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Alkali-Activated Natural Pozzolan/Slag Binder for Sustainable Concrete

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ALKALI-ACTIVATED NATURAL POZZOLAN/SLAG BINDER FOR SUSTAINABLE CONCRETE

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Alkali-Activated Natural Pozzolan/Slag Binder for Sustainable Concrete

is approved in partial fulfillment of the requirements for the degree of

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ABSTRACT

This study aimed to fully replace Portland cement (PC) with environmentally friendly binders capable of improving longevity of concrete. The new binders consisted of different proportions of natural Pozzolan and slag which were alkaline-activated with various combinations of sodium hydroxide and sodium silicate. A step-by-step research program was designed to (1) develop alkali-activated natural Pozzolan/slag pastes with adequate fresh and strength properties, (2) produce alkali-activated natural Pozzolan/slag mortars to assess the effects of dominant variables on their plastic and hardened properties, and (3) finally produce and assess fresh, mechanical, dimensional, transport and durability properties of alkali-activated natural Pozzolan/slag concretes. The major variables included in this study were binder combination (natural Pozzolan/slag combinations of 70/30, 50/50 and 30/70), activator combination (sodium silicate/sodium hydroxide combinations of 20/80, 25/75 and 30/70), and sodium hydroxide concentration (1, 1.75 and 2.5M). The experimental program assessed performance of alkali-activated natural Pozzolan/slag mixtures including fresh properties (flow and setting times), unit weights (fresh, demolded and oven-dry), mechanical properties (compressive and tensile strengths, and modulus of elasticity), transport properties (absorption, rapid chloride penetration, and rapid chloride migration), durability (frost resistance, chloride induced corrosion, and resistance to sulfuric acid attack), and dimensional stability (drying shrinkage). This study also compared the performance of alkali-activated natural Pozzolan/slag concretes with that of an equivalent reference Portland cement concrete having a similar flow and strength characteristics.

The results of this study revealed that it was doable to find optimum binder proportions, activator combinations and sodium hydroxide concentrations to achieve adequate plastic and hardened properties. Nearly for all studied alkali-activated concretes, workability and setting times were in the acceptable ranges. Overall, a 50/50 combination of natural Pozzolan and slag developed the highest strengths. Increasing slag content to 70%, however, was useful for mixtures with high NaOH concentrations (2.5M) and for acceleration of initial reactions. The strength of alkali-activated concretes improved with increases in sodium silicate portion of activator. Regarding effects of sodium hydroxide concentration on strength properties, there were optimum NaOH molarities which increased with an increase in slag portion of the binder. A 50/50 combination of natural Pozzolan and slag also proved to be the optimum combination for the results of absorption test. NaOH concentration and sodium silicate dosage had marginal effects on the absorption and volume of permeable voids. The chloride penetration depth reduced with decreases in natural Pozzolan portion of the binder (particularly from 70 to 50%), sodium silicate dosage, and NaOH concentration. A nearly similar trend was seen for the drying shrinkage of studied alkali-activated natural Pozzolan/slag concretes, as reduction of these variables also reduced the drying shrinkage. The mass loss of alkali-activated concretes subjected to acid attack increased with increases in slag content, sodium silicate dosage, and sodium hydroxide concentration. The failure time in corrosion test improved (increased) with increases in natural Pozzolan content, sodium silicate dosage, and sodium hydroxide concentration. The frost resistance of alkali-activated concretes improved as slag portion of the binder was increased. An increase in sodium silicate dosage was beneficial in improving frost resistance of concretes made with binders having 50 and 70% slag. An opposite trend was seen when slag portion of the binder was reduced to 30%.

The mechanical properties (compressive strength, tensile strength and elastic modulus) of alkali-activated concretes made with activators having 20 and 25% sodium silicate were lower than those of the reference Portland cement concrete. As sodium silicate dosage of activator was increased to 30%, the compressive strengths of alkali-activated concretes were similar to those of the reference Portland cement concrete. Absorption of the studied alkali-activated natural Pozzolan/slag concretes was averagely 26% lower than that of the reference Portland cement concrete. Their chloride penetration depths were significantly lower (averagely about 80%) than that of the reference Portland cement concrete. The average drying shrinkage of alkali-activated natural Pozzolan/slag concretes was lower than that of reference PC concrete by nearly 26%. While the drying shrinkage of the worst performed alkali-activated natural Pozzolan/slag concrete was about 25% higher than that of the reference Portland cement concrete, there were several alkali-activated concretes that shrank considerably less than the reference Portland cement concrete. The corrosion and acid attack resistances of alkali-activated natural Pozzolan/slag concretes were significantly higher than that of the reference Portland cement concrete. The frost resistance of alkali-activated concretes having binders made with 50 and 70% slag was significantly higher than that of the reference Portland cement concrete. On the other hand, the frost resistance of concretes made with binders having 30% slag was similar to or less than (depending on sodium silicate content) that of the reference Portland cement concrete.

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I would like to express my profound gratitude to my academic advisor, Dr. Nader Ghafoori, for his scholastic advice and technical guidance throughout this investigation. His devotion, patience, and focus on excellence allowed me to reach this important milestone in my life. I also wish to extend my acknowledge to my examination committee members, Dr. Samaan Ladkany, Dr. Mohamed Kaseko, Dr. Harry Teng, and Dr. Pradip Bhowmik for their guidance and suggestions.

I wish to thank Mr. Peter Faught, the research shop technician, for providing unlimited assistance and technical supports during the experimental program. I thank Mr. Mohammadreza Sharbaf for being my teammate during this memorable journey.

DEDICATION

This study is dedicated to my parents, Mr. Naser Najimi and Mrs. Pouran Samavari. Without their continued and unconditional love and support, I would not be the person I am today.

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CHAPTER 1- INTRODUCTION

1.1. Why alkali-activated binders?

Concrete is known as the most widely used man-made construction material. The prevailing binder used to make concrete is Portland cement (PC) with an annual production of 3 billion tons (Pacheco-Torgal et al. 2012). The projections for the global demand of PC show that in the next 40 years it will have a two-fold increase reaching 6 billion tons per year. Production of one ton of PC generates 0.94 tons of CO_2 (Pacheco-Torgal et al. 2012). Other authors reported that the cement industry emits, on average, 0.87 kg of CO_2 for every kg of cement produced (Pacheco-Torgal et al. 2012). It is estimated that PC production accounts for nearly 7% of the world's total CO_2 emissions (Huntzinger et al. 2009, Pacheco-Torgal et al. 2012). As such, carbon dioxide gas emission as a result of cement and concrete production is becoming a global concern.

Contrary to the common belief, PC concrete is not free of severe degradation problems. Recently, durability of PC concrete structures became a major issue in dealing with longevity of concrete structures. In the U.S, the direct cost of corrosion in highway bridges exceeds billions of dollars per year, and indirect costs to users due to traffic delays and lost productivity have been estimated to be ten times as much (ACI 222 2001, Kirkpatrick et al. 2002, Lindquist et al. 2006). According to the latest Annual Urban Mobility Report (Schrank et al. 2012), congestion in 2011 caused urban Americans to travel 5.5 billion hours more and to purchase an extra 2.9 billion gallons of fuel for a congestion cost of $121 billion. This issue can be further recognized considering the fact that the average age of existing bridges in the U.S. is 42 years. With a design lifespan of 50 years, more than 200,000 of approximately 600,000 highway bridges are 50 years old or older. This number will double by 2030 according to the U.S. Department of Transportation National Bridge Inventory (U.S. DOT 2013). Hence, the U.S. transportation network is expected to face several challenges due to the aging of the network components as more than one out of ten existing bridges already fall in the category of “structurally deficient,” requiring major maintenance, rehabilitation, or even replacement (ASCE 2013). The problem is not limited to concrete bridges. Several problems have also been observed in concrete pavements. Concrete pavements are aging and deteriorating. They have shown varying signs of deteriorations due to age, harsh environment, excessive loading and other detrimental factors. It was reported that one third of the U.S. road system, about 1.3 million miles, is in poor condition or worse, receiving a grade of D in the American Society of Civil Engineers report card (Van Dam et al. 2011). Roadway agency budgets continue to fall short of needed funds, with an estimated $115.7 billion annual shortfall from funding required to substantially improve pavement conditions (Van Dam et al. 2011). As such, the need for production of high performance concrete has never been more urgent.

The desire to reduce CO_2 emissions and to produce more durable concrete has given impetus to search for new binders. Several studies have been conducted in recent years to find alternative binders for PC. These research investigations have resulted in introducing different types of binders including alkali-activated binders, calcium aluminates cements, calcium carbonate cements, magnesium oxy-carbonate cements, Bellite-calcium sulphoaluminate-ferrite cements, and partially pre-hydrated C-S-H based binders. Although far more research is needed for the afore-mentioned alternative binders, several researchers suggested that alkali-activated binders may have the potential to lead the transition to the cement of the future. The discovery of alkali-rich pozzolans in the ancient monuments, which have been durable over millennia, can be considered an undeniable proof of this potential (Glukhovsky 1959, Jackson et al. 2010). This indicates that alkali-activated Pozzolanic materials may prove to be a viable solution to concrete durability concerns. Also, these binders can significantly reduce CO_2 emission of concrete production. Different studies estimated 40 to 80% reduction in carbon-dioxide gas emission by replacing Portland cement with alkali-activated binders. Davidovits was the first author to address CO_2 emissions of alkali-activated binders stating that they generate just 0.184 tons of CO_2 per ton of binder (Davidovits et al. 1990). Duxson et al. (2007c) estimated that the reduction in CO_2 emission varies between 50 to 100% when PC was replaced by alkali-activated binders. McLellan et al. (2011) reported a 44% to 64% reduction in greenhouse gas emissions of alkali-activated binders when compared to PC. Duxson and Van Deventer (2009) mentioned a study in which a low-emission Portland cement (0.67 ton/ton) and alkali-activated binders were compared, reporting that the latter had 80% lower CO_2 emissions. Alkali-activated binders are not only a more sustainable and economical choice due to reducing PC consumption and providing adequate durability, but also they (1) incorporate industrial by-products such as slag and fly ash resulting in reduction of disposal sites, and (2) are suitable for stabilization/solidification of hazardous and radioactive wastes (Shi and Fernandez Jimenez 2006; Vance and Perera 2009; Provis 2009). Depending on the design and the starting materials, following are a list of other advantages that alkali-activated materials may provide (Duxson et al. 2007a, Provis and Van Deventer 2014):

- Adequate flexural and compressive strength, and high strength gain;
- High-temperature resistance, including thermal insulating properties;
- Stability under chemical (including acid) attack;

- Dimensional stability in service;
- Not subject to deleterious alkali–aggregate reactions;
- Strong adhesion to metallic and nonmetallic surfaces;
- Effective passivation of reinforcing steel;
- Low permeability to fluids and chloride ions;
- Low cost; and
- Beneficiation and/or valorization of industrial wastes

Despite these benefits and the facts that it has long been introduced to the cement and concrete industry, there is a need for significantly more research studies in order for alkali-activated binders to become recognized as technically and economically viable construction materials.

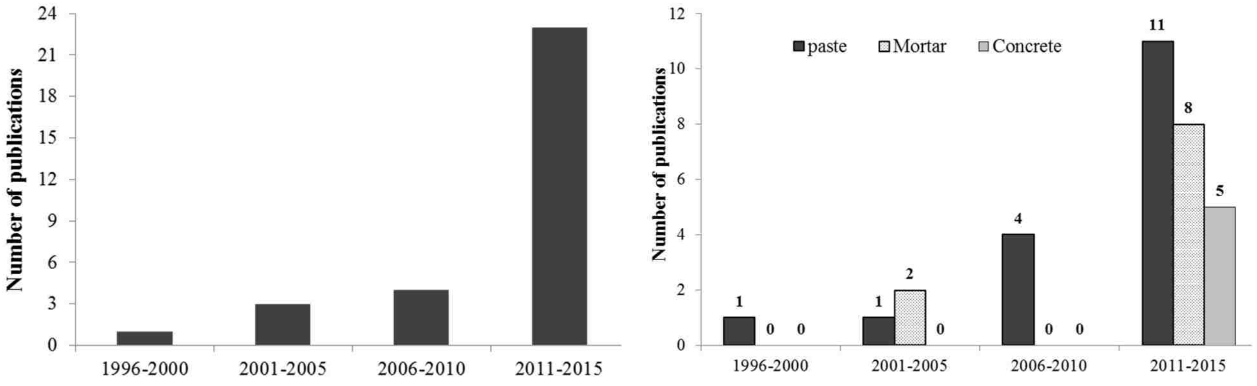
1.2. Why combination of low-calcium and high-calcium binders?

For several decades, a great deal of research has been dedicated to alkali activation of blast furnace slag (high-calcium binders). In recent decades, the research has been shifted towards activation of low-calcium binders including fly ash, to a larger extent, and metakaolin and natural Pozzolans, to a lesser extent. Today, literature is silent on alkali-activation of combined high-calcium and low-calcium binders. Figure 1.1 shows the number of publications on blended fly ash/slag mixtures as an example of combined binders. It can be seen that while there is a growing trend in recent years (period of 2011 to 2015), the conducted research is very limited in scope. These studies have mainly focused on a few properties of pastes or mortars. There are only five publications on alkali-activated fly ash/slag concretes with limited information for their short-term properties. In the case of combination of natural Pozzolan and slag, the availability of past study is far more scarce. There is only one study reported till 2015 (in 2011) which unsuccessfully attempted to combine slag and natural Pozzolans to produce alkali-activated pastes. To date, no published studies on properties of alkali-activated mortars and concretes containing natural Pozzolan and slag as binders can be found.

Each of these alkali-activated binders, i.e. high-calcium and low-calcium binders, provide certain benefits; in particular in terms of durability. The N-A-S-H gel (Na_2O-Al_2O_3-SiO_2-H_2O) as the main reaction product of low-calcium binders offers excellent chemical and thermal resistances, while C-(N)-A-S-H (Na_2O-Cao-Al_2O_3-SiO_2-H_2O) or C-A-S-H (Cao-Al_2O_3-SiO_2-H_2O) as the primary reaction products of high-calcium binders provide chemical binding of water which reduces permeability. “The N-A-S-H gel may also offer some scope for anion-binding mechanisms that retard chloride ingress, thus increasing the service life of a reinforced concrete by prolonging the time taken to initiate corrosion of embedded steel” (Provis and Van Deventer 2014). Accordingly, it can be suspected that combinations of high-calcium and low-calcium binders may offer mutual benefits, leading to production of sustainable binders with excellent long-term performances.

Alkali-activated binders have been linked with a number of limitations. Aside from usage of alkaline activators which requires safety precautions, long setting time and the need for curing at elevated temperatures are the major drawbacks of alkali-activated low-calcium binders, which can limit their applications to precast systems only. Fast setting times have been found where a combination of sodium hydroxide and sodium silicate was used to activate high-calcium slag binders. Different types of retarding admixtures, from commercially available to chemically potent retarders of Portland cement, have found to be ineffective in slowing down setting times of alkali-activated slags. Some acids (malic and phosphoric acids) have shown successful in retarding setting times, but their applications defeated the purpose through noticeable reduction in strength. With proper proportioning, it may be possible to use the benefits of high-calcium binders to avoid the need for elevated temperatures and to take advantage of the long setting time of low-calcium binders to hinder the quick setting process of high-calcium binders.

In summary, it’s hypothesized that combination of these two binder types can lead to development of high-performance alkali-activated concretes. Integration of high-calcium and low-calcium binders (1) eliminates the need for curing at elevated temperatures, (2) counteracts the fast setting of high-calcium binders and long setting of low-calcium binders, (3) takes advantage of unique benefits offered by each of these two binder types, and (4) offers an alternative to Portland cement as a sustainable and durable binder.



(a) (b)

Figure 1.1 Total number of research on fly ash/slag mixtures from 1996 to 2015; (a) in different periods, (b) categorized by subjects; obtained from Scopus database searched by different keywords in the “article title, abstract, keywords” section

1.3. Why combination of natural Pozzolan and blast furnace slag?

Since blast furnace has been the promising source for high-calcium binders used in the concrete, for the purpose of this study, it was selected as the calcium-rich portion of the combined binder. Amongst the low-calcium binders, metakaolin has limited application due to the high temperature (560 to 580°C) needed for its production and its high hydration liquid demand. These issues result in higher cost and pollution, limiting its application. Fly ash and natural Pozzolan have close characteristics; except that the former is a by-product and the latter is natural. They both have shown potential for use as low-calcium binders. Therefore, they have been considered for the selectin of low-calcium binders.

Figure 1.2 presents the number of publications on fly ash/slag and natural Pozzolan/slag combinations from 1996 till 2015. While there are a total of 31 publications on fly ash/slag mixtures, as of 2015, there has been only one research study reported on natural Pozzolan/slag combination used for production of pastes having 5, 15 and 25% slag. Considering the low percentages and unsuccessful activation of slag in this publication, it can be considered that there is almost no reported fundamental study in this field as of this date. Therefore, natural Pozzolan was selected as the low-calcium binder for this study. While fly ash could have been selected, as more research is needed on alkali-activated fly ash/slag composites, selection of natural Pozzolan provided more research originality.

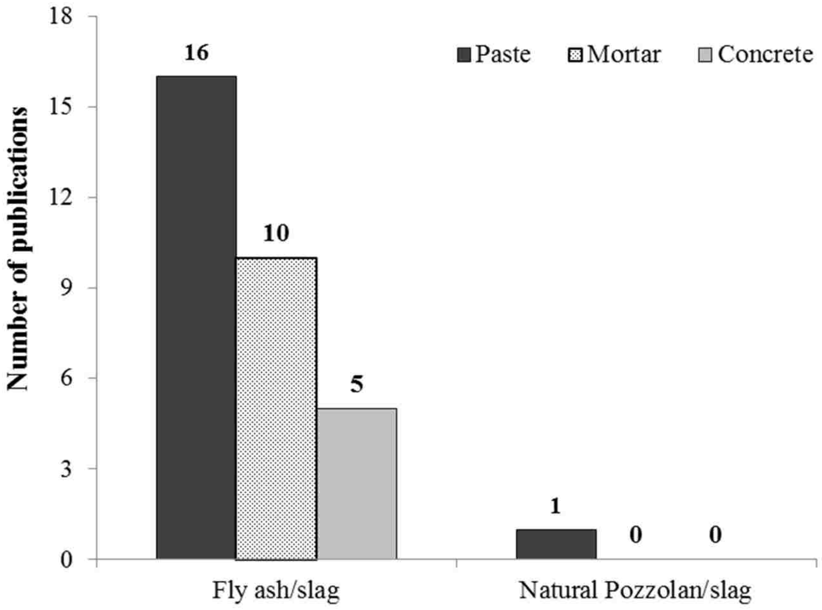


Figure 1.2 The number of research on fly ash/slag and natural Pozzolan/slag mixtures till 2015, obtained from Scopus database searched by different keywords in the "article title, abstract, keywords" section

1.4. Research objectives and outline of dissertation

The main goal of this dissertation is to fully replace Portland cement with alkali-activated Portland cement free binders to produce sustainable concrete with a similar or superior performance to that of Portland cement concrete. It's hypothesized that this goal can be achieved through proper combinations of natural Pozzolan and slag (slag as high-calcium part and natural Pozzolan as low-calcium part) and alkaline activators.

It's well-understood that replacement of Portland cement is only possible through a step-by-step process from developing proper pastes with adequate fresh and strength properties, producing strong and durable mortars, and finally working towards development of high-performance concretes. Accordingly, this dissertation is devised on the basis of the following objectives to:

- *Produce Portland cement-free binders by alkali-activation of natural Pozzolan and slag.*
- *Develop alkali-activated natural Pozzolan/slag pastes with adequate flow, proper setting time, and adequate compressive strength.*
- *Produce alkali-activated natural Pozzolan/slag mortars and assess their fresh, mechanical and durability properties.*
- *Develop alkali-activated natural Pozzolan/slag concretes and evaluate their performances.*

The followings are the outline designed to achieve the above-mentioned objectives:

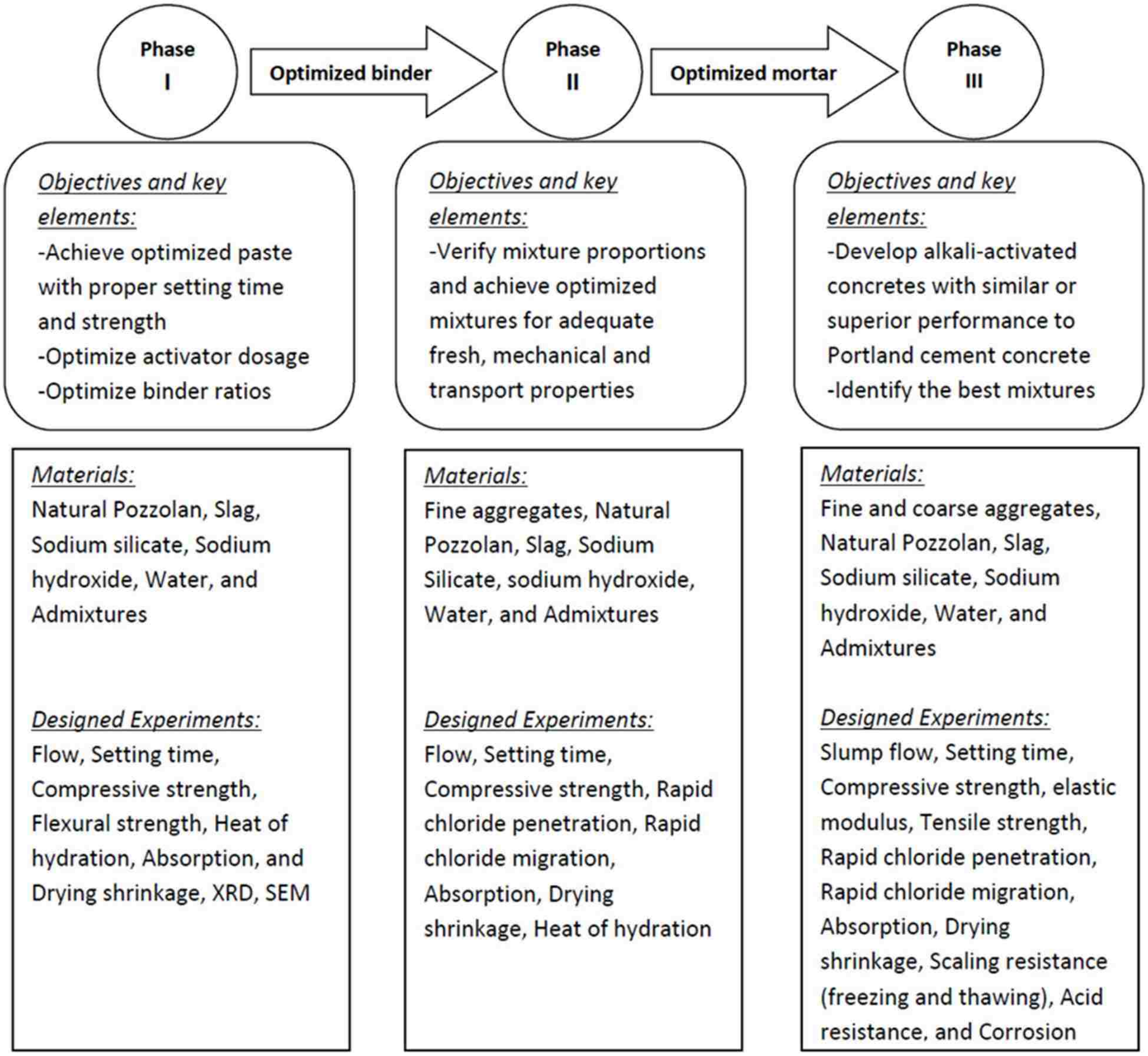
Step (1)- Literature review: The first task is to review the state of the art on different alkali-activated binders. This task, which is covered in Chapter 2, presents the history of alkali-activated binders, the ingredients used for production of alkali-activated materials, performance of different cementitions components activated with alkaline activators, chemical reactions of alkali-activated binders, suggested models, and final reaction products. The findings of this task are used in selection of materials and experimental program.

Step (2)- Development of alkali-activated natural Pozzolan/slag pastes with adequate flow, proper setting time, and enough compressive strength: The second task is devoted to production of alkali-activated natural Pozzolan/slag pastes with satisfactory fresh and hardened properties. The aim is to produce pastes that can provide similar fresh properties, particularly setting time, to those of Portland cement pastes, as well as adequate strength. This task is presented in Chapter 4. The X-ray diffraction (XRD) and scanning electron microscope (SEM) are also considered as additional tools which may help in identification of reaction products and explanation of the observed behaviors.

Step (3)- Production of alkali-activated natural Pozzolan/slag mortars and assessment of their properties: This task, which is covered in Chapter 5, is designed to serve as a transition between paste and concrete. Fine aggregate are added in this task to find if properties of the produced binder can be enhanced when blended with fine aggregate. This task also verifies the activator dosages and molarities, and the selected mixture proportions.

Step (4)- Development of alkali-activated natural Pozzolan/slag concretes and evaluation of their performances: In this task, alkali-activated concretes are designed based on the results obtained in Tasks 2 and 3. A comprehensive experimental program is carried out to assess performance of the studied alkali-activated concretes through properties including flow, setting times, strength and stiffness, fluid migration, dimension stability, and durability. A reference Portland cement concrete having a nearly similar flow and compressive strength is used for comparison purpose. Chapter 6 documents the findings of this task.

The experimental program, developed in Tasks 2 to 4, is briefly summarized in Figure 1.3.



Objectives and key elements:
-Achieve optimized paste with proper setting time and strength
-Optimize activator dosage
-Optimize binder ratios

Materials:
Natural Pozzolan, Slag, Sodium silicate, Sodium hydroxide, Water, and Admixtures

Designed Experiments:
Flow, Setting time, Compressive strength, Flexural strength, Heat of hydration, Absorption, and Drying shrinkage, XRD, SEM

Objectives and key elements:
-Verify mixture proportions and achieve optimized mixtures for adequate fresh, mechanical and transport properties

Materials:
Fine aggregates, Natural Pozzolan, Slag, Sodium Silicate, sodium hydroxide, Water, and Admixtures

Designed Experiments:
Flow, Setting time, Compressive strength, Rapid chloride penetration, Rapid chloride migration, Absorption, Drying shrinkage, Heat of hydration

Objectives and key elements:
-Develop alkali-activated concretes with similar or superior performance to Portland cement concrete
-Identify the best mixtures

Materials:
Fine and coarse aggregates, Natural Pozzolan, Slag, Sodium silicate, Sodium hydroxide, Water, and Admixtures

Designed Experiments:
Slump flow, Setting time, Compressive strength, elastic modulus, Tensile strength, Rapid chloride penetration, Rapid chloride migration, Absorption, Drying shrinkage, Scaling resistance (freezing and thawing), Acid resistance, and Corrosion

Figure 1.3 Experimental laboratory program

CHAPTER 2- LITERATURE REVIEW

2.1. History/background

‘’The concept of alkali-activated materials as an alternative to Portland cement has been known since at least 1908’’ (Provis and Van Deventer 2014). Provis and Van Deventer (2009) stated Purdon as the first researcher who developed scientific basis for these binders in 1940 in Belgium (Purdon 1940). Purdon (1940) activated more than 30 different slags by use of sodium hydroxide or combinations of calcium hydroxide and sodium salts. He achieved strength development rate and ultimate strengths comparable to those of Portland cement mixtures. He also commercialized alkali-activated materials in Belgium in the 1950s. Several buildings were constructed that still stand more than 60 years later (Provis and Van Deventer 2014). According to Shi et al. (2011), however, Kuhl (a German cement chemist and engineer) was the first who developed alkali-activated binders in 1930. Recently, a patent of Kuhl was recognized which dates back to 1908 (see Figure 2.1). This work is considered now the first use of alkali-activated materials as an alternative for Portland cement.

UNITED STATES PATENT OFFICE.

HANS KÜHL, OF BLANKENESE, NEAR HAMBURG, GERMANY, ASSIGNOR, BY MESNE ASSIGNMENTS, TO THE ATLAS PORTLAND CEMENT COMPANY, OF NEW YORK, N. Y., A CORPORATION OF PENNSYLVANIA.

SLAG CEMENT AND PROCESS OF MAKING THE SAME.

No. 900,939. Specification of Letters Patent. Patented Oct. 13, 1908.

Application filed July 3, 1907. Serial No. 381,960.

Figure 2.1 The 1908 patent of Kuhl (Provis and Van Deventer 2014)

Although the research started in Western Europe, it didn’t continue there or was limited till 1980s. The research shifted eastward to Soviet Union and China for several decades. The shortage of cement led the researchers and manufacturers of these countries to look for alternatives. Glukhovsky (1959) was the first and the most distinguished researcher who focused on alkali-carbonate activation of metallurgical slags. Glukhovsky (1959) also sought to investigate the cement binders used in ancient Roman and Egyptian buildings. His studies showed that these monuments were consisted of alkali-rich Pozzolan mortars, being extremely durable over millennia. These findings, which confirmed later by the other researchers, indicated that the first application of alkali-activated binders was indeed thousand years ago (ancient times). These observations revealed the promising performances of these binders as well. Glukhovsky also focused on explaining the difference between the compositions of Portland cement and other minerals found in the earth’s crust (Roy 1999). He found that Portland cement forms C-S-H and $Ca(OH)_2$ as hydration products, whereas the other minerals predominantly form zeolites, also called aluminum silicate hydrates, that lead to enhanced durability (Roy 1999). He then developed an alkali-activated binder which he named “soil-cement”; the soil to represent a ground rock and cement to represent its cementitious properties. The “soil-cement” consisted of ground alumino-silicates mixed with alkali-rich industrial wastes (Glukhovsky 1959).

Davidovits (1979) was another researcher who made significant progress in this field by developing and patenting several aluminosilicate-based formulas for niche applications in France. Davidovits further defined these developed binders as geo-polymers in a study on alkali-activation of metakaolin. He combined "polymer" and "geo" due to the ability of these binders to transform, polymerize, and harden at low temperatures, and being inorganic, hard, and stable at high temperatures (Davidovits 1979). He was also the first author to address CO_2 emissions of alkali-activated binders stating that they generate just 0.184 tons of CO_2 per ton of binder (Davidovits et al. 1990).

During 1980s, an especial type of alkali-activated concrete known as F-concrete was developed and commercialized in Northern Europe (Provis and Van Deventer 2014). “Through the 1980s and 1990s, a high-early-strength hybrid Portland/alkali-activated concrete termed Pyrament was marketed in North America” (Provis and Van Deventer 2014). Wastiels et al. (1994) introduced alkali-activated fly ash in the early 1990s.

From then, research on alkali-activated binders has grown dramatically, in particular due to the development of new techniques capable of identifying mineralogical and microstructural characteristics of alkali-activated materials and recent attention to sustainability. Since the 1990s, research on this topic expanded to all corners of the globe, “with more than 100 active research centers (academic and commercial) now operating worldwide, and detailed research and development activity taking place on every inhabited continent” (Provis and Van Deventer 2014). Most of these research have been dedicated to (1) development of binders with acceptable performance or comparable performance to that of Portland cement, (2) microstructural characterization of these binders, and (3) activation of raw materials available in each location. A summary of the important events in the history of alkali-activated materials is documented in Table 2.1.

Table 2.1 Important events in history of alkali-activated materials (Li et al. 2010)

Year	Author	Significance
1908	Kuhl	US Patent: Slag cement and process of making the same
1939	Feret	Slags used for cement
1940	Purdon	Alkali-slag combinations
1959	Glukhovsky	Theoritical basis and development of alkaline cements
1965	Glukhovsky	First called 'alkaline cements'
1979	Davidovits	Geopolimer' term
	Malinowski	Ancient aqueducts characterized
1983	Forss	F-cement (slag-alkali-superplasticizer)
1984	Langton and Roy	Ancient building materials characterized
1985	Davidovits and Sawyer	Patent of 'Pyrament' cement
1986	Krivenko	DSc Thesis, R_2O-RO-SiO_2-H_2O
	Malolepsy and Petri	Activation of synthetic melilite slags
	Malek et al.	Slag cement-low level radioactive wastes forms
1987	Davidovits	Ancient and modern concretes compared
1989	Deja and Malolepsy	Resistance to chlorides shown
	Kaushal et al.	Adiabatic cured nuclear wastes forms from alkaline mixtures
	Roy and Langton	Ancient concretes analogs
	Majundar et al.	$C_{12}A_7$-slag activation
	Talling and Brandstetr	Alkali-activated slag
1990	Wu et al.	Activation of slag cement
1991	Roy et al.	Rapid setting alkali-activated cements
1992	Roy and Silsbee	Alkali-activated cements: an overview
	Palomo and Glasser	CBC with metakaolin
1993	Roy and Malek	Slag cement
1994	Glukhovsky	Ancient, modern and future concretes
	Krivenko	Alkaline cement
1995	Wang and Scrivener	Slag and alkali-activated microstructure
1996	Shi	Strength, pore structure and permeability of alkali-activated slag
1997	Fernandez-Jimenez and Puertas	Kinetic studies of alkali-activated slag cements
1998	Katz	Microstructure of alkali-activated fly ash
1999	Davidovits	Chemistry of geopolymeric systems, technology
	Roy	Opportunities and challenges of alkali-activated cements
	Palomo	Alkali-activated fly ash-a cement for the future
2000	Gong and Yang	Alkali-activated red mud-slag cement
	Puertas	Alkali-activated fly ash/slag cement
2001	Bakharev	Alkali-activated slag concrete
2003	Palamo and Palacios	Immobilization of hazardous wastes
2004	Grutzeck	Zeolite formation
2006	Sun	Sialite technology
2007	Duxson	Geopolymer technology: the current state of the art
2008	Hajimohammadi et al.	One-part geopolymer
2009	Provis and van Deventer	Geopolymers: structure, processing, properties and industrial applications
2011	Bondar et al.	Progress in alkali-activation of natural Pozzolans
2014	Pacheco-Torgal et al.	Handbook of alkali-activated cements, mortars, and concretes

2.2. Starting materials (components)

Alkali-activated binders (also known as alkali-activated cements or geopolymers in literature) are “essentially the result of an alkaline attack on amorphous or vitreous natural materials or industrial by-products.” Accordingly, these binders are composed of two main components: (1) an alkaline activator or combination of alkaline activators, and (2) a cementitious component or combinations of cementitious components. Figure 2.2 shows the major ingredients used in production of alkali-activated binders (Pacheco-Torgal et al. 2015). This section briefly reviews these ingredients.

2.2.1. Cementitious components

As shown in Figure 2.2, different materials have been used as cementitious component of alkali-activated materials. Amongst them, blast-furnace slags and fly ash are the most commonly used cementitious components. Metakaolin and natural Pozzolans are the other sources that have been used to a lesser extent. The typical chemical compositions of these materials are presented in Table 2.2.

