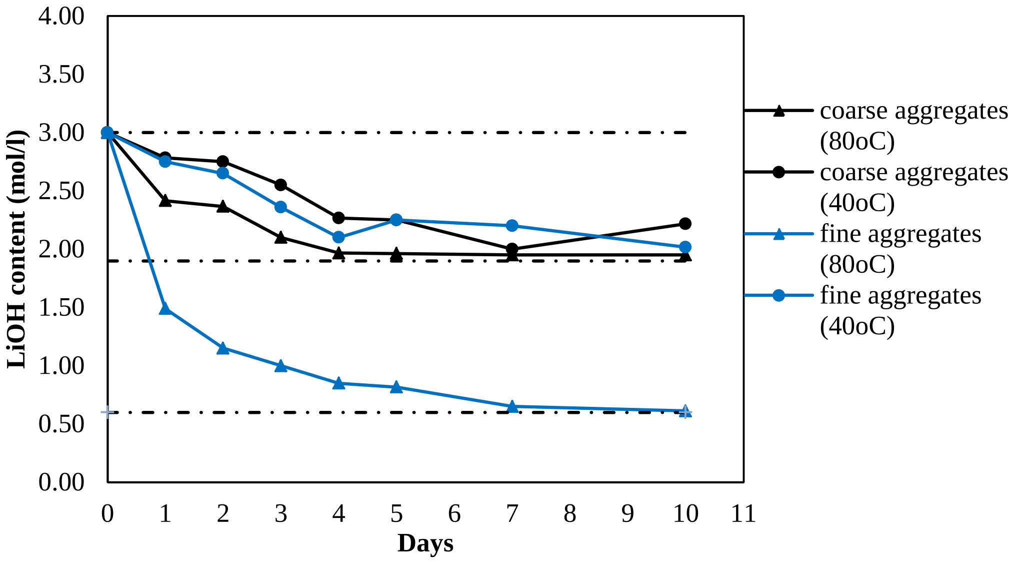

Fig. 5.8 Aggregates immersion in 3M of $LiOH^{\cdot}H_2O$ (Andesite-2) for 10 days

When reactive aggregates were immersed in 3M of $LiOH^{\cdot}H_2O$ solution, coarse aggregates absorbed $LiOH^{\cdot}H_2O$ about 1.05 mol/l at 80^o C & absorbed about 1.00 mol/l at 40^o C. Meanwhile, Fine aggregates absorbed $LiOH^{\cdot}H_2O$ about 2.35 mol/l at day 7 at 80^o C & absorbed about 0.9 mol/l at 40^o C. The absorbtion results of coarse and fine aggregates for andesite-1 and andesite-2 can be summarized in **Table 5.7**.

Table 5.7 $LiOH^{\cdot}H_2O$ absorption in coarse and fine aggregate (mol)

Temperature	**Immerse (Days)**	**Andesite-1**		**Andesite-2**			
		4M of coarse	**4M of fine**	**3M of coarse**	**3M of fine**	**4M of coarse**	**4M of Fine**
80^{o}C	5	1.52	2.87	1.04	2.18	1.35	2.89
	10	-	-	1.05	2.39	1.25	2.96
40^{o}C	5	-	-	0.75	0.75	0.7	1.10
	10	-	-	0.78	0.98	1.09	1.13

Pictures of reactive aggregates after immersing and titrating can be seen in **Photo 5.4 (**a for andesite-1; b,c,d,e,f,g: andesite-2, example: 4M-80C-10 days means immersed in 4M at 80^{o}C for 10 days).

a. 4M-80C-5 days b. 3M-80C-10 days, c. 3M-40C-10 days

d. 4M-80C-10 days, e. 4M-40C-10 days f. 4M-80C-5 days g. 4M-40C-5 days

Photo 5.4 Reactive aggregates observation after one week of titration test

It can be observed that the aggregates immersed in 4M at 80^{o}C for 5 and 10 days showed white color on the surfaces of the aggregates. It might lithium silicate layer has been created. However, when aggregates immersed at 40^{o}C the silicate layer was not so bright. Moreover, when the aggregates immersed in 3M at 80^{o}C and 40^{o}C for 5 and 10 days, the silicate layer was not so clear.

5.3.3 Discussion on $LiOH^{\cdot}H_2O$ effectiveness

Several mechanisms for the effectiveness of $LiOH^{\cdot}H_2O$ in reducing expansion have been proposed such as: Lithium may alter the product of ASR composition, resulting in less expansive product, Lithium may reduce silica dissolution, Lithium may decrease the repolymerization of silica and silicates, and Lithium may reduce repulsive forces between colloidal ASR gel particles (5.5 (5.6). However, the author is more inclined to the opinion that lithium can reduce silica dissolution and protect it to react with alkali, because when soaking reactive aggregates and place inside the oven at temperature 80°C, $LiOH^{\cdot}H_2O$ directly react with silica in the aggregates. Then, lithium silicate layer is created. As well as the opinion of the researchers as follows: Lawrence M et al. showed that increasing lithium hydroxide concentrations, thus silica solubility decreased(5.7). However, increasing sodium or potassium hydroxide concentrations, thus silica solubility increased. Lawrence M et al. suggested that formation of surface layer of lithium silicate caused agglomeration(5.7).

Diamond and Ong showed that the amount of lithium increases in gel product proportional to the amount of sodium and potassium, so expansion of the mortar bar decreases(5.8). Stark proposed that during ASR, when the lithium concentration was enough, lithium-alkali (and possibly calcium) formed silicates that have less capacity for expansion(5.9). Furthermore, lithium was an alkali metal, and its binding within the C-S-H structure will be likely increased in FA mixtures where the Ca:Si was decreased (Batty and Greening 1978) (5.10), (Stade 1989) (5.11). The usage of fly ash in portland cement-based materials was known to decrease the Ca to Si ratio in the calcium silicate hydrate (C-S-H). Fly ash with its lower or no CaO content has a bigger effect on lowering the Ca:Si. A lower Ca:Si in the C-S-H can increase alkali binding within cement hydration product. Collins et al. (5.12), Berubé et al. (5.13) also stated that the binding of lithium in the cement hydrates may be preferable to binding of Na^+ or K^+. Moreover, it can be seen from the results of titration test that coarse aggregate of andesite-1 absorbed $LiOH{\cdot}H_2O$ about 1.52 mol/l at day 5. Then, coarse aggregates of andesite-2 absorbed $LiOH{\cdot}H_2O$ about 1.35 mol/l in day 5 and about 1.25 mol/l in day 10. Furthermore, maximum absorbtion of $LiOH{\cdot}H_2O$ 1.75 mol/l in day 7. It can be thought that the effective immersion of aggregates was at day 7.