Based on the chemical compositions, these materials can be divided into two main groups: cementitious materials (or high-calcium binders) and Pozzolanic materials (or low-calcium binders). High-calcium binders contain a considerable amount of calcium oxides, so they have cementing property on their own. Low-calcium binders contain high silica and alumina and low calcium oxide. Accordingly, they don’t have cementing property on their own and can’t harden without use of high-calcium binders or alkaline activators. Their alkaline activation produces an amorphous alkaline aluminosilicate hydrate (N-A-S-H gel) which differs substantially from the semi-crystalline C-S-H gels or C-A-S-H gels that form due to alkaline activation of high-calcium binders. A brief review of these materials is presented below:

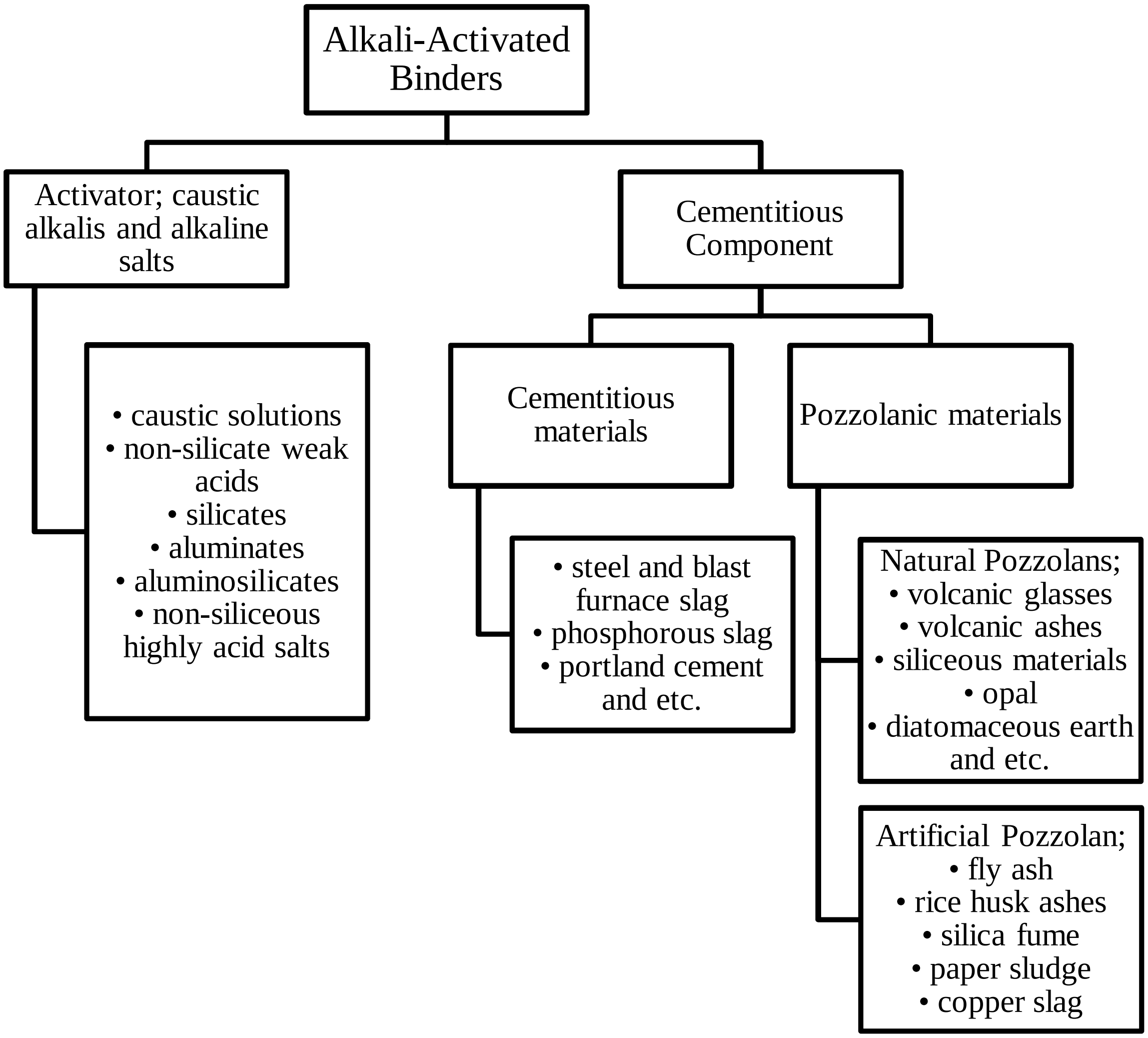


Figure 2.2 Different components of alkali-activated binders (Pacheco-Torgal et al. 2015)

Table 2.2 Chemical compositions of cementitious materials (ACI 232.1 2012, Pacheco-Torgal et al. 2015)

Component	Blast Furnace Slag	Class C Fly Ash	Class F Fly Ash	Metakaolin	Natural Pozzolans
SiO_2	27-40%	34.1%	42.6-59.8%	40-70%	45-86%
CaO	30-50%	38%	2.8-7%	--	3-10%
Al_2O_3	5-35%	14.2%	21.8-34.5%	20-35%	2-20%
Fe_2O_3	<1%	7.2%	6.3-18.1%	<1%	2-10%
MgO	1-2.%1	1.5%	1.2-2.6%		0.5-4.5%
SO_3	<3%	4.2%	0.19-1.9%		
Na_2O	1-3%*	0.44%	0.15-0.94%		0.4-11%[+]
K_2O		1.4%	0.38-6%		

* The summation of Na_2O and K_2O

[+] Na_2O plus 0.658 K_2O

2.2.1.1. Blast furnace slag

Different slags with different origins and properties have been utilized in production of alkali-activated binders including steel, phosphorous, and blast-furnace slags (also known as ground granulated blast furnace slag (GGBFS) in literature). Amongst them, GGBFS is the most commonly used type of slag for the purpose of alkali-activation. GGBFS is a by-product of iron production (refining iron). In the process of refining iron, which is shown in Figure 2.3 (Shi et al. 2006b), iron ore, iron scrap, fluxes, and coke as fuel are charged into the blast furnace. These materials go through numerous chemical and physical reactions while descending to the bottom of the furnace. The coke, entered from the top, descends to the level where the preheated air or hot blast enters the blast furnace. The reaction of hot air with coke produces carbon monoxide (CO). Carbon monoxide reduces iron oxides in the iron ores to pure iron and produces carbon dioxide (CO_2), which leaks out of the furnace at the top. The limestone, which is another element enters from the top, descends in the blast furnace and decomposes at high temperatures into calcium oxide (CaO) and additional carbon dioxide. Calcium oxide becomes the blast furnace flux for the slag and removes Sulphur and other impurities. The slag forms from any remaining silica, alumina, magnesia or lime that enters with the iron ore or coke. “The molten slag appears above the pig iron at the bottom since it has a lower density. Its temperature is close to that of the molten pig iron, which ranges between 1400 and 1600°C. The slag rises to the surface and is trapped off from time to time” (Shi et al. 2006b).

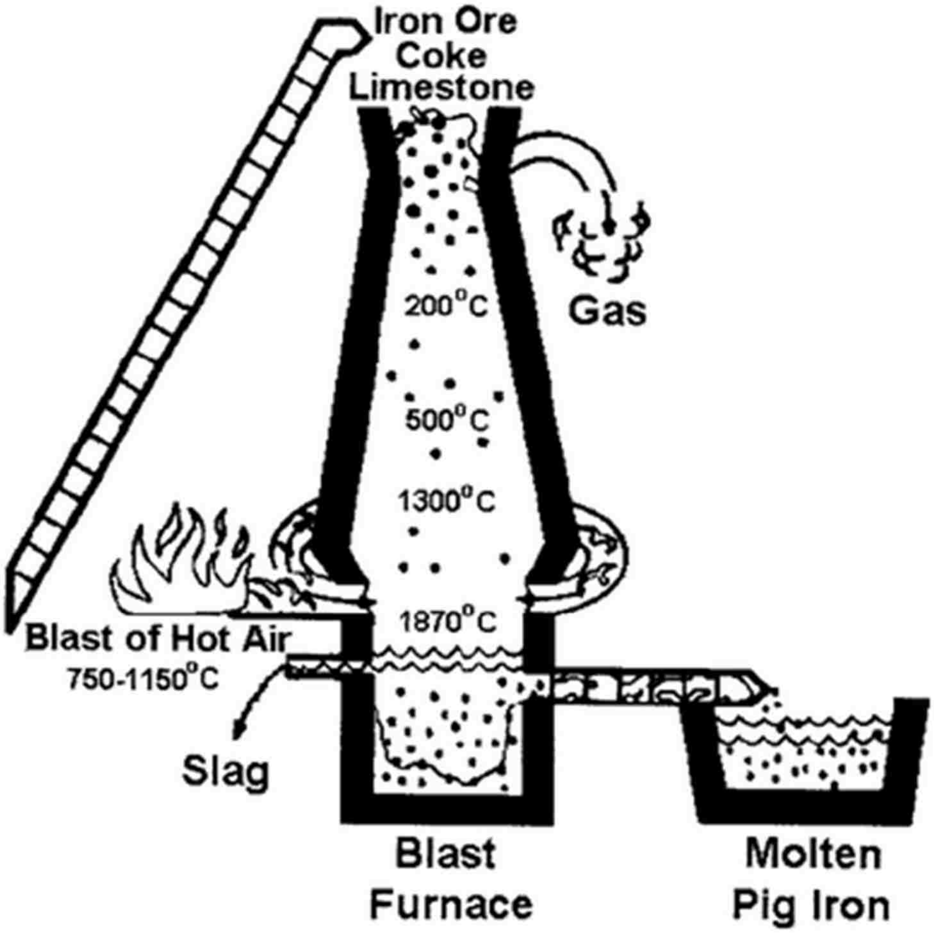


Figure 2.3 Schematic representation of a blast furnace (Shi et al. 2006b)

2.2.1.2. Coal fly ash

Fly ash (primarily class F) has been commonly used in production of alkali-activated materials. Fly ash is a by-product of power generation at coal-fired power plants. It is collected by the electrostatic or mechanical precipitators that separate the solid particles from the smoke, resulting in a less harmful smoke for the environment (Shi et al. 2006b).

The chemical composition of fly ash varies widely, depending on the coal composition, substances injected into the coal, or gas steam. Use of limestone and dolomite for desulphurization increase the amounts of calcium and magnesium oxides. Inclusion of conditioning agents for improvement of collection efficiency (such as sodium carbonate and bicarbonate, Sulphur trioxide, sodium sulfate, magnesium oxide, water, phosphorous, ammonia, and tri-ethylamine) affects the fly ash composition as well (Shi et al. 2006b).

Depending on the chemical composition, fly ash is classified into two groups of class C and class F. Class F fly ash contains less than 10% calcium oxide (low CaO), whereas class C fly ash has CaO content of higher than 10% (usually between 15 and 30%). On the other hand, Class F fly ash contains high silica and alumina. The summation of silica, alumina, and iron oxide is more than 70% for class F fly ash, while this summation is between 50 to 70% for class C fly ash.

2.2.1.3. Metakaolin

Metakaolin is an amorphous, highly reactive aluminosilicate, which has shown promising performance as a starting binding component of alkali-activated materials. Its application, however, has been limited to laboratory-scale tests and ceramic-type applications due to (1) the high temperature needed to produce metakaolin which results in high cost and pollution, and (2) its high hydration liquid demand.

Metakaolin ($Al_2O_3.2SiO_2$) is produced by firing kaolinitic ($Al_2(Si_2O_5)(OH)_4$), which is a clay mineral family phyllosilicate (Pacheco-Torgal et al. 2015). Different stages of firing kaolinitic clay change its atomic structure and result in a highly reactive aluminosilicate, called metakaolin. The starting kaolinitic clay loses inter-layer water or moisture between 100° and 250°C. Dehydration begins between 300° to 400°C and accelerated between 500° and 600°C. At these temperatures, dehydration of clay is completed and all the clay atomic structure is destroyed, thus resulting in a highly Pozzolanic material. If aluminum presents in the structure, alumina forms at 950°C. The general process of producing metakaolin from kaolinitic clay is presented in Eq. (1) (Shi et al. 2006b).

$$Al_2(Si_2O_5)(OH)_4 \xrightarrow{560-580℃} Al_2O_3.2SiO_2 + 2H_2O \qquad \text{(Eq. 1)}$$

The chemical composition of the resulting metakaolin is strongly dependent on the chemical and mineralogical composition of the starting clay. The time and temperature of firing process are both dependent on the type of clay.

2.2.1.4. Natural Pozzolans

Natural Pozzolans are the other types of aluminosilicates that have the potential to be activated by use of alkaline activators. Although they have high potential for activation and “it’s estimated that about 5% of the solid surface of the earth is covered by volcanic rocks or effusive (Lorenz 1985),” there are limited research on alkali-activation of natural Pozzolans to date.

Natural Pozzolans are usually results of volcanic eruptions which cooled quickly under different conditions and formed amorphous or vitreous materials. The volcanic-type natural Pozzolans include (1) volcanic glasses and (2) volcanic Tuffs.

Volcanic glasses such as volcanic ash, pumice and pumicite derived from volcanic rocks in which amorphous glass is produced from fusion. Of these, “volcanic ashes are formed during explosive eruptions by shattering of solid rocks and violent separation of magma (molten rock) into tiny pieces. Explosive eruptions are generated when ground water is heated by magma and abruptly converted to steam and also when magma reaches the surface so that volcanic gases dissolved in the molten rock expand and escape (explode) into the air extremely rapidly. Volcanic ash is composed of fragments of rock, minerals and glass that are less than 2mm (0.08in) in diameter” (Shi et al. 2006b). Pumice and Pumicite are other forms that form during eruptions. “During an explosive eruption, volcanic gases dissolved in the liquid portion of magma also expand rapidly to create a foam or froth; the liquid part of the froth quickly solidifies to glass above ground” (Shi et al. 2006b). Therefore, pumice is actually a kind of glass and not a mixture of minerals.

Volcanic Tuffs were formed by the action of groundwater on volcanic glass under high temperature. Their properties varied depending on the characterization of volcanic glass, properties of ground water, temperature and pressure. Natural zeolite is an especial type of natural Pozzolans (volcanic Tuffs) which formed over millions of years by nature. It’s from alteration and crystallization of volcanic ash in alkaline waters under high pressure.

Siliceous materials such as diatomaceous earths, diatomaceous stone, opal and chert are considered another type of natural Pozzolans that “usually formed from the precipitation of silica from solution or from the remains of organisms” (Shi et al. 2006b).

2.2.2. Alkaline activator

Caustic alkalis (hydroxides) and alkaline salts have been utilized for the purpose of alkaline activation. These activators can be classified into following groups, where M is the alkaline cation (Provis and Van Deventer 2009).

- Caustic alkalis (MOH) such as LiOH, NaOH, KOH, RbOH and CsOH
- Non-silicate weak acid salts (M_2CO_3, M_2SO_4, M_3PO_4, MF)
- Silicate ($M_2O.nSiO_2$)
- Aluminates ($M_2O.nAl_2O_3$)
- Aluminosilicates
- Non-siliceous strong acid salts (M_2SO_4)

A brief review of the used alkaline activators is presented in following sections:

2.2.2.1. Caustic alkalis

While different alkali hydroxides such as LiOH, NaOH, KOH, RbOH and CsOH can be used for the purpose of alkali activation, the most commonly used ones are sodium and potassium hydroxides.

- *Lithium hydroxide*

Lithium hydroxide is at the lower end of the useful alkalinity range for hydroxide activators. It had minor importance in the previous research on alkali-activated binders. The only literature on lithium hydroxide come from the patent work using it as an accelerator for polymerization or from the general reviews mentioning lithium as a possible alkali cation metal for geopolymerization (Provis and Van Deventer 2009).

- *Sodium hydroxide*

Sodium hydroxide is the cheapest and most available alkaline hydroxide. Therefore, it has been the most commonly utilized activator. There are some concerns, however, that can affect its applications. The highly corrosive nature of concentrated NaOH or other alkali hydroxides necessitates specialized processing equipment for large-volume productions. This issue and the performance issues resulted in preference of silicate activation. In addition, the phase diagram of NaOH-H_2O system, which is shown in Figure 2.4, is complicated. While solubility of sodium hydroxide at 25°C is 53.3% by mass (28.57 mole), it reduces to 30% by mass (10.73 mole) at 0°C. It also has a complex phase diagram between 0°C to 25°C. Therefore use of concentrated NaOH (high molarity) at cooler climates can be complicated (Provis and Van Deventer 2009).

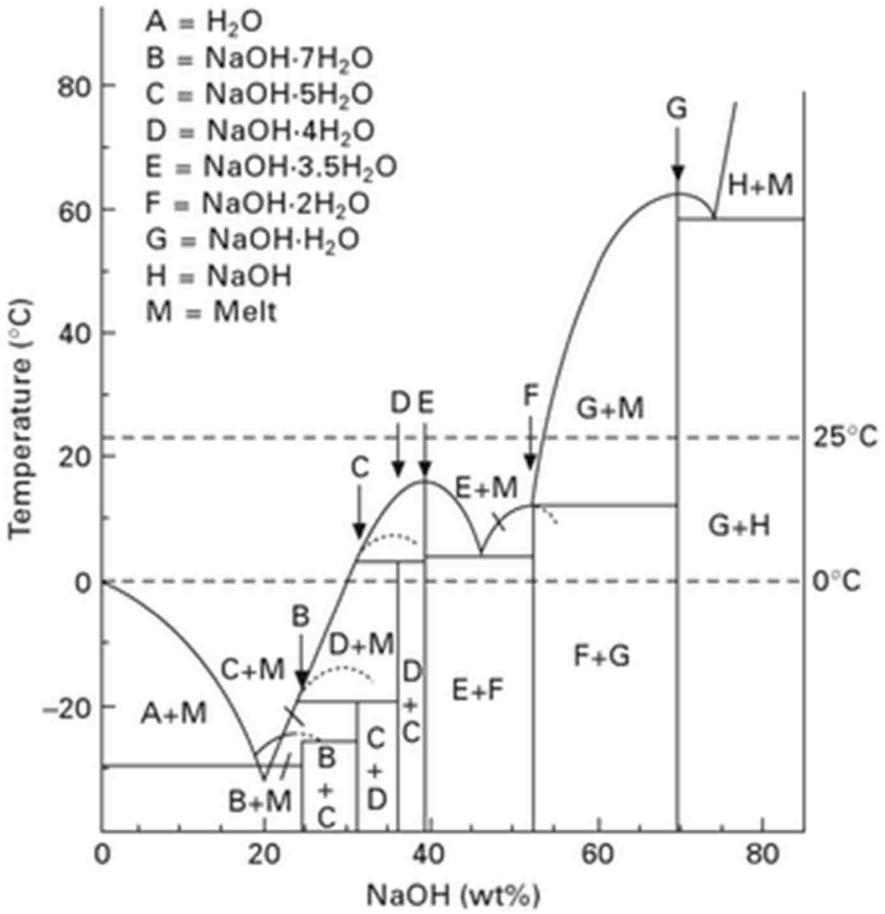


Figure 2.4 Phase diagram of NaOH-H_2O system (Provis and Van Deventer 2009)

- *Potassium hydroxide*

Potassium hydroxide is another main hydroxide source that can be used for alkali-activation. Potassium hydroxide has much simpler phase diagram than NaOH- H_2O system. It's therefore not problematic under realistic activation conditions. However, it has been shown that crystallization is slower in KOH/metakaolin and KOH/fly ash systems as compared to NaOH/metakaolin and NaOH/fly ash systems (Provis and Van Deventer 2009, Duxson et al. 2007b, Fernandez-Jimenez et al. 2006a). In particular, Fernandez-Jimenez et al. (2006a) noticed considerably suppressed crystallization due to activation by KOH, when they activated fly ash with NaOH and KOH.

- *Rubidium hydroxide*

Rubidium hydroxide (RbOH) is rarely studied, if any, in the literature. Lack of data can be seen from Gurvich et al. (1997) review indicating the best currently available thermochemical data of this compound from a 1906 study. The lack of research could be due to its cost and relative scarcity.

- *Cesium hydroxide*

Cesium hydroxide (CsOH) has also been used for the purpose of alkali-activation. Although it's less rare than Rubidium hydroxide, it's still sufficiently exotic to be used for large-scale applications. Its most desirable application can be for niche ceramic-type usage requiring high thermal resistance and very low thermal expansion (Provis and Van Deventer 2009).

The most conducted research on use of CsOH in geopolymerization process has been on: (1) immobilization of radioactive Cesium in geopolymers, mainly as a minor component in mixed-alkali systems, and (2) for X-ray scattering studies, as it provides very good X-ray contrast and leads to obtaining valuable data (Provis and Van Deventer 2009).

2.2.2.2. Sodium silicate

Sodium silicate, also known as waterglass, has been widely used for the purpose of alkali-activation. It’s also considered the most effective alkaline activator for many cementing systems (Shi et al. 2006b).

“Sodium silicate is the generic name for a series of compound with the formula $Na_2O.nSiO_2$” (Shi et al. 2006). Commercial liquid sodium silicates have n value of 1.60 to 3.85, which is also called the ratio of silica-to-sodium oxide or modulus of sodium silicate. While “n” can theoretically be any number, the liquid sodium silicate outside the range of 1.60 to 3.85 have limited stability, thus is not practical (Shi et al. 2006b).

2.2.2.3. Sodium carbonate

Sodium carbonate, also commercially known as soda ash, is another activator that has shown satisfactory performance for different cementing components. Sodium carbonate is a “white anhydrous powdered or granular material containing well above 99% Na_2CO_3”, which is almost equivalent to 58% Na_2O (Shi et al. 2006b). Sodium carbonate has been used for activation of GGBFS in eastern and central Europe for more than 50 years and for different applications such as buildings, civil infrastructure and demonstration projects. The reason for interest in sodium carbonate is its lower environmental impacts in comparison with hydroxide or silicate solutions. It also induces lower pH which is beneficial in terms of occupational health and safety. They, however, found less interest from both academia and industry as they develop strength much slower than sodium hydroxide and sodium silicate systems.

2.2.2.4. Sodium sulfate

Different studies have shown sodium sulfate as an effective alkaline activator for lime-based cementing components.

Sodium sulfate (Na_2SO_4) can be found in two major forms; anhydrous Na_2SO_4 (Thenardite) and $Na_2SO_4.10H_2O$ (Mirabilite). “Sodium sulfate is obtained either directly from mining (natural resources of over 10^9 tonnes are estimated to exist worldwide), or as a byproduct from the manufacture of many other industrial chemicals” (Provis and Van Deventer 2014). Accordingly, if activation with sodium sulfate results in satisfactory performance, its usage provides significant scope for Greenhouse savings in binder production (Provis and Van Deventer 2014).

2.2.2.5. Sodium aluminate

There have been a few studies using sodium aluminate for the purpose of activation. In these studies, it was shown that viable binders can be made using sodium aluminate (Phair and Van Deventer 2002, Rees 2007, and Brew and Mackenzie 2007).

2.2.2.6. Final note

Of these activators, sodium hydroxide, sodium silicate, sodium carbonate, and sodium phosphate are the most available and economical activators (Shi et al. 2006b). Sodium and potassium hydroxide and silicate are the most commonly used activators for the purpose of geopolymerization. Potassium compounds, however, will have a very limited application due to (1) their availability and costs, and (2) the existing literature indicating their similar properties to sodium compounds. Thus, for the purpose of this study, sodium hydroxide and sodium silicate were selected as alkaline activators.

2.3. Literature on different types of alkali-activated materials

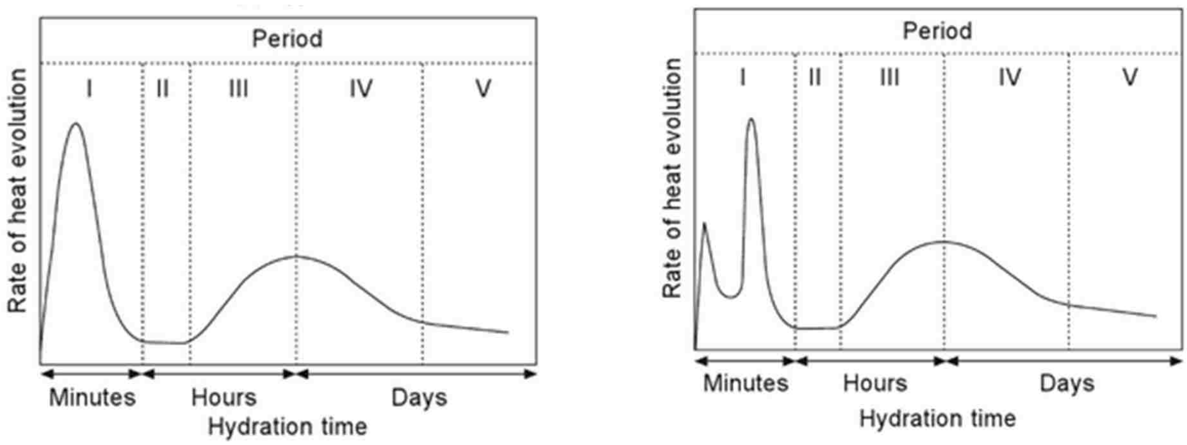
As mentioned earlier, blast-furnace slag and fly ash (Class F) are the most used cementitious components in production of alkali-activated binders. To a lesser extent, metakaolin and natural Pozzolans have been used as well. From these materials, metakaolin has limited application due to the high temperature (560 to 580°C) needed for its production and its high hydration liquid demand. These issues result in a higher cost and pollution to limit its application. Therefore, the state of the art in this section is devoted to alkali-activation of (1) slag, (2) fly ash, (3) natural Pozzolan, (4) combination of fly ash and slag, and (5) combination of natural Pozzolan and slag. As sodium hydroxide and sodium silicate are selected for this research, the focus of the literature review is mainly on these two types of activators.

2.3.1. Slag

The most research in the field of alkali-activated materials have been dedicated to activation of slags; in particular blast furnace slag. The state of the art on different properties of alkali-activated slag pastes, mortars, and concretes are presented in the sections to follow.

2.3.1.1. Heat of hydration

Heat of hydration of alkali-activated slags has been studied by different researchers. Figure 2.5 presents typical heat of hydration models of sodium hydroxide- and sodium silicate-activated slags. Figure 2.5.a shows the typical pattern observed for slags activated with sodium hydroxide or high pH activators. This type of curve is similar to that of Portland cement and includes 5 stages; “(1) Initial (pre-induction) period, (2) induction period, (3) acceleration (post-induction) period, (4) deceleration period, and (5) diffusion period” (Pacheco-Torgal et al. 2015). In this process, there are two peaks; one initial peak at pre-induction period and acceleration peak after induction period. The magnitude and positions of these peaks are dependent on different variables. The first peak is related to wetting and dissolution of slag particles, whereas the second peak is attributed to the accelerated hydration of slag.



(a) (b)

Figure 2.5 Heat of hydration; (a) typical pattern for sodium hydroxide-activated slag, (b) typical pattern for sodium silicate-activated slag (Pacheco-Torgal et al. 2015)

Figure 2.5.b presents a typical pattern that can be observed when slag activates with sodium silicate. It can be seen that this curve includes three peaks; two peaks in pre-induction period and another one after induction period. While the first peak is related to the wetting and dissolution of slag particles, the second peak (additional initial peak) is related to the reaction between dissolved Ca^{2+} coming from slag and anions of activators. It should be noted that the

two initial peaks may merge together depending on the activator dosage, slag reactivity and hydration temperature. Also, the presented models will change, if combination of two or more activators will be used.

In addition to the nature of activator (shown in Figure 2.5), several other factors affect heat of hydration of alkali-activated slags including activator dosage, water-to-slag ratio, nature of slag, pH of activator solution, and temperature. In general, increases in activator dosage accelerate the hydration process and increase the cumulative heat of hydration. Depending on the activator used, water-to-slag ratio (W/S) can significantly affect heat of hydration too (see Figure 2.6). As can be seen while increases in W/S from 0.45 to 0.6 had minor effects for NaOH-activated slags (slight reduction in hydration peak), similar changes in W/S substantially changed the hydration curve of sodium silicate-activated slag. There was not an obvious induction period for W/S of 0.45, whereas induction period last for almost 15hr for W/S of 0.60. The increases in W/S also modified the sharp accelerated peak to a very diffuse peak.

Some publications also suggested that increases in initial pH of activator accelerate early hydration of slag (Yuan et al. 1987, Roy et al. 1992, Song et al. 2000). They stated that for a given amount of Na_2O, sodium hydroxide solution has higher pH than the other sodium-containing activators, so sodium hydroxide-activated slag mixtures has the shortest induction period and the highest accelerated hydration peak. Other researchers argued that the hydration relies more upon the nature of anion of the activator than its initial pH (Shi et al. 1989). Temperature is another important factor that can significantly affect heat of hydration and the time of accelerated peak. In general, for every 10°C increase in temperature, the chemical reactions will be doubled, the peak value will be nearly doubled, and the time of peak appearance will be almost halved.

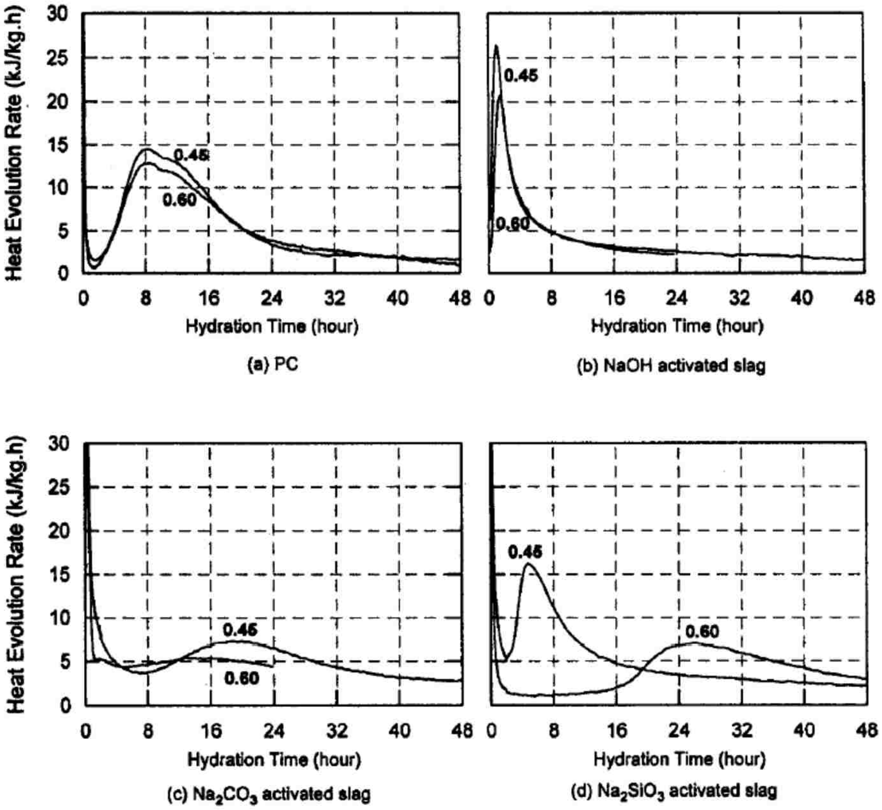


Figure 2.6 Effect of W/S and W/C on heat of hydration; (a) Portland cement, (b) sodium hydroxide-activated slag, (c) sodium carbonate-activated slag, and (d) sodium silicate-activated slag (Shi and Day 1996b)

2.3.1.2. Setting time

Setting times, in particular initial setting time, is of important characteristics of cementitious materials as they represent the time available for transporting, placing, compacting, and finishing. Controlling setting time has been one of the main issues regarding use of alkali-activated slags, in particular when sodium silicate was part of the activator. Use of liquid sodium silicate results in fast setting, which may cause problems for mixing and placement. Table 2.3 presents initial and final setting times of the study conducted by Shi and Li (1989). It can be seen that the initial setting times were less than 7 and 32min when modulus of sodium silicate was 2.5 and 1.5, respectively. For the same modulus of sodium silicate, i.e. 2.5 and 1.5, final setting times were lower than 12 and 80 min (less than 30 min in case of 3% Na_2O), respectively. In another study, Atis et al. (2009) measured setting time of alkali-activated pastes activated with different activators such as liquid sodium silicate, sodium hydroxide, and sodium carbonate containing 4 to 8% sodium. Initial and final setting times of slag pastes activated with sodium hydroxide varied between 4 to 21 min and 28 to 59 min, respectively. These values were in the range of 15 to 35 min and 47 to 77 min for pastes activated with sodium silicate depending on the modulus of sodium silicate. These results show the quick setting time of alkali-activated slags having sodium hydroxide or sodium silicate as alkaline activators. The setting time of sodium carbonate-activated slag pastes were close to that of Portland cement paste; ranging between 170 to 190 min for initial setting time and 288 to 306 min for final setting time.

Table 2.3 Effect of sodium silicate modulus on setting time of alkali-activated slags (Shi and Li 1989)

Activator		Setting time	
Sodium hydroxide concentration (in weight of Na_2O)	Modulus of sodium silicate	Initial (min)	Final (min)
2	0	112	228
2	0.5	62	134
2	1.5	32	79
2	2.5	7	12
3	0	85	216
3	0.5	47	112
3	1.5	11	24
3	2.5	5	7

Since setting time was found to be an important and controlling factor for alkali-activated slag binders, it has been the main focus of several studies. It was found that setting time of these binders are strongly dependent on the type and dosage of activator or activators, nature of slag, and the used admixtures and additives.

Type and dosage of activator are considered the main factor affecting setting time of alkali-activated slag. In general, slags activated with sodium carbonate exhibit longer setting time than slag activated with sodium silicate or sodium hydroxide (Anderson and Gram 1987, Atis et al. 2009). The comparison between sodium hydroxide and sodium silicate is not simple. While Anderson and Gram (1987) concluded generally longer setting time of sodium hydroxide-activated slag than sodium silicate-activated slag, Atis et al. (2009) observed the contrary. The opposite observations are related to substantial dependence of setting time of sodium silicate-activated slags on modulus of sodium silicate. Increases in modulus of sodium silicate solution reduce the setting time. As presented in Table 2.3, Shi and Li (1989) showed that how setting time can reduce substantially when modulus increased from 1.5 to 2.5. Atis et al. (2009) used modulus of 0.75 to 1.5, and observed longer setting time in sodium silicate-activated slags than sodium hydroxide-activated slags. It can speculate that they could observe different, if they used higher modulus such as 2.5. Accordingly, it can be concluded that sodium silicate-activated slags can set quicker or slower than sodium hydroxide-activated slags depends on modulus of sodium silicate. An increase in dosage of activator generally reduces the setting time as well (Chang 2003). Wu (1999) activated slag with sodium silicate and different dosages of Na_2O including 2, 4, 6, 8, and 10%. While increasing the dosage from 2 to 4% didn't significantly change the setting time, the initial setting time reduced from 90 min to 34 min when dosage increased from 4% to 8%. This increase (4 to 8%) significantly affected the final setting time, reducing it from 425 min to 45 min. In case of 10% Na_2O, alkali-activated slag set too fast to allow for measurement of the setting time.

Nature of slag is another parameter affecting setting time. Purdon (1940) stated that setting times of slags from different sources vary, even when they have similar chemical compositions. The basicity of slag ($(CaO+MgO)/SiO_2$) also affects the setting time, as "higher basicity will likely result in shorter setting time regardless of the nature of activator used" (Krivenko 1992). The Blaine fineness of slag affects the setting time as well. Anderson and Gram (1987) observed a very sharp reduction in setting time of alkali-activated slags when Blaine fineness increased from 530 to 670 m^2/kg. They, however, didn't observe a considerable influence when Blaine fineness increased from 350 to 530 m^2/kg.

Combination of activators and use of additives are of the other factors affecting setting process of alkali-activated slag. It has been observed that addition of K_2SO_4 to sodium hydroxide-activated slag or K_2CO_3 to sodium silicate-activated slag increase the setting time.

Similarly, phosphoric acid, potassium sodium tetrate, molasses and melic acid showed slight to considerable retarding effects (Wu et al. 1993, Brough et al. 2000). Brough et al. (2000) also reported significant retarding effect when they added 8% NaCl to sodium silicate-activated slag. On the other hand, they observed accelerating effect by adding 1 or 4% NaCl (Brough et al. 2000). Bilim et al. (2013) didn't find set-retarding admixture effective in hindering setting of alkali-activated slag mortars.

2.3.1.3. Workability

"Workability is defined as the amount of mechanical work or energy required to compact concrete without segregation." While there are several terms describing fresh properties of pastes, mortars, and concretes such as consistency, flowability, mobility, pumpability, finishability and harshness, workability has often been used to represent all these properties.

In general, alkali-activated slags have higher tendency for formation of cementitious structure than Portland cement. It means that ultimate resistance to shear (viscosity) of alkali-activated slag paste is higher than that of Portland cement paste, thus the former has generally less workability than the latter (Glukhovsky et al. 1981, Jolicoeur et al. 1992, Collins and Sanjayan 1999a). The lower workability of alkali-activated slag pastes in comparison with that of Portland cement paste can be seen in Table 2.4 (Jolicoeur et al. 1992).

Workability of alkali-activated slag pastes, mortars and concretes are affected by different factors such as nature of slag, type and dosage of activator or activators, use of chemical and mineral admixtures, and timing for addition of activator. Effects of these factors are presented in the following subsections.

Table 2.4 Mini-slump area of alkali-activated slag and Portland cement pastes (Jolicoeur et al. 1992)

W/C	Concrete type, NaOH dosage in Na_2O	Time of testing (min)		
		10	30	60
0.40	Portland cement	40	34	31
	Alkali, 0	32	20.6	20
	Alkali, 2	30	12	2
	Alkali, 4	35	20	6
0.50	Portland cement	119	110	78
	Alkali, 0	100	84	70
	Alkali, 0.5	92	23	8
	Alkali, 1	66	18	10
	Alkali, 2	72.5	26	7
	Alkali, 4	69	43	18

2.3.1.3.1. Effect of activators' type and dosage

Type of activators and their dosages can significantly affect workability of alkali-activated slag mixtures. In case of sodium silicate-activated slags, the modulus of sodium silicate is a key factor too.

Shi (1987) and Shi and Li (1989) found that there was less water required to attain a normal consistency for sodium silicate-activated slag paste in comparison with the amounts needed for sodium hydroxide and sodium carbonate-activated slag pastes to reach the same consistency. Jolicoeur et al. (1992) measured flow of Portland cement and alkali-activated slag pastes having different dosages of sodium hydroxide; their results are reported in Table 2.4. It can be seen that all alkali-activated slag pastes had lower flow and quicker slump loss in comparison with those of Portland cement pastes. Use of 0.5, 1 and 2% Na_2O in the system of pastes resulted in quicker slump loss than inclusion of 0 or 4% Na_2O. Jolicouer et al. (1992) also assessed effects of sodium silicate modulus on setting time; indicating its substantial role in workability of alkali-activated slag systems. Figure 2.7 shows the mini-slump test results of alkali-activated slag pastes having different sodium silicate' modulus (Jolicouer et al. 1992). It can be seen that for modulus of less than 0.5, workability is low. For modulus of 0.5 to 1, mini-slump flow is very high with minimal slump loss within 60 min. For sodium silicate' modulus of above 1, workability reduced significantly with increases in modulus. In case of modulus of 2, workability was lost within few minutes (less than 10 min) after mixing.

In another study, Jiang (1997) studied rheological properties of slag pastes with or without sodium hydroxide. Use of sodium hydroxide resulted in increases in the apparent viscosity and yield stress of the pastes, in particular for lower water-to-slag ratios. Collins and Sanjayan (1999a) compared the slump flow and slump loss of different types of alkali-activated slag concretes with those of Portland cement concrete. They found that the initial slump of concretes activated with liquid sodium silicate or combination of sodium hydroxide and sodium carbonate was lower than that of PC concrete. These concretes also showed quicker slump loss than PC concrete. The authors reported an opposite trend when they used solid sodium silicate as an alkaline activator.

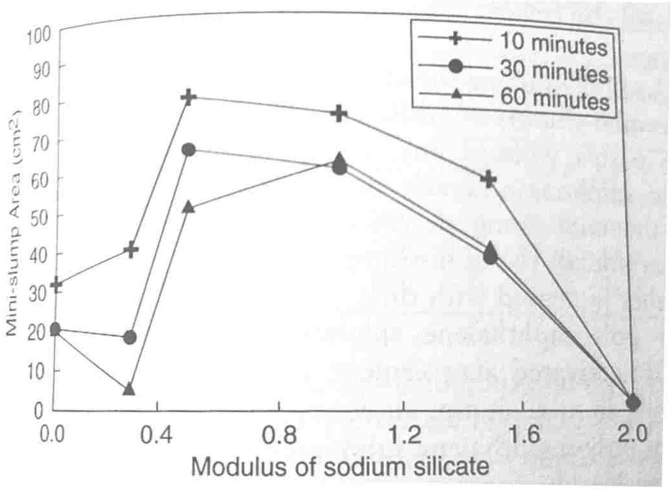


Figure 2.7 Effect of sodium silicate modulus on mini-slump flow (Jolicouer et al. 1992)

2.3.1.3.2. Effect of chemical admixtures

The chemical admixtures, used for PC concrete, don’t necessary work for alkali activated concretes. The high alkaline environment of alkali-activated binders in their fresh state may dissolve or destroy the admixtures, making them ineffective. Accordingly, contradictory results have been reported in the literature on influence of chemical admixtures in workability of alkali-activated slags. Isozaki et al. (1986) used sodium lignosulphonate and formalin condensates of β-naphthalene sodium sulfonate as superplasticizers. While the former provided plasticizing effect, the latter didn’t. Douglas and Brandstetr (1990) applied similar superplasticizers. They didn’t observe any change in consistency except by using 9% sulfonated naphthalene-based superplasticizer. This addition, however, resulted in a significant reduction in one-day strength. Jolicoeur el at. (1992) tried sodium poly-naphthalene sulfonate and Na-gluconate admixtures for sodium hydroxide-activated slags. Use of these admixtures resulted in reasonable increases in workability. The slump loss, however, was rapid for both of these admixtures. They observed similar trend for slags activated with sodium silicate having modulus of less than 0.5. For higher modulus, none of these admixtures could increase the workability (Jolicoeur et al. 1992). Gifford and Gillott (1997) used different types of high-range water reducers; they stated that very high and impractical dosages were required to achieve reasonably workable mixtures. Collins and Sanjayan (2001) reported addition of lignosulphonate water-reducing retarder or sulfonate-based superplasticizers or combination of both effective in improving workability of solid sodium silicate-activated slag pastes. This behavior, however, was attributed to use of solid sodium silicate. Zhu et al. (2001) found an effective retarder which keeps the workability of concrete during first several hours without affecting the early and late-age strengths. However, not much detail was provided by the authors. Puertas el al. (2003b) found newly developed superplasticizers such as vinyl co-polymer- and polyacrylate co-polymer-based admixtures ineffective in improving workability of alkali-activated slags.

2.3.1.3.3. Effect of mineral admixtures or additives

Use of mineral admixtures or additives can affect workability of alkali-activated slag as well. While workability of Portland cement mixture decreases with inclusion of silica fume and increases by use of fly ash, it was found that replacing 10 to 20% of slag with either of them can greatly increase workability of alkali-activated slag mixtures (Skvara 1985, Talling and Brandstetr 1989, Gifford and Gillott 1997, Collins and Sanjayan 1999a). On the other hand, addition of lime resulted in reduction of flow and quicker loss of workability for sodium silicate-activated slags (Jolicoeur et al. 1992, Chen and Liao 1992, Cheng and Sarkar 1994).

2.3.1.4. Strength

“The strength of cement and concrete materials is perhaps the most important overall measure of quality, although other properties may also be critical” (Shi et al. 2006b). Nature of slag, type and dosage of activator or activators, water-to-slag ratio, curing temperature, slag fineness, time of addition of activator, additives or mineral admixtures, and compaction pressure for system with very low water-to-slag ratio are of the main factors affecting strength of alkali-activated slag mixtures. A brief review of the main influential factors is presented below:

2.3.1.4.1. Type and dosage of activator

Results of different studies showed that type of activator and its dosage are the most important factors affecting the strength of alkali-activated slag binders. Atis et al. (2009) studied compressive strength of several alkali-activated slag mortars activated with sodium hydroxide, liquid sodium silicate, and sodium carbonate, containing 4 to 8% sodium. The compressive strength test results are presented in Table 2.5. The 28-day strength of mortars was in the ranges of 35.5 to 81.1 MPa for sodium silicate-activated mortars, 23.9 to 29.2 MPa for sodium hydroxide-activated mortars, and 24.7 to 35.7 MPa for sodium carbonate-activated mortars. It can be seen that liquid sodium silicate was the best followed by sodium carbonate and sodium hydroxide. Higher strengths were developed when higher sodium concentrations were used. They also investigated effect of sodium silicate modulus on strength properties; indicating that there is an optimum SiO_2-to-Na_2O ratio (see Figure 2.8; Atis et al. 2009). Other studies also confirmed the significant effect of sodium silicate modulus on strength properties. Shi and Li (1989) assessed compressive strength of phosphorous slag activated with sodium silicate having modulus of 0.5 to 2.5 or sodium hydroxide. While the strength of sodium hydroxide-activated slag was always lower than that of sodium silicate-activated slag, they concluded that optimum modulus of sodium silicate was between 1 and 1.5. Similarly, Wang et al. (1994) found modulus of 1 to 1.5 as an optimum modulus as well (See Figure 2.9). Similar results were obtained by Wu (1999). Bin (1988) also noticed increases in strength by increasing sodium silicate modulus up to 1.7. The further increase didn't cause any significant effect (Bin 1988).

Table 2.5 Effect of activator type on compressive strength (Atis et al. 2009)

Activator type	Concentration	Compressive strength (MPa)		
		7-days	28-days	3-months
Liquid sodium Silicate	8% Na, Ms=0.75	67	81.1	84.2
	8% Na, Ms=1.00	66.7	80.9	85.6
	8% Na, Ms=1.25	52.3	58.9	62.6
	8% Na, Ms=1.50	47.3	57.5	59.2
Sodium hydroxide	4% Na	19.7	23.9	23.2
	6% Na	22.7	26.2	31.1
	8% Na	22.1	29.2	33.2
Sodium carbonate	4% Na	16.8	24.7	26.4
	6% Na	21.7	27.6	28.3
	8% Na	24.7	35.7	37.3

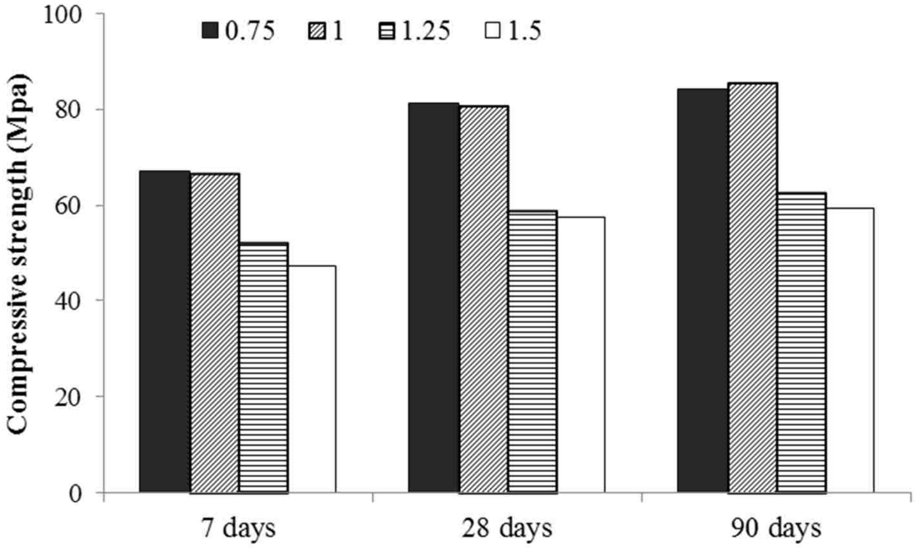


Figure 2.8 Effect of sodium silicate modulus on strength properties (Atis et al. 2009)

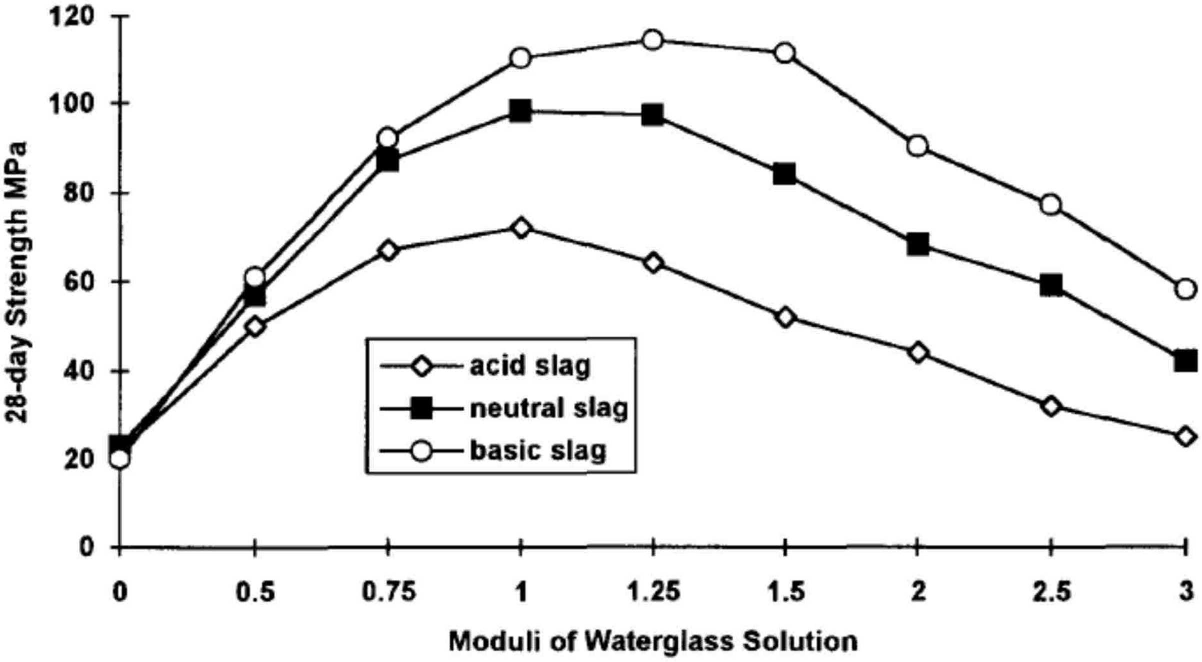


Figure 2.9 Effect of sodium silicate modulus on strength properties (Wang et al. 1994)

About the effect of sodium (or potassium) hydroxide dosage, different observations have been reported in the literature. Overall, it can be concluded that there is a minimum amount of activator needed for a successful activation. There is an optimum or maximum level as well. The minimum, optimum and maximum levels vary in the literature as different materials and conditions were used in different investigations. Purdon (1940) suggested the optimum of NaOH to be about 5 to 8% of mixing water. Jolicoeur et al. (1992) noticed strength reductions when less than 5% sodium hydroxide (by Na_2O) was used. Chen and Liao (1992) reported increases in strength with increases in dosage to a level, after which use of higher dosage didn't increase the strength, nor reduced it. Cheng and Chiu (2003) reported strength reduction, when molarity of alkaline activator (KOH) increased from 10 to 15M. Chi (2012) increased dosage of Na_2O in alkali-activated slag concrete activated with combined sodium hydroxide and sodium silicate; reporting improvement in strength properties with increases in dosage of activator.

Combination of activators is another subject that has been investigated. Majority of the conducted studies stated increases in strength by combination of activators. Krivenko (1994b) assessed effects of combination of different anions on the strength of alkali-activated slag mixtures. The test results, presented in Table 2.6, revealed that the combination of two types of anions produced higher strengths than either one of them. Fernandez-Jimenez et al. (1999) compared strength properties of slags activated using sodium hydroxide, sodium carbonate, and combination of sodium hydroxide and sodium silicate. They noticed that the combination of sodium hydroxide and sodium silicate led to significantly higher strength than the other activators. Li and Sun (2000) also stated that combination of sodium hydroxide and sodium carbonate resulted in higher strengths than those activated by either one of them. On the other hand, Jolicoeur (1992) reported that for sodium silicate with modulus of 1 and 1.5, addition of sodium carbonate resulted in strength reduction for all the ages tested. In case of sodium silicate with modulus of 0.5, addition of sodium carbonate increased the one-day strength, but didn't affect strength thereafter (Jolicoeur et al. 1992). Fernandez-Jimenez and Puertas (2003) also observed reduction in strength through inclusion of sodium carbonate. They used combinations of sodium silicate, sodium hydroxide and sodium carbonate for the purpose of activation, and assessed their effects on strength properties of alkali-activated slag mixtures. They stated that presence of silicate ions improved the strength, whereas carbonate ions decreased the strength.

Table 2.6 Effect of onions of activator on strength of alkali-activated slag (krivenko 1994b)

Anion	Compressive strength (MPa)	Flexural strength (MPa)
OH^-	36.6	4.05
OH^-+Cl^-	38.3	4.20
$OH^-+SO_4^{2-}$	28.2	3.80
$OH^-+SiF_6^{2-}$	64.1	6.80
CO_3^{2-}	45.6	5.36
$CO_3^{2-}+Cl^-$	48.4	5.65
$CO_3^{2-}+ SO_4^{2-}$	50.2	5.80
$CO_3^{2-}+ SiF_6^{2-}$	55.5	5.85
SO_3^{2-}	34.8	4.20
$SO_3^{2-}+Cl^-$	36.7	4.38
$SO_3^{2-}+ SO_4^{2-}$	35.1	4.85
$SO_3^{2-}+ SiF_6^{2-}$	65.9	5.20
SiO_3^{2-}	81.8	8.26
$SiO_3^{2-}+Cl^-$	87.8	8.40
$SiO_3^{2-}+ SO_4^{2-}$	95.7	8.70
$SiO_3^{2-}+ SiF_6^{2-}$	100.9	9.20

2.3.1.4.2. Effect of nature and fineness of slag

The strength properties of alkali-activated slag systems vary depends on origin and nature of slag. “Variation of chemical composition among different blast furnace slag results in different hydration products for a given activator” (Shi et al. 2006b, Shi and Day 1996c). Figure 2.10 highlights these differences by presenting results of two studies conducted by Shi and Day (1996) activated two different slags by use of sodium hydroxide and sodium silicate. A totally opposite trend can be seen in these studies. Figure 2.9 shows results of another study conducted by Wang et al. (1994) on acidic, neutral and basic slags. It can be seen that the higher was the alkalinity of the slag, the higher was the strength.

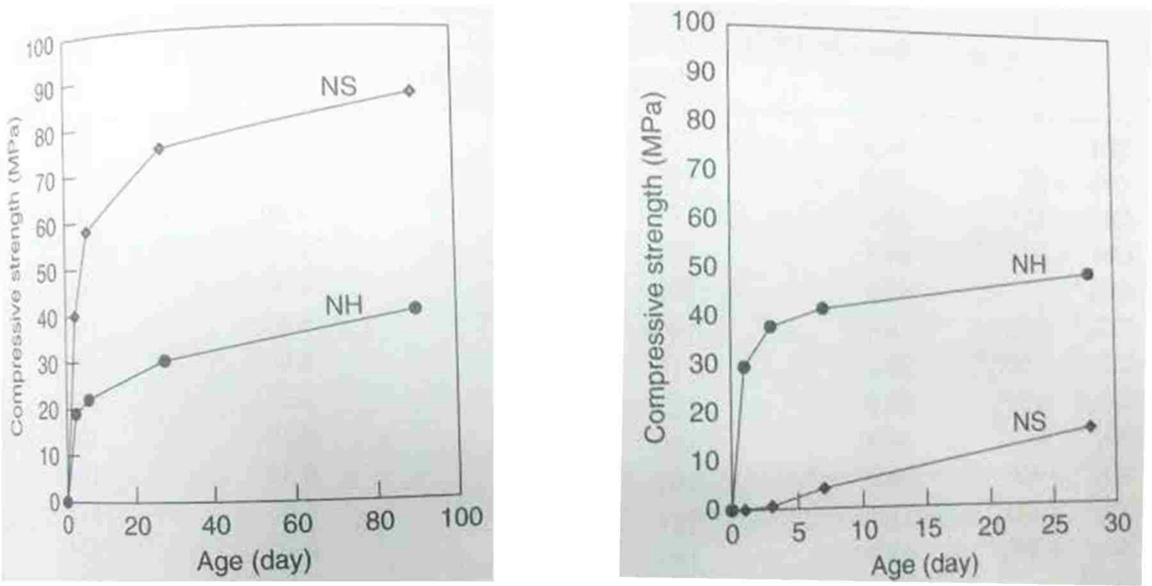


Figure 2.10 Effect of slag nature on strength properties (Shi and Day 1996c); (NS: Sodium silicate-activated mixture, NH: Sodium hydroxide-activated mixture)

Fineness of slag can significantly influence the strength of alkali-activated slag mixtures too. Shi and Li (1989) studied effects of slag fineness (for phosphorus slag) on the strength by varying fineness in the range of 200 to 600 m^2/kg. While increases in fineness from 200 to 400 m^2/kg increased the strength, in particular at early ages, further increases didn't provide additional benefits. Parameswaran and Chatterjee (1986) used similar fineness range to evaluate its influence on the strength of sodium hydroxide-activated slags. They observed significant strength increases with increasing fineness from 300 to 400 m^2/kg, a slight strength increase between fineness of 400 to 500 m^2/kg, and strength reductions when fineness increased from 500 to 600 m^2/kg. Similarly, Wang et al. (1994) stated that the strength reduction happens in fineness between 500 to 600 m^2/kg depends on alkalinity of slag. Accordingly, it can be concluded that "the Blaine fineness may be controlled to about 400 to 500 m^2/kg to obtain proper strength development rate" (Shi et al. 2006b).

2.3.1.4.3. Effect of mineral and chemical admixtures

There are different studies in the literature investigating effect of additives on strength development of alkali-activated slag mortars and concretes. In these studies, it was found that addition of small amounts of Portland cement clinker (5 to 7%) or lime (2%) can improve strength of alkali-activated slag mortars, in particular at early ages (Cheng et al. 1991, Chen and Liao 1992, Krivenko 1994a). Douglas et al. (1991) stated that combination of lime and silica fume led to higher strength than using lime alone. Chen and Liao (1992) reported reduction in strength by addition of silica fume alone to alkali-activated slag binders, whereas Collins and Sanjayan (1999b) observed improvements in strength of alkali-activated slag concrete by replacing 10% of slag with condensed silica fume. Collins and Sanjayan (1999b) also noticed improvements in strength by replacing 10% of slag with ultra-fine slag. On the other hand, they reported strength reduction by replacing 10% of slag with ultra-fine fly ash.

Puertas et al. (2003b) studied effects of chemical admixtures on strength of alkali-activated slags. They observed significant reduction in strength by use of vinyl co-polymer superplasticizer. They also reported that addition of polycrylate co-polymer-based superplasticizer didn’t show any effect on the strength of alkali-activated slags (Puertas et al. 2003b).

2.3.1.4.4. Curing conditions

Similar to Portland cement, curing conditions have major influences on the properties of alkali-activated slags. Collins and Sanjayan (2001b) studied strength development of alkali-activated concretes under three different curing conditions of water bath, sealed and exposed to air. The water bath-cured concretes developed the highest strength followed by sealed-cured concretes. The exposed-cured concretes not only produced the lowest strength, but also experienced strength loss after 28 days. The water bath-cured concretes showed slight strength increase up to 1 year. The sealed-cured concretes experienced strength gain for up to 90 days. From then, their strength didn’t increase possibly due to lack of moisture.

Curing temperature is also effective in strength development of alkali-activated slags. Use of elevated temperature increases the chemical reaction, thus accelerating the strength gain. Shi et al. (1991) reported that the strength gained in several months under standard curing temperature (25°C), could be developed within few hours using elevated temperatures (for example 65°C or 95°C). However, they observed lower ultimate strength using elevated temperatures instead of ambient temperatures.

2.3.1.5. Stress-strain relationship and elastic modulus

Stress-strain relationship and modulus of elasticity are of important parameters in structural design. In terms of these properties, there are a few conducted research investigating the difference between Portland cement and alkali-activated slag concretes. The overall finding of these studies is that there are not obvious differences between them (Hakkinen 1986, Douglas et al. 1992).

Hakkinen (1986) compared stress-strain relationship of alkali-activated slag concrete and Portland cement concrete; concluding that the secant modulus of elasticity of alkali-activated slag concrete can be estimated from the same equation recommended by ACI 318 for Portland cement concrete. Douglas et al. (1992) compared experimental and theoretical elastic modulus of alkali-activated slag concretes; their results are documented in Table 2.7. It can be seen that the experimental values were very much in agreement with the theoretical values calculated by use of ACI equation.

Table 2.7 Compressive strength and elastic modulus of alkali-activated slag concretes (Douglas et al. 1992)

Water-to-binder ratio	Sodium silicate-to-slag ratio	Compressive strength (MPa)		Theoretical modulus of elasticity (GPa)		Experimental modulus of elasticity (GPa)	
		28 days	91 days	28 days	91 days	28 days	91 days
0.48	0.48	42.4	46.3	30.8	32.2	30.2	31.1
0.48	0.48	43.4	51.6	31.2	34.0	29.7	31.2
0.48	0.39	36.2	42.3	28.5	30.8	30.7	32.3
0.48	0.37	39.0	43.9	29.5	31.3	33.7	34.8
0.48	0.33	39.0	43.9	29.5	31.3	33.7	34.8
0.41	0.32	41.2	48.4	30.4	32.9	29.4	32.1
0.49	0.48	36.3	43.4	28.1	31.2	28.3	30.9

2.3.1.6. Shrinkage

Shrinkage is the reduction in volume at constant temperature without external loading, which has significant effects on long-term performance of structures. High shrinkage has been another major issue of alkali-activated slag mixtures (Bin 1988, Jiang et al. 1997).

Figure 2.11 shows autogenous shrinkage of alkali-activated slag pastes activated with sodium hydroxide or different dosages of sodium silicate (Cincotto et al. 2003). It can be seen that autogenous shrinkage of all alkali-activated pastes was higher than that of Portland cement paste. Sodium silicate-activated pastes exhibited higher autogenous shrinkage than sodium hydroxide-activated slag paste. They attributed these observations to the much larger mesopores of sodium silicate-activated paste than those of sodium hydroxide-activated paste. Higher dosage of silicate led to higher autogenous shrinkage as well.

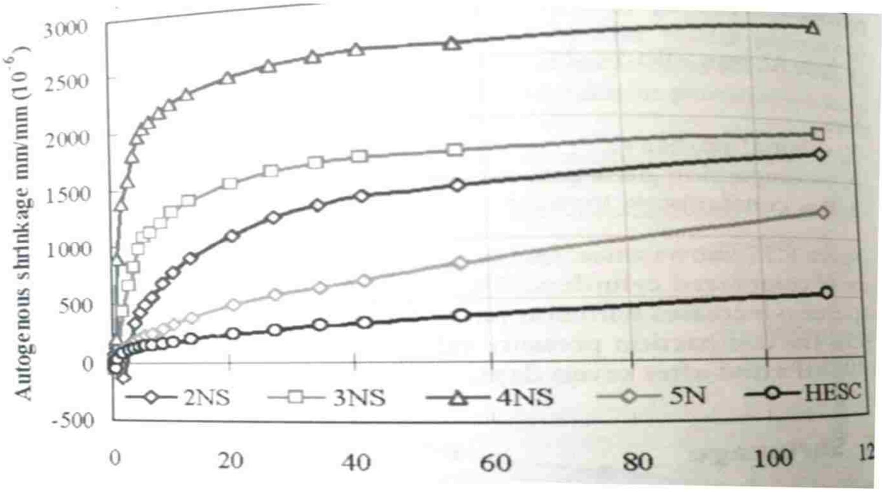


Figure 2.11 Autogenous shrinkage (Cincotto et al. 2003); HESC: High early age strength Portland cement, 2NS: 2.5% sodium silicate (by Na_2O), 3NS: 3.5% sodium silicate (by Na_2O), 4NS: 4.5% sodium silicate (by Na_2O), 5N: Sodium hydroxide-activated slag

The shrinkage Problem is not limited to the autogenous shrinkage. Drying shrinkage of alkali-activated slag is also higher than that of Portland cement. Douglas et al. (1992) noticed that sodium silicate-activated slag concretes experienced higher drying shrinkage than that of Portland cement concrete having equivalent water-to-cementitious materials ratio and workability. Atis et al. (2009) also showed that the drying shrinkage of sodium hydroxide- and sodium silicate-activated slag mortars were 2 to 3 and 3 to 6 times of that of PC mortar, respectively, depending on the sodium concentration and modulus of sodium silicate (See Figure 2.12).

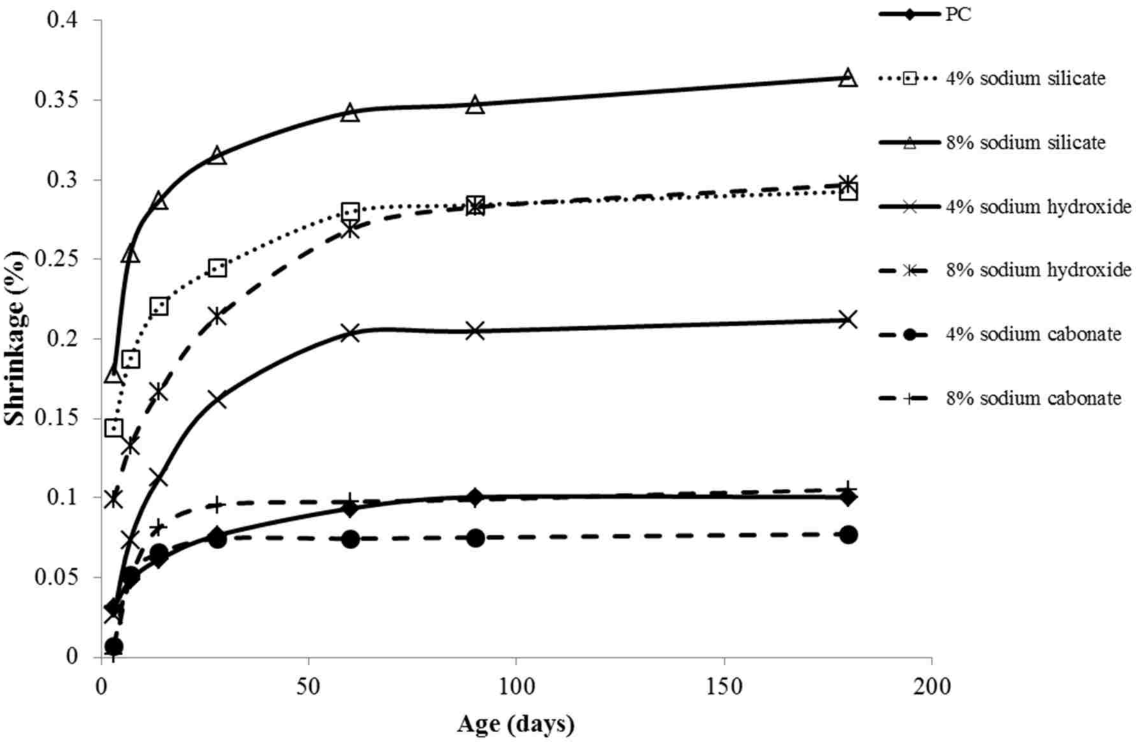


Figure 2.12 Drying shrinkage test results of Atis et al. (2009)

Several factors can affect the drying shrinkage of alkali-activated slags including nature of slag, activator type and dosage, water-to-slag ratio, degree of hydration, curing temperature, additives, relative humidity, and rate and time of drying. Of these factors, activator type is the most important factor which has been studied by different researchers. Anderson and Gram (1987) noticed higher drying shrinkage for sodium silicate-activated slag pastes in comparison with sodium hydroxide- and sodium carbonate-activated slag pastes. They found that all alkali-activated slag pastes exhibited higher drying shrinkage than Portland cement paste. They also observed that eight hours of steam curing at 80°C could significantly reduce the problem. Except for slags activated with high sodium silicate' modulus, majority of steam-cured pastes experienced almost similar shrinkage to that of Portland cement paste. Similarly, Bakharev et al. (1999) observed higher drying shrinkage in sodium-silicate activated slag pastes than sodium hydroxide-, sodium carbonate- and sodium phosphate-activated slag pastes. Collins and Sanjayan (1999c) also observed higher drying shrinkage in sodium silicate-activated slag concrete than sodium hydroxide/sodium carbonate-activated slag concrete. In another study conducted by Atis et al. (2009), shown in Figure 2.12, sodium silicate-activated slag mortars shrank as almost as twice as sodium hydroxide-activated slag mortars and 4 to 6 times of sodium carbonate-activated slag mortars. The drying shrinkage of sodium carbonate-activated slag mortars was almost similar to that of Portland cement mortar.

There has been several research trying different methods to reduce drying shrinkage of alkali-activated slags. Similar to Anderson and Gram (1987) who showed steam curing at 80°C useful in reducing drying shrinkage, Bakharev et al. (1999) found use of curing at elevated temperature to be effective. Collins and Sanjayan (1999c) found longer curing time in lime-saturated water effective in reduction (slight reduction) of drying shrinkage. Bakharev et al.

(2000) also reported air-entraining admixture, shrinkage reducing admixture, and gypsum (6%) effective in limiting drying shrinkage. They also observed slight reduction in drying shrinkage by use of lignosulphonate-based admixtures. On the other hand, they noticed a considerable increase in drying shrinkage using naphthalene-based superplasticizers. Similar to Bakharev et al. (2000), Chang et al. (2005) reported reduction in drying shrinkage by use of gypsum. They noticed increases in drying shrinkage using phosphoric acid as a retarder. Bilim et al. (2013) noticed reduction in drying shrinkage of alkali-activated mortars using shrinkage reducing admixtures. However, the shrinkage values were still significantly higher than that of Portland cement mortars.

2.3.1.7. Transport properties

There are different processes that may cause deterioration of a concrete structure. A concrete structure can be severely damaged due to reinforcement corrosion, sulfate attack, frost damage and alkali-silica reaction. The common characteristic with all of these processes is that they require something to be transported into the concrete from outside or out from inside the concrete (Claisse 2005). Even alkali-silica reaction, which is a reaction between components which are already present inside a structure, requires water for the reaction to take place (Claisse 2005). Therefore, transport properties are considered durability indices and can provide valuable measure of concrete durability.

As microstructure and properties of alkali-activated materials are strongly dependent on the characteristics of the used activators, the transport properties vary from one study to another. In general, several research studies showed that “for a given water-to-cement or water-to-slag ratio, a properly designed alkali-activated slag cement paste can exhibit a significantly lower total porosity and a lower portion of capillary pores than a Portland cement paste does" (Shi et al. 2006). The lower pores result in lower permeability as well. Shi and Day (1996a) and Shi et al. (1992) compared total porosity and pore structure characteristics of Portland cement and alkali-activated slag pastes. The results of this study are documented in Table 2.8. It can be seen that alkali-activated slag pastes had lower porosity and finer pore structure than Portland cement paste. Shi and Day (1996b) also observed that the porosity of sodium silicate-activated slag mortar was significantly lower than that of Portland cement mortar, whereas sodium hydroxide-activated slag mortar had higher porosity than Portland cement mortar. This observation confirmed by Song et al. (2000), noticing higher porosity in sodium hydroxide-activated slag paste than Portland cement paste.

Table 2.8 Pore structure characteristics of 28-day Portland cement and alkali-activated slag pastes (Shi and Day 1996a, Shi et al. 1992)

Type of binder	Porosity (%)	Pore volume (%)		
		18-100 A°	100-1000 A°	> 1000 A°
Alkali-activated slag	12.77	80.98	15.10	3.92
Portland cement	22.30	18.87	69.68	11.45

Different researchers compared permeability of Portland cement and alkali-activated slag mixtures. Wu et al. (1993) and Davidovits (1994) showed that permeability of alkali-activated slag concretes and pastes were several times lower than those of Portland cement concrete and paste, respectively. Similarly, Shi (1996) reported significantly lower water permeability in alkali-activated slag mortars than Portland cement mortars. Shi (1996) also conducted mercury intrusion measurement on alkali-activated slag mortars; reporting that sodium silicate-activated slag mortar had much lower porosity and finer pore structure than and sodium carbonate- and sodium hydroxide-activated mortars, and Portland cement mortar.

There are also a few studies conducted assessing chloride permeability and diffusion of alkali-activated slag mixtures. Hakkinen et al. (1987) compared chloride diffusion of alkali-activated slag paste and Portland cement paste; stating that the former had 30 to 40 times slower diffusion rate than the latter. Douglas et al. (1992) conducted rapid chloride permeability test (RCPT) on alkali-activated slag concretes. They reported 28-day passed charges of 1311 to 2547 coulombs and 91-day passed charges of 676 to 1831 coulombs. These values are considered low permeability. They also observed that the passed charge increased with increases in sodium silicate-to-slag ratio, which could be attributed to the increases of alkali concentration in the concrete pore solution. Roy et al. (2000) studied effect of addition of alkalis to blended cements containing Portland cement and slag. They observed significant reduction in chloride diffusion as a result of alkali-activation.

2.3.1.8. Frost resistance

“In cold climates, frost action in the form of freezing and thawing cycles is one of the major problems” (Pacheco-Torgal et al. 2015), which can cause severe damage to concrete infrastructure. Accordingly, the frost resistance is of the most important properties of concrete in areas where freezing occurs.

The freezing point, deformation and frost resistance of alkali-activated slags are different than those of Portland cement mainly due to the difference in their pore solution chemistry. For Portland cement mixtures, the freezing point of water in capillary pores is lower than that of normal water, ranging between -4°C for pore radius of 300A° and -8°C for pore radius of 150

A°. “Frost destruction of water-saturated Portland cement pastes happens mainly during a spasmodic freezing of micro-capillary pore water from the freezing temperature to around -20°C” (Shi et al. 2006b). The capillary pores’ solution of Portland cement paste freezes spasmodically and the meniscus disappears. On the other hand, the capillary pores’ solution of alkali-activated slag pastes freezes gradually and the meniscus remains during freezing. The freezing point of pore solution is also different for alkali-activated pastes. It’s not only affected by the pore size, but also by the type of activator. For instance, when sodium carbonate is the activator, the freezing point of the eutectic mixture is -2.1°C, whereas it’s -36°C when potassium carbonate uses as the activator (Shi et al. 2006b).

The frost resistance of alkali-activated slag concrete is dependent on type of activator, pore solution’ chemistry, porous network, freezing rate, and curing conditions. Of the influential factors, activator type affects both pore chemistry and pore structure of alkali-activated concretes, thus having significant influence on their frost resistance. Glukhovsky (1979) and Glukhovsky et al. (1988) stated that the sodium silicate-activated slag concretes usually have the least porous structure, highest strength, and best frost resistance. They observed that a properly designed alkali-activated slag concrete with sodium silicate or sodium hydroxide could provide more frost resistance than Portland cement concrete. Similarly, Timkovich (1986) reported superior frost resistance of sodium silicate-activated slag concrete to Portland cement and sodium carbonate-activated slag concretes. Skurchinskaya and Belitsky (1989) didn’t observe any visible deterioration in sodium silicate-activated slag concretes after 45, 60, and 100 freezing-thawing cycles in 5% NaCl, $MgSO_4$, and $CaCl_2$, respectively. In another study, Pu et al. (1991) didn’t notice any mass loss in alkali-activated slag concretes subjected to 200 freezing and thawing cycles. Fu et al. (2011) used combination of sodium hydroxide and sodium silicate to develop alkali-activated slag concretes. The frost resistance of produced concretes was assessed based on ASTM C666, procedure A. They observed less than 12% reduction in elastic dynamic modulus and below 1% mass loss after 300 freezing-thawing cycles; both indicating satisfactory frost resistance of alkali-activated slag concretes. The excellent performance was attributed to the compact structure of concrete made it impermeable to water penetration, as well as high compressive strength which made it durable in negative temperatures. The same team (Cai et al. 2013) used response surface methodology to study the frost resistance of the similar concrete. They concluded that the frost resistance is dependent on the porous network of concrete; greater frost resistance develops as a result of smaller air bubble spacing coefficient. They also concluded that the influential factors on frost resistance are solution-to-slag ratio and slag content, to a larger extent, and sand content, to a lesser extent. The best performance was observed using lower solution-to-slag ratio and higher slag content. Sand content had very little effect on frost resistance.

There are also a few studies in the literature using air-entraining admixtures in order to increase frost resistance of alkali-activated slag concretes. Hakkinen (1986) was of the first researchers who tried to introduce air-entraining admixture to alkali-activated slag concretes; this experience wasn't successful. However, alkali-activated concrete without air-entrainment displayed better frost resistance than Portland cement concrete. Byfors et al. (1989) assessed inclusion of different commercial air-entraining admixtures for alkali-activated concretes including Vinsol resin, alkylalcoholsulfonate tenside, polyglycolether-sulfonate tenside, and hollow plastic microspheres. Their results showed two of these admixtures, i.e. alkylcoholsulfonate tenside and polyglycolether-sulfonate tenside, were effective. However, higher dosage of admixture was needed in comparison to Portland cement to introduce air in alkali-activated concretes. In another study, Douglas et al. (1992) assessed frost resistance of air-entrained alkali-activated slag concretes according to ASTM C666, procedure A. The results of their work are presented in Table 2.9. Except for one mixture, the air-entrained alkali-activated slag concretes showed satisfactory frost resistance. While the acceptance limit is 40% loss of the initial dynamic modulus and 0.10% expansion after 300 freezing-thawing cycles, these mixtures were well below the limits after 500 cycles. The air-void spacing factor for the frost-resistant alkali-activated slag concretes was in the range of 270 to 340 μm, which is higher than the recommended upper limit of 220 μm for Portland cement concrete. The authors related mediocre behavior of one of the mixtures to its lower sodium silicate content. They also noticed that while it was relatively easy to introduce air into the fresh mixture, the air content reduced in hardened concrete, possibly due to incompatibility of air-entraining admixture (sulfonated hydrocarbon type) and alkaline activators.