5.3.4 Workability, compressive strength and elastic modulus

There was almost no change in slump of concrete compare to control concrete when $LiOH{\cdot}H_2O$ was used in mixture proportions. It can be noted that setting time of concrete was accelerated by the usage of $LiOH{\cdot}H_2O$, especially when aggregates were immersed in $LiOH{\cdot}H_2O$ solution. The effect of $LiOH{\cdot}H_2O$ was also not significant on air content. It was also supported by Hooper et al. confirmed that no changes in slump of concrete when $LiOH{\cdot}H_2O$ was used(5.14). The results of compressive strength test at 28 days are shown in **Fig. 5.9** and **Fig. 5.10.**

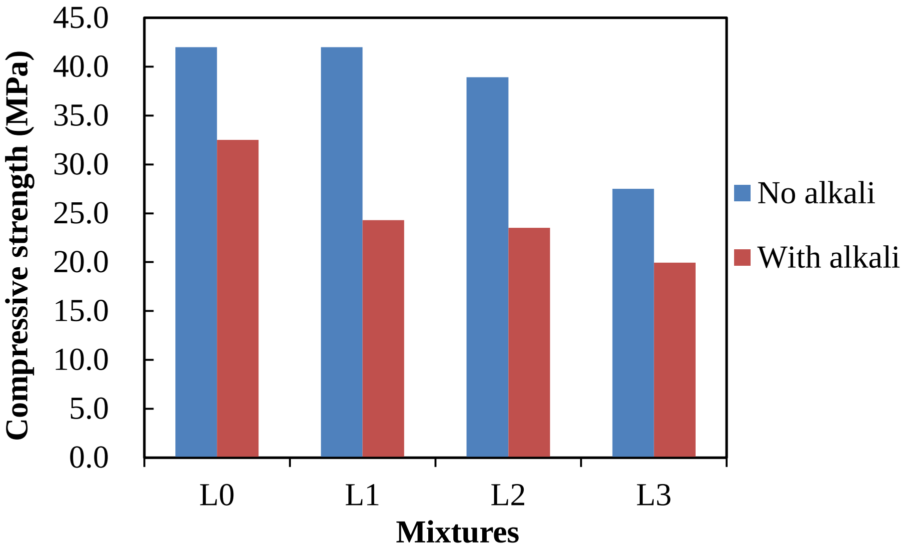

Fig. 5.9 Compressive strength of concrete at 28 days (Andesite-1)

It can be noticed that the usage of $LiOH{\cdot}H_2O$ could influence the compressive strength values. The compressive strength of concrete with $LiOH{\cdot}H_2O$ are smaller than strength of control concrete. It also can be observed in concrete without alkali. $LiOH{\cdot}H_2O$ reduced compressive strength of the concrete. The strength reduction of the compressive strength is related to the properties of $LiOH{\cdot}H_2O$ that $LiOH{\cdot}H_2O$ may retard hydration. As a result, $LiOH{\cdot}H_2O$ slows the rate of hardening and reduces the compressive strength. Further, in **Fig. 5.10**, it can be seen that compressive strength of concrete with 4M of $LiOH{\cdot}H_2O$ are smaller than 3M of $LiOH{\cdot}H_2O$.

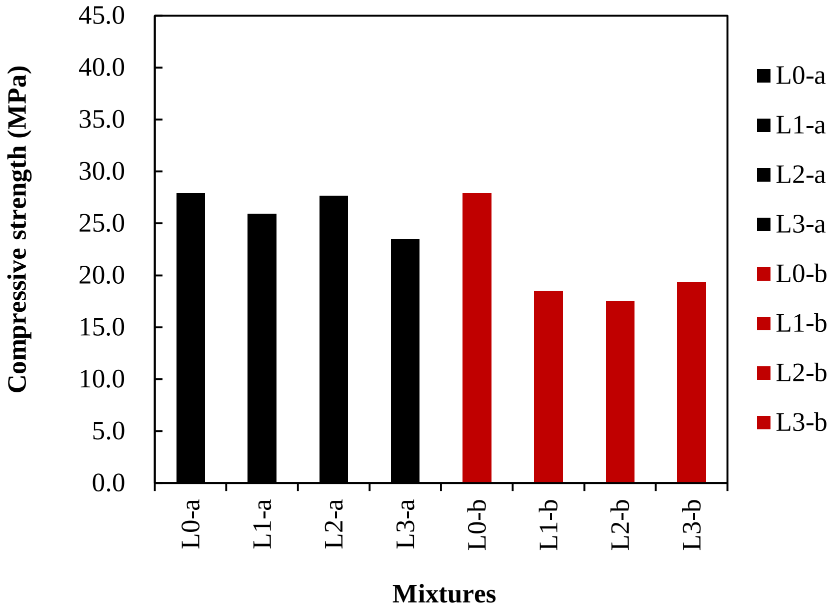

Fig. 5.10 Compressive strength of concrete with alkali at 28 days (Andesite-2)

To determine concrete quality, the compressive strength is the most common measurement. The effect of Lithium compounds on compressive strength are reported with different effect by some researchers. Marcus J. Millard mentioned that lithium nitrate may accelerate hydration in the first 24 hours, but may retard hydration after 1 day(5.15). Wang et al. examined that the usage of LiOH in concrete was not generally affected the strength(5.16). Furthermore, Wang et al. said the compressive strength of concrete with high alkali cements (Na_2Oe of 0.8% or more) at 28 days, the strength was reduced as much as 25% in the presence of lithium. Moreover, Wang et al. observed that $LiOH{\cdot}H_2O$ can act as a hydration retarder(5.16). Meanwhile, McKeen et al. concluded that compressive strength of concrete contained Lithium exhibited higher at 7, 14, 28, 56, and 90 days, but strength increase were not significant(5.17). Thomas et al. found that concrete contained lithium (a 75% and 100% of the standard $LiNO_3$ dosages), its compressive strength identical to concrete without lithium at ages 3, 7, 28, 56, and 90 days(5.18). Lane explained that compressive strength was decreased when $LiOH{\cdot}H_2O$ was used at a 100% dosage rate(5.19). Hooper et al. mentioned that reductions in 28-day compressive strength were possible in concrete containing $LiOH{\cdot}H_2O$ (5.14).

The relationship between compressive strength and elastic modulus at 28 days are shown in **Fig. 5.11** and **Fig 5.12**.

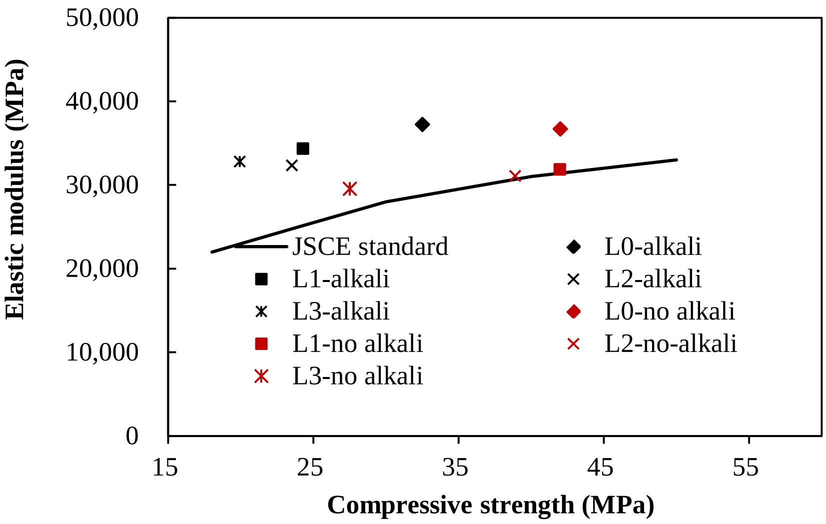

Fig. 5.11 Relationship between compressive strength and elastic modulus for concrete with and without alkali (Andesite-1)

It can be observed that the higher compressive strength, the higher elastic modulus. Most of the relation between compressive strength (f'_c) and modulus elasticity (E_c) are above JSCE standard. However, a good linear correlation between compressive strength and elastic modulus is acquired.

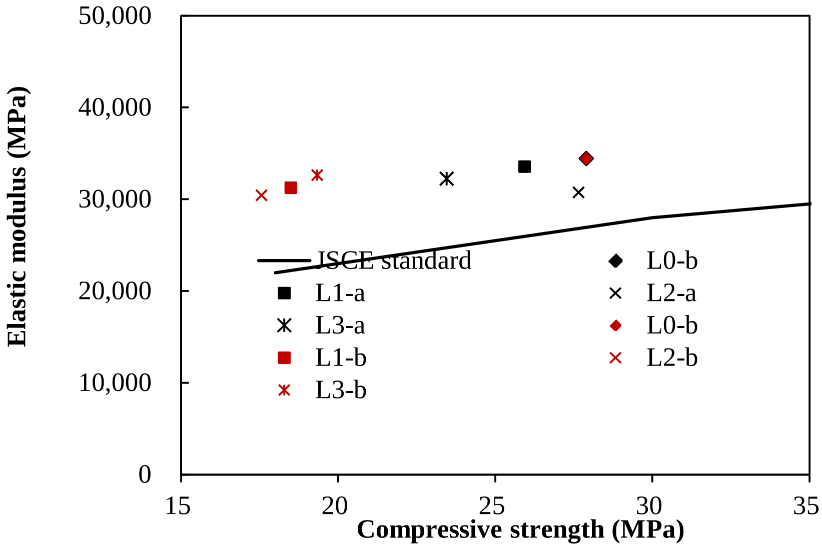

Fig. 5.12 Relationship between compressive strength and elastic modulus for concrete with 3M and 4M of $LiOH^{.}H_2O$ (Andesite-2)

5.3.5 Ultrasonic pulse velocity (UPV) test

Test results of UPV are depicted in **Fig. 5.13** The values are in range of 3.89 km/s to 4.24 km/s. The results indicate that the concrete quality is good. All values were higher than 3.7 km/s (IS:13311-1-1992). Comparison of UPV results among concrete with $LiOH^{.}H_2O$ to concrete control, it seems that concrete with $LiOH{\cdot}H_2O$ contribute to improve the concrete quality at all ages. The UPV results of concrete with L1, L2, L3 are higher than control concrete. Most of UPV values for each mixture increase with time. Furthermora, relationship between expansion and UPV can be seen in **Fig. 5.14**. It can be observed that the larger the UPV values the lower the expansion.