In another study, Gifford and Gillott (1996a) found a commercial air-entraining admixture (aqueous solution of modified salts of a sulfonated hydrocarbon) ineffective in producing stable air and increasing the frost resistance.

Table 2.9 Properties of alkali-activated slag concretes after 500 freezing and thawing cycles (Douglas et al. 1992)

	Alkali-activated mixture				
	1	2	3	4	5*
Sodium silicate-to-slag ratio	0.48	0.48	0.39	0.37	0.33
Air content of fresh concrete (%)	6.2	5.2	7.3	7.2	5.7
Air content of hardened concrete (%)	3.9	4.2	4.5	6.2	4.7
Spacing factor of air bubbles (μm)	270	325	336	286	377
Initial compressive strength (MPa)	30.2	29.7	30.7	32.1	33.7
After 500 cycles					
Length variation (%)	0.03	0.04	0.07	0.09	0.18
Weight variation (%)	-3.7	-1.0	-2.7	-2.9	-2.6
Resonant frequency variation (%)	1.8	3.4	-1.4	-0.1	-29.9
Pulse velocity variation (%)	-1.0	0.8	-3.6	-8.1	-29.0
Relative dynamic modulus of elasticity (%)	104	107	97	100	50
Residual flexural strength (%)	62	63	58	67	32

* Estimated at 300 cycles

There are also a few applications of alkali-activated slag concretes in real structures constructed in countries where frost resistance is an issue. These structures include several high residential buildings and prestressed reinforced concrete railway sleepers in Russia, and a 330m long concrete road in Ukraine; all were built between 1986 and 1994 (Pacheco-Torgal et al. 2015). The inspections showed that they are still in good conditions without cracking, deterioration or defects on the surface. Also, the alkali-activated slag concrete road in Ukraine experienced less surface deterioration than Portland cement concrete roads (Pacheco-Torgal et al. 2015).

2.3.1.9. Sulfate attack

Portland cement concrete can deteriorate for several reasons and sulfate attack is reported to be a major contributor to concrete premature failure. It was reported that concrete deterioration due to sulfate attack is the second major durability problem, after reinforcement corrosion. Sulfates can come from a variety of sources such as groundwater, high clay-content soils, seawater, organic materials in marshes, mining pits, and sewer pipes, and in different forms including magnesium sulfate, sodium sulfate, calcium sulfate, potassium sulfate, and ammonium sulfate. Sulfate attack can be either in the form of internal attack, which is the result of chemical reactions between constituents of cement paste and sulfate ions; or external attack, which mostly manifests itself in the form of surface scaling similar in appearance to that of freezing and thawing damage. Upon contact and diffusion of sulfate ions into the concrete, chemical reactions happen, resulting in formation of gypsum, ettringite, thaumasite or a combination of these phases. Formation of these compounds cause expansion, stress, and mass and strength losses, thus deteriorating the Portland cement concrete.

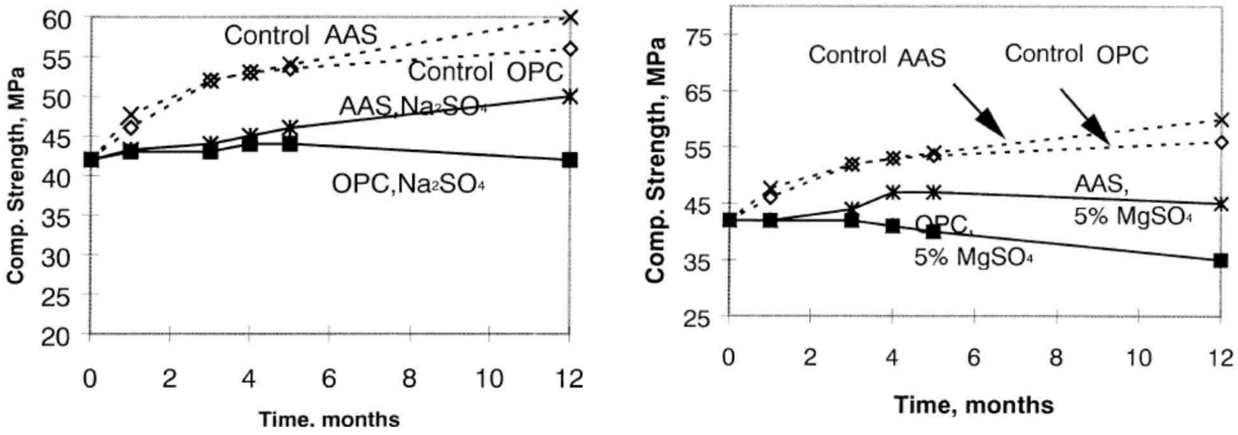
Since alkali-activated slags contained lower calcium content than Portland cement, it’s expected that they don’t experience the same level of attack or experience sulfate attack with different mechanisms. It was also found that some modifications may be required to the test methods, which were originally designed for assessing sulfate resistance of Portland cement mixtures, in order to become useful for evaluation of alkali-activated mixtures. Following is a brief review on sulfate resistance of alkali-activated slag binders to date.

Krivenko (1986) measured flexural strength of different types of alkali-activated slag concretes immersed in different sulfate solutions such as Na_2SO_4, $ZnSO_4$, $CuSO_4$, $NiSO_4$,

$Al_2(SO_4)_3$, $(NH_4)_2SO_4$, $MgSO_4$ and $MnSO_4$. The author compared their performance with that of regular and sulfate-resistant Portland cement concretes. All alkali-activated slag concretes performed better than the regular Portland cement concrete in all different sulfate solutions, and even superior to sulfate-resistant concrete in sodium sulfate solution. In case of exposure to sodium sulfate solution, all alkali-activated slag concretes displayed excellent resistance to sulfate attack regardless of their compositions. This observation was attributed to lack of formation of deteriorating compounds. Immersion of alkali-activated slags in other sulfate solutions could result in formation of hydrosilicate, hydroxides, and gypsum, which don't have any cementing property. The most corrosive environments were in the following order: $MnSO_4$, $MgSO_4$, $(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $NiSO_4$, $CuSO_4$, $ZnSO_4$, and Na_2SO_4. Krivenko (1986) also found that use of acidic slag and high modulus sodium silicate increase the sulfate resistance to a similar or even better level than that of sulfate-resistant Portland cement concrete.

Hakkinen (1986, 1987) measured compressive and flexural strengths of Portland cement and alkali-activated slag concretes immersed in 1 and 10% sodium and magnesium sulfates. Both concretes didn't experience any strength loss after two years of immersion in 1% sodium sulfate solution. Alkali-activated slag concrete didn't experience any strength loss in 1% magnesium sulfate too, whereas Portland cement concrete lost 25% of its strength. While Portland cement concrete was destroyed in both 10% sodium and magnesium sulfates, alkali-activated slag concrete survived 10% sodium sulfate immersion.

Bakharev et al. (2002) observed less strength loss in alkali-activated slag concretes than Portland cement concrete when they were immersed in 5% sodium or magnesium sulfate solutions (See Figure 2.13). While no ettringite was formed in alkali-activated slag concrete immersed in sodium sulfate, ettringite was detected in Portland cement concrete exposed to the same solution. They observed considerable amounts of gypsum and ettringite in Portland cement concrete immersed in magnesium sulfate. Considerable amount of gypsum was also found in alkali-activated slag concrete exposed to magnesium sulfate solution, resulted in some softening as well as cracks in concrete corners. Similarly, Douglas et al. (1992) didn't observe any noticeable change in weight, length, pulse velocity and dynamic modulus of elasticity of sodium silicate-activated slag concretes immersed 4 months in 5% sodium sulfate.



(a) (b)

Figure 2.13 Compressive strength of Portland cement concrete (OPC) and Alkali-activated concretes (AAS) subjected to 5% sodium sulfate and magnesium sulfate; (a) sodium sulfate, and (b) magnesium sulfate (Bakharev et al. 2002)

Puertas et al. (2002) assessed sulfate resistance of alkali-activated slag mixtures having sodium hydroxide or sodium silicate as alkaline activators. Sodium silicate-activated mixture showed satisfactory sulfate resistance, whereas sodium hydroxide-activated mixture lost 15 to

25% strength in comparison with the samples cured in water. They found traces of ettringite formation in sodium hydroxide-activated slags.

Recently, Chi (2012) adopted a test method from ASTM C88 and used it to compare sulfate resistance of Portland cement and alkali-activated slag concretes. This method included mass loss measurement after 5 cycles of immersion in saturated sodium sulfate solution followed by drying at 105±5°C. The mass loss of alkali-activated slag concrete was lower than that of Portland cement concrete. The author couldn't find any general trend for strength loss of the studied concretes.

Komlijenovic et al. (2013) immersed alkali-activated slag mortars and blended Portland cement/slag mortars for 90 days in 5% sodium sulfate solution. The alkali-activated slag mortars didn't lose any strength, whereas Portland cement mortars experienced strength loss due to formation of gypsum and ettringite. The satisfactory performance of alkali-activated mortars was attributed to the absence of Portlandite and unavailability of aluminum for reaction with sulfates.

2.3.1.10. Acid attack

In recent decades, deterioration of cementitious materials as a result of acid attack has drawn more attention; particularly due to deterioration of concrete sewer pipes and concrete structures in municipal wastewater treatment plants, as well as concerns regarding acid resistance of cement-solidified wastes (Shi et al. 2006b).

In general, the process of acid attack on Portland cement concrete can be briefed in ion exchange, reaction, reduction of concrete alkalinity, and thus decomposition and deterioration of the hydration products. When acid attacks to a Portland cement concrete and reacts with hydrated and unhydrated compounds, the pH decreases. It’s well documented that “all hydrated Portland cement compounds are stable only in solutions with well-defined ranges of concentrations for Ca^{2+} and OH^- ions” (Pacheco-Torgal et al. 2015). Therefore, as pH reduces, the hydration components become unstable and decompose. It happens for calcium hydroxide at pH of 12.6, ettringite at pH of 10.7, and calcium silicate hydrate (C-S-H) at pH of almost 10.5, successively. Finally, calcium aluminate and ferrite hydrates decompose. The final products are generally calcium salts of the acid and a decalcified residue of cement hydration products.

Alkali-activated concretes contain lower calcium than Portland cement, so a different process of acid attack is expected. Also, higher resistance against acid attack is anticipated for alkali-activated concretes due to absence of Portlandite and lower Ca-to-Si ratio. The studies conducted on alkali-activated slags confirmed this expectation indicating superior acid resistance of alkali-activated slag mixtures to Portland cement mixtures. Shi and Stegemann (2000) compared acid resistance of Portland cement and alkali-activated slag pastes, using nitric and acetic acids with pH of 3. They observed that corroded depth of alkali-activated slag pastes were almost 50 and 67% lower than that of Portland cement pastes for nitric acid and acetic acid, respectively. Bakharev et al. (2003) immersed Portland cement and alkali-activated slag concretes for 12 months in acetic acid having pH of 4. Portland cement concrete samples experienced 47% strength reduction in comparison with water-cured samples, whereas alkali-activated slag concrete lost 33% of its strength. Recently, Bernal et al. (2012) compared acid resistance of Portland cement and alkali-activated slag mortars exposed to hydrochloric, nitric, and sulfuric acid solutions having pH of 3, and acetic acid solution with pH of 4.5. They observed that acetic acid was more detrimental than mineral acids. While the strength loss of both types of mortars was negligible during exposure to mineral acids, strength of both Portland cement and alkali-activated slag mortars was reduced due to exposure to acetic acid. The strength reduction, however, was significantly lower for alkali-activated slag mortars than Portland cement mortar.

In literature review, a number of parameters were found effective in acid resistance of alkali-activated slag mixtures or in improving their acid resistance. It was stated that addition of dehydrated magnesium silicate into alkali-activated slag could improve the acid resistance of the paste by 1.5 to 2 times. Addition of NaA, NaX and NaY zeolite also increased the acid resistance of alkali-activated slags. The highest resistance was found for mixtures containing 30% NaA or 20% NaX zealites (Krivenko et al. 1991b, Brodko 1992). Blaakmeer (1994) noticed significant increases in acid resistance by partial replacement of slag with fly ash. However, this replacement resulted in decreases in strength. Pu et al. (1999) concluded that slag with lower basicity provide better acid resistance.

2.3.1.11. Corrosion

Chloride-induced corrosion of reinforcing steel is the most important cause for failure of concrete infrastructures. Chloride contamination of bridge decks, marine structures, and parking garages due to use of deicing salts, exposure to the harsh environments, and harmful chloride ions presented in concrete as a result of using contaminated ingredients are of the main sources of such corrosion. Given the high alkalinity of alkali-activated concretes and concomitant position on the Pourbaix diagram, it has been hypothesized that use of alkali-activated concretes should limit corrosion of reinforcing steel to negligible levels (Pacheco-Torgal et al. 2015).

The state of the art on corrosion of steel reinforcement embedded in alkali-activated slag is limited. The conducted research, however, didn’t confirm the above-mentioned hypothesis.

Deja et al. (1991) and Malolepszy et al. (1994) measured corrosion of steel in alkali-activated slag mortars. Their results indicated that the corrosion current in alkali-activated slag mortars was much higher than that in Portland cement mortars. They, however, mentioned that the corrosion current decreased by extending the time. Similarly, Aperador et al. (2009) noticed higher corrosion current density ($i_{corrosion}$) in sodium silicate-activated slag mortars than Portland cement mortars. On the other hand, polarization resistance of Portland cement mortar was higher than that of alkali-activated slag mortar. These results are presented in Figure 2.14.

Aperador et al. (2012) also compared corrosion potential of reinforcing steel embedded in Portland cement and sodium silicate-activated slag concretes. These concretes were immersed in 3.5% NaCl solution for 12 months. The results, which are shown in Figure 2.15, indicated almost similar corrosion potential for both types of concretes after 3 to 6 months of immersion. The negative potential remained constant for Portland cement concrete after 6 months, whereas it increased for alkali-activated slag concrete increasing the corrosion potential.

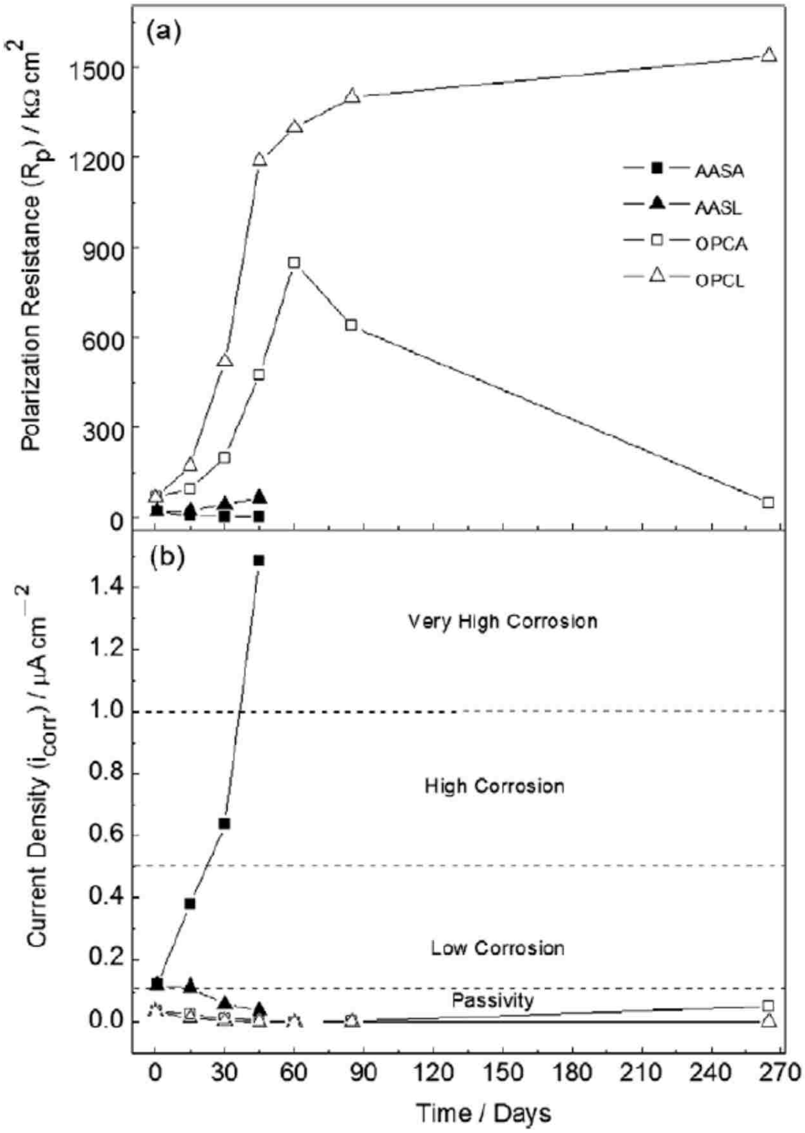


Figure 2.14 Corrosion potential of Portland cement and alkali-activated slag mortars (Aperador et al. 2009); AASA and AASL are alkali-activated mortars, OPCA and OPCL are Portland cement mortars

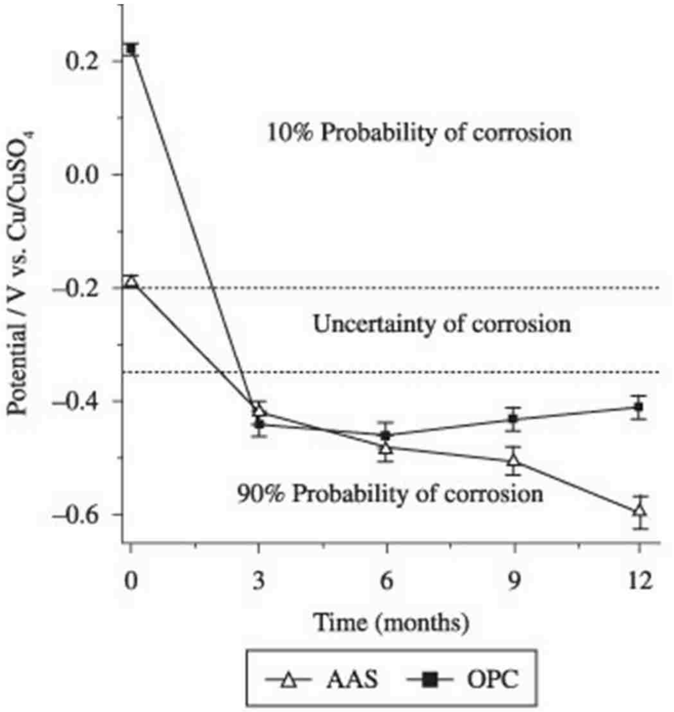


Figure 2.15 Corrosion potential for Portland cement and alkali-activated slag concretes (Aperador Chaparro et al. 2012); AAS: alkali-activated concrete, OPC: Portland cement concrete

2.3.1.12. Resistance to alkali-aggregate reactions

Alkali-aggregate reaction (AAR) is one of the major durability-related issues of Portland cement concrete. The reaction of alkaline hydroxides with poorly crystallized or amorphous silica (alkali-silica reaction or ASR) or dissolution of dolomite of carbonate rocks (alkali-carbonate reaction or ACR) produce expansive compounds, which induce stresses and crack concrete. As high concentration of alkaline ions is a critical condition for alkali-aggregate reaction, there is a concern regarding this durability issue in alkali-activated concretes when reactive aggregate is used. On the other hand, it’s well documented that the replacement of Portland cement with proper amounts of slag can reduce or eliminate alkali-aggregate reactions, which can be considered a positive point for the alkali-activated slag mixtures facing AAR. In addition, C-S-H formed in alkali-activated slags has lower Ca/Si than C-S-H produced in hydration of Portland cement, thus alkali-activated slag uptakes higher R^+ than Portland cement. Accordingly, free R^+ (Na^+ or K^+) of alkali-activated slag is less than what originally assumed (Shi 2003, Shi et al. 2006b).

There exist limited studies for ACR of alkali-activated slag mixtures. This section mostly discusses these mixtures as affected by ASR. The existing literature on ASR of alkali-activated slag mixtures is quite controversial. While most of the studies indicated lower expansion of alkali-activated slag mixtures than that of Portland cement mixtures, there are a few research showing the contrary. Figure 2.16 presents results of the main studies conducted on this subject, which summarized by Pouhet (2015). Based on the performance, Pouhet (2015) divided these studies in 3 groups: (1) For the first group, alkali-activated slag mixtures had slight expansions which were lower than or similar to that of Portland cement mixtures, (2) In case of the second group, the expansions of alkali-activated slag mixtures were lower than that of Portland cement mixture, but it was not negligible. In fact, some of the expansions were above the allowable limits, and (3) Alkali-activated mixtures of the third groups experienced considerable expansion that was higher than that of Portland cement mixtures.

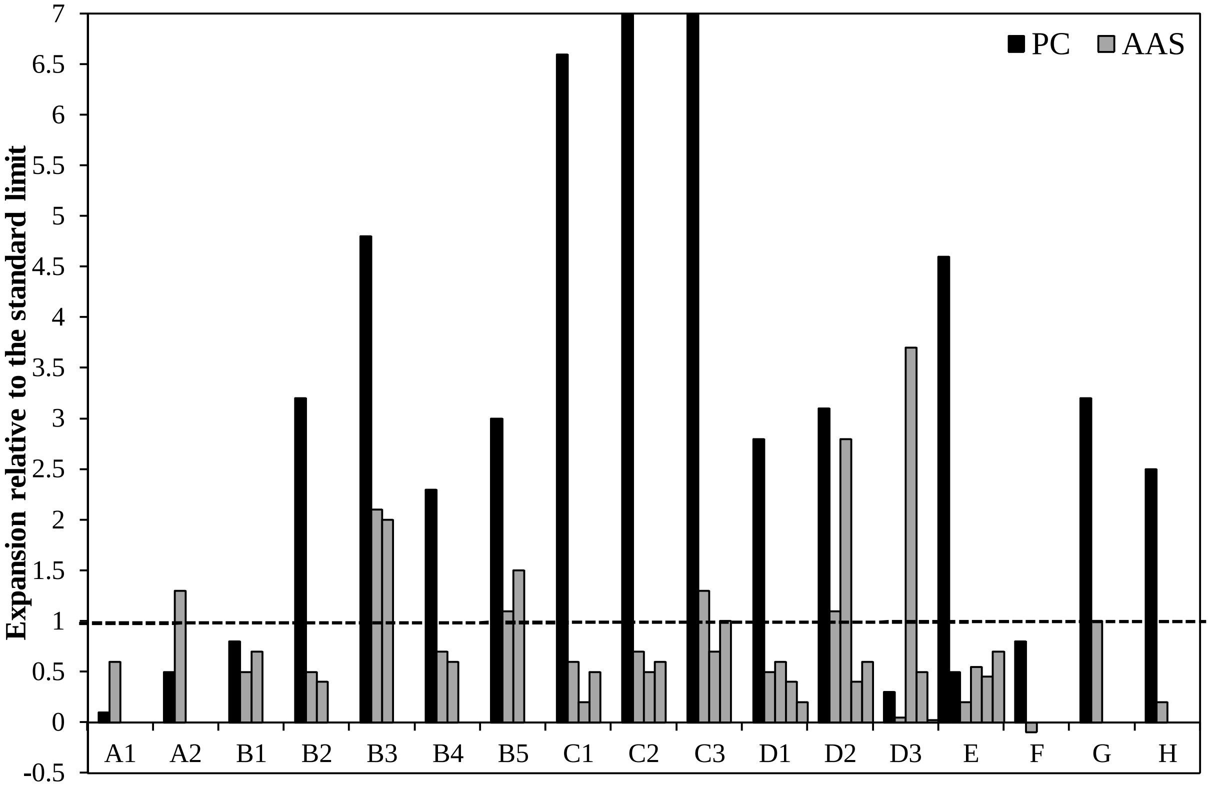


Figure 2.16 ASR expansion relative to the standard limits for different studies (Pouhet 2015); PC: Portland cement mixture, AAS: Alkali-activated mixture; (A value higher than 1 means expansion higher than the suggested limits)

While it seems impossible to generalize about the ASR of alkali-activated mixtures in comparison with Portland cement mixtures due to use of different parameters and tests in literature, the following conclusions can possibly be drawn: (1) For majority of the cases, alkali-activated slag mixtures had lower ASR expansion than Portland cement mixture, (2) The first conclusion doesn’t mean negligible expansion. Almost 25% of alkali-activated slags had higher expansion than the allowable limit, (3) Use of sodium silicate resulted in higher expansion. Increases in alkaline content did the same, and (4) When the used aggregate was not reactive, the expansion was below the permitted limit and ASR was not a problem. The literature review is presented in more detail below:

Metso (1982) was of the first researchers who studied the alkali-aggregate reaction of alkali-activated slag mortars. The experiment was conducted according to ASTM C277 and on Portland cement and two types of slag. Opal was added in different percentages to increase the reactivity of aggregates. Except for one of the alkali-activated mortars (one of the two types of slag having high opal and alkaline contents), the expansion of alkali-activated slag mortars were significantly lower than that of Portland cement mortar. The author stated that different slags may have different behavior, even if they are activated similarly. It was also concluded that higher alkalinity can strengthen the ASR susceptibility. Shi (1988) used a rapid autoclave method to assess expansion of alkali-activated slag mixtures; He claimed that low-alkali-activated slag having opal aggregates didn't exceed the expansion limits. Gifford and Gillott (1996b) assessed ASR and ACR of alkali-activated slag concretes. They used sodium silicate or sodium carbonate as alkaline activators and provided 6% $(Na_2O)_{eq}$ per mass of slag. They compared the expansion of alkali-activated slag concretes with that of Portland cement concrete having $(Na_2O)_{eq}$ of 1.25% of cement weight. A comparison study was conducted using six different aggregates; one non-reactive, four potentially reactive to ASR (siliceous), and one dolomitic limestone potentially reactive to ACR. Results of their work are shown in Figure 2.17 for alkali-silica reactivity. Their results showed significantly lower expansion in all alkali-activated slag concretes than Portland cement concretes. Two of alkali-activated slag concretes, however, experienced expansion higher than the standard allowable limit. In case of alkali-carbonate reaction, alkali-activated slag concrete performed worse than Portland cement concrete. They expanded nearly twice as that of Portland cement concrete.

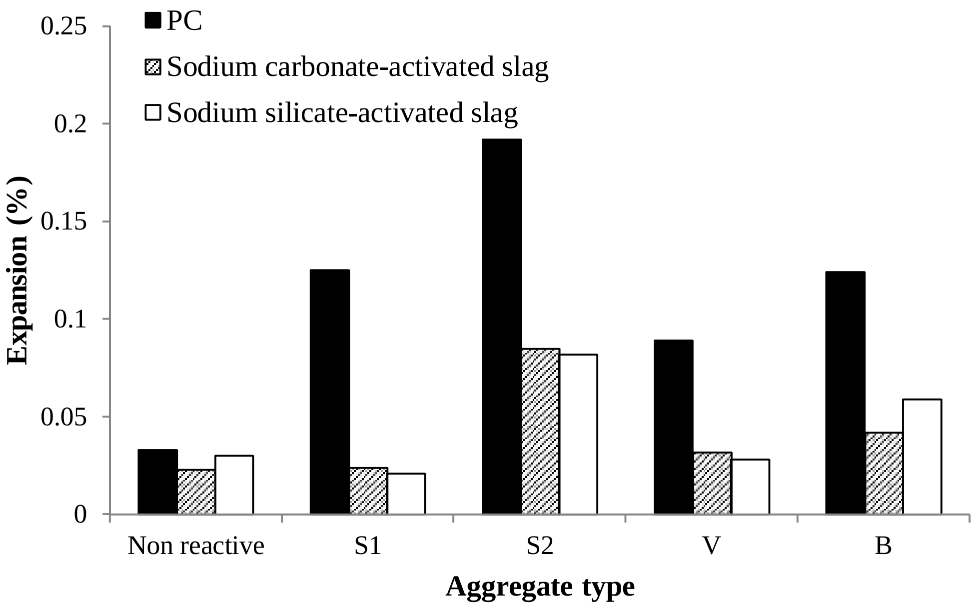


Figure 2.17 One-year expansion due to ASR (S_1, S_2, V and B are different aggregates potentially reactive to ASR) (Gifford and Gillott 1996b)

Fernandez-Jimenez and Puertas (2002) compared ASR of Portland cement and alkali-activated slag mortars kept in 1M sodium hydroxide at 80°C. They observed significantly lower expansion in alkali-activated slag mortars than Portland cement mortars. Due to slower rate of expansion in first days, they stated that this accelerated test may not be suitable for assessing ASR of alkali-activated slags. Chen et al. (2002) studied ASR of different alkali-activated slags using three different slags (basic, neutral and acid slags), and four types of activators (sodium carbonate, sodium hydroxide, sodium sulfate and sodium silicate). ASR expansion of these mixtures was compared with that of Portland cement mixture. The results of this study revealed that the expansion of alkali-activated slag mixtures was significantly lower than that of Portland cement mixture. This observation was related to significant reduction in free alkalis by reactions which formed alkali hydrates and produced gels that absorb alkalis very strongly. They also found that sodium silicate- and sodium hydroxide-activated slag mixtures had the highest and lowest expansions, respectively. The expansions increased with increases in alkaline content and reduced with decreases in alkalinity of the slag. The basic slag gained the highest expansion, whereas the acid slag experienced the lowest expansion.

Al-Otaibi (2007) activated slags with sodium silicate or sodium metasilicate having 4% or 6% Na_2O content. They measured their ASR expansion and compared the results with pure and blended Portland cements (60% Portland cement plus 40% slag) being cast with and without extra alkalis. They noticed higher ASR expansion with increasing the alkaline content. The expansion levels of alkali-activated slag concretes were in the same level of Portland cement mixtures without added alkalis; both were significantly lower than the expansion of Portland cement concretes with added (extra) alkalis. Puertas et al. (2009) also observed considerably lower ASR expansion in alkali-activated slag mortars than Portland cement mortars. However, they declared that the expansion of alkali-activated slag mortars was close to the acceptable limits and cannot be ignored. Wang et al. (2010) compared ASR expansion of alkali-activated slag/metakaolin mixtures (activated with mixture of sodium silicate and sodium hydroxide) with that of Portland cement mixture. They observed that Portland cement mixture expanded nine times more than alkali-activated slags mixture. All the alkali-activate mixtures had lower expansion than the acceptable limit. The authors attributed the satisfactory performance to dissolution of silica by alkalis, which resulted in rapid reactions thus reducing the available alkalis for ASR. They also observed reduction in expansion by decreases in modulus of sodium silicate or increases in sodium silicate content.

While majority of studies pointed out on lower ASR expansion of alkali-activated slag mixtures than Portland cement mixtures, there are few studies indicating opposite findings. Hakkinen (1986) stated that while the expansion of alkali-activated slag concrete was in the same level of Portland cement concrete for alkali content of 2% by mass of slag, their expansion increased by increase in alkali content from 2.2 to 5.3% (for an opal content of 8%) reaching higher levels of expansion than Portland cement concrete. In another study, Bakharev et al. (2001a) compared ASR expansion of alkali-activated slag concrete with that of Portland cement concrete; concluding that the former was more likely to be deteriorated due to ASR than the latter. While alkali-activated slag concretes experienced considerable expansion exceeding the limit in 2 months, Portland cement mixture didn't reach the limit in a year.

A series of studies were also conducted to reduce, control or eliminate the ASR expansion in alkali-activated slag mixtures. Pu and Chen (1991) and Yang (1997) found use of silica fume effective in eliminating ASR in alkali-activated slag mixtures. Yang (1997) also found use of 30 to 50% low-calcium fly ash effective in reducing expansion due to alkali-aggregate reactivity. Chen et al. (2002) recommended use of acidic slags to control the impact of alkali-aggregate reactivity, knowing that it might decrease the activity of alkali-activated slag. Krivenko et al. (2013) found partial replacement of slag with metakaolin effective in eliminating ASR expansion. In their research, while the expansion of alkali-activated slag mixture was only 25% lower than the acceptable limit, use of 15% metakaolin in the mixture reduced expansion to zero or even to a slight shrinkage. It's worth repeating that alkali-activated slag/metakaolin mixture, produced by Wang et al. (2010), had significantly lower ASR expansion than that of Portland cement mixture.

2.3.1.13. Carbonation

Carbonation refers to reaction of cement-based materials with carbon dioxide. In Portland cement concrete, carbonation can cause serious problems by forming HCO_3^- (a weak acid) in pore solutions of concrete which reacts with calcium-rich hydration products (including Portlandite, calcium silicate hydrate, calcium aluminate hydrate, and ettringite), and forms calcium carbonate. These reactions result in (1) strength loss and (2) pH reduction which destroys the protective passive layer around reinforcement leading to corrosion of the reinforcing steel. Carbonation usually accompanied by shrinkage which can crack concrete as well.

The carbonation mechanism for alkali-activated slag concretes is not as yet fully understood. However, it has been suggested to happen in following two steps: (1) carbonation of pore solution resulting in pH reduction and precipitation of Na-rich carbonates, followed by (2) decalcification of Ca-rich phases or secondary phases presented in alkali-activated concretes. The conducted research in this field also indicated that the accelerated carbonation test, which designed for cement-based systems, doesn’t represent the natural carbonation process for alkali-activated slags. There were inconsistency between natural carbonation rates of alkali-activated concretes and the results of accelerated tests. In the following sections, a brief review of the conducted research on this subject is discussed.

Byfors et al. (1989) compared carbonation of Portland cement and alkali-activated slag concretes. They claimed that the carbonation of alkali-activated slag concretes were faster than that of Portland cement concrete. Similarly, Bakharev et al. (2001b) noticed higher susceptibility to carbonation for alkali-activated concretes than Portland cement concrete. Hakkinen (1993) and

Shi (2003a) observed serious cracking in alkali-activated slag mixtures exposed to carbon dioxides.

On the other hand, Ionescu and Ispas (1986) noticed the same carbonation depth in Portland cement and alkali-activated slag/fly ash mixtures. Xu and Pu (1999) declared lower carbonation depth in alkali-activated slag concretes than Portland cement concretes. Malolepszy and Deja (1999) and Deja (2002) studied the carbonation of sodium carbonate- and sodium silicate-activated slag mortars by exposing them for two years to 0.1MPa pressure of carbon dioxide at 20°C and 90% relative humidity. They observed low carbonation depth in both mortars. Their strengths were even higher than those of normally-cured mortars. They related this observation to the high relative humidity. It’s generally accepted that carbonation rate is faster at relative humidity of 50 to 70%. The carbonation rate reduces at higher and lower relative humidity.

In recent years, Puertas et al. (2006) noticed more carbonation depth in sodium silicate-activated slag mortars than sodium hydroxide-activated slag mortars. More recently, Bernal et al. (2014) found that MgO content of slag can affect the extension and mechanism of carbonation of alkali-activated slag mixtures. They observed significant reduction in the carbonation extent of alkali-activated slag mixtures by increases in MgO content. This was related to the formation of layered doubled hydroxides which absorb carbon dioxide. Higher formations of these products, as a result of increases in MgO content, improved the performance considerably.

As final note, it should be mentioned that the weak performance of alkali-activated slag mixtures in accelerated carbonation tests, which doesn’t match the performance under normal conditions, could be related to the unsuitability of the test method for alkali-activated mixtures.

Alkali-activated slag mixtures are more susceptible to shrinkage-related problems. Dry conditions promote desiccation of the reaction products, resulting in structural changes and causing superficial micro cracking which facilitates CO_2 ingress. Therefore, the pre-conditioning of the specimens prior to accelerated carbonation testing can severely change the superficial permeability of alkali-activated mixture as a result of drying shrinkage. This can lead to exaggerated carbonation than what can be experienced under natural carbonation conditions. Also, it has been found that acceleration process change the resulting carbonated products compared to what form under natural condition. This change can considerably reduce the degree of pore blockage compare to normal condition, which results in higher permeability under accelerated conditions. Accordingly, a revised test method is needed to assess carbonation of alkali-activated slag concretes (Bernal 2015).

2.3.1.14. Resistance to other types of chemical attack

Chloride salts can be a source of problem for Portland cement concrete. It’s well documented that a high concentration of calcium chloride can deteriorate Portland cement concrete. Deja and Malolepszy (1989, 1994) compared the chloride salt resistance of Portland cement and sodium hydroxide-activated copper slag mortars. They measured strength development of these mixtures immersed in water, sodium chloride, magnesium chloride, and potassium chloride solutions. While they observed significant reduction for Portland cement concretes immersed in corrosive solutions, the strengths of alkali-activated mortars increased slightly regardless of the immersion condition. These results indicated better corrosion resistance of alkali-activated slags in comparison with Portland cement. Similar performance was observed by Kurdowski et al. (1994) for sodium carbonate-activated slag. They didn’t notice any visual trace of corrosion within 7 years of immersion in the same solutions. Shi (2003a) compared behavior of alkali-activated slag mortar with Portland cement mortar immersed in 30% calcium chloride solution. While Portland cement mortar were corroded starting with small cracks in corner followed by swelling and appalling of the surface, alkali-activated slag mortars provided excellent resistance.

Other salts and alkaline conditions can also deteriorate Portland cement concrete. Even though hydrated cement has a high pH, it still can be deteriorated in alkaline environment. Deng et al. (1989) studied effects of corrosive solutions such as sodium sulfate, magnesium sulfate, sodium hydroxide and sodium chloride on strength of alkali-activated slag pastes in comparison with Portland cement pastes. While the strength of Portland cement pastes significantly reduced in all the above-mentioned solutions, alkali-activated slag pastes didn’t experience any strength loss. Although far more research is needed for alkali-activated slag binders, they seem to be more resistant in highly alkaline conditions.