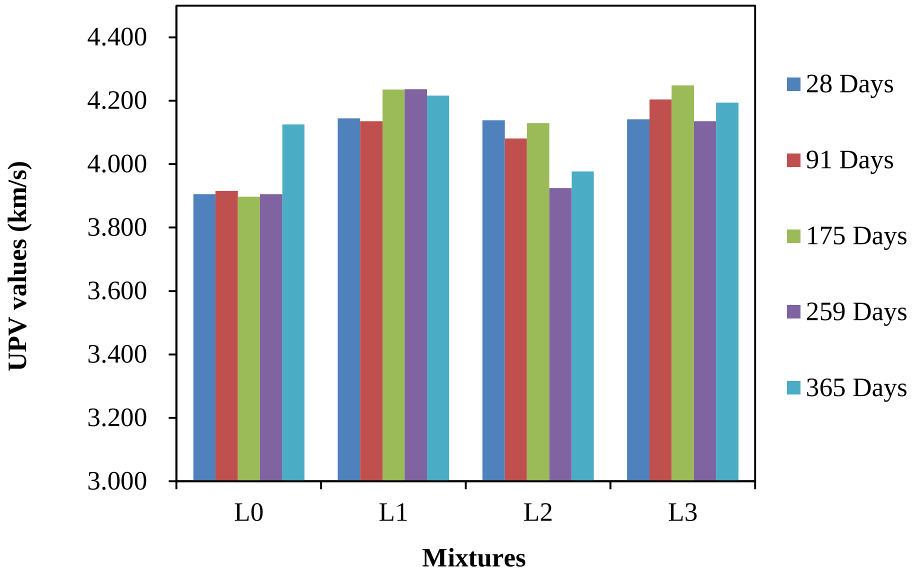

Fig.5.13 UPV results of concrete

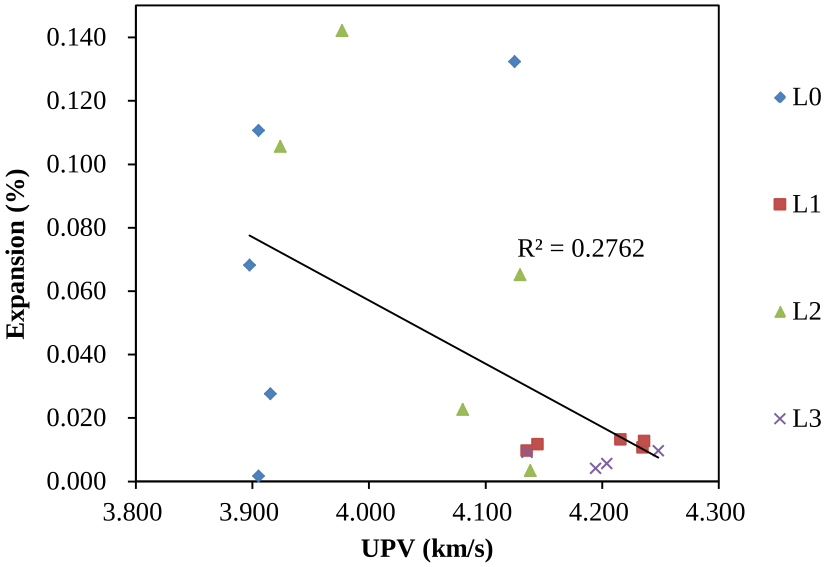

Fig.5.14 Relationship between expansion and UPV

5.4. Summary

In order to investigate the treatment of reactive aggregate with $LiOH \cdot H_2O$, concrete prism and mortar bar were made and tested, then cured at 40°C and 80°C. The following conclusions are obtained based on the results of investigations:

1. Treatment of reactive aggregate with cement paste (w/c=0.5) containing 3M and 4M of $LiOH \cdot H_2O$ can not avoid the silica in aggregate to react with alkali.
2. Reactive aggregates that immersed in 4M of $LiOH \cdot H_2O$ solution in oven at temperature 80°C for 5 days can reduce expansion for andesite-1. Expansion reduction is under 0.05% that classified as non-reactive.
3. Reactive aggregates that covered with cement paste (w/c=0.5) containing 4M of $LiOH \cdot H_2O$ then immersed in 4M of $LiOH \cdot H_2O$ solution for 5 days can also reduce expansion for andesite-1. Expansion reduction is under 0.05% that classified as non-reactive.
4. Reactive aggregates that immersed in 4M of $LiOH \cdot H_2O$ solution in controlled room at 80°C for 10 days can reduce expansion for andesite-2. Expansion reduction is under 0.05% that classified as non-reactive.
5. Reactive aggregates that covered with cement paste (w/c=0.5) containing 4M of $LiOH \cdot H_2O$ then immersed in 4M of $LiOH \cdot H_2O$ solution for 10 days can reduce expansion for andesite-2. Expansion reduction is under 0.05% that classified as non-reactive.
6. Duration of immersing and temperature of treatment are important in treating of reactive aggregates for suppressing expansion.
7. Coarse aggregates of andesite-1 absorbed $LiOH \cdot H_2O$ about 1.52 mol/l. Further, Coarse aggregates of andesite-2 absorbed $LiOH \cdot H_2O$ about 1.75 mol/l.
8. Based on the results of coarse aggregates of andesite-2 showed that maximum absorption of $LiOH \cdot H_2O$ max = 1.75 mol/l at temperature 80°C. Then, effective immersing period for passivation of aggregates was at day 7.

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CHAPTER 6. THE EFFECTIVENESS OF COMBINATION OF FLY ASH AND LITHIUM HYDROXIDE MONOHYDRATE ($LiOH{\cdot}H_2O$)

6.1 Introduction

Mineral admixtures such as fly ash (FA) have been used to reduce expansion. FA at the level of 15%, and 25% usually can reduce expansion very well. However, at level smaller than 15%, FA was not enough in reducing expansion. Based on the expansion results of **chapter 3** in **Fig. 3.22** and Fig. **3.23**, it can be seen that FA at level 15% is not enough to reduce expansion. Expansion result of FA15: 0.069% is larger than 0.05%. However, expansion result of FA at level 25%: 0.011 is lower than 0.05%. As a results, FA at the level of 10 % and 15% will be used with Lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$) as chemical admixtures.

This study is intended to find out the combination effect of mineral and chemical admixtures. Moreover, this study is conducted in efforts to reduce alkali-silica reaction that focuses on the usage of FA and $LiOH{\cdot}H_2O$. FA is used at the level of 10% and 15% and the reactive aggregates is treated by using $LiOH{\cdot}H_2O$ solution. Lithium hydroxide is used to create a lithium silicate layer by immersing the fine reactive aggregates in $LiOH{\cdot}H_2O$ solution prior to use. Reactive aggregates will be immersed in 2M or 3M of $LiOH{\cdot}H_2O$ solution inside sealed stainless container. In this study, the treatment of fine reactive aggregates is combined with non reactive aggregates in pessimum ratio 30:70. Moreover, mortar bars were made to investigate the effectiveness of FA with $LiOH{\cdot}H_2O$ in reducing expansion. Mortar bars were made based on JIS A 1146. Specimens were treated in controlled room at 40°C, and R.H. 100%.

6.2 Material and mixture proportions

6.2.1 Materials

There two types of binder are used in this study, namely: ordinary portland cement (OPC), and fly ash (FA). OPC, and FA meet the requirements of JIS R 5202 and JIS A6201, respectively. Chemical compositions of cement and FA are shown in **Table 6.1**.

Table 6.1 Chemical compositions of OPC and FA

Constituents	OPC	FA
SiO_2, %	20.89	54.96
MgO, %	0.92	1.30
SO_3, %	2.02	0.49
Na_2O, %	0.35	1.07
K_2O, %	0.36	1.30
CaO, %	64.25	3.18
LoI, %	1.87	2.37

Pictures of reactive aggregates were immersed in $LiOH\cdot H_2O$ solution can be seen in **Photo 6.1**.

Photo 6.1 Fine reactive aggregates immersed in $LiOH\cdot H_2O$ solution

Meanwhile, the physical properties of material are presented in **Table 6.2.** Two aggregates were used in this experiment; one was classified as alkali silica reactive (andesite-2) and another was classified as non-reactive (limestone).

Table 6.2 Physical properties of materials

Material	Description
Cement, OPC	Density = 3.16 g/cm^3, Specific Surface Area = 3330 cm^2/g
Fly ash, (Type II)	Density = 2.26g/cm^3, Specific Surface Area = 3970 cm^2/g
Fine aggregates (Limestone)	Density (SSD) = 2.70 g/cm^3, Water absorption = 0.61%, Rc = 8 mmol/l. Sc = 1 mmol/l.
Fine aggregates (Andesite-2)	Density (SSD) = 2.68 g/cm^3, Water absorption = 1.56%, Rc = - mmol/l. Sc = - mmol/l.

6.2.2 Mixture proportions

Mortar bars were made based on JIS A 1146. Reactive coarse aggregates were crushed into fine aggregates that matches requirement of particle size distribution in JIS A 1146. Crushed reactive aggregates were immersed in 2M or 3M of $LiOH\cdot H_2O$ solution, and place them in oven at temperature 40°C for 5 days. Before soaking the aggregates, 500 ml of $LiOH\cdot H_2O$ solution was prepared for each 900 g of reactive aggregates. Furthermore, aggregates and solution were allowed to cool to room temperature after removing from the oven. Then, reactive aggregates were placed in sealed plastic bucket in SSD condition. Water to cement ratio of mortar was adjusted to 0.50 and alkali content was set such that Na_2Oeq of cement 1.2 wt% by adding NaOH solution (1 mol/l) into mixing water. Mixture proportions of mortar are shown in **Table 6.3**.

Table 6.3 Mixture proportions of mortar

No	Mix	w/c	Water+ NaOH (g)	Cementitious Material (g)		Aggregates (g)	NaOH (ml)
				OPC	FA		
1	C	0.50	300	600	-	1350	120
2	FA10	0.50	300	540	60	1350	108
3	FA15	0.50	300	510	90	1350	102
4	C-2M	0.50	300	600	-	1350	120
5	C-3M	0.50	300	600	-	1350	120
6	FA10-2M	0.50	300	540	60	1350	108
7	FA15-2M	0.50	300	510	90	1350	102
8	FA10-3M	0.50	300	540	60	1350	108
9	FA15-3M	0.50	300	510	90	1350	102

Mixture C was made for control, no treatment for reactive aggregates. Mixture 2, FA was used at level 10% (FA10), Mixture 3, FA was used at level 15% (FA15). Mixture 4 and Mixture 5 used 2M and 3M of $LiOH{\cdot}H_2O$. Mixture 6, FA was used at level 10% and reactive aggregates were immersed in 2M of $LiOH{\cdot}H_2O$ solution in sealed stainless container, then place inside oven at temperature 40°C for 5 days, (FA10-2M). Description of other mixtures can be seen in **Table 6.4**.

Table 6.4 Mixtures description treatment for reactive aggregates

Description		FA		
		0%	10%	15%
$LiOH{\cdot}H_2O$	No treatment	C	FA10	FA15
	2M	C-2M	FA10-2M	FA15-2M
	3M	C-3M	FA10-3M	FA15-3M

6.2.3 Titration test procedure

Titration test was conducted to find out content of lithium in aggregates and solution during immersing, and to determine effective immersing period. Samples of fine aggregates: coarse aggregates were crushed and graded to have distribution as specified in JIS A 1146 (Mortar bar test). Samples of coarse aggregates: maximum size is: 2 cm. Test procedure: 1) 45 g of aggregates and 25 ml of 3M & 4M of $LiOH{\cdot}H_2O$ (hereinafter, "LiOH") was placed and soaked in sealed HDPE bottle and place inside oven at $40^{O}C$ & $80^{O}C$. 2) The bottle was removed from oven at day 1, 2, 3, 4, 5, 7, 10 days. After the removal, the aggregates and solution was allowed to cool to room temperature. 3) Then, the aggregates and solution are filtered under vacuum, and the filtrate collected. During the filtering process, deionized water was used to rinse the aggregates and HDPE bottle. 4) After filtrating, total solution was 200 ml (25 ml of $LiOH{\cdot}H_2O$ solution + rinse water), 5) Then 0.8 ml solution was taken from step number 4. Further, deionized water was added to 0.8 ml up to 20 ml. Furthermore, the sample was ready to be titrated against potassium hydrogen phthalate (KHP) to determine the concentration of the $LiOH{\cdot}H_2O$ in the aggregates. 6) $LiOH{\cdot}H_2O$ solution was also examined (blank test).