Other chemicals that can affect Portland cement and alkali-activated materials are organic liquids. Research in this area is very limited. Table 2.10 documents a comparison between performance of Portland cement and alkali-activated slag concretes immersed in different organic liquids (Gontcharov 1984). These results showed significantly higher resistance of alkali-activated slag concretes to organic fluids than Portland cement concrete. It was also observed that large molecule fluid organics are much less aggressive to alkali-activated slag concrete than Portland cement concrete. Alkali-activated slag concretes showed almost 3 times more resistance to mineral oil, animal fat and 30% sugar solution when compared with Portland cement concrete.

Table 2.10 Corrosion resistance in liquid organics (Gontcharov 1984)

Liquid organics	pH value	Titratable acidity mol/l	Coefficient of resistance after 720 days of immersion	
			Alkali-activated slag cement	Portland cement
Gasoline	-	0.0005	0.98-0.99	0.98-0.99
Benzol	-	0.0007	0.96-1.00	0.70-0.90
Kerosene	-	0.0008	0.92-0.99	0.60-0.78
Mineral oil	-	0.0011	0.64-0.96	0.50-0.70
Diesel fuel	-	0.0009	0.72-0.94	0.50-0.67
Sulphur petroleum	-	0.0013	0.50-0.97	0.56-0.40
Animal (Pig) fat	-	0.0500	0.56-0.97	Destroyed
Sugar solution (30% concentration)	-	0.0100	0.68-1.18	0.30-0.64
Salt brine of meat packing plant	-	-	0.68-1.18	0.30-0.64
Acetic acid (10% concentration)	2.8	-	0.25-0.45	0.15-0.24
Milk acid (10% concentration)	3.45	-	0.30-0.79	0.20-0.35

Decalcification is another process that can weaken Portland cement concrete. This process involves dissolution and leaching of calcium ions from $Ca(OH)_2$ and C-S-H in pure water. This process can affect concretes that are in contact with water for a long time such as dams, water pipes and tunnels. As decalcification is a slow process, accelerated tests have been designed using ammonium nitrate instead of water. In case of alkali-activated slag, there is only one research assessing their decalcification process. Komljenovic et al. (2012) compared performance of alkali-activated slag mortar with that of Portland cement mortar exposed to 6M ammonium nitrate. While strength loss was observed in both mixtures, alkali-activated slag mortars experienced considerably lower strength reduction than Portland cement mortars. Portland cement mortar lost 81% of its strength in 2 months, whereas alkali-activated slag mortar experienced only 9% strength loss in the same period. The authors related this resistance to the absence of calcium hydroxide, high level of polymerization of silicate network, relatively low level of aluminum substitution for silicon in C-S-H gel structure, and formation of a protective layer of polymerized silica gel. It’s worth mentioning that “decalcification resistance of a binder material is of great importance in the structures used for radioactive waste disposal containers,” (Pacheco-Torgal et al. 2015). This study showed promising performance of alkali-activated slags for stabilization/solidification processes. Previous research also confirmed high potential of alkali-activated binders for use in stabilization/solidification of hazardous and radioactive wastes (Shi and Fernandez-Jimenez 2006; Vance and Perera 2009; Provis 2009).

2.3.2. Fly ash

In recent years, a great deal of research has been devoted to alkali-activation of fly ash. Although the research in this area is still in its primary stage, this binder has shown the potential for production of high-strength and high-performance concretes. However, it should be noted that the need for curing in elevated temperature may limit their applications to only precast systems.

Similar to the alkali-activated slag mixtures, type and dosage of alkaline activator, nature of fly ash, and alkaline solution-to-binder ratio are of the factors affecting properties of alkali-activated fly ash binders. Curing conditions including curing temperature, available moisture, and curing time are of other factors that can considerably affect their properties. A brief review on assessed properties of alkali-activated fly ash mixtures are described below.

2.3.2.1. Fresh properties

There has been very limited research assessing fresh properties of alkali-activated fly ash binders. These works has been mainly focused on evaluation of their setting time and workability.

2.3.2.1.1. Setting time

Similar to the alkali-activated slag binders, setting time has been a major concern for alkali-activated fly ash binders. Long setting time is an issue for class F fly ash binders, whereas quick setting is a concern of class C fly ash binders. Setting time of alkali-activated class F fly ash binders can be extended to longer than a day at ambient temperatures. In fact, their low reactivity necessitates use of curing at elevated temperatures (usually within the range of 40 to 90°C). On the other hand, class C fly ash can set within 1 to 2 hours at ambient temperatures.

There are several factors affecting setting times of alkali-activated fly ash mixtures including chemical composition of fly ash, type and dosage of activator, alkaline solution-to-binder ratio or water-to-binder ratio, and use of compatible admixtures. As the main difference of class C and F fly ash is their CaO contents, thus it is a key factor affecting their setting time. Figure 2.18 shows influence of CaO content on setting time of alkali-activated fly ash mixtures; indicating setting acceleration with increases in lime content. Recent research has also shown silica-to-alumina ratio and the initial precipitation of C-A-S-H critical in setting of alkali-activated class C fly ash binders. For class C fly ash binders activated with sodium hydroxide and sodium silicate, increases in both silica and alumina shorten the setting time due to formation of C-A-S-H gel which is the dominant gel in the setting process.

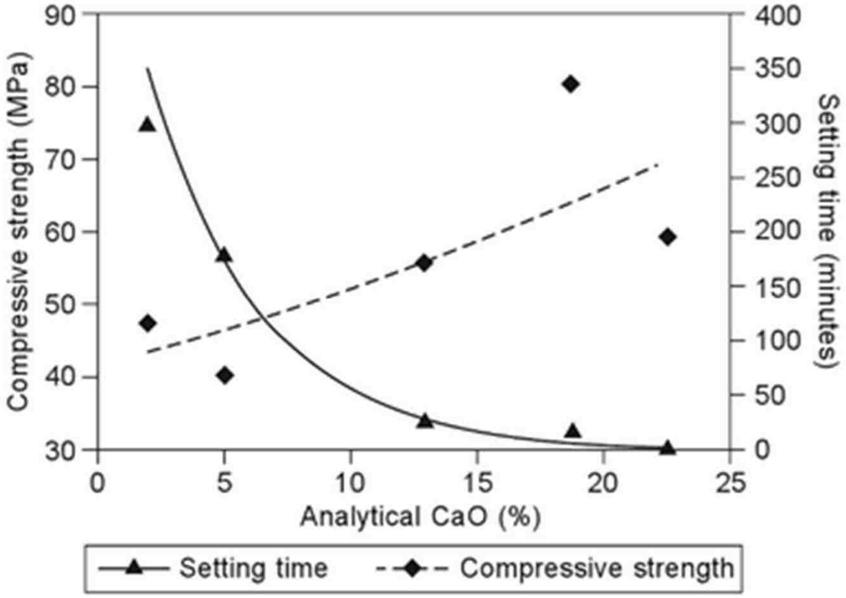


Figure 2.18 Effect of CaO content on setting time (Diaz et al. 2010)

Recently, Sierra (2015) conducted a study in the UNLV Concrete Research Laboratory on alkali-activated class F fly ash mortars using elevated temperature. In her study, she assessed effects of sodium hydroxide concentration and solution-to-binder ratio on the setting time. The setting time results are presented in Table 2.11. These results revealed that the initial and final setting times of alkali-activated class F fly ash mortars can vary from a few hours up to 2 days or more. The findings of this study also indicated that NaOH molarity and solution-to-binder ratio are of influential parameters that can significantly affect the setting times. Increases in molarity and reduction in solution-to-binder ratio reduced the setting time of the selected mortars to the same level of Portland cement mortars.

Table 2.11 Setting times of alkali-activated class F fly ash mortars (Sierra 2015)

Property	Solution-to-binder ratio	NaOH molarity (M)			
		5	7.5	10	12.5
Initial setting time (hrs)	0.42	9.88	8.35	7.47	3.03
	0.46	12.50	9.37	9.22	7.68
	0.50	27.20	14.47	10.75	10.97
Final setting time (hrs)	0.42	22.08	10.23	8.80	5.50
	0.46	23.23	12.33	12.17	10.97
	0.50	41.72	17.77	13.97	13.62

In a few studies, accelerators and retarders have been tried to adjust setting time of alkali-activated fly ash mixtures. Lee and van Deventer (2002) used inorganic salts to accelerate setting process of class F fly ash pastes activated with combinations of potassium hydroxide and sodium silicate. They found calcium and magnesium salts effective for acceleration purposes. They also noticed delay in setting time using right compositions of chloride, carbonate and nitrate salts. In the case of class C fly ash, proper amounts of sucrose was found effective in delaying the setting time. On the other hand, use of calcium chloride resulted in acceleration of the reactions, thus shortening the setting time of alkali-activated class C fly ash pastes (Rattanasak et al. 2011).

2.3.2.1.2. Workability

In terms of workability, there is not any particular research comparing the flow of alkali-activated fly ash and Portland cement mixtures. Considering nature of fly ash and the results of the exiting literature, it can be concluded that workability can’t be a regular issue for alkali-activated fly ash mixtures; in particular for class F fly ash. In this regard, Hardjito (2005) stated that at ambient temperatures, alkali-activated class F fly ash can be handled for up to two hours without indication of setting or evidence of degradation in their strength properties (Hardjito 2005). In a recent study conducted in the Concrete Research Laboratory at UNLV, Sierra (2015) confirmed that workability is not much of an issue for alkali-activated class F fly ash mortars. From the results of her research, study shown in Figure 2.19, it can be seen that workability is significantly dependent on alkaline concentration and type of activators. While solution-to-binder ratio didn’t show significant effect on flow, increases in alkaline concentration or sodium silicate content resulted in considerable reduction of flow. From these results, one can easily deduce that depending on the alkalinity or activator type, flow of alkali-activated fly ash mixtures can be more or less similar to that of Portland cement mixtures. Therefore, with a proper mixture proportioning design, workability is not an issue for alkali-activated fly ash mixtures.

In another study with similar objectives, Ryu et al. (2013) studied effects of alkaline concentration and different combinations of sodium hydroxide and sodium silicate on flow of alkali-activated class F fly ash mortars. They included sodium hydroxide concentrations of 6, 9, and 12M, and sodium hydroxide/sodium silicate combinations of 100/0, 75/25, 50/50, 25/75 and 0/100. They found reduction in slump flow with increases in sodium hydroxide concentration and sodium silicate content. The only exception was sodium hydroxide/sodium silicate combination of 50/50 which had higher flow than 25/75 and 75/25 combinations.

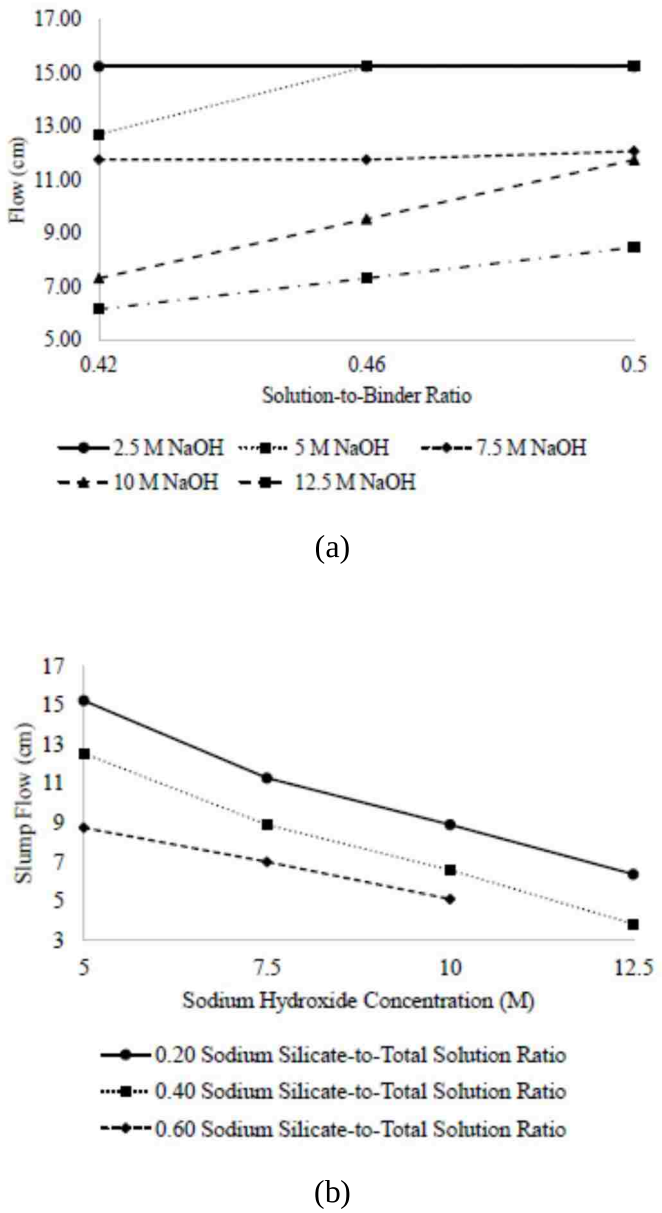


Figure 2.19 Workability of alkali-activated class F fly ash mortars (Sierra 2015)

2.3.2.2. Compressive strength

Compressive strength of alkali-activated fly ash mixtures depends on type of alkaline activator, alkaline concentration, fly ash composition and type, curing condition, and solution-to-binder ratio. Depending on the combinations of these factors, it’s possible to produce concretes with low, normal or medium, and high strength. While use of low-molarity activator or curing at room temperature result in low strengths, high-strength binders can be made by use of elevated temperatures, high-concentration activator and inclusion of sodium silicate as a partial activator. For instance, Fernandez-Jimenez et al. (2006b) produced high-strength alkali-activated class F fly ash concretes using high-molarity sodium hydroxide, partial inclusion of sodium silicate and curing at 85°C for 20 hours. They used two different combinations of activators; (1) AAFA-N containing 8M NaOH solution, and (2) AAFA-W having 85% of a 12.5M solution of sodium hydroxide plus 15% sodium silicate. Compressive strengths of the produced alkali-activated concretes are shown in Figure 2.20 along with Portland cement concretes having w/cm of 0.5 which cured for 20 hours at 22 or 40°C and 98% relative humidity. These results showed higher strengths of alkali-activated fly ash concretes than those of Portland cement concretes. These results also proved that a really high strength (almost 45 MPa) could be developed within a day by use of elevated temperatures and proper combinations of activators.

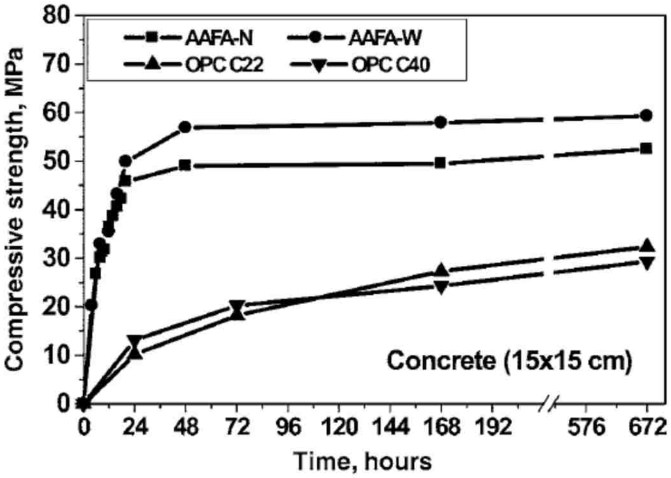


Figure 2.20 Compressive strength of Portland cement and alkali-activated fly ash concretes (Fernandez-Jimenez et al. 2006b)

In the following sections, effects of influential factors on compressive strength of alkali-activated fly ash mixtures are briefly reviewed.

2.3.2.2.1. Effect of activator type

Similar to the alkali-activated slag mixtures, type of activator can significantly affect the strength of alkali-activated fly ash mixtures. Criado et al. (2005) compared effects of two different curing conditions and two types of alkaline activators (solely sodium hydroxide and combination of sodium hydroxide with sodium silicate) on polymerization reactions of alkali-activated class F fly ash. They found that addition of sodium silicate allowed for further polymerizations, which in turn led to higher strength than when only sodium hydroxide was used as an activator. Similarly, Panias et al. (2007) found addition of sodium silicate to sodium hydroxide effective in strength improvement. Use of sodium silicate resulted in higher soluble silicate content which favored strength development.

Komljenovic et al. (2010) evaluated compressive strength of alkali-activated fly ash mortars using calcium hydroxide, sodium hydroxide, potassium hydroxide and sodium silicate as activators. The highest strength was observed for sodium silicate-activated mortars followed by sodium hydroxide-activated mortars. The high silicon contents, which ease the reactions, led to higher reaction products and thus higher strengths of sodium silicate-activated mortars. The activation potential was found in the following order:

$$KOH < NaOH+Na_2CO_3 < NaOH < Na_2O.nSiO_2$$

2.3.2.2.2. Effect of activator concentration (sodium hydroxide molarity)

The concentration of alkaline activator has been known as the most important factor affecting properties of alkali-activated fly ash binders. In general, increases in concentration of hydroxide ions lead to increases in solubility of aluminosilicates, which in turn, result in higher compressive strengths. The effects of alkaline concentration, however, have not always been that simple. While some studies suggested that a minimum amount of alkaline are needed for a successful activation, there are different studies showing adverse effects of high alkaline concentrations on the strength properties of alkali-activated fly ash binders. Based on all the observed results, it can be concluded that there are minimum, optimum, and maximum levels for activator concentration.

Katz (1998) assessed effect of sodium hydroxide concentration on compressive strength of alkali-activated fly ash mixtures using different molarities of 1, 2, 3 and 4M. The compressive strength increased with increases in molarity of sodium hydroxide, which was attributed to the increase in degree of reactivity due to higher concentration of activator.

Hardjito et al. (2004a) used combinations of sodium hydroxide (8 and 14M) and sodium silicate to activate fly ash concretes. They used sodium silicate-to-sodium hydroxide mass ratio of 0.4 and 2.5. They observed increases in compressive strength by increases in alkaline concentration and sodium silicate-to-sodium hydroxide ratio. Similarly, Komljenovic et al. (2010) and Ravikumar et al. (2010) observed increases in compressive strength with increases in sodium hydroxide concentrations in the ranges of 10 to 15% Na_2O and 4 to 8M, respectively.

Vargas et al. (2011) activated class F fly ash using sodium hydroxide cured at elevated temperatures. They studied effects of Na_2O/SiO_2 molar ratio by varying it between 0.2 and 0.4. They noticed higher strength in mixtures having higher Na_2O-to-SiO_2 molar ratio. Arioz et al. (2012) measured compressive strength of alkali-activated fly ash mixtures which were activated using combination of sodium hydroxide (4, 8 and 12M) and sodium silicate. Their results also revealed improvements in compressive strength by increases in NaOH concentration.

While the above-mentioned studies showed increases in strength with increases in alkaline concentration, there are other investigations showing that there is an optimum level for increasing activator concentration. Palomo et al. (1999) stated that an excess of OH^- concentration in the system could result in strength reduction of alkali-activated fly ash systems. Xu and Van Deventer (2000) concluded that extra alkaline couldn’t lead to strength improvements. Similarly, Kaps and Buchwald (2002) reported no strength improvement for more than a certain amount of NaOH. They also showed that measurable strength could not be gained below a minimum NaOH content. Strength reduction was also observed for alkali-activated slags, when molarity of alkaline activator (KOH) increased from 10 to 15M (Cheng and Chiu 2003). Similarly, Rajamma et al. (2012) reported an optimum sodium hydroxide concentration when activating biomass fly ash with 8, 10, 12, and 18M NaOH. Their results showed increases in strength when molarity increased from 8 to 10M. The strength, however, decreased for molarity of more than 10M.

2.3.2.2.3. Effect of curing conditions

Curing condition is another influential parameter affecting properties of alkali-activated fly ash binders. The main factors in selection of curing conditions are curing temperature, available sample moisture and oven moisture environment, and curing age; all of which are briefly described below.

> (1) Curing temperature: reactions of fly ash; particularly Class F, are extremely slow at ambient temperatures. Use of elevated temperatures catalyzes the reactions of alkali-activated binders and helps them to form a strong network of hydrates, which in turn, substantially increase their compressive strengths. The previously conducted research have shown improvements in the compressive strength of alkali-activated fly ash mixtures when temperatures increased in the ranges of 30 to 90°C. Beyond 90°C, however, increases in temperature may result in adverse effects.
>
> (2) Curing age: prolonging the curing time also improves the polymerization process, thus increasing the compressive strength. However, when elevated temperatures used, increases in strength beyond 48 hours was found insignificant. Even some researchers indicated that a few hours of curing at elevated temperatures led to completion of

majority of geopolymerization process, after which secondary treatment is not required.

(3) Available sample moisture and moisture environment in oven: when cured in the oven (elevated temperatures), conditions of samples can significantly affect the properties of alkali-activated mixtures. It was found that the moisture condition or relative humidity are effective in strength development. The strength differs if samples are sealed-cured or moist-cured or dry-cured (exposed).

Followings are a brief review of different studies assessing effects of curing environment on compressive strength of alkali-activated fly ash binders:

Katz (1998) assessed effects of curing temperatures on compressive strength of alkali-activated fly ash mixtures by using different temperatures of 20, 50 and 90°C. The compressive strength increased with increases in curing temperatures. Similarly, Hardjito et al. (2004a) observed improvements in strength of alkali-activated fly ash concretes by increasing the temperature in the same range.

Criado et al. (2005, 2010 and 2012) used two methods of curing in the oven: (1) for the first method, “the molds were placed in air-tight receptacles containing a certain amount of water, which was not, however, in contact with the molds.” The relative humidity was almost 90%, (2) for the second method, “the molds were introduced directly into the oven alongside a porcelain capsule containing water.” Relative humidity was 40 to 50%. The samples cured by the first method developed considerably higher strengths than those cured using the second method. They attributed the lower strength of the second method to lack of moisture and carbonation of the samples.

Kovalchuk et al. (2007) tried three different curing conditions in order to optimize the curing process. These conditions were: (1) Sealed curing: the molds with samples inside them were covered by plastic bags (sealed) and cured for 8 hours at 95°C, (2) Dry curing: the covered molds were cured in oven for 2 hours at 95°C. Then samples were demolded and subjected to a thermal ramp from room temperature to 150°C in 3 hours, followed by 6 hours curing at 150°C and cooling to room temperatures in 3 hours, and (3) Steam curing: the conditions were similar to dry curing except that 95°C was used instead of 150°C and 100% relative humidity was maintained during the curing process. The sealed curing led to the highest strengths, followed by steam curing. The dry-cured samples developed the lowest strengths. This observation was related to availability of moisture for chemical reactions. As was stated, the sealed and steam curing conditions encapsulate the moisture of samples, which allowed for higher degree of reactions and microstructural developments, resulting in higher strength.

Ravikumar et al. (2010) found increases in strength of alkali-activated fly ash concretes by increasing temperature and time of curing. Similar conclusion was drawn by Vargas et al. (2011).

Mustafa Al Bakari et al. (2011) assessed strength properties of alkali-activated class F fly ash mixtures cured at room temperature, 50, 60, 70, and 80°C. They found the highest strength in samples cured at 60°C. They noticed that temperatures beyond 60°C not only didn’t increase the strength, but also resulted in moisture loss thus hindering the strength development.

Joseph and Matthew (2012) assessed the influence of curing temperature on strength of alkali-activated class F fly ash concretes by varying curing temperatures between 30 to 120°C (30, 60, 70, 80, 90, 100, 110, and 120°C). The compressive strength results are presented in

Figure 2.21. It can be seen that compressive strength improved by increasing temperature up to 100°C and experienced reduction for temperatures beyond 100°C. They attributed the strength loss to lack of moisture.

Recently, Sierra (2015) and Ghafoori et al. (2014) compared effects of different curing conditions on compressive strength of alkali-activated class F fly ash mortars. They used three different curing conditions in oven; namely exposed (dry), sealed, and moist in an air-tight container (not in contact with water). Samples were cured at 80°C. Overall, the highest strength was observed for moist curing, followed by sealed curing. The exposed cured samples developed the lowest strengths due to carbonation.

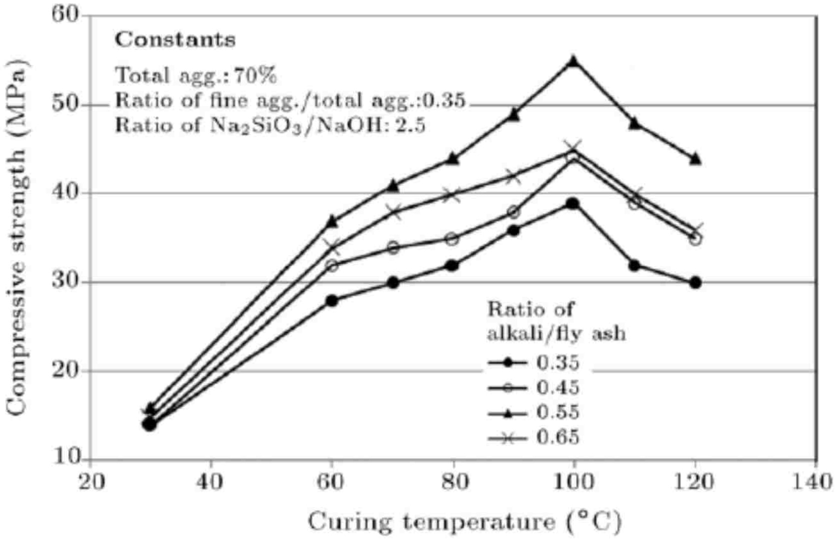


Figure 2.21 Effect of curing temperature and alkali/fly ash on strength (Joseph and Matthew 2012)

2.3.2.2.4. Effect of solution-to-binder ratio

Solution-to-binder ratio is another factor that can affect properties of alkali-activated binders. The majority of previous studies concluded that, similar to Portland cement, reduction in solution-to-binder ratio or water-to-binder ratio led to higher compressive strength for alkali-activated binders. There are, however, a few investigations refuting the above-mentioned findings.

Palomo et al. (1999) studied the effect of activator-to-fly ash ratio by using two ratios of 0.25 and 0.30. They couldn't found any obvious trend between these two different activator-to-fly ash ratios. For some of the activators or curing temperatures, mixtures with activator/fly ash of 0.25 had higher strength, while opposite trend was seen in the other mixtures. On the other hand, Hardjito et al. (2004a) and Panias et al. (2007) observed increases in compressive strength by reduction of water-to-solid mass ratio. Ravikumar et al. (2010) found increases in strength by decreasing activator-to-binder ratio. They stated that although use of higher activator-to-binder ratio increased the amount of alkaline activator in the mixture, the porosity was also increased thus lowering the compressive strength.

Xie and Kayali (2014) studied effect of water content for alkali-activated class F fly ash mixtures cured in ambient temperatures or with use of elevated temperatures. While the reduction of water content was found effective in strength improvement of samples cured in ambient temperatures, they didn't observe any significant effect for heat-cured samples.

More recently, Sierra (2015) and Ghafoori et al. (2016) assessed strength properties of alkali-activated class F fly ash mortars having different solution-to-binder ratios of 0.42, 0.46

and 0.50. They also observed improvements in compressive strength by reduction in solution-to-binder ratio.

2.3.2.2.5. Effect of fly ash composition and origin

Composition of fly ash has a significant influence on the properties of alkali-activated fly ash mixtures; not only strength properties of binders containing class C and F fly ashes significantly differ, but also fly ashes with almost similar characteristics but coming from different origins can produce considerably different results. Unfortunately, there is not enough research assessing these differences for alkali-activated fly ash mixtures. There is, however, a comprehensive study conducted by Diaz-Loya et al. (2011) activating 25 different fly ashes from different origins. Results of their study are presented in Table 2.12.

Considering only class F fly ashes, it can be seen that the strengths varied in the range of 10.34 to 49.24 MPa with an average of 36.17 MPa. For class C fly ashes, the range was even wider. The compressive strength of alkali-activated class C fly ashes varied in the range of 2.73 to 80.37 MPa with an average of 50.31 MPa. These results can easily show the effect of fly ash type and origin on properties of fly ash geopolymers.

Table 2.12 Strength properties of alkali-activated fly ashes with different origins (Diaz-Loya et al. (2011)

Fly ash type	Sample	SiO_2	Al_2O_3	CaO	Fe_2O_3	Compressive strength, MPa	Flexural strength, MPa	Elastic modulus, MPa
C	1	37.77	19.13	22.45	7.33	59.5	4.48	33.633
C	2	32.41	18.40	28.07	7.17	52.28	4.72	34.377
C	3	55.61	19.87	12.93	4.52	55.89	4.3	37.108
F	4	58.52	20.61	5.00	9.43	40.35	4.14	28.599
F	5	61.01	20.06	5.48	7.00	47.55	5.58	29.475
F	6	61.23	19.20	5.64	7.27	46.69	5.3	29.358
F	7	62.12	19.59	5.01	6.88	46.79	4.61	28.517
F	8	59.32	19.72	6.90	7.22	46.11	4.71	26.455
C	9	48.70	16.60	18.72	6.93	80.37	5.27	42.878
F	10	55.07	28.61	1.97	6.22	47.44	5.12	25.635
F	11	56.22	27.15	5.43	3.73	12.2	2.24	7040
F	12	56.39	27.36	4.69	3.34	12.82	2.38	6812
F	13	57.11	28.18	5.18	4.00	20.68	3.5	7960
F	14	57.35	27.78	5.57	3.65	10.34	2.74	7460
F	15	40.75	22.79	4.64	17.76	46.56	6.31	28.744
F	16	36.18	17.70	2.26	10.59	49.24	4.66	19.278
C	17	39.25	21.09	23.53	4.99	61.38	6.23	31.447
C	18	33.02	19.82	26.19	6.75	39.19	4.19	19.064
F	19	59.25	18.43	9.23	5.61	43.38	4.24	25.607
C	20	56.42	17.63	11.66	5.74	53.7	4.43	28.91
C	21	27.15	17.57	33.39	6.08	36.54	3.58	26.972
C	22	31.26	19.76	28.53	6.47	57.18	5.27	29.448
C	23	30.85	17.07	28.47	6.79	42.81	5.18	22.567
C	24	55.15	23.55	10.60	4.63	62.19	4.83	29.896
C	25	33.38	14.72	26.80	7.69	2.73	0.62	1868
F	Minimum	36.18	17.70	1.97	3.34	10.34	2.24	6812
	Maximum	62.12	28.61	9.23	17.76	49.24	6.31	29.475
	Average	55.42	22.86	5.15	7.13	36.17	4.27	20.842
C	Minimum	27.15	14.72	10.60	4.52	2.73	0.62	1868
	Maximum	56.42	23.55	33.39	7.69	80.37	6.23	42.878
	Average	40.08	18.77	22.61	6.26	50.31	4.42	28.181

2.3.2.3. Other strength/mechanical properties

The splitting tensile and flexural strengths of alkali-activated fly ash concretes are generally similar to or higher than that of the Portland cement concrete having the same compressive strength.

Hardjito (2005) observed tensile strengths of 4.43 to 7.43 MPa for alkali-activated fly ash concretes which were similar to those of Portland cement concrete. Sofi et al. (2007) also stated that tensile and flexural strengths of alkali-activated fly ash concretes can fit in the models developed for Portland cement concrete. Ryu et al. (2013) assessed the tensile strength-to-compressive strength ratio of alkali-activated fly ash concretes. They found this ratio to be between 7.8 to 8.2% which is similar to the typical ratio of Portland cement concrete. Tho-in et al. (2012) developed pervious geopolymer concrete using high-calcium fly ash and sodium silicate. The mechanical properties of the developed pervious geopolymer concrete were similar to those of conventional pervious concretes.

Other studies showed superior performance of alkali-activated fly ash concretes to Portland cement concrete in terms of tensile and flexural strengths. Jing et al. (2006) showed that under special curing conditions, it’s possible to develop alkali-activated fly ash mixtures with a Brazilian tensile strength of more than 10 MPa. Sarker et al. (2011) evaluated the bond and tensile strength of alkali-activated fly ash concrete with reinforcing steel. Their bond and tensile strength were higher than those of Portland cement concrete having similar compressive strength. They observed more brittle modes of failure in alkali-activated fly ash concretes than Portland cement concretes of similar compressive strength due to the denser interfacial transition zone, higher bond and tensile strength of alkali-activated fly ash concretes (Sarker et al. 2013).

Higher stresses were needed for formation of cracks in alkali-activated fly ash concretes when compared with Portland cement concrete. Similarly, Diaz-loya et al. (2011) noticed higher flexural strength-to-compressive strength ratio for alkali-activated fly ash concretes than typical ratios of Portland cement concrete. Olivia and Nikraz (2012) optimized synthesis condition properties of alkali-activated fly ash concretes by using Taguchi method. The produced concretes had the compressive strengths of about 56 to 60 MPa. They also made Portland cement concretes with similar compressive strength. Afterwards, they compared tensile and flexural strengths of alkali-activated fly ash and Portland cement concretes; their results are presented in Table 2.13. It can be seen that the studied alkali-activated fly ash concretes showed higher tensile and flexural strengths than Portland cement concretes having a similar compressive strength.

Table 2.13 Strength properties of Portland cement and alkali-activated fly ash concretes (Olivia and Nikraz 2012)

Mixture id.	Compressive strength (MPa)		Flexural strength (MPa)		Splitting strength (MPa)		Modulus of elasticity (GPa)	
	28 days	91 days	28 days	91 days	28 days	91 days	28 days	91 days
PC (control)	56.22	65.15	7.33	7.02	3.97	4.25	34.16	37.64
T7	56.49	56.51	7.39	9.21	4.13	4.18	25.33	27.18
T4	56.24	58.85	8.99	9.36	3.96	4.1	26.95	28.03
T10	60.2	63.29	8.38	9.85	4.29	4.79	29.05	26.80

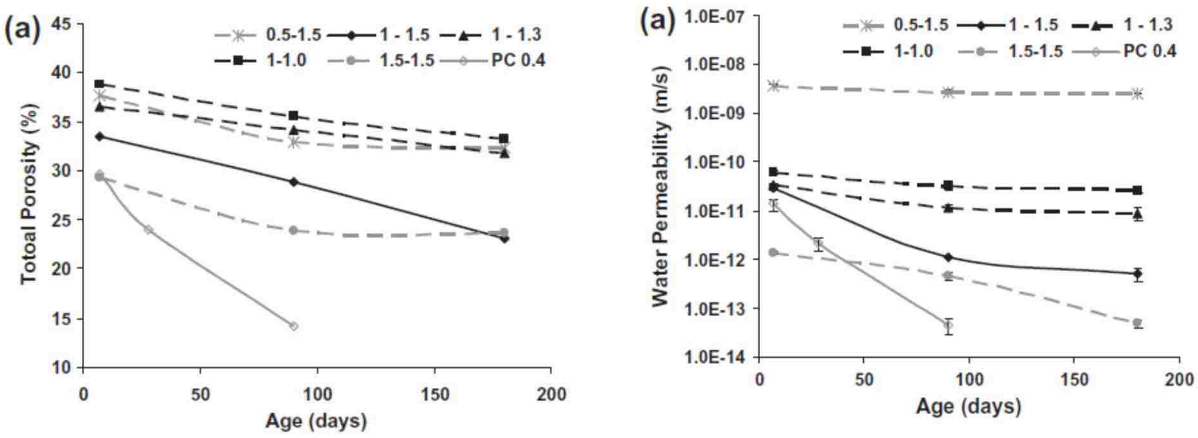
In terms of elastic modulus, the findings are quite controversial. Hardjito (2005) assessed the mechanical properties of alkali-activated class F fly ash concretes. The measured Young's modulus and Poisson's ratio of alkali-activated concretes were similar to those of Portland cement concrete. The stress-strain relationship of alkali-activated fly ash concretes was found to fit well with equations originally developed for Portland cement concretes. These results were later confirmed by Sarker (2009) and Yost et al. (2013).

On the other hand, there are a number of studies showing lower elastic modulus of alkali-activated fly ash concretes than that of Portland cement concrete. Fernandez-Jimenez et al. (2006b) and Olivia and Nikraz (2012) observed lower elastic modulus in alkali-activated fly ash concretes than Portland cement concretes (also see Table 2.13). Sofi et al. (2007) noticed that the modulus of elasticity of alkali-activated fly ash concretes was less than that of Portland cement concrete having the same compressive strength. Diaz-loya et al. (2011) measured modulus of elasticity of 25 different alkali-activated fly ash concretes having fly ash of different classes and origins. They concluded that the elastic modulus of alkali-activated fly ash concretes were generally lower than that of Portland cement concrete.

2.3.2.4. Transport properties

In general, lower permeability is expected for alkali-activated fly ash binders in comparison with a Portland cement binder having similar total porosity. This is mainly due to the much finer pore size of the alkali-activated fly ash mixtures than Portland cement mixtures.

Ma et al. (2013) measured total porosity and water permeability of alkali-activated fly ash and Portland cement mixtures. Their results are presented in Figure 2.22. It can be seen that the 7-day porosity of mixtures 1.5-1.5 and PC0.4 (Portland cement mixture) were almost similar. The water permeability of Portland cement mixture, however, was 10 times higher than that of mixture 1.5-1.5 with similar porosity. As the curing age was extended, the total porosity and permeability of alkali-activated fly ash mixtures didn’t change considerably, as expected. On the other hand, total porosity of Portland cement mixture was significantly modified (to almost half at 90 days), which in turn, significantly reduced its permeability. In another study, Nasvi et al. (2014) compared carbon dioxide permeability of alkali-activated fly ash paste with that of an oil well cement paste (type G cement). For the same porosity, the permeability of cement paste was several times higher than that of alkali-activated fly ash paste. This observation was attributed to the finer pore size of geopolymers in comparison with that of cement paste.