6.3 Results and discussions

6.3.1 Expansion test

Expansion behavior of mortar with FA is shown in **Fig. 6.1**. In the case of mortar without FA and no treatment of reactive aggregates with $LiOH \cdot H_2O$, expansion was large and fast from the beginning until the end of observation period. It can be observed that there was expansion reduction due to usage FA. The expansion rate of mortar with FA10 was lower compared to mortar expansion for control (C). Then, The expansion rate of mortar with FA15 was lower compared to mortar with FA10.

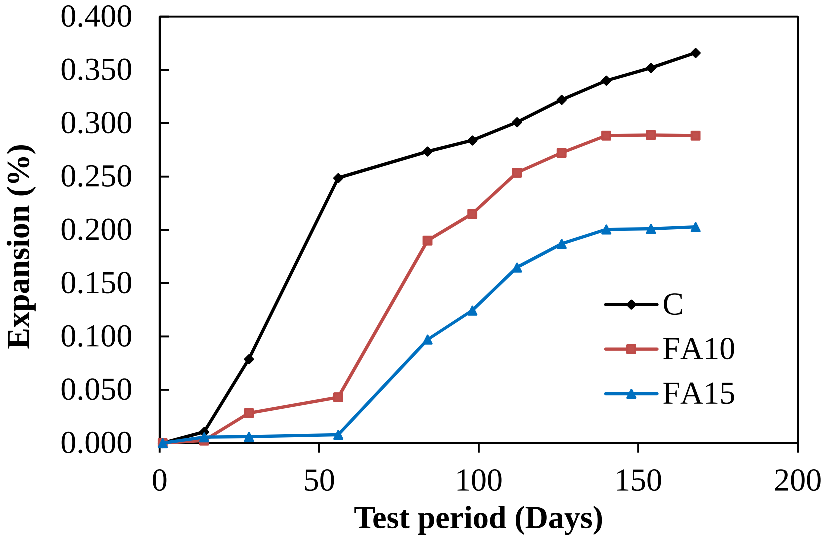

Fig. 6.1 Test results of mortar bar with FA

Furthermore, **Fig. 6.2** shows expansion behavior of mortar with 2M and 3M of $LiOH \cdot H_2O$.

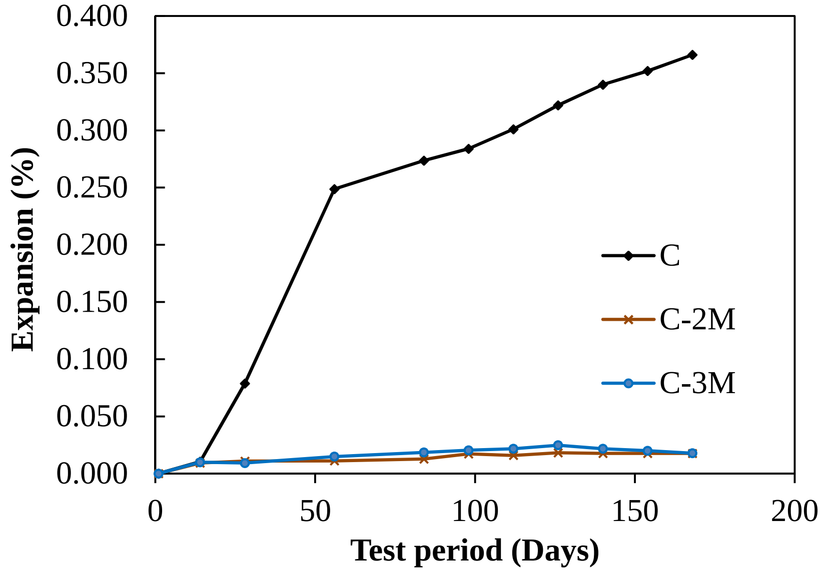

Fig.6.2 Test results of mortar bar with $LiOH \cdot H_2O$

In case of mortar without treatment of reactive aggregates with LiOH·H_2O, expansion was large and fast from the beginning until end of the period. Expansion of mortar with 2M of LiOH·H_2O was lower than control (C). Then, Expansion of mortar with 3M of LiOH·H_2O was lower than mortar with 2M LiOH·H_2O. There was expansion reduction due to increase dosage/level of LiOH·H_2O. Expansion reduction of mortar C-2M and mortar C-3M were under 0.1% that classified as innocuous. Further, **Fig. 6.3** Expansion of control (C) was large and fast until end of the period. There was expansion reduction of mortar with FA10. Even the expansion of mortar with FA at level 10% was lower than control (C). The expansion of mortar with FA at level 10% was quite large. When the reactive aggregates were immersed in 2M & 3M of LiOH·H_2O solution and used together with FA10%. Then, the expansion was lower than expansion of mortar with FA10% itself. There was expansion reduction due to combination of FA at level 10% and FA with 2M & 3M of LiOH·H_2O. Expansion reduction of mortar FA10-2M & mortar FA10-3M were under 0.1% that classified as innocuous.

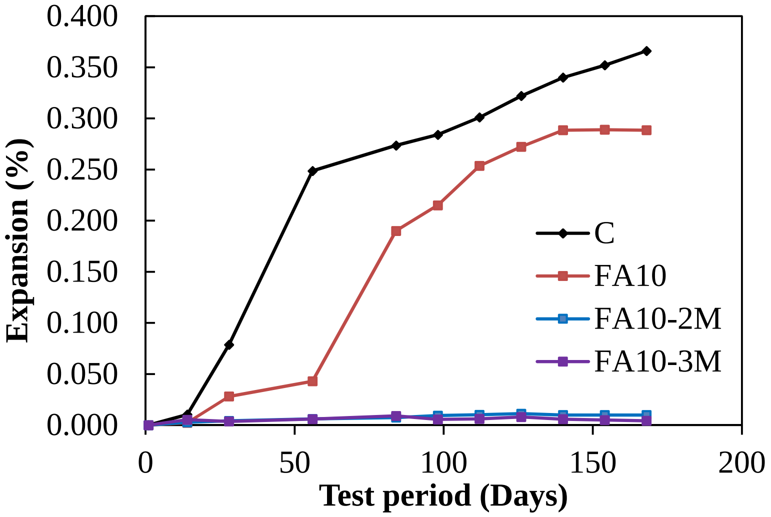

Fig. 6.3 Test results of mortar bar with FA10 and LiOH H_2O

Moreover, **Fig. 6.4** shows expansion behavior of mortar with FA at level 15%, and mortar combination of FA15% with 2M and 3M of LiOH·H_2O.