(a)

(b)

Figure 2.22 Porosity and water permeability of alkali-activated fly ash mixtures; (a) total porosity, (b) water permeability (Ma et al. 2013)

A few studies have been conducted assessing effects of curing conditions, activator dosage, and activator-to-binder ratio on transport properties of alkali-activated fly ash mixtures. Kovalchuk et al. (2007) measured the total porosity of alkali-activated fly ash mixtures under three different curing conditions of sealed curing, dry curing and steam curing (these curing conditions were described in section 2.3.2.2.3). The lowest porosity was observed in the sealed-cured samples. The total porosity of dry-cured samples was slightly lower than that of steam-cured samples.

Ravikumar et al. (2010) noticed reduction in porosity of alkali-activated fly ash mixtures by increases in activator dosage (alkaline concentration) and decreases in activator-to-binder ratio.

Ma et al. (2013) measured the total porosity and water permeability of alkali-activated fly ash mixtures activated with different dosages of silica and Na_2O (see Figure 2.22). The activator solutions were: 0.5M SiO_2 and 1.5M Na_2O, 1.0M SiO_2 and 1.5M Na_2O, 1.0M SiO_2 and 1.3M Na_2O, 1.0M SiO_2 and 1.0M Na_2O, and 1.5M SiO_2 and 1.5M Na_2O. They reported reductions in water permeability and total porosity by increasing silica and alkaline contents.

In another study, Gorhan and Kurklu (2014) observed reduction in volume of permeable voids by increasing curing time and temperature.

Recently, Sierra (2015) studied effects of alkaline concentration and sodium hydroxide solution-to-binder ratio on absorption and total porosity of NaOH-activated fly ash mortars (class F). The results are presented in Figure 2.23. The variables were NaOH molarity of 5, 7.5, 10 and 12.5M, and solution-to-binder ratios of 0.42, 0.46 and 0.50. Significant reduction in absorption was observed by increases in molarity of activator. The absorption also decreased with reduction in solution-to-binder ratio. These reductions, however, were minimal in comparison to those observed due to the increases in activator concentration. Nearly, similar trends were observed in rapid chloride penetration and migration tests (Sierra 2015).

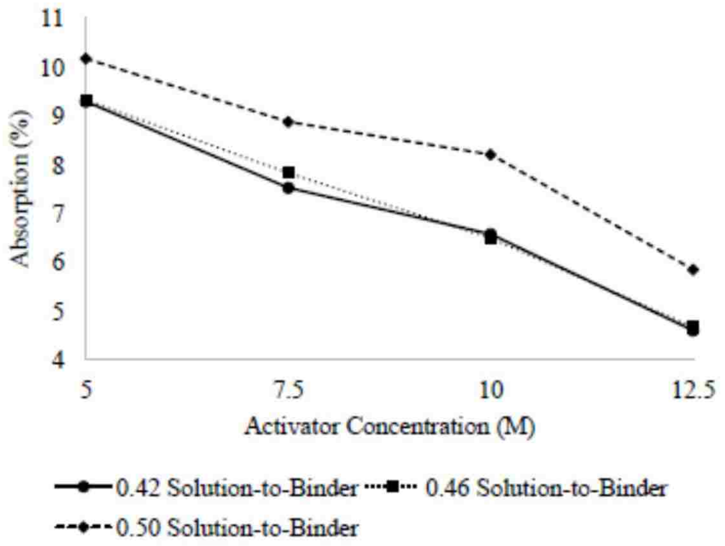


Figure 2.23 Effects of alkaline concentration and solution-to-binder ratio on absorption (Sierra 2015)

2.3.2.5. Resistance to chemical attacks

Majority of the conducted research showed proper resistance of alkali-activated fly ash mixtures against sulfate attack. Hardjito et al. (2004a) studied sulfate resistance of alkali-activated fly ash concretes over a period of 12 weeks immersion in sodium sulfate. They observed minimal changes in compressive strength and length of the studied concretes; indicating their great sulfate resistance. Skvara et al. (2005) evaluated sulfate resistance of alkali-activated fly ash pastes and mortars immersed in sodium sulfate and magnesium sulfate solutions. They didn’t observe any mass loss, length change, or formation of new crystalline phases over a period of 2 years. Even, compressive strength of alkali-activated mortars increased over the exposure time. Fernandez-Jimenez et al. (2007) measured strength change of alkali-activated fly ash mortars immersed in 4.4% sodium sulfate. After fluctuations in strength at early age, they observed increases in strength of samples by extending the exposure time. They didn’t observe any difference in performance of sodium hydroxide- and sodium silicate-activated mortars. Sata et al. (2012) compared sulfate resistance of Portland cement and alkali-activated lignite bottom ash mixtures exposed to 5% sodium sulfate. The sulfate-induced expansion of alkali-activated mixtures was considerably lower than that of Portland cement mixtures. Chindaprasirt et al. (2013) noticed some strength losses in alkali-activated high calcium fly ash mixtures after 6 months of exposure to 5% magnesium sulfate.

In terms of acid attack, alkali-activated fly ash mixtures provided greater resistance than Portland cement mixtures. Rostami and Brendley (2003) compared acid resistance of Portland cement and alkali-activated fly ash concretes by immersing them in different acids including 100% solution of acetic acid, 70% solution of nitric acid, and 20% solutions of hydrochloric and sulfuric acids. The alkali-activated fly ash concretes experienced significantly less mass loss than Portland cement concretes after a year of immersion in all different acids. In the worst case scenario alkali-activated fly ash concretes lost less than 5% of their mass in a year, whereas Portland cement concretes lost more than 25% of their mass in less than 3 months (2 hrs in nitric acid, a week in hydrochloric acid, a month in acetic acid, and 3 months in sulfuric acid). Portland cement concretes were severely damaged after 2 hours of exposure to nitric acid, whereas the alkali-activated fly ash concretes didn’t show any sign of degradation after more than a week immersion.

In another study, Bakharev (2005) noticed greater acid resistance (acetic and sulfuric acids) of alkali-activated fly ash pastes in comparison with Portland cement pastes containing purely cement or combination of 80% cement and 20% fly ash.

Fernandez-Jimenez et al. (2007) also observed less mass and strength losses in alkali-activated fly ash mortars than Portland cement mortars when they were immersed for 90 days in hydrochloric acid with pH of 1. Similarly, Chaudhary and Liu (2009) noticed greater resistance of alkali-activated fly ash concretes to hydrochloric acid in comparison with Portland cement concrete. Sata et al. (2012) showed the same behavior in sulfuric acid. They compared resistance of Portland cement and alkali-activated lignite bottom ash mortars exposed for 120 days to 3% sulfuric acid. The mass loss of Portland cement mortar was significantly higher than that of alkali-activated mortar.

Ariffin et al. (2013) prepared alkali-activated concretes using pulverized fuel ash, palm oil ash or combination of them. They exposed alkali-activated and Portland cement concretes to 2% sulfuric acid for 18 months. All the alkali-activated concretes experienced lower mass and strength losses than Portland cement concrete. The blended alkali-activated concrete lost 35% of its initial strength after 18 months of immersion, while the strength loss of Portland cement concrete was 68%. In a more recent study, Sierra (2015) didn’t report any mass or strength losses after 2 months immersion of alkali-activated fly ash mortars in sulfuric acid.

There is only one research showing contrary. Lloyd et al. (2012) immersed 28-day cured Portland cement and alkali-activated fly ash binders in sulfuric acid. They observed lower corroded depth in Portland cement binders than alkali-activated fly ash binders. This behavior was in contrary with observations of Shi and Stegemann (2000) on 1-year cured pastes. Lloyd et al. (2012) also noticed improvements in acid resistance by increases in alkaline content of the studied mixtures. They didn’t detect any considerable change in acid resistance due to variation of water-to-binder ratio, alkaline type and the content of dissolved silica in activator.

2.3.2.6. Frost resistance

The research on frost resistance of alkali-activated fly ash mixtures is limited. The results of these research have shown their superior performance to not-air-entrained Portland cement mixtures.

Skvara et al. (2005, 2006) assessed frost resistance of alkali-activated fly ash mortars. They didn’t observe any mass loss or disintegration after 150 cycles of freezing-thawing; stating that ‘’the fly ash-based geopolymers were very resistant to freeze-thaw’’. The strength after 150 cycles, however, was lower than that of reference samples maintained in laboratory condition. Rostami and Brendley (2003) compared the frost resistance of Portland cement and alkali-activated fly ash concrete concretes. Results of their study are presented in Figure 2.24. It can be seen that the frost resistance of not-air-entrained alkali-activated fly ash concretes was similar to that of air-entrained Portland cement concrete and significantly better than that of not-air-entrained Portland cement concrete. Use of air-entraining admixture didn’t provide any stable air for alkali-activated concretes, thus not modifying their frost resistance.

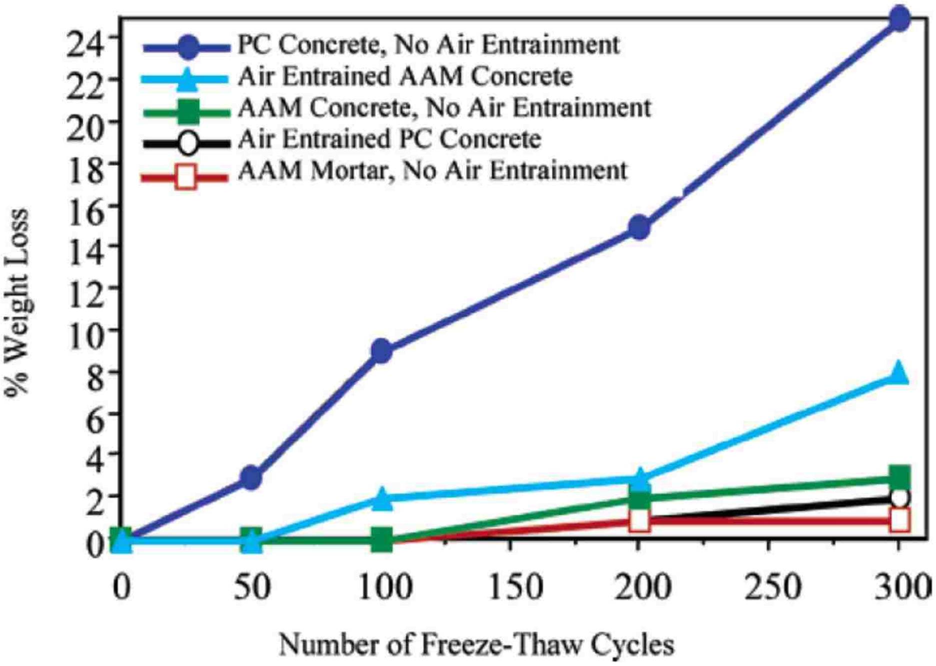
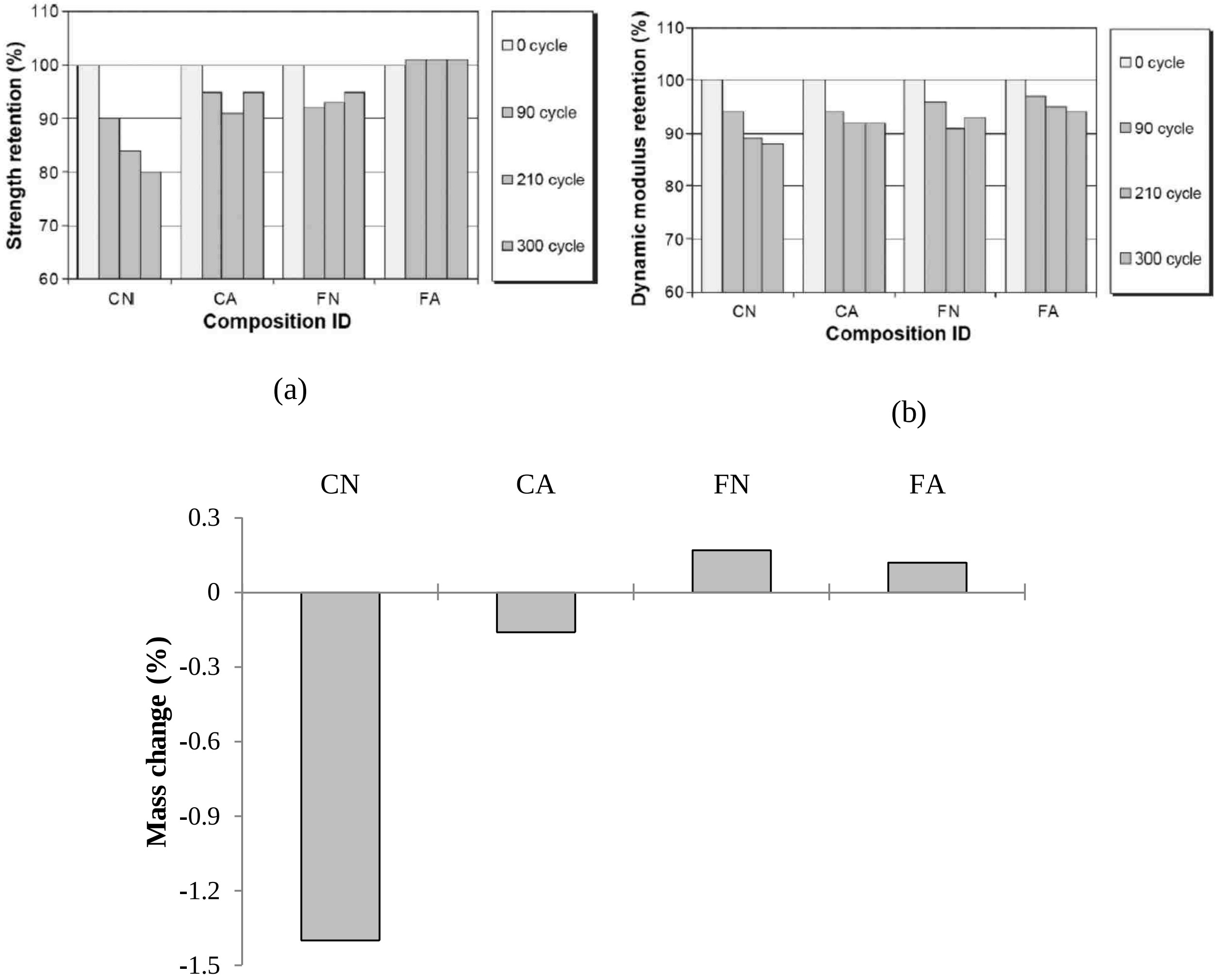


Figure 2.24 Freeze-thaw resistance of Portland cement and alkali-activated mixtures testing based on ASTM C666, procedure A. AAM: alkali-activated mixture, PC: Portland cement mixture (Rostami and Brendley 2003)

Sun (2005) and Sun and Wu (2013) also assessed frost resistance of air-entrained and not-air-entrained alkali-activated fly ash contained mortars according to ASTM C666. They compared their performance with those of air-entrained and not-air-entrained Portland cement mortars. Results of the study are shown in Figure 2.25. It can be seen that the resistance of air-entrained and not-air-entrained alkali-activated fly ash mortars were similar or superior to that of air-entrained Portland cement mortar. Both of alkali-activated mortars were significantly more resistant to freeze-thaw cycles than not-air-entrained Portland cement mortars. Use of air-entrained admixture, however, didn’t provide noticeable positive effect on the performance of alkali-activated mortars. Shi (2012) (cited by Montes et al. 2013 and Pacheco-Torgal et al. 2015) stated an opposite observation. While alkali-activated class F fly ash failed ASTM C666 criteria only after 100 to 120 freezing-thawing cycles, the air-entrained alkali-activated class F fly ash mixtures were able to resist 300 freeze-thaw cycles by losing only 10% of their initial dynamic modulus.



(a)

(b)

(c)

Figure 2.25 Freeze-thaw resistance of Portland cement and alkali-activated mortars; (a) strength retention, (b) dynamic modulus retention, (c) mass change; CN (PC mortar without air entraining agent) CA (PC with air entraining) FN (alkali-activated without air entraining) and FA (alkali-activated with air entraining); (Sun and Wu 2013)

2.3.2.7. Other properties

There are a few more properties of alkali-activated fly ash mixtures that have been recently studied including corrosion, shrinkage and alkali-aggregate reaction.

In case of corrosion, Miranda et al. (2005) noticed that alkali-activated fly ash mortars passivate reinforcing steel as rapidly and effectively as Portland cement mortars. Corrosion rate of alkali-activated fly ash mortar was at the same level of that of Portland cement mortar. They concluded that the corrosion of alkali-activated fly ash mixtures will not limit their applications.

Drying shrinkage is another property of alkali-fly ash concretes which have been evaluated. The main research in this area was done at the Curtin University, Australia by Hardjito et al. (2002, 2004a, 2004b, 2005), Hardjito and Rangan (2005), Wallah et al. (2004, 2005), Wallah and Rangan (2006), Sumajouw et al. (2007), Rangan et al. (2005, 2006). Their results revealed very low drying shrinkage of alkali-activated fly ash concretes cured at elevated temperatures; the maximum shrinkage was almost 100 microstrain (Pacheco-Torgal et al. 2015). This behavior was related to the evaporation of most of the water during curing process. As the remaining water in the concrete micropores was low, the drying shrinkage was low too. On the other hand, these researchers observed very high shrinkage in alkali-activated fly ash concretes cured at ambient temperatures (with a maximum shrinkage of around 1200 microstrain). The remaining water (water not used for chemical reactions) possibly evaporated over a period of time causing extensive shrinkage.

In another study, Lee (2007) compared drying shrinkage of alkali-activated class C and class F fly ash concretes with that of Portland cement concrete. The mean drying shrinkage of alkali-activated class C fly ash concrete was 520 microstrain which was considerably lower than that of Portland cement concrete experiencing 820 microstrain. The mean drying shrinkage of alkali-activated class F fly ash concretes were 550, 720 and 920 microstrain for different mixtures with nominal compressive strengths of 20, 60 and 45 MPa, respectively.

Lee (2007) also reported that alkali-activated fly ash concretes may have a high early-age shrinkage potential or high rate of shrinkage in the first one or two days. For the standard drying shrinkage test methods, the zero reading starts at 3, 7 or 28 days depend on the standard and composite system. For example above-mentioned studies used a zero reading of 3 or 7 days. Therefore, standard methods may need revisions in order to correctly assess shrinkage of alkali-activated concretes cured at elevated temperatures.

Alkali-aggregate reaction (AAR) is another property that has been investigated. Almost all the conducted studies concluded that alkali-activated fly ash mixtures or other activated aluminosilicates experienced less abnormal swelling due to AAR, even when very reactive aggregates were used. Between 1994 and 2005, Davidovits reported no deterioration due to AAR expansion for the studied geopolymers (Pacheco-Torgal et al. 2015). Fernandez-Jimenez et al. (2007) and Garcia-Lodeiro et al. (2007) observed significantly lower ASR expansion in alkali-activated fly ash mortars than Portland cement mortars. It was, however, mentioned that alkali-activated fly ash mixtures can’t be considered totally safe as a few mixtures exceeded the allowable limits.

2.3.3. Natural Pozzolans

The research on alkali-activation of natural pozzolans is very limited. There are only a few studies in this field which have been mainly focused on properties of pastes and mortars, and carried out by only a few groups of researchers. These studies can be divided in three groups: (1)

the main group of these studies was carried out by Bondar and her colleagues in Iran. Their research started with feasibility study on activation of natural Pozzolans, followed by activation of natural Pozzolan from different origins. They recently assessed limited properties of alkali-activated natural Pozzolan concretes as well; (2) a few studies have been carried out by other researchers assessing limited properties of natural pozzolan pastes, and (3) a more recent work on alkali-activated natural pozzolan mortars conducted in the UNLV Concrete Research Laboratory by Ghafoori, Radke and Najimi (Ghafoori et al. 2016, Najimi et al. 2016). This section discusses each of these groups, signifying the need for additional studies in this field.

2.3.3.1. Works by Bondar and her colleagues

Use of natural pozzolans in Iran dates back to thousands years ago. According to ACI 232.1 (2012), the first use of natural pozzolan was 5000-4000 B.C., using diatomaceous earth form of natural pozzolan from the Persian Gulf. There are different dormant volcanos and thus various sources of natural pozzolans in Iran. On the other hand, there has not been any source of fly ash there till recent years. Accordingly, there has been a growing interest for application and research on natural Pozzolans in Iran.

The first attempt for alkali-activation of natural Pozzolans dates back to 2005, when Bondar and her colleagues conducted preliminary experiments (a feasibility study) on natural pozzolans from two different sources; namely Taftan and Shahindej (Bondar et al. 2005). The activation was made with various combinations of sodium silicate and potassium hydroxide having molarities of 2.5, 5 and 7.5M. They cured the produced pastes for 28 days at 40°C before their strengths were measured. While this preliminary work couldn’t be considered a success, there were evidences indicating the possibility of producing a binder with sufficient strength for structural elements. The compressive strength of alkali-activated Shahindej and Taftan pastes reached 10 and 18MPa at their best, respectively. These values were not considerable, but it should be considered that the studied pastes were cured at only 40°C. From the observed difference between strength of these two types of Pozzolans, effect of natural pozzolan origin on properties of alkali-activated mixtures can be detected as well.

Bondar et al. (2011a) later investigated effect of activator' type, form and dosage on compressive strength of alkali-activated natural pozzolan pastes using similar sources of natural Pozzolan; i.e. Taftan and Shahindej (Bondar et al. 2011a). They used sodium and potassium hydroxides with different molarities of 2.5, 5, 7.5 and 15M, and sodium silicate as activators. Industrial sodium silicate in three forms of powder, granular and solution were used. The authors also made sodium silicate with SiO_2-to-Na_2O ratios of 2.1, 2.4 and 3.1. Three different curing conditions at 40°C, 60°C, and autoclave curing were used for the purpose of their study. They noticed that potassium hydroxide-activated Pozzolans achieved higher strengths than sodium hydroxide-activated Pozzolans. Potassium hydroxide in the range of 5 to 7.5M was found to generate the highest compressive strength. While lower molarity (2.5M) resulted in lower dissolution of natural Pozzolans and thus lower strengths, 10 and 15M KOH didn't lead to higher strength as well. This was related to the fact that the excess water needed longer time or higher temperature to be evaporated from the system before forming the geopolymer responsible for strength development. There wasn't any obvious trend for NaOH-activated natural Pozzolan pastes. The samples cured at 60°C achieved higher strengths than those cured at 40°C. However, 40°C was found enough to achieve the minimum strength required for structural concrete. Also, it was found that autoclave curing at 2.5MPa and 150°C for 3 hr could produce strengths similar to curing at 60°C for 28 days. The solution and granular forms of sodium silicate was found the most and least suitable forms for activation purposes, respectively. For low-calcium oxide natural Pozzolans (having high soluble silica), sodium silicate modulus of 2.1 was found optimum, whereas the sodium silicate modulus of 3.1 was found optimum for high-calcium oxide natural Pozzolans (calcinated Pozzolan). Bandar et al. (2011b) also assessed effects of heat treatment and calcination on natural pozzolans from 5 different origins. The calcination was only effective for two types of natural Pozzolans that contained Montmorillonite.

The same research team also tried to use alkali-activated natural pozzolans in production of concrete (Bondar et al. 2011b and 2012). They studied effects of curing conditions (sealed and fog curing), curing temperatures (20, 40 and 60°C) and water-to-binder ratio (0.4, 0.41, 0.45, 0.5 and 0.55) on strength and transport properties of concretes. Followings are the major findings of their work:

- While the early-age strength of alkali-activated natural Pozzolan concretes were lower than those of Portland cement concrete, their late-age strength reached to similar or higher values than those of Portland cement concrete. Similar trend was observed for modulus of elasticity.

- The ultrasonic pulse velocity of alkali-activated natural Pozzolan concrete was lower than that of Portland cement concrete having the same strength.

- The drying shrinkage of alkali-activated natural Pozzolan concretes was considerably lower than that of Portland cement concrete.

- Sealed curing was found to be superior to fog curing. For sealed curing condition, lower w/b and higher temperature led to lower shrinkage.

- Oxygen permeability of alkali-activated natural Pozzolan concretes were 10 to 35% lower than that of Portland cement concrete at late age (90 days). Opposite trend was observed at 7 days.

- Increases in curing temperature improved strength and permeability of alkali-activated concretes.

- The rapid chloride permeability test (RCPT) gave misleadingly high results.

Bondar et al. (2015) also assessed sulfate resistance of alkali-activated natural pozzolan mortars and concretes activated using potassium hydroxide and sodium silicate. The maximum expansion within their studied mortars was 0.074% after 6 months of immersion; which was well below the 0.1% limit of ASTM C1012 for Portland cement concretes. The concretes immersed in sulfate solution for 2 years had 8 to 19.5% lower strength than that of the reference concrete cured outside of the sulfate solution.

2.3.3.2. The limited research around the world

Villa et al. (2010) used sodium hydroxide and sodium silicate to activate natural zeolite. They used different sodium silicate-to-sodium hydroxide ratios of 0.4, 1.5, 5, 10 and 15, and curing temperatures of 25, 40, 60, and 80°C. The results are presented in Figure 2.26. It can be seen that the room temperature-cured natural zeolite exhibited the lowest compressive strengths. However, their strength increased with time up to a sufficient level at 90 days. The natural zeolites cured by use of elevated temperatures reached their ultimate strength after 7 days of curing. Their strengths were at the same level of Portland cement mixtures. Sodium silicate-to-sodium hydroxide ratio of 0.4 was found low for strength development at all curing temperatures. The ratio of 1.5 produced a satisfactory strength for all curing conditions. The ratio of 5 and 10 could have resulted in good performance depending on the selected temperature. On the other hand, the ratio of 15 resulted in strength reduction as compared to that obtained using other ratios.

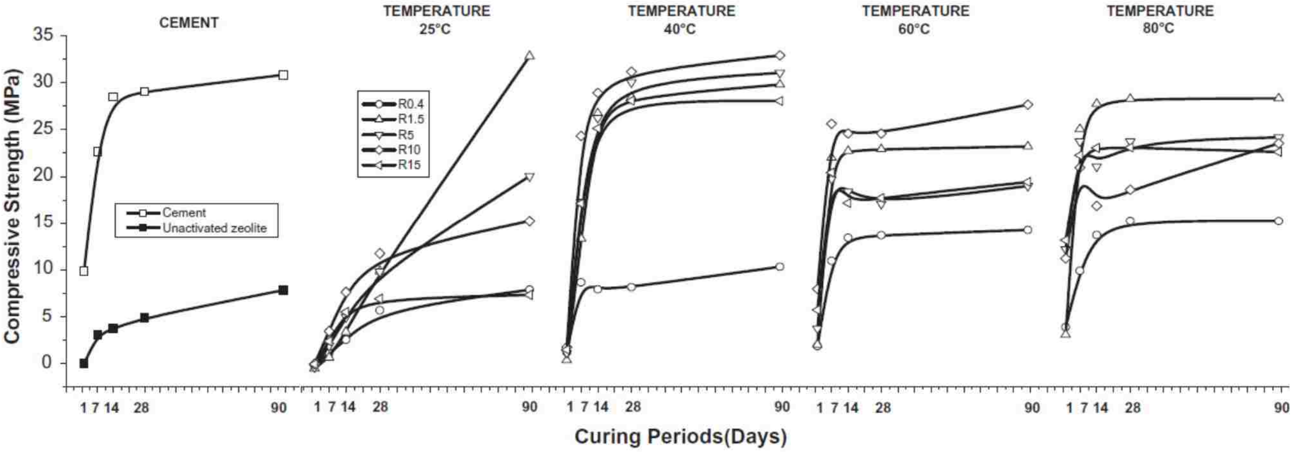


Figure 2.26 Compressive strength of alkali-activated natural zeolite by Villa et al. (2010); R0.4, R1.5, R5, R10 and R15 are related to sodium silicate-to-sodium hydroxide ratios of 0.4, 1.5, 5, 10 and 15, respectively

Lemougna et al. (2011) activated volcanic ash using sodium hydroxide as alkaline activator. They used three different curing temperatures of 40, 70, and 90°C, and two curing conditions of dry (exposed) and wet in the water. Results of their work are shown in Figure 2.27. They noticed increases in the strength as curing temperature increased up to 90°C. They also reported reduction in strength, when temperature increased beyond 90°C. As temperature rose to 250°C, the strengths were nearly halved as a result of loss of structural water as well as formation of micro-cracks. The alkali-activated natural Pozzolans cured under dry condition achieved higher strength than those cured under wet condition.

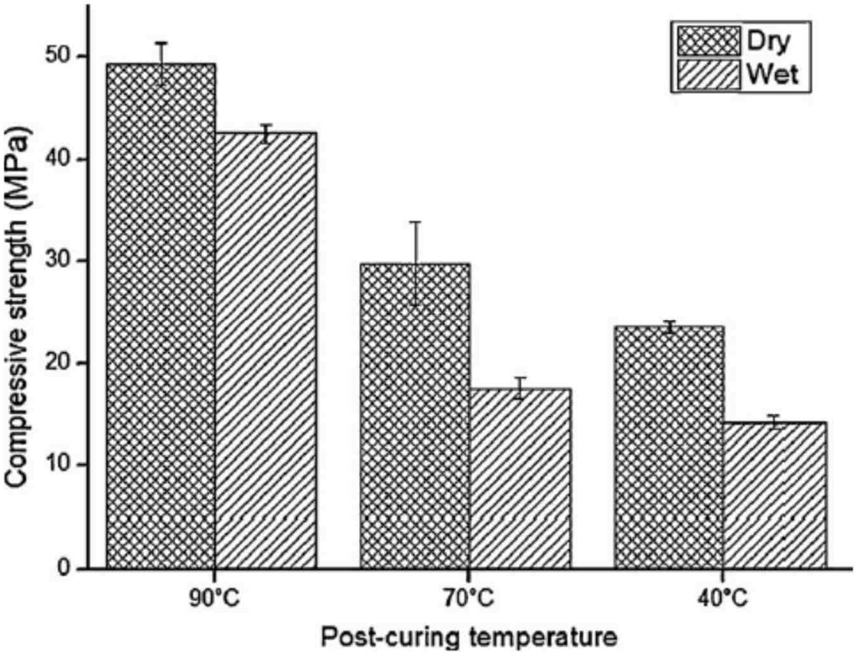


Figure 2.27 Effect of curing condition and temperature on compressive strength of alkali-activated volcanic ash (Lemougna et al. 2011)

Najafi Kani and Allahverdi (2011) evaluated shrinkage of alkali-activated natural Pozzolan pastes activated with combinations of sodium hydroxide and sodium silicate. They used different combinations of activators to provide various SiO_2/Na_2O of 0.3, 0.45, 0.6, 0.75 and 0.9, Na_2O/Al_2O_3 of 0.77, 0.92, 1.08 and 1.23, and H_2O/Al_2O_3 of 7.5, 8, 9 and 9.5. They also assessed effect of hydrothermal curing on the shrinkage. They found that (1) the geopolymerization process resulted in significant shrinkage, (2) the chemical composition, in particular SiO_2/Na_2O, substantially affects the shrinkage, (3) drying shrinkage reduced with decreases in SiO_2/Na_2O, Na_2O/Al_2O_3 and H_2O/Al_2O_3, and (4) hydrothermal curing with short pre-curing in humid atmosphere was found considerably effective for reduction of shrinkage.

In another study, Tchakoute et al. (2013) were able to achieve reasonable strengths for ambient temperature-cured alkali-activated natural Pozzolan pastes through activation with combinations of sodium hydroxide and sodium silicate. They achieved 28-day strengths of 9 to 19 MPa and 23 to 50 MPa for two different types of Pozzolans and by using different SiO_2-to-Na_2O molar ratios. The higher SiO_2-to-Na_2O molar ratios resulted in higher strengths. Their results also indicated the importance of Pozzolan' amorphous contents, which were different between the studied Pozzolans.

Moon et al. (2014) also confirmed the feasibility of using alkali-activated natural Pozzolans as a sustainable binder for use in construction materials. Their designed pastes reached strengths of 33 and 47 MPa when activated with sodium hydroxide and combination of sodium hydroxide and sodium silicate, respectively. It's worth mentioning that they used curing condition of 80°C and 100% relative humidity.

2.3.3.3. Research in Concrete Research Laboratory, UNLV

Ghafoori, Radke, and Najimi (Ghafoori et al. 2016, Najimi et al. 2016) evaluated effects of sodium hydroxide concentration, sodium hydroxide solution-to-binder ratio (S/B), and curing condition on properties of alkali-activated natural Pozzolan mortars. They made several mortars with different sodium hydroxide molarities of 2.5, 5, 7.5, 10 and 12.5M, and various S/B of 0.50, 0.54 and 0.58. The produced mortars were cured at 80°C under three different conditions of exposed (dry), sealed (wrapped) and moist until testing at ages of 1, 3, and 7 days. Multiple tests were conducted on the alkali-activated natural Pozzolan mortars including flow spread, compressive strength, flexural strength, PH measurement, absorption, and rapid chloride migration. Compressive strength test results under the above-mentioned curing conditions are presented in Table 2.14. These results revealed that the sealed curing condition was most conducive to strength gain, whereas the exposed curing condition caused dehydration and/or carbonation within the samples, and the moist curing condition did not allow for full removal of excess water resulting in reduced bond formations. The moist oven-cured mortars produced higher strength than the exposed cured mortars when alkaline activator with lower molarities was used. The opposite trend was observed for the higher molarities mortars. The compressive and flexural strengths, absorption and depth of penetrated chloride improved when NaOH concentration increased and S/B decreased. Some of these observations are presented in Table 2.15 and Figure 2.28. The authors also cured a series of samples in standard curing room (at ambient temperature and 100% relative humidity); their results are presented in Table 2.16. It can be seen that ambient temperature-cured samples showed no significant strength gain.

Table 2.14 Compressive strength of alkali-activated mortars cured in the oven (Ghafoori et al. 2016, Najimi et al. 2016)

S/B	NaOH Concentration (M)	Age (days)	Exposed (MPa)	Moist (MPa)	Sealed (MPa)
0.50	2.5	1	3.8	4.2	4.6
		3	5.2	6.2	5.4
		7	4.6	10.0	5.9
	5	1	7.2	4.8	5.4
		3	9.0	7.5	9.7
		7	8.8	11.2	12.5
	7.5	1	10.4	6.6	7.4
		3	14.5	11.2	16.5
		7	15.3	17.3	20.5
	10	1	13.6	8.7	9.4
		3	27.7	15.9	22.3
		7	26.2	22.9	31.9
0.54	2.5	1	3.5	4.2	4.5
		3	5.0	5.9	5.7
		7	4.6	9.5	5.7
	5	1	6.0	4.1	4.4
		3	6.6	6.8	8.4
		7	6.8	10.5	11.4
	7.5	1	9.8	5.3	5.8
		3	11.0	9.2	14.8
		7	11.5	13.7	17.9
	10	1	12.8	6.7	7.9
		3	25.3	13.5	21.6
		7	24.2	21.1	28.2
	12.5	1	15.7	7.3	10.4
		3	30.8	16.3	24.1
		7	27.6	25.7	30.8
0.58	2.5	1	2.4	2.6	2.9
		3	3.0	3.9	3.4
		7	3.0	6.1	3.9
	5	1	4.7	2.5	3.0
		3	5.5	4.6	6.8
		7	5.1	7.0	8.4
	7.5	1	8.1	3.3	3.5
		3	10.1	6.5	12.6
		7	8.6	8.5	14.9
	10	1	11.9	5.0	5.7
		3	21.9	8.9	17.5
		7	21.6	15.0	27.1
	12.5	1	14.0	5.7	7.4
		3	32.4	17.4	23.3
		7	31.8	26.6	37.7

Table 2.15 Results of rapid chloride migration and rapid chloride penetration tests (Ghafoori et al. 2016, Najimi et al. 2016)

Molarity	S/B	Rapid chloride migration			RCPT (Charge passed for Voltage of 10V)
		DNSSM×10^{-12} (m^2/s)	Rate of chloride penetration (mm/Vh)	Chloride penetration depth (mm)	
2.5	0.5	194.77	0.538	32.29	6118
	0.54	214.57	0.587	35.19	6308
	0.58	285.21	0.760	45.62	6800
5	0.5	112.56	0.331	19.88	6625
	0.54	121.01	0.352	21.09	--
	0.58	181.20	0.503	30.17	6776
7.5	0.5	41.33	0.144	8.63	6239
	0.54	64.55	0.206	12.38	6433
	0.58	71.65	0.225	13.48	7080
10	0.5	21.38	0.088	5.26	2407
	0.54	21.80	0.089	5.33	3463
	0.58	23.10	0.092	5.53	6397
12.5	0.54	15.63	0.071	4.23	1054
	0.58	17.08	0.075	4.49	1065

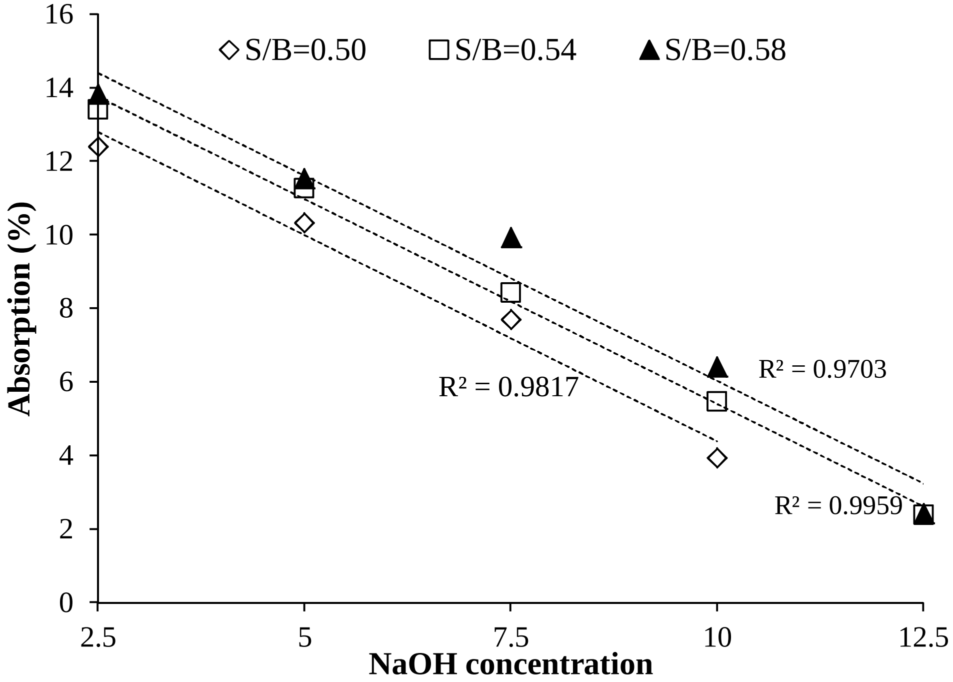


Figure 2.28 Results of absorption test on the studied alkali-activated mortars (Ghafoori et al. 2016)

Table 2.16 Compressive strengths of standard moist cured mortars (Ghafoori et al. 2016)

S/B	NaOH Concentration (M)	Compressive strength (MPa)	
		7 days	28 days
0.50	2.5	2.8	3.8
	5	3.2	5.3
	7.5	3.2	5.6
	10	3.8	5.6
0.54	2.5	3.4	5.1
	5	2.2	3.6
	7.5	2.9	4.8
	10	2.7	4.4
	12.5	2.5	3.4
0.58	2.5	2.0	2.9
	5	1.6	3.0
	7.5	1.5	3.0
	10	1.6	3.6
	12.5	1.6	2.4

2.3.4. Fly ash/slag combination

In recent years, there is a growing trend to combine fly ash and slag for cementitious components as combination of the two benefits the system. The N-A-S-H gel as the main reaction product of low-calcium binders offers excellent chemical and thermal resistances, while C-A-S-H as the reaction product of high-calcium binders provide chemical binding of water which reduces permeability (Provis and Van Deventer 2014). Thus, it’s hypothesized that a proper combination may lead to an excellent performance.