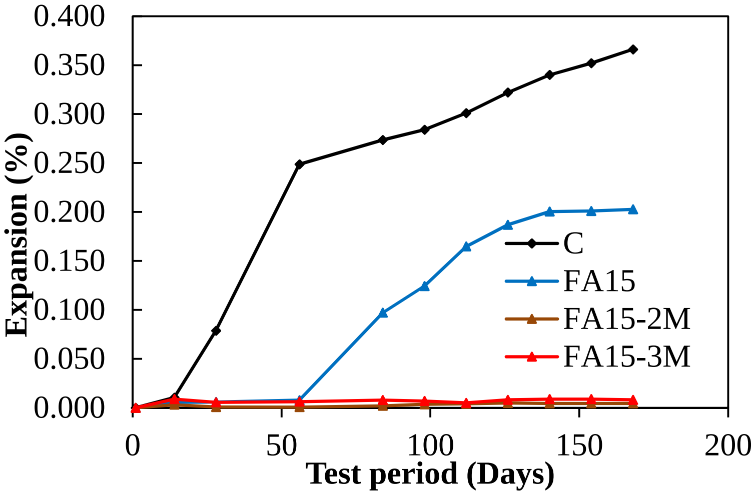

Fig. 6.4 Test results of mortar bar with FA15 and LiOH·H_2O

Expansion of mortar combination of FA at level 15 with 2M & 3M of $LiOH{\cdot}H_2O$ was lower than control (C) and FA15. There was expansion reduction due to combination of FA at level 15 with 2M & 3M of $LiOH{\cdot}H_2O$. Expansion reduction of mortar FA15-2M and FA15-3M were under 0.1% that classified as innocuous.

6.3.2 Titration test

Titration test results of fine aggregates (andesite-2) can be seen in **Fig. 6.5** and **Fig. 6.6**.

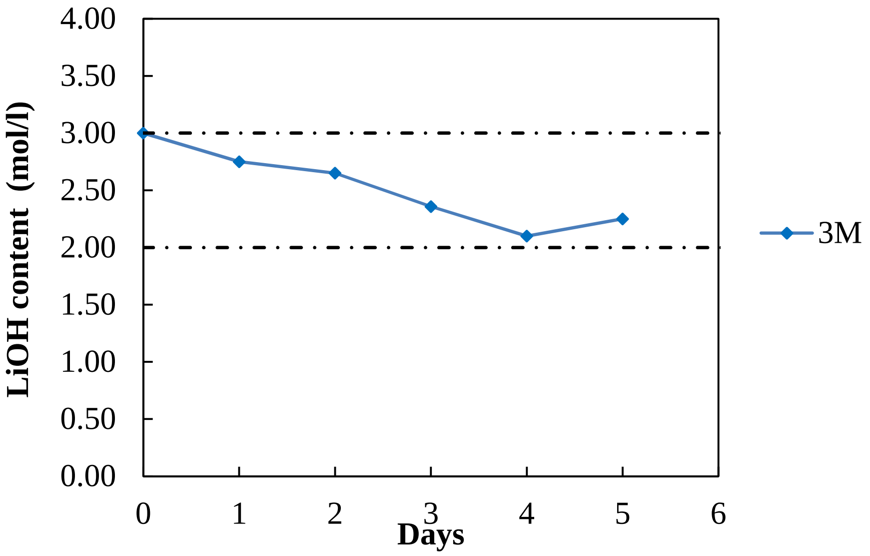

Fig. 6.5 Fine aggregates immersion in 3M of $LiOH{\cdot}H_2O$ for 5 days at 40°C

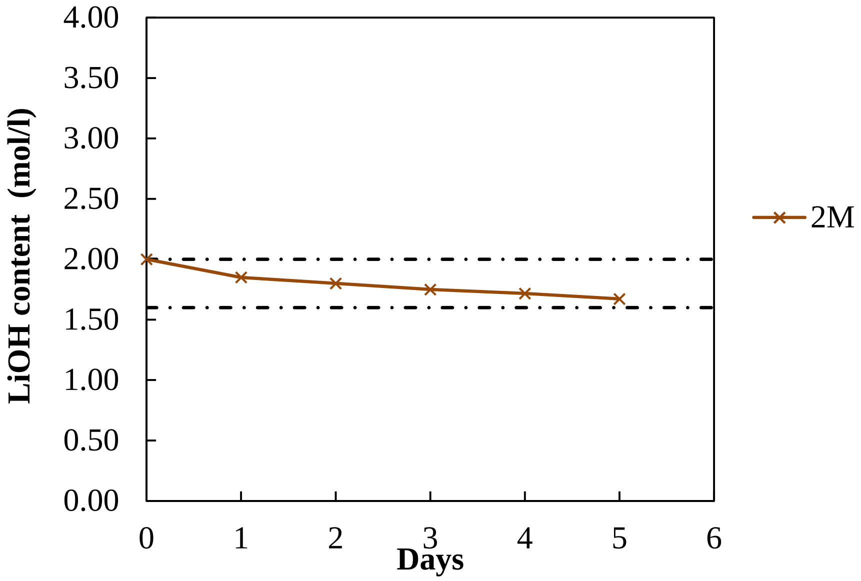

Fig. 6.6 Fine aggregates immersion in 2M of $LiOH{\cdot}H_2O$ for 5 days at 40°C

Fine aggregates absorbed $LiOH{\cdot}H_2O$ about 0.90 mol/l at day 4, when they were immersed in 3M of $LiOH{\cdot}H_2O$. Then, fine aggregates absorbed $LiOH{\cdot}H_2O$ about 0.33mol/l, when they were immersed in 2M of $LiOH{\cdot}H_2O$.