Table 2.17 documents the research studies for which combinations of fly ash and slag, as cementitious components, for the purpose of alkaline activation were used. Figure 2.29 shows the number of articles on this subject published in the past 20 years. It can be seen that there has been growing interest in this subject. Also, it can be seen that the majority of these studies have been dedicated to obtaining a few properties of pastes and mortars. The research on alkali-activated fly ash/slag concretes, in particular on their durability properties, is very limited. Therefore, the research in this field is still in its infancy and far more studies are needed before their applications are materialized. Followings are a brief review of the major studies conducted in this field to date.

Table 2.17 Previous works on alkali-activated fly ash/slag systems

Year	Total number of research	Authors	Mixture type	Studied properties
2000	1	Puertas et al.	paste	compressive strength, mineralogical characteristics
2002	1	Puertas et al.	mortar	sulfate resistance
2003	2	Puertas and Fernandez-Jimenez	paste	mineralogical and microstructural characteristics, compressive strength
		Puertas et al.	mortar	compressive and flexural strengths, freeze-thaw
2006	1	Escalante Garcia	paste	compressive strength, XRD
2007	1	Zhao et al.	paste	setting time, SEM, XRD
2010	2	Kumar et al.	paste	strength properties, setting time, heat of hydration
		Izquiredo et al.	paste	leaching
2012	2	Xin et al.	paste	use of specified design method/ simulation
		Wang et al.	paste	addition of metakaolin; mineralogical and microstructural characteristics, compressive strength
2013	7	Puligilla and Mondal	paste	ultrasonic, compressive strength
		Lee and Lee	paste/ concrete	setting time and mechanical properties
		Kar et al.	concrete	compressive strength, ultrasonic
		Chi and Huang	mortar	strength, water absorption, drying shrinkage, SEM, XRD
		Ismail et al.	paste	sulfate resistance, mineralogical characteristics
		Ismail et al.	mortar/ concrete	compressive strength, transport properties
		Rashad	concrete	flow, strength, shrinkage
2014	4	Ismail et al.	paste	SEM, XRD, FTIR, TGA
		Jang et al.	paste	setting time, flow, heat of hydration
		Ghafoori and Najimi	mortar	fresh, mechanical and transport properties
		Lee et al.	paste/ mortar	shrinkage, XRD
2015	10	Gao et al. (**3** studies)	paste	heat of hydration, compressive strength, mineralogical characteristics
		Chi et al.	mortar	compressive strength, length change, water absorption, SEM, XRD
		Marjanovic et al.	mortar	compressive strength, SEM
		Marjanovic et al.	mortar	shrinkage, strength properties
		Deb et al.	concrete	compressive strength, shrinkage
		Wang et al.	paste	flow, compressive strength, ultrasonic, sulfate attack
		Wardhono et al.	mortar	compressive strength
		Lee and Lee	paste	microstructure, reaction products
2016	1	Abdalqader et al.	paste	compressive strength, SEM, XRD, TGA, hydration

* No publications for the years that are not mentioned

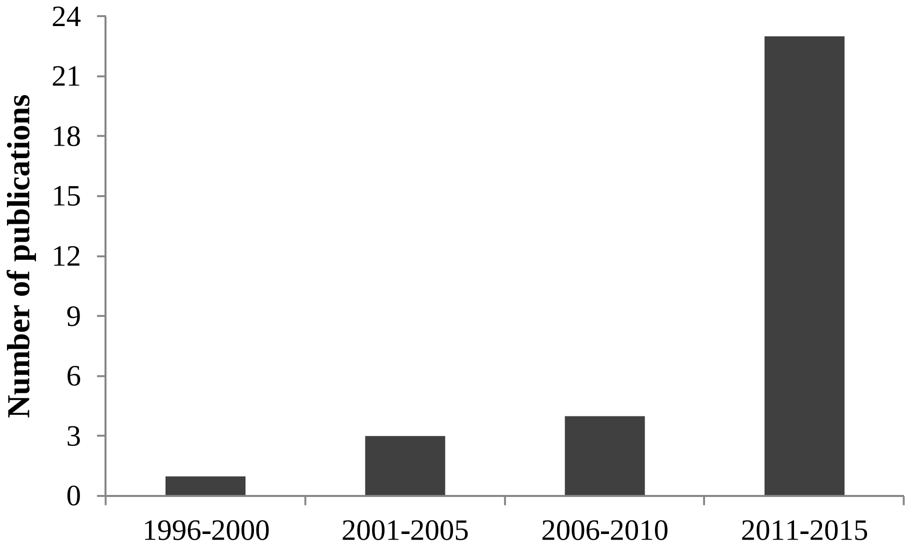


Figure 2.29 Number of publications related to alkali-activated fly ash/slag systems, obtained from Scopus database searched by different keywords in the “article title, abstract, keywords” section

Puertas et al. (2000) developed alkali-activated fly ash/slag pastes using sodium hydroxide solutions (2 and 10M) as activators. They selected different fly ash/slag combination of 100/0, 70/30, 50/50, 30/70 and 0/100. The produced pastes cured under two curing conditions: (1) at 25°C and 98% relative humidity, and (2) 5 hrs at 65°C followed by the same conditions of the first method. They concluded that compressive strength increased with increases in slag content and molarity of sodium hydroxide. Except for the early-age strengths, use of elevated temperature caused lower late-age strengths (28 and 90 days). They found ‘’a hydrated calcium silicate of the CSH gel type with high tetrahedrically coordinated Al amounts and interlayer Na ions in its structure’’ as the main reaction products of pastes having 50% slag and 50% fly ash.

Puertas and Fernandez-Jimenez (2003) evaluated mineralogical and microstructural characteristics, and strength of alkali-activated fly ash/slag pastes having 50% fly ash and 50%

slag. They used 10M NaOH for activation and a liquid-to-binder ratio of 0.35. The ambient temperature-cured pastes gained 7-day and 28-day compressive strengths of 31.9 and 63.5 MPa, respectively. The 7-day and 28-day flexural strengths were 6.3 and 13.5 MPa, respectively. These values proved that it’s possible to develop high strengths at ambient temperatures when the two activators are combined. They also stated that the main reaction product was a “low-crystalline calcium silicate hydrate rich in Al, which included Na into its structure”.

Puertas et al. (2003) also assessed freeze-thaw resistance of 3 different alkali-activated mortars and compared their performances with that of a control Portland cement mortar. The alkali-activated mortars included (1) an alkali-activated slag mortar activated by use of sodium silicate and sodium hydroxide solutions and cured at room temperature, (2) an alkali-activated fly ash mortar which activated with 8M sodium hydroxide and cured for the first day at 85 °C, and (3) a 50/50 alkali-activated fly ash/slag mortar activated with 8M sodium hydroxide and cured at room temperature. These mixtures, cast with and without fiber, were subjected to 50 cycles of freeze-thaw at the age of 28 days. Figure 2.30 presents the ratio of mortars’ strength after freeze-thaw cycles-to-strength of mortars not subjected to the freeze-thaw cycling. While alkali-activated fly ash mortar showed weak resistance to freezing-thawing cycles, the slag contained mortars (both 100% slag and 50% slag mixtures) performed superior to Portland cement mortar. The combined mortar performed in between the alkali-activated fly ash and alkali-activated slag mortars. Use of fiber didn’t significantly affect the freeze-thaw resistance.

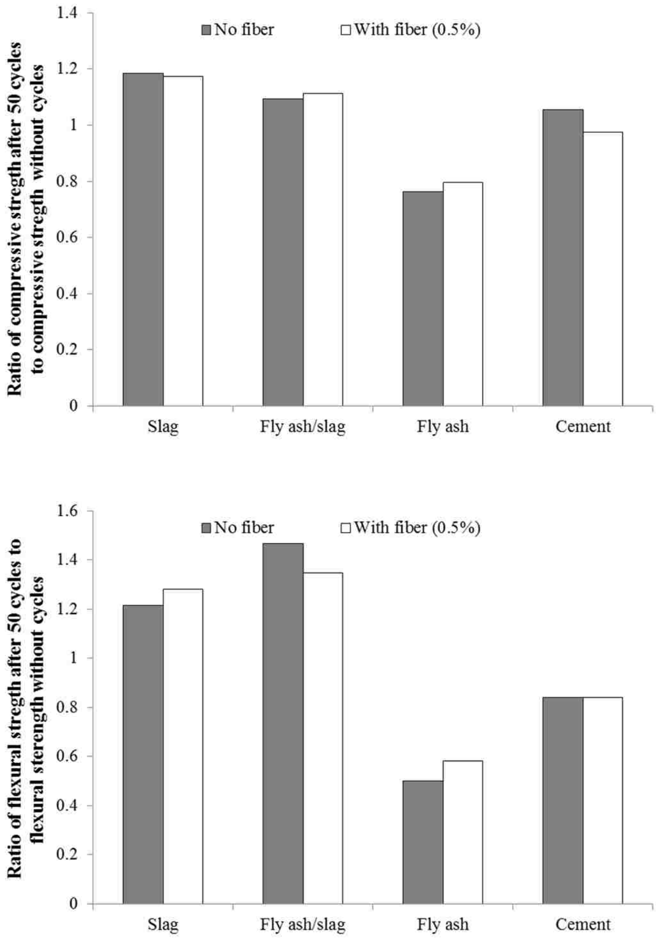


Figure 2.30 Effect of freeze-thaw cycles on strength of alkali-activated mortars (Puertas et al. 2003)

Escalante Garcia et al. (2006) produced alkali-activated fly ash/slag pastes with different fly ash-to-slag proportions of 100-0, 75-25, 50-50, 25-75, and 0-100. The used activators were combinations of sodium silicate and 4 to 8% Na_2O. The produced pastes were cured for a day at 75°C, followed by 28 days at 20°C before testing for compressive strength. While the activated paste containing only fly ash reached 25 MPa at its best performance, alkali-activated slag pastes gained strengths in the range of 80 to 85 MPa. The other studied pastes developed strengths between the above-mentioned values; indicating strength reduction by increases in fly ash content. The authors also found modulus of 1 to 1.5 as an optimum modulus for sodium silicate, when sodium silicate with modulus of 0, 0.75, 1, 1.5, and 2 were utilized. Similarly, Zhao et al. (2007) observed reduction in strength of alkali-activated pastes when up to 50% of slag was replaced with fly ash.

Kumar et al. (2010) replaced up to 50% of fly ash with slag and assessed effects of this replacement on properties of alkali-activated fly ash-based pastes. Increases in slag content led to significant increases in strength and heat of hydration, and considerable reduction in setting time. While alkali-activated pastes having purely fly ash developed less than 5 MPa strength (about 3 MPa at 28 days), the 28-day strength reached 30 MPa by replacing 35 to 50% of fly ash with slag. Setting time reduced substantially by inclusion of slag in the mixtures. Setting time of alkali-activated fly ash paste (without slag) was reported to be nearly 300 min. It was reduced to almost 100 min and 50 min by replacing 5 and 15% of fly ash with slag, respectively. Similarly, Puligilla and Mondal (2013) observed increases in strength and heat of hydration of alkali-activated pastes, when they replaced up to 15% of fly ash with slag.

Lee and Lee (2013) measured setting time and strength properties of alkali-activated fly ash/slag pastes and concretes having slag content of 10 to 30% by mass of total binder. They used combinations of sodium hydroxide (with molarity of 4, 6, and 8M) and sodium silicate to produce sodium silicate-to-sodium hydroxide ratios of 0.5, 1, and 1.5. The studied pastes set quickly. For instance, the initial setting time of alkali-activated paste having 20% slag, NaOH molarity of 4M and sodium silicate-to-sodium hydroxide ratio of 0.5 was only 20 min at 28°C and 60 to 80 min at 17°C. The setting time was reduced with increases of NaOH molarity, sodium silicate-to-sodium hydroxide ratio, and slag content. The 28-day strengths of concretes were in the range of 15 to 30 MPa. The appropriate slag content was found to be 15 to 20% considering setting time, workability and compressive strength. Use of high dosage of phosphoric acid (more than 2.25%) was found effective in retarding the setting time. However, it resulted in an average strength reduction of about 30%.

Kar et al. (2013) made different alkali-activated fly ash/slag concrete mixtures in order to assess the feasibility of use of nondestructive testing techniques for prediction of mechanical properties. They concluded that “effective relationship can be established to predict compressive strength and modulus of elasticity from the ultrasonic pulse velocity with reasonable accuracy” (Kar et al. 2013).

Chi and Huang (2013) compared properties of alkali-activated fly ash/slag and Portland cement mortars having similar solution (or water)-to-binder ratio. They used sodium silicate as the main activator which was combined with enough NaOH to maintain Na_2O level at 4 and 6%. The selected fly ash/slag combinations were 100/0, 70/30, 50/50, 30/70, 0/100. Results of their studies revealed higher strength and lower absorption of alkali-activated mortars in comparison with Portland cement mortars. Fly ash/slag combination of 50/50 showed the best performance in strength and absorption tests. On the other hand, drying shrinkage of all alkali-activated mortars was higher than that of Portland cement mortar. The higher slag content resulted in higher drying shrinkage.

Ismail et al. (2013b) assessed microstructural changes of alkali-activated fly ash/slag pastes exposed to sulfate solutions. They used fly ash-to-slag ratio of 1, and water-to-binder ratios of 0.4, 0.5 and 0.6. They immersed the produced pastes in sodium and magnesium sulfates for 3 months. The magnesium sulfate was found more aggressive to alkali-activated pastes than sodium sulfate. While gypsum was formed in pastes immersed in magnesium sulfate, it didn't form in sodium sulfate-exposed pastes. Use of lower water-to-binder ratio led to higher resistance to sulfate attack. Ismail et al. (2013a) also compared permeability of alkali-activated fly ash/slag mortars and concretes with that of Portland cement mixtures. They selected slag/fly ash proportion of 75/25, 50/50, 25/75 and 0/100 for the studied mortars, and 100/0, 75/25 and 50/50 for the studied concretes. They used sodium meta-silicate granules dissolved in tap water as activators. Except for the mixture having purely fly ash, the strength of alkali-activated fly ash/slag mixtures was close to that of Portland cement mixture. Similar trend was observed for absorption and capillary absorption. Chloride migration and diffusion of alkali-activated concretes were significantly lower than those of Portland cement concrete. Increases in slag content led to improved chloride permeability.

Rashad (2013) produced alkali-activated fly ash concrete using sodium silicate and sodium hydroxide as activators. He replaced up to 15% of fly ash with slag (5, 10 and 15%) and cured the produced samples for 2 days at 80°C. Partial replacement of fly ash with slag significantly improved the strength properties. This replacement, however, increased the drying shrinkage.

Jang et al. (2014) assessed effects of Polycarboxylate-based and naphthalene-based superplasticizers on fresh properties and strength of alkali-activated fly ash/slag pastes which activated with combinations of sodium silicate and sodium hydroxide. They found both superplasticizers effective in improving the flow. The effect of Polycarboxylate-based superplasticizer, however, was more significant than that of naphthalene-based superplasticizer. The used Polycarboxylate-based admixture also provided a retarding effect resulting in reduced slump loss, whereas the naphthalene-based admixture didn’t cause any retarding effect. Use of Polycarboxylate-based superplasticizer, however, resulted in reduction of ultimate strength.

Ghafoori and Najimi (2014) evaluated fresh, strength and transport properties of alkali-activated fly ash/slag mortars, and compared their performances with those of Portland cement mortar. They made three mixtures including two alkali-activated and a Portland cement mortars. Alkali-activated mortars contained 50% fly ash and 50% slag as binders, and two different combinations of sodium hydroxide and sodium silicate solutions as alkaline activators (sodium hydroxide-sodium silicate combinations of 50/50 and 70/30). The authors assessed flow, setting times, compressive strength, elastic modulus, absorption, void content, and chloride migration and penetration of the above-mentioned mortars. The results of study revealed higher strength of alkali-activated mortars than those of Portland cement mortar (See Figure 2.31). Their 3-days strengths were 34 and 41 MPa, being in a suitable range for repair applications. The alkali-activated mortars showed superior performance in RCPT, RMT, water absorption, and void content results compared to those of Portland cement mortar. Their setting times, however, were considerably shorter than those of the Portland cement mortar.

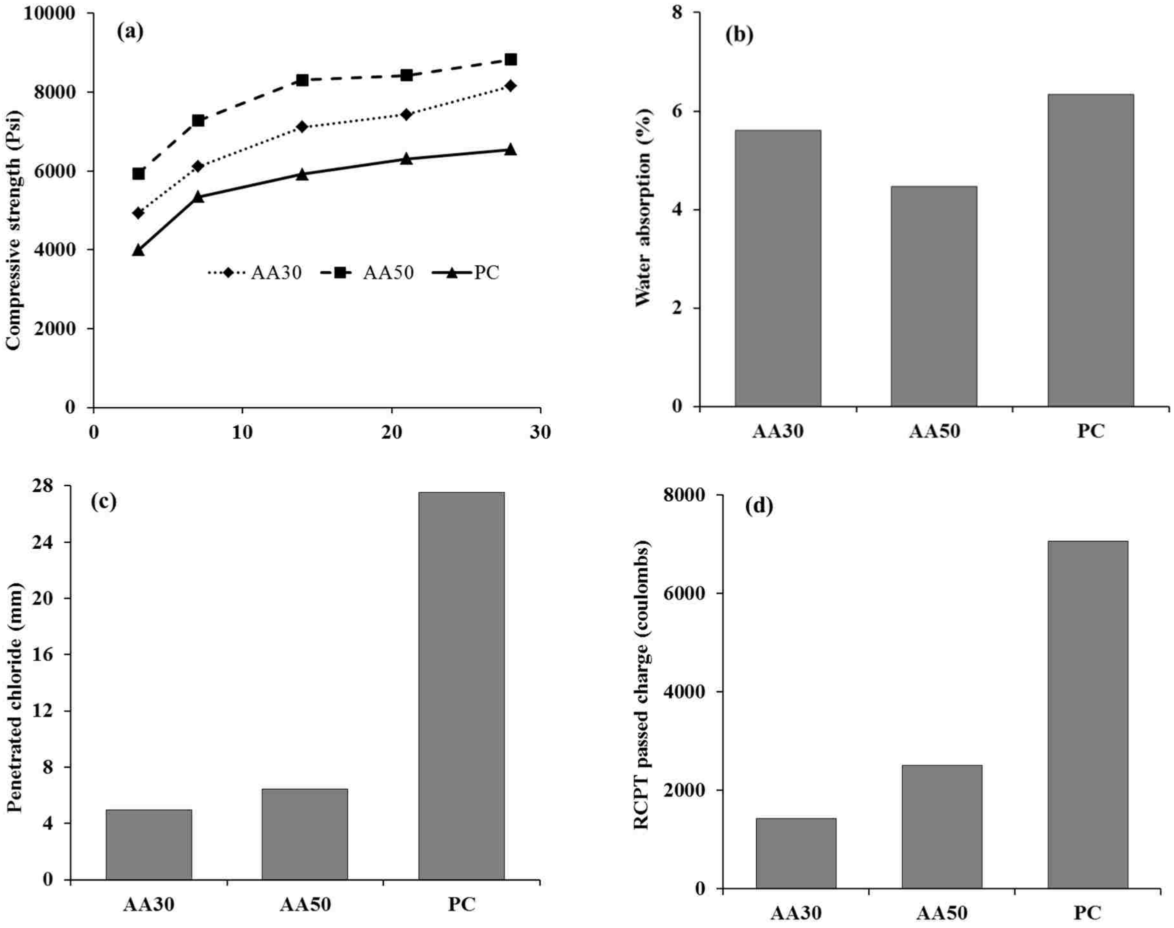


Figure 2.31 Results of alkali-activated fly ash/slag mortars in comparison with that of a standard PC mortar, (a) compressive strength, (b) water absorption, (c) depth of migrated chloride, (d) rapid chloride penetration test results (AA30 is the mixture having 30% silicate and 70% sodium hydroxide solution. AA50 contains 50% silicate and 50% sodium hydroxide solution) (Ghafoori and Najimi 2014).

Lee et al. (2014) measured shrinkage of alkali-activated fly ash/slag pastes and mortars having slag contents of up to 30%. They compared the results with those of Portland cement mixtures. The chemical shrinkage of alkali-activated mixtures was lower than that of Portland cement mixtures, whereas the opposite trend was observed in case of autogenous and drying shrinkages. They also noticed increases in chemical, autogenous and drying shrinkages by increases in slag content. Use of higher slag, however, led to improved strength.

Gao et al. (2015c) replaced up to 50% of slag with fly ash and evaluated the gel character and strength of developed alkali-activated slag-based pastes. They used sodium hydroxide and sodium silicate as alkaline activators. Similar to the previous results, use of fly ash reduced the early- and late-age strengths. The cumulative heat of hydration was reduced by increases in fly ash content. All the studied pastes experienced the same typical reaction stages including initial dissolution, induction, acceleration, deceleration, and stable periods. The authors noticed C-A-S-H type gels as the major reaction product. N-A-S-H gel was not detected in reaction products.

Chi et al. (2015) designed an alkali-activated fly ash/slag mortar with a fly ash-to-slag ratio of 1 (50/50) using sodium hydroxide and sodium silicate as alkaline activators. They assessed compressive strength and drying shrinkage of the produced mortar, and compared the results with those of Portland cement, alkali-activated fly ash, and alkali-activated slag mortars. They stated that the alkali-activated fly ash/slag mortars achieved the highest strengths. Its drying shrinkage, however, was only lower than that of alkali-activated slag mortar.

In another study, Marjanovic et al. (2015) measured compressive strength of alkali-activated fly ash/slag mortars. They used curing temperature of 95°C and fly ash-to-total binder ratios of 1, 0.75, 0.5, 0.25 and 0. The strength of studied mortars increased with higher replacement of fly ash with slag. There was, however, an optimum for such replacement as mortar with fly ash-to-total binder ratio of 0.25 had higher strength than mortar with no fly ash (purely slag).

Deb et al. (2015) measured drying shrinkage and compressive strength of alkali-activated fly ash/slag concretes having only two fly ash/slag combinations of 90/10 and 80/20. They observed that concrete containing 20% slag performed superior (higher compressive strength and lower drying shrinkage) to the concrete having 10% slag. Their best-performed concrete (with proportion of 80/20) shrank almost 11% more than Portland cement concrete.

Wang et al. (2015) assessed fresh and hardened properties of alkali-activated fly ash/slag pastes having fly ash contents of up to 60% of total binder (0, 20, 40 and 60%). They used sodium silicate and sodium hydroxide as activators. They observed higher flow and setting time by replacing a portion of slag with fly ash. On the other hand, this replacement resulted in lower strengths.

Wardhono et al. (2015) produced alkali-activated fly ash/slag mortars containing fly ash up to 50% of the total binder. A combination of sodium silicate and sodium hydroxide was used as alkaline activators. They noticed reduction in the early age-strength through inclusion of fly ash (3 and 7 days), whereas contrary was seen for the 28-day strength.

Abdalqader et al. (2016) used sodium carbonate for activation of alkali-activated fly ash/slag pastes. They used slag/fly ash combinations of 100/0, 75/25, and 50/50, and applied 5 and 10% sodium carbonate for activation. They also used two methods of curing; i.e. at temperature of 20±2°C in water tank or sealed. They observed that higher strengths can be achieved by use of higher dosage of sodium carbonate and sealed curing. While replacing up to 25% of slag with fly ash resulted in slight reduction of compressive strength, use of higher fly ash caused significant strength reduction. The authors detected C-(N)-A-S-H as the main binding phase.

2.3.5. Natural Pozzolan/ slag combination

Combination of natural Pozzolan and slag has been rarely investigated to date. In fact, there are only 3 studies in this field which are limited to the pastes. From these studies, one is conducted by Allahverdi et al. (2011), which used up to 25% slag as natural Pozzolan replacement. This study could also be considered as a research of alkali-activated natural pozzolans instead of natural pozzolan/slag combinations. The other two studies have been published in 2016 by Robayo et al. (2016) and Jafari Nadoushan and Ramezanianpour (2016). A brief review of these three studies is presented below:

Allahverdi et al. (2011) replaced 5, 15 and 25% of natural pozzolan with blast-furnace slag. In addition to SEM and XRD test, they assessed effects of these replacements on compressive strength and setting time of the produced pastes. They reported that the setting times of mixtures were long and use of slag didn’t considerably affect the setting times. If checking the individual value in their paper, setting times even slightly increased by replacing a portion of natural Pozzolan with slag. They also observed that the strength of pastes having natural Pozzolan and slag was similar to or slightly lower than that of pastes containing only natural Pozzolan. The observation of this study was in contrast with all the speculation driven from the literature on use of blast-furnace slag. The authors related this observation to the increases in Si/Al of binder by use of slag stating that the increase was against strength development. The observed behavior, however, could be inferred to unsuitability of the used slag for the purpose of alkaline activation. Robayo et al. (2016) did almost similar study by replacing 10, 20, 30% of natural Pozzolan with slag. They measured setting time, heat of hydration and compressive strength of the produced pastes. In contrast to the result of Allahverdi et al. (2011), they noticed significant increase in compressive strength and considerable reduction in setting times through partial replacement of natural Pozzolan with slag. These replacements also led to considerable increase in heat of hydration.

In the most recent study, Jafari Nadoushan and Ramezanianpour (2016) replaced 5, 10, 15, 20, 50, 75 and 100% of slag with natural pozzolans (pumice) and assessed flow and strength of the produced pastes. For the purpose of activation, they used sodium or potassium hydroxide (6 and 8M) combined with sodium silicate and provided a constant sodium silicate-to-hydroxide ratio of 0.4. In general, flow of alkali-activated pastes reduced by inclusion of natural Pozzolans. This observation was related to the higher specific surface area of pumice in comparison with that of slag. They also noticed improvement in 91-day strength of studied pastes by replacing 5 to 25% of slag with natural pozzolan. The higher replacement level resulted in considerable strength reduction. The optimum replacement level was found to be 5 to 10%.

2.4. Chemistry of alkali activated binders

During the last few decades of research on alkali-activated binders, a wide variety of materials have been activated and different alkali-activated binders have been produced. These binders can generally be categorized into two main groups on the basis of the primary reaction products which is strongly dependent on the calcium content of the starting material.

(1) High-calcium binders ($(Na,k)_2O$-Cao-Al_2O_3-SiO_2-H_2O)

When the starting material is rich in calcium and silicon (such as blast furnace slag) and it’s activated under relatively moderate alkaline condition, the main reaction product is a calcium silicate hydrate gel (C-A-S-H). This gel is almost similar to the C-S-H gel, the main product of

Portland cement hydration, which takes up *Al* in the gel structure. “The C-A-S-H type gels almost always coexist with secondary products of the layered double-hydroxide group” (Provis and Van Deventer 2014).

(2) Low-calcium binders ((Na,k)$_2$*O- Al*$_2$*O*$_3$*- SiO*$_2$*- H*$_2$*O)*

When the starting material is rich in silicon and aluminum and low in calcium such as class F fly ash, more aggressive conditions are necessary to start the reactions (i.e. highly alkaline activators and elevated temperatures). Under these conditions, the main product is alkaline aluminosilicate hydrate gel (N-A-S-H or K-A-S-H) that can be regarded as a zeolite precursor. It should be noted that unlike C-A-S-H, H (water) is not a major structural component of N-A-S-H or K-A-S-H (Provis and Van Deventer 2014).

Figure 2.32 and Table 2.18 present the general process and reaction products of high-calcium and low-calcium alkali-activated binders. It can be seen that the general process of alkali-activation include dissolution of aluminosilicate sources, rearrangement of the dissolved species, gel nucleation, and formation of reaction products. The reaction produces include C-A-S-H and hydrotalcite-like (Mg, Al)-layered double hydroxides for high-calcium binders, and N-A-S-H and zeolites for low-calcium binders. It has been proven recently that the two primary gels (C-A-S-H and N-A-S-H) can coexist in blended systems. If a combination of low-calcium and high-calcium binders is used, the reaction products can be close to products of either one of these binders or combination of these products which vary depending on the type of activators, proportions of the binders, activator dosage, curing conditions, and etc. The activation patterns, general mechanisms, proposed models, and final products of each group of alkali-activated binders are briefly described in the following sections:

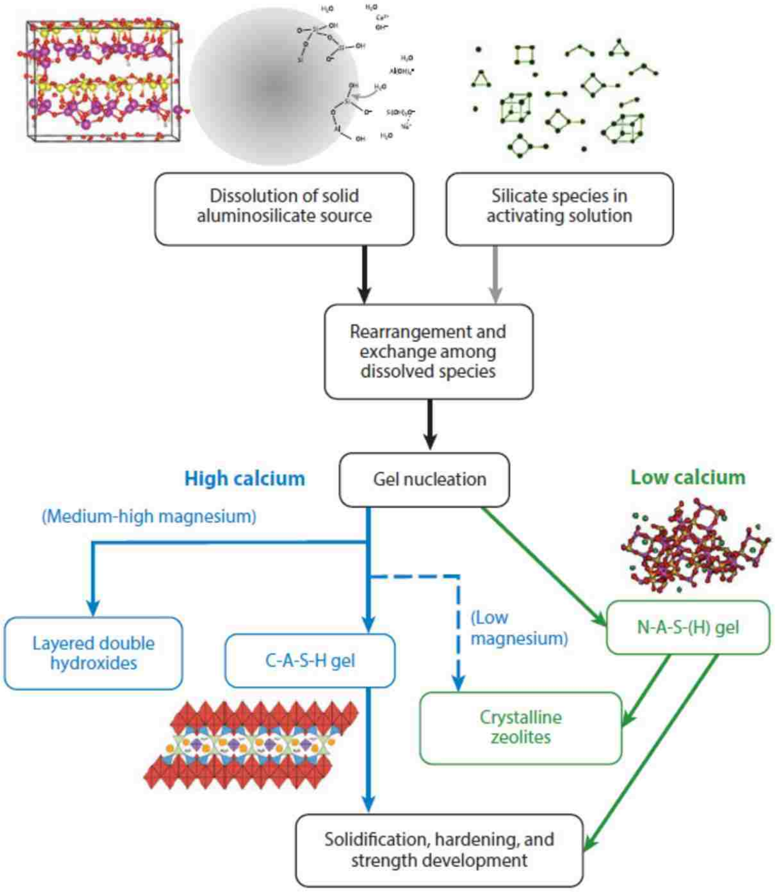


Figure 2.32 Process and reaction products of alkali-activation (Provis and Van Deventer 2014)

Table 2.18 Reaction products of Portland cement and alkali-activated binders (Pacheco-Torgal et al. 2015)

Reaction product	Binder type		
	Portland cement	Alkali-activated binders	
		High-calcium binders	Low-calcium binders
Primary	C-S-H	C-A-S-H	N-A-S-H
Secondary	$Ca(OH)_2$ AFm AFt	Hydrotalcite $[Mg_6Al_2CO_3(OH)_{16}H_2O]$ C_4AH_{13} $CASH_8$ C_4AcH_{11} $C_8Ac_2H_{24}$	Zeolites: hydroxysodalite, zeolite P, Na-chabazite, zeolite Y, faujasite
C= CaO, S=SiO_2, A=Al_2O_3, N=Na_2O, H=H_2O, c=CO_2			

2.4.1. High-calcium binders

Blast furnace slag is the most commonly used material for production of calcium-rich (high-calcium) alkali-activated binders. As presented in Table 2.2, slag is rich in calcium oxide (30-50%) and silica (27-40%). The other major components are alumina, and magnesium oxide. “Slag contains both network-forming anions $(SiO_4)^{4-}$, $(AlO_4)^{5-}$, and $(MgO_4)^{6-}$, and network-modifying cations Ca^{2+}, Al^{3+} and Mg^{2+}” (Pacheco-Torgal et al. 2015).

Slag reactivity in alkaline activation process depends mainly on the vitreous phase content (a depolymerized calcium silicate); which has been recommended to be over 90%. Degree of depolymerization $(DP=[n(CaO)-2n(MgO)-n(SO_3)]/[(SiO_2)-2n(MgO)-0.5n(Al_2O_3)])$ was found as a key parameter that has a direct relationship with slag reactivity. The higher the degree of depolymerization (or the lower the degree of polymerization in the glass), the higher is the silicate network which means higher reactivity.

When a slag activates with alkaline activators, a series of reactions happens which can be simply summarized with following equations (Glukhovsky 1967, 1994, Krivenko 1994b). The alkali-activation of slag, however, is a more complex process having different stages including destruction of slag (dissolution), followed by polycondensation and formation of reaction products.

$$=Si–O^- + R^+ \rightarrow =Si–O–R \qquad \text{Eq. (2)}$$

$$=Si–O–R + OH^- \rightarrow =Si–O–R–OH^- \qquad \text{Eq. (3)}$$

$$=Si–O–R–OH^- + Ca^{2+} \rightarrow =Si–O–Ca–OH + R^+ \qquad \text{Eq. (4)}$$

During the reactions, the produced gel takes up Al in the gel structure. The alkaline cation (R^+) acts as a mere catalyzer in the initial phases of hydration. Glukhovsky and Krivenko (Glukhovsky 1967, 1994, Krivenko 1994b) also believed that the alkaline cations are taken up into the structure, as reaction advances.

Figure 2.33 also presents a theoretical model showing the reaction mechanisms (Pacheco-Torgal et al. 2015). This model shows C-S-H formation which takes up Al into the structure. Accordingly, the primary reaction product in this process (also shown in Table 2.18) is C-A-S-H gel which is a calcium silicate hydrate (C-S-H) similar to the Portland cement hydration with aluminum in its composition. This gel, however, is slightly different from Portland cement C-S-H, as it has lower CaO-to-SiO_2 ratio (C/S). Several authors also observed small amounts of alkalis in this gel, which neutralize the charge imbalance created when a *Si* is replaced by an *Al* tetrahedron. Therefore, it was proposed that this gel is actually C-(N)-A-S-H gel. The secondary reaction products include hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}.4H_2O$), C_4AH_{13}-type phases, C_4AcH_{11}, and $C_8Ac_2H_{24}$ (Pacheco-Torgal et al. 2015). The structure of C-A-S-H gel and presence of secondary phases depend on the properties of used slag, type and dosage of alkaline activator, and curing conditions. It should be also noted that some researchers noticed formation of zeolites such as Gismondine and Garronite when MgO is low, as well as AFm-like layers in C-S-H structure (Bernal et al. 2011, Provis and Van Deventer 2014).