6.4 Summary

In order to investigate the effectiveness of FA with $LiOH\cdot H_2O$, mortar bars were made. The following conclusions are obtained based on the results of investigations:

1. When FA at the level of 10% and 15% was not enough to reduce exansion, then reactive aggregates that immersed in $LiOH\cdot H_2O$ solution can be used together with FA.
2. Combination of FA at level 10% and 15% with 2M and 3M of $LiOH\cdot H_2O$ can be used to reduce expansion.
3. Expansion reduction of mortar FA10-2M, FA10-3M, FA15-2M and FA15-3M are under 0.1% that classified as innocuous.

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CHAPTER 7. CONCLUSIONS AND RECOMMENDATION

7.1 Conclusions

The purpose of study on mitigating alkali silica reaction by using mineral admixtures and chemical admixtures (lithium hydroxide monohydrate-$LiOH{\cdot}H_2O$) is hopely to be applied on concrete durability problem in Japan and Indonesia. Hence**,** the performance of chemical admixtures and mineral admixtures were evaluated by making mortar and concrete specimen based on JIS A 1146 and RILEM AAR-3. The effectiveness of combination of these materials were examined. Then, optimum level of mineral and the effectiveness of combination minerals as cement replacement are recommended to be used in construction industry for suppressing expansion due to ASR. The results of each study are described as follow:

In **Chapter 3**, silica fume (SF) with high content SiO_2 and no content of alkalis were used. Mortar and concrete mixtures were made with aggregates in pessimum ratio 30:70 between reactive and non reactive aggregates. The results showed that SF at the level 10% of cement replacement can reduce expansion, and in the concrete with additional alkali, SF can refine pore size distribution of the concrete.

The effectiveness of combination fly ash (FA) with silica fume (SF) in order to suppress expansion due to ASR were investigated. The combination were conducted at the level 15% and 25% of FA. At level 15% of FA, the combination was FA 10% and SF 5% (FA10SF5), and at level 25% of FA, the combination was FA 15% and SF 10%, (FA15SF10). The results showed that incorporation of FA and SF were very good in suppressing expansion. Their expansion were lower than FA, expansion of FA10SF5 and FA15SF10 were under 0.005% that classified as non reactive. Futhermore, the combination between these minerals can also refine pore size distribution of the concrete.

The usage of expanded perlite powder (EPP), and the combination between fly ash (FA) with EPP was also investigated in order to reduce ASR. The combination was conducted at the level 15% and 25% of FA. At level 15% of FA. The combination was FA 10% and EPP 5%, (FA10EPP5), and at level 25% of FA, the combination was FA 15% and EPP10%, (FA15EPP10). At the level 15% of EPP can suppress expansion. Furthermore, incorporation of FA and EPP, their expansion were also lower than FA. However, combination FA with EPP (FA15EPP10) is under 0.05%, that classified as non reactive. Furthermore, the combination between these minerals can also refine pore size distribution of the concrete.

In **Chapter 4**, the reasons why FA, SF, and EPP can reduce expansion were described in this chapter. The contents of SiO_2 is important component to increase the ash effectiveness and lower the expansion not only in single mineral but also in mineral combination.

In **Chapter 5**, previous study showed that when 4M of $LiOH{\cdot}H_2O$ solution was used to immerse reactive aggregates to create passivated aggregates greatly reduced expansion in accelerated mortar bar tests compared to non passivated aggregates. 4M of $LiOH{\cdot}H_2O$ was also used to create passivated aggregate layer in mortar and concrete. Three types of treatment were prepared. Firstly, reactive aggregates were immersed in $LiOH{\cdot}H_2O$ solution in the temperature 80°C (L1) for 5 days. Secondly, reactive aggregates were covered with cement paste (w/c=0.5) used water contain $LiOH{\cdot}H_2O$ solution (L2). Lastly, Reactive aggregates were covered with cement paste (w/c=0.5) used water contain $LiOH{\cdot}H_2O$ solution, then be immersed in LiOH H_2O solution at the temperature 80°C (L3) for 5 day. The expansion was greatly decreased. The expansion of concrete with L1 and L3 treatment was under 0.05% and lower than control concrete, and the expansion of concrete with L3 was the lowest of all. Duration of immersing and temperature of treatment are important in treating of reactive aggregates for suppressing expansion.

In **Chapter 6** the effectiveness of combinations, between FA and $LiOH{\cdot}H_2O$ were investigated. First step, experiment was conducted with fly ash (FA) at level 10% and 15%. Second step, $LiOH{\cdot}H_2O$ was used at dosage 2M, 3M to treat reactive aggregates. Then, combination between FA and $LiOH{\cdot}H_2O$ were used to reduce expansion. When FA at level 10% and 15% was not enough to reduce expansion. Then, reactive aggregates can be treated by immersing in 2M and 3M of $LiOH{\cdot}H_2O$ solution and use together with FA to reduce expansion.

7.2 Recommendations and future works

7.2.1 Recommendations

Combination mineral between FA with SF : FA10SF5, FA15SF10, and combination FA with EPP: FA15EPP10 can be used to reduce expansion.

7.2.2 Future works

In order to develop investigations that have been conducted and reported in this dissertation, the following aspects were expected for the next research. As it was revealed in this study that the combination between the two minerals, its expansion was quite good and can be used to reduce expansion caused by ASR. Combination FA with SF, or FA with EPP, the expansion value was lower than the value of expansion of FA itself. Making it very interesting if one’s try to combine other minerals, for instance: SF with perlite, or FA with ground glanulated blast furnace slags (GGBFS), or a merger among the three minerals are also worthy to be conducted.

Mineral admixtures such FA, SF, metakaolin (MKP), etc are not always available. So, experiment with combining mineral admixtures with chemical admixtures, various of mineral such as SF, GGBFS, MKP etc. and various lithium compounds or other chemicals are also needed to be conducted. Experiments that are reported in this study, conducted in a laboratory where conditions such as temperature, relative of humadity controlled very well. Therefore, it is very interesting to conduct same experiment in a real environmental conditions. So that, the results obtained could be comparable to what was done in the laboratory.