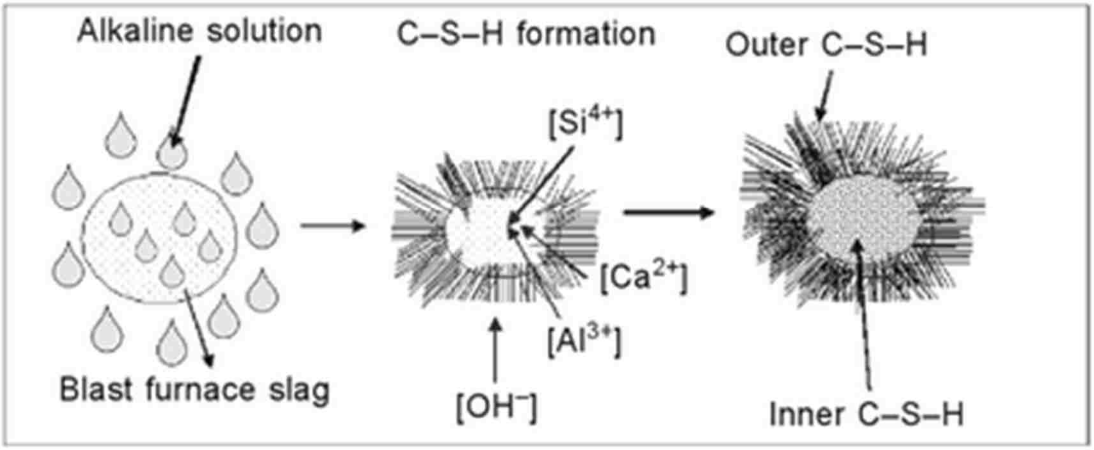


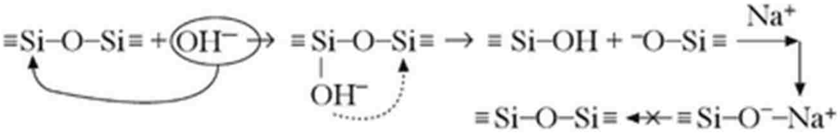
Figure 2.33 Theoretical model of alkali-activation of slag (Pacheco-Torgal 2015)

2.4.2. Low-calcium binders

Fly ash, to a larger extent, and metakaolin, to a lesser extent are the most commonly used materials in production of low-calcium alkali-activated binders (geopolymers). Natural Pozzolan is the other low-calcium material (aluminosilicate) that has been rarely used and investigated.

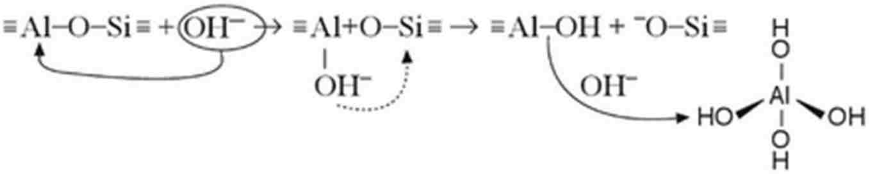
In general, the alkali-activation of low-calcium binders is less thoroughly understood when compared with high-calcium binders. It’s suggested by Glukhovsky (1994) that the general mechanism includes three main stages; destruction-coagulation or dissolution, coagulation-condensation or hydrolysis, and condensation-crystallization or condensation (Glukhovsky 1994). In this model, the reactions start with breaking Si-O-Si bonds by OH^- ions (destruction or dissolution stage). The negative ions (OH^-) “redistribute their electronic density around the silicon atoms, weakening the Si-O-Si bonds.” As a result, Si-O-Si bonds breaks, and -Si-OH (silanol) and $-Si-O^-$ (sialate) form. The positive cation (Na^+) neutralizes sialate and form Si-O-

Na$^+$. The last reaction (between sialate and positive cation) hinders the reverse reaction which could result in formation of Si-O-Si bonds. Eq. (5) shows this process (Pacheco-Torgal 2015):



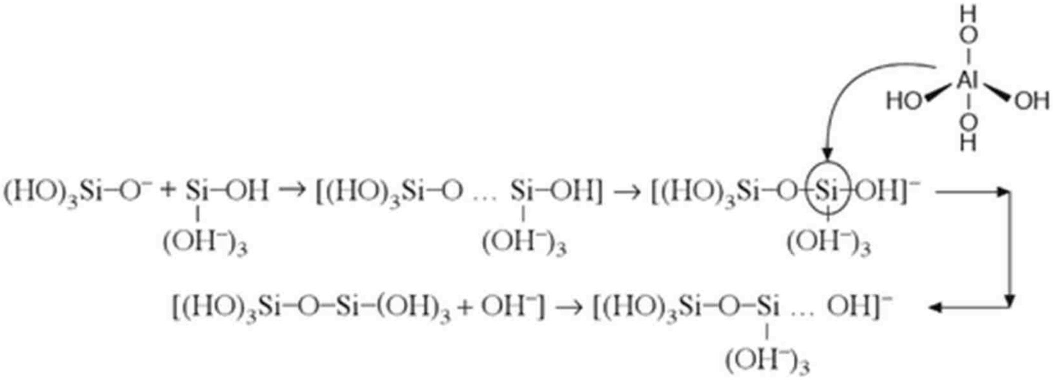
Eq. (5)

Similarly Si-O-Al bonds dissolves and forms complex species; mainly Al(OH)$^{4-}$ anions, as show in Eq. (6) (Pacheco-Torgal 2015).



Eq. (6)

In coagulation-condensation stage, “the accumulation of ionic species favors the contact between the disaggregated products and polycondensation begins, giving rise to coagulated structures” (Pacheco-Torgal 2015). Eq. (7) shows how silica monomers forms Si-O-Si bonds (dimers), which builds polymer as a result of interaction with the other monomers. Hydroxides (OH$^-$ ions) catalyze this stage. The formed clusters grow in all direction, forming colloids. It can be seen in Eq. (7) that Al(OH)$_4$ may participate in the process and replace silicon tetrahedra.



Eq. (7)

In the condensation-crystallization stage, the reaction products precipitate. In this stage, “the presence of solid particles in initial solid phase furthers the reaction product precipitation.”

Other models also proposed which are generally in agreement with the above-mentioned model. A zeolite synthesis model was proposed by Palomo et al. (2005) which consist of two main stages; nucleation and growth. Nucleation stage includes dissolution of the aluminates and the formation (polymerization) of complex ionic species. This stage covers the first two stages of Glukhovsky’ model. The growth stage is when the nuclei reach a critical size and crystals grow. This stage results in production of N-A-S-H gel (zeolite precursor) that would eventually evolve into a zeolite.

Figure 2.34 presents another model which is the result of several revisions on the former model. In this model, the aluminosilicate dissolves into several species; particularly silica and alumina monomers. The monomers interact and form dimers. The dimers react with monomers and form trimers, tetramers and so on. As the process continues, solution saturates and N-A-S-H gel precipitates. It should be noted that as bonds of Al-O are weaker than Si-O bonds, the produced gel is initially Al-rich (gel 1). As the reaction continuous, more Si-O bonds dissolve. Thus silicon concentrations of N-A-S-H gel increase and Si-rich gels form (gel 2). This model can also be seen in Figure 2.35, showing dissolution, silicate and aluminate formation, solution saturation (equilibrium), gelation (formation of gel 1), reorganization and formation of gel 2, and polymerization (Duxson et al. 2007a).

Table 2.18 also presents the reaction products of activation of low-calcium binders. As discussed, the primary product is N-A-S-H gel. The other reaction products include different zeolites such as hydroxysodalite, zeolite P, Na-chabazite, zeolite Y and faujasite, which vary depending on the nature of starting binder, activator type and dosage, and curing conditions.

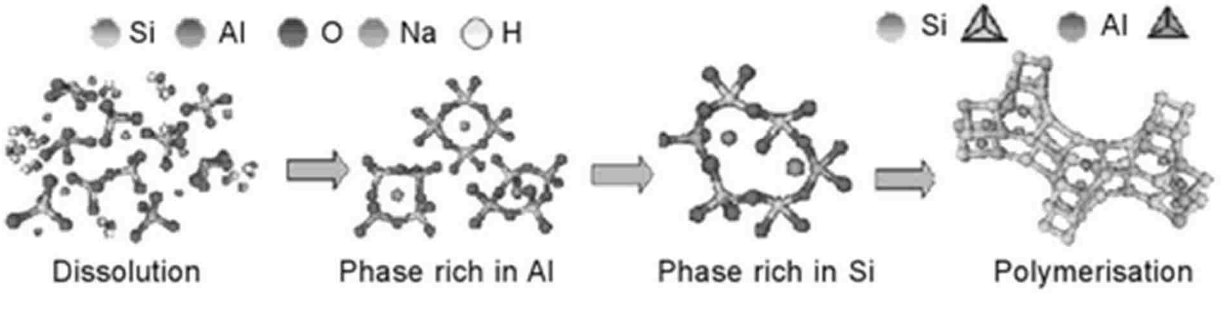


Figure 2.34 Model proposed for low-calcium binders (Fernandez-Jimenez et al. 2005b, Shi et al. 2011, Pacheco-Torgal 2015)

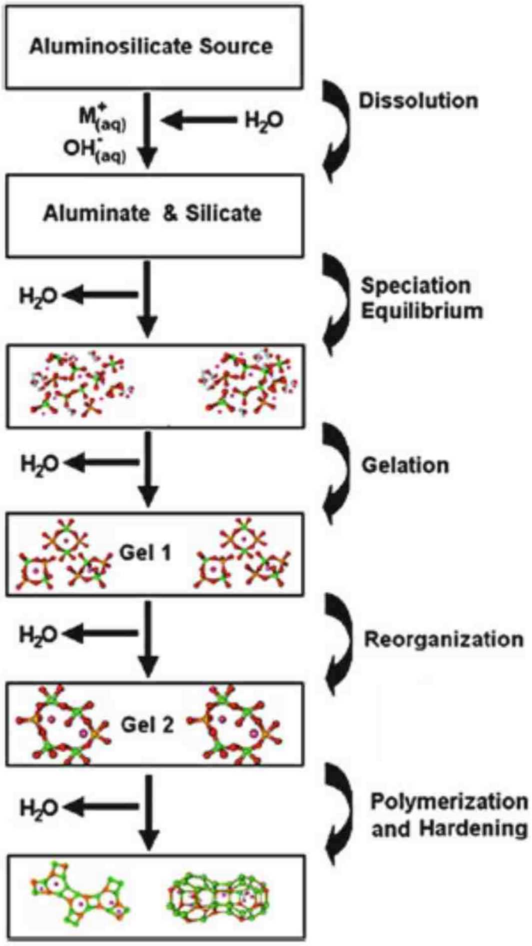


Figure 2.35 Geopolymerization model proposed by Duxson et al. (2007a)

2.4.3. Combined binders (blend of high-calcium and low-calcium binders)

Due to the limited research on combined binders (high-calcium and low-calcium binders), their reaction processes and final products are less understood. From the conducted research, it can generally conclude that:

- The reaction products of combined binders are intricate mixes of different gels, which depend mainly on the reaction conditions.

- Co-precipitation of C-A-S-H and N-A-S-H gels is possible, in particular at early ages. It has been proven that these two gels can coexist, although they don’t develop singly as two separate gels. They interact, which result in structural and compositional changes.
- It has been noticed that when enough calcium is in the system, the final products may evolve toward C-A-S-H gel which is more stable than N-A-S-H gel. This process takes a long time and requires special conditions. The reaction products are usually a combination of C-A-S-H and (N,C)-A-S-H gels.

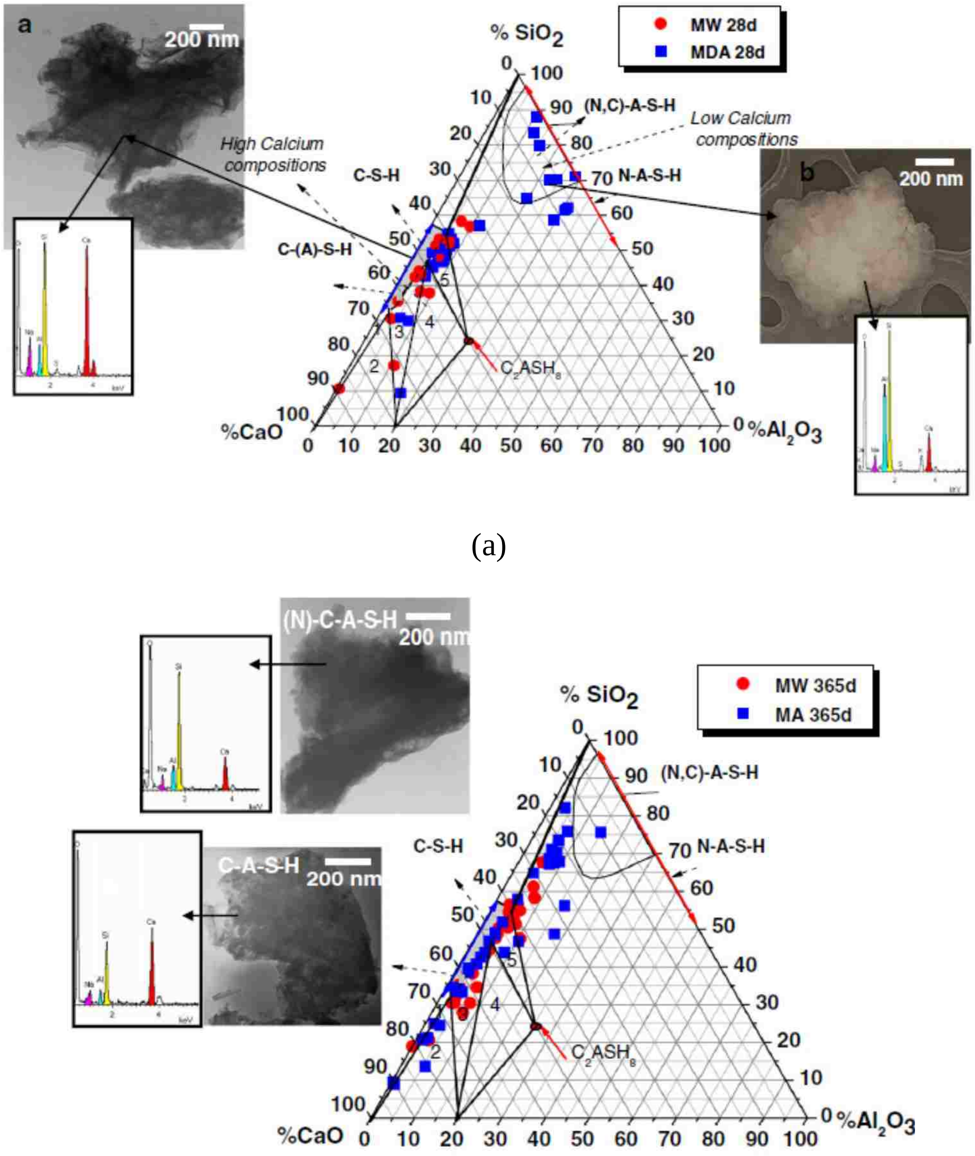
The following section presents a brief review of the major studies in this field. It provides the detected reaction products in these studies as well as a proposed model for the activation process. It should be noted that further research are required to verify and modify these findings.

Yip et al. (2005) assessed co-existence of C-A-S-H and N-A-S-H gels in alkali-activated slag/metakaolin blends. They showed that the two gels can coexist together, but it’s highly dependent on the alkalinity of the mixture. They concluded that (1) These two gels only coexist at low pH values, (2) When high sodium hydroxide concentration (7.5M) was used, N-A-S-H was predominant and took up small amounts of calcium, and (3) Only when adequate reactive calcium was present, these two gels co-existed.

Palomo et al. (2007) developed a blended binder containing 70% fly ash and 30% Portland cement clinker, which was activated with sodium hydroxide and sodium silicate. They noticed a complex mix of amorphous gels (C-A-S-H+(N,C)-A-S-H) as reaction products. The C-S-H and N-A-S-H co-existence was only detected at early ages (28 days at most).

Garcia-Lodeiro et al. (2013) activated the same system of 70% fly ash and 30% Portland cement with use of sodium hydroxide and sodium silicate. While they observed a combination of C-A-S-H and N-A-S-H gels at the age of 28 days, C-A-S-H gel was the dominant gel after a year of reaction (see Figure 2.36). Almost all of the EDX analysis results at 1 year were located inside the composition range of C-A-S-H type gel. They also observed that (N-C)-A-S-H gels evolved into compositions with higher calcium and lower aluminum contents. They concluded that "In the presence of aluminum C-S-H gel development was C-S-H→C–(A)–S–H→C-A-S-H, whilst in the presence of calcium, N-A-S-H gel evolved as N-A-S-H→(N,C)-A-S-H→C-A-S-H. This last conversion was not complete in these systems because the amount of calcium present was thought to be insufficient."

Similarly, Garcia Lodeiro et al. (2009, 2010, 2011) realized in their other investigations that formation of C-A-S-H gel is favored over time. These authors studied compatibility of synthetically produced N-A-S-H and C-A-S-H gels at different pH values (Garcia Lodeiro et al. 2011). They also evaluated effect of Na and Al addition to C-S-H gel and Ca addition to N-A-S-H gel. They concluded that (1) presence of dissolved calcium modified N-A-S-H gels into (N,C)-A-S-H gel by partial replacement of sodium with calcium, (2) presence of aluminum species and high pH had substantial effects on C-S-H gel, and aluminum was taken up to the structure, and (3) pH was a governing factor. When pH was high (over 12) and system contained sufficient calcium, C-A-S-H gel was favored over N-A-S-H gel (see Figure 2.37).



(a)

(b)

Figure 2.36 EDX analysis of water hydrated (MW) and alkali-activated (MA) fly ash/Portland cement blends projected onto the $CaO-Al_2O_3-SiO_2$ plane, (a) 28 days, (b) 1 year (Garcia-Lodeiro et al. 2013)

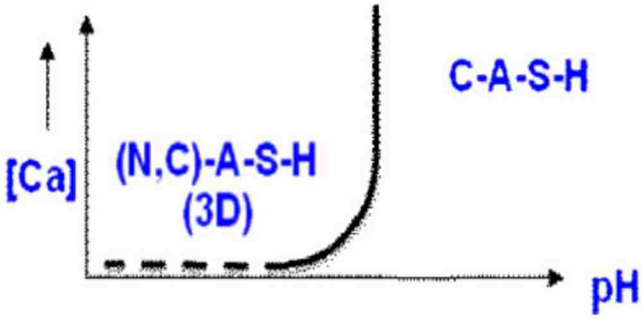


Figure 2.37 Model proposed for stability of N-A-S-H gel in terms of calcium content and pH (Garcia-Lodeiro et al. 2011)

Ismail et al. (2014) studied the reaction products of sodium silicate-activated fly ash/slag systems for up to 180 days. The fly ash-slag combinations were 100-0, 75-25, 50-50, 25-75 and 0-100. Results of their study are presented in Figure 2.38. It can be seen that while C-A-S-H was the reaction product of slag-based system (without fly ash, see Figure 2.38.A) and N-A-S-H was formed in fly ash-based system (without slag, see Figure 2.38.E), both of these gels were formed in combined systems. The hybrid gel (N,C)-A-S-H was also formed for fly ash/slag combinations of 50/50 and 75/25 (see Figures 2.38.C and 2.38.D). The formation of this gel was related to either calcium substitution into the N-A-S-H gel, or sodium sorption or substitution in the C-A-S-H gel.

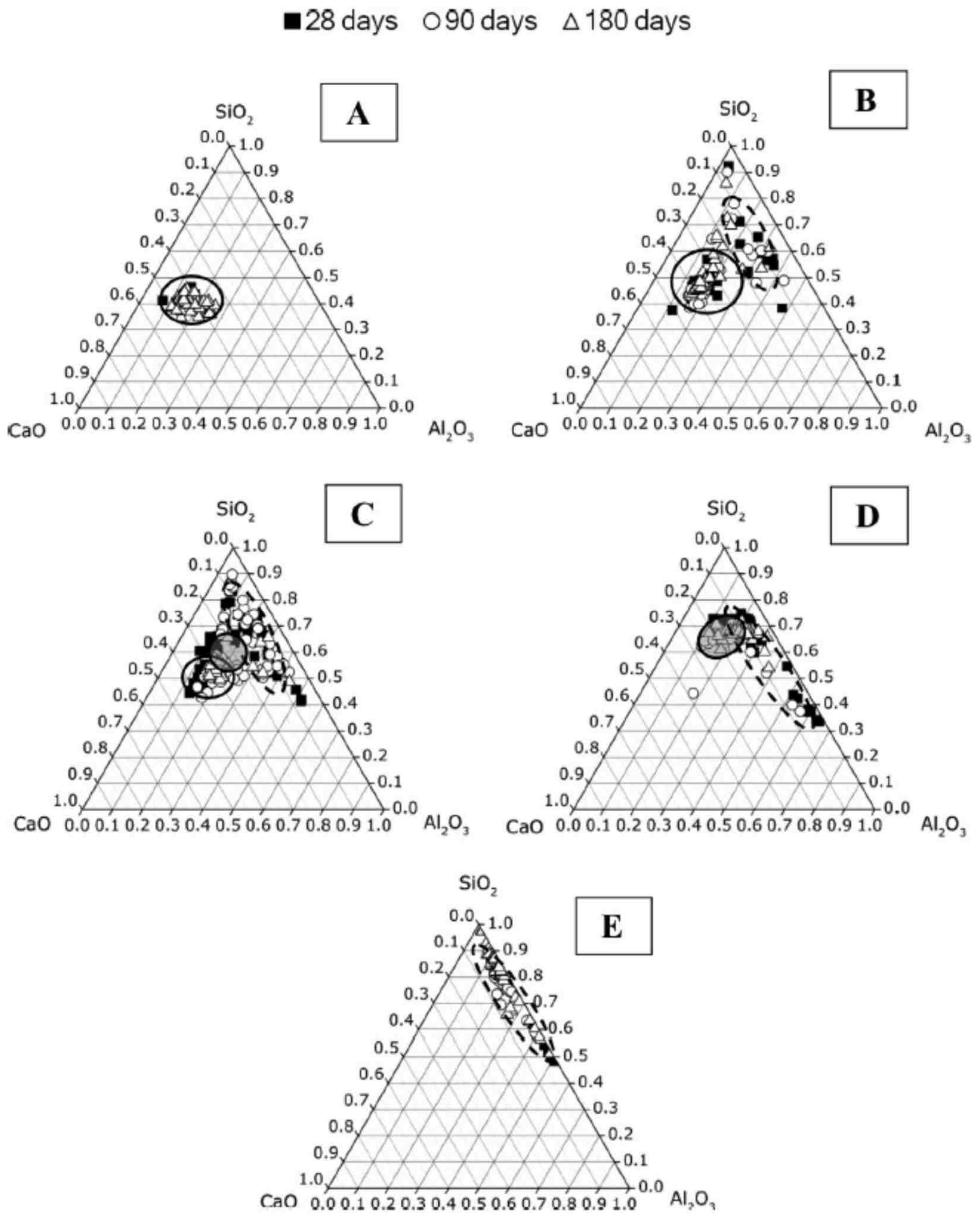


Figure 2.38 EDX analysis of alkali-activated fly ash/slag binders projected onto the CaO-Al_2O_3-SiO_2 plane, (A) 100% slag, (B) 75% slag-25% fly ash, (C) 50% slag-50% fly ash, (D) 25% slag-75% fly ash, (E) 100% fly ash (Ismail et al. 2014)

Abdalqader et al. (2016) also found (N,C)-A-S-H gel as the main binding phase of pastes containing 50% slag and 50% fly ash which was activated by use of sodium carbonate (See Figure 2.39). For lower percentages of fly ash in the paste (higher slag content), however, the reaction product shifted towards C-A-S-H gel. It should be noted that these observations was made at the age of 28 days.

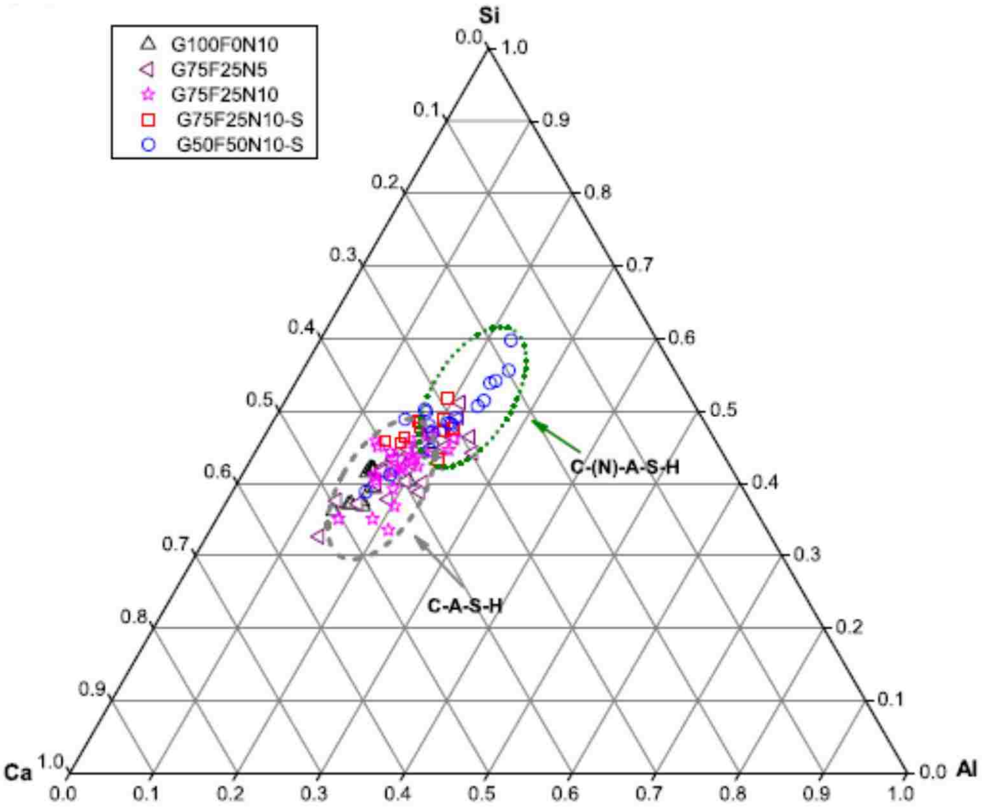


Figure 2.39 EDX analysis of sodium carbonate-activated fly ash/slag binders projected onto the Ca-Al-Si plane. GxFyNz means x% slag, y% fly ash, and z% sodium carbonate (Abdalqader et al. 2016)

Garcia-Lodeiro et al. (2013) also proposed a model for the reaction process of the combined binders which is shown in Figure 2.40. This model was mainly suggested based on their studied binder which was a system of high silica and alumina and fairly low calcium (70% fly ash plus 30% Portland cement activated with sodium hydroxide and sodium silicate). The proposed model includes 5 stages as follows:

(1) Stage A: This process starts with dissolution of aluminosilicates of low-calcium binder (fly ash in their studies) and calcium silicates of high-calcium binder (Portland cement in their studies) in alkaline solution.

(2) Stage B: When the solution saturates, C-S-H and N-A-S-H (gel 1 with Si/Al~1) gels precipitate.

(3) Stage C: As the reaction progresses, more Si-O groups dissolve increasing the silicon concentration. The dissolved silicon uptake in both gels. While it enhances the C-S-H gel polymerization, the N-A-S-H gel changes from type 1 gel to type 2 gel with Si/Al of approximately 2.

(4) Stage D: In this stage, the Calcium and Aluminum ions diffuse to the formed gels. A small amount of calcium ions, which have not participated in C-S-H gel, interact with N-A-S-H gel and form (N,C)-A-S-H gel. As sodium and calcium ions have similar ionic radius and electronegative potential, sodium ions are replaced by calcium via ion exchange reminiscent of the mechanism observed in clay and zeolites. Therefore, this replacement keeps the three-dimensional structure of the gel. Similarly, as the aluminum content rises, C-S-H converts to C-A-S-H gel. While C-S-H has a one-dimensional structure, the inclusion of tetrahedral aluminum may lead to generation of two-dimensional structure.

(5) Stage E: If there is enough calcium available, it diffuses into the pores and interact with (N,C)-A-S-H gel. When Ca^{2+} ions interact and form Si-O-Ca bonds, their polarizing effects distort Si-O-Al bonds, which ultimately break the bonds releasing Al to the system. As N-A-S-H gel ((N,C)-A-S-H) releases aluminum, less polymerized structure such as C-A-S-H gel form. Simultaneously, the C-A-S-H gel formed in prior stages take up more silicon and aluminum that was released. Given sufficient time and experimental conditions (enough calcium concentration and pH), the system would evolve in a hypothetical stage toward a single C-A-S-H gel which is a more thermodynamically stable gel. It should be mentioned that these compositional and structural changes in N-A-S-H gels apparently don’t impact materials strength.

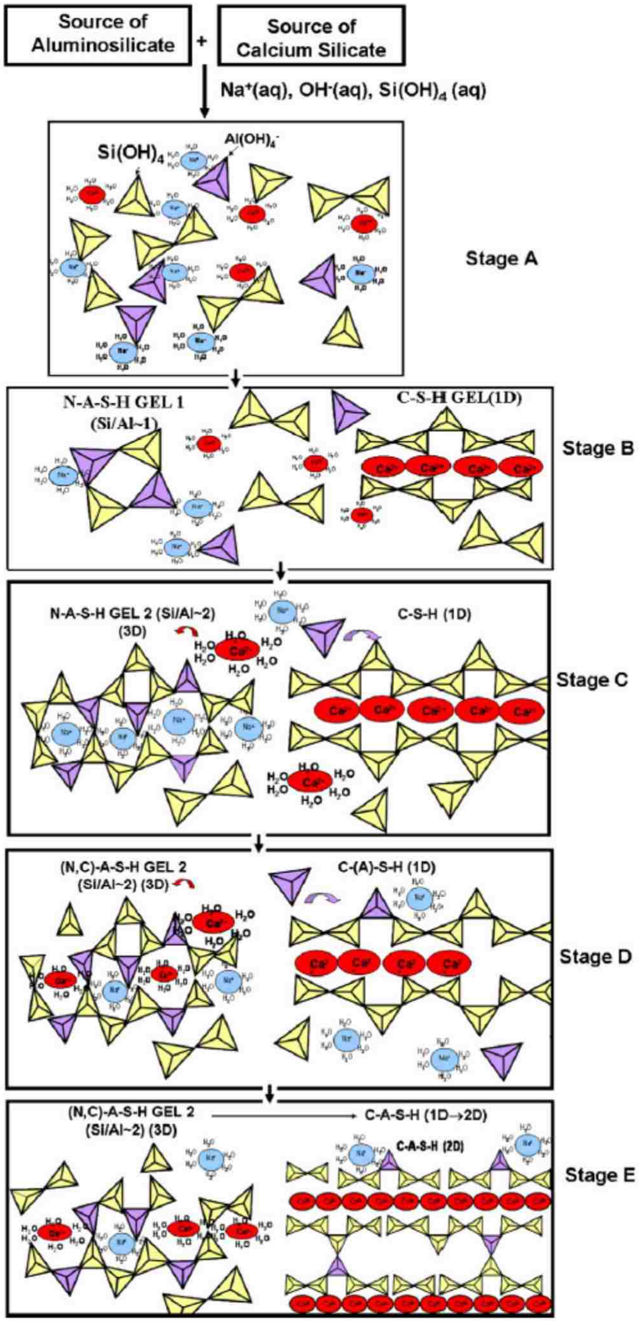


Figure 2.40 Reaction process model for combined binders (Garcia-Lodeiro et al. 2013)

CHAPTER 3- EXPERIMENTAL PROCEDURE

3.1. Materials

The materials used in this study included natural Pozzolan and slag as binders, sodium hydroxide and sodium silicate solutions as alkaline activators, fine and coarse aggregates, and distilled water. Type V Portland cement was also used to produce reference (control) Portland cement mixtures. The following sections present physical and chemical properties of the raw materials used in this investigation.

3.1.1. Natural Pozzolan

The natural Pozzolan, used in production of alkali-activated mixtures, was obtained from the Nevada Cement Company in Fernley. It was sourced from a vitrified rhyolite deposit near Dayton, Nevada. The used natural Pozzolan was naturally amorphous and as a felsic volcanic was high in silica and aluminum. During this project, natural Pozzolan was provided twice from this source, which was slightly different. The chemical properties of natural Pozzolan are documented in Table 3.1. Table 3.2 presents the chemico-physical requirements of natural Pozzolan based on ASTM C618.

The summation of silica, alumina and iron oxide was 78.4% for the used natural Pozzolan, exceeding the 70% minimum level for class N raw and calcined natural Pozzolans specified in ASTM C618. The calcium oxide content was low (3.2%), indicating that this material was not cementitious on its own. The 7-, and 28-day strengths of mortars having 20% natural Pozzolan were 85 and 92% of a prepared standard reference mortar, respectively; which were well above minimum requirement of 75% specified in ASTM C618. The used natural

Pozzolan had a considerably high specific surface (6088 cm^2/gr). Its fine particle size can be seen in Table 3.2, as only 13.5% was retained on sieve#325 (45 μm). The particle size distribution of natural Pozzolan is shown in Figure 3.1. The median particle size (50% passing size) of natural Pozzolan was almost 15.8 micron which was similar to that of Portland cement.

Table 3.1 Chemical composition of natural Pozzolan

Compound, %	Natural Pozzolan (Phase I)	Natural Pozzolan (Phases II and III)
Calcium oxide (CaO)	3.2	2.3
Silica (SiO_2)	68.8	71.0
Alumina (Al_2O_3)	8.5	7.9
Iron oxide (Fe_2O_3)	1.1	0.7
Sodium oxide (Na_2O)	2.6	3.2
Potassium oxide (K_2O)	3.9	4.3

Table 3.2 Chemical and physical properties of natural Pozzolan according to ASTM C618

Requirements			Natural Pozzolan results	
			Phase I	Phases II and III
Chemical requirements	$SiO_2+Al_2O_3+Fe_2O_3$, %	min, 70.0	78.4	79.6
	Sulfur trioxide (SO_3), %	max, 4.0	0.1	0.1
	Moisture content, %	max, 3.0	0.7	0.2
	Loss on ignition, %	max, 10.0	3.7	3.4
Physical requirements	Amount retained when wet-sieved on 45 μm sieve, %	max, 34	13.5	8.7
	[1]Strength activity index, at 7 days, percent of control	min, 75	85	84
	[1]Strength activity index, at 28 days, percent of control	min, 75	92	91
	Water requirement, percent of control	max, 115	103	98
	Autoclave expansion or contraction, %	max, 0.8	0	0
	Specific gravity	--	2.29	2.33
	Specific surface, cm^2/g	--	6088	4505

[1] The strength activity index is determined based on ASTM C311 by replacing 20% of cement with natural Pozzolan.

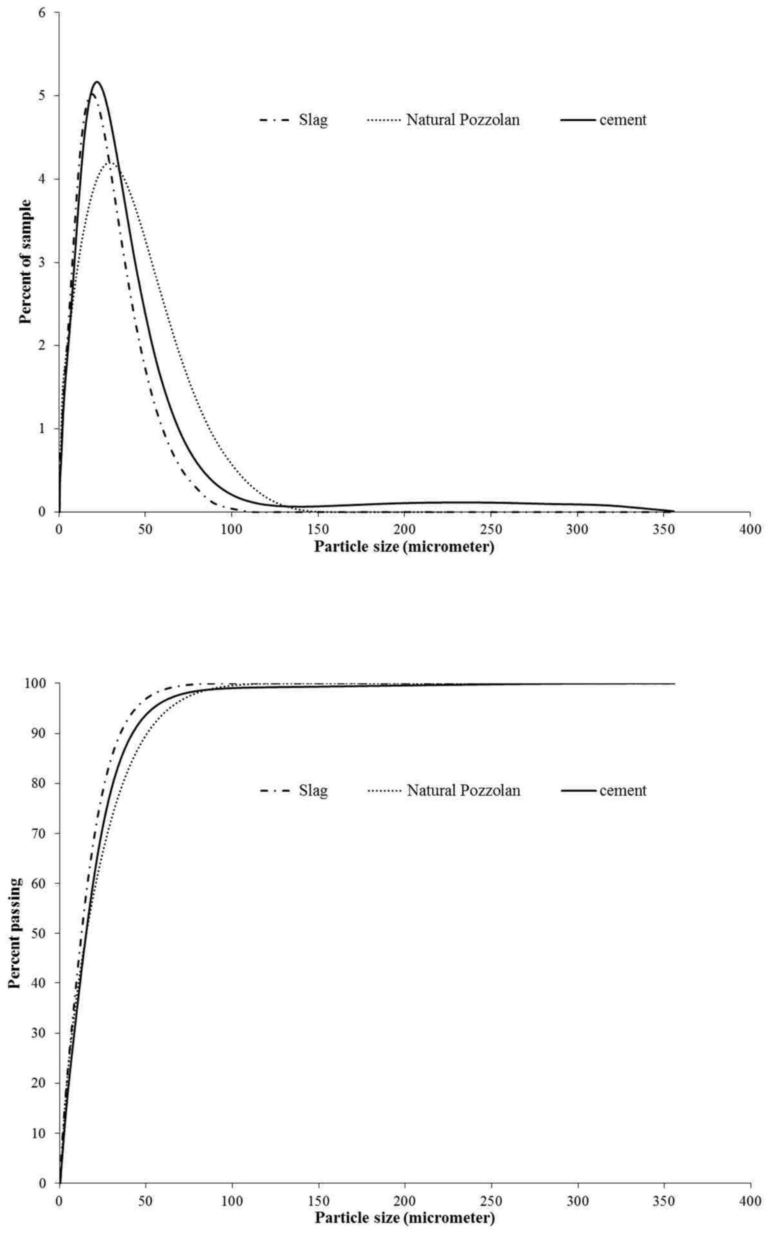


Figure 3.1 Particle size distribution of different binders

3.1.2. Slag

The used slag was donated by Lafarge-North America, which is located in Seattle. Its chemical and physical properties are reported in Tables 3.3 and 3.4, respectively. It can be seen that the used slag contained 43.6% calcium oxide, so it had cementitious properties. Its other major compounds were silica (31%) and alumina (11.5%). The particle size distribution of slag is shown in Figure 3.1. It can be seen that slag particles were finer than those of natural Pozzolan and Portland cement. The median particle size of slag was almost 12.6 micron, whereas median particle size of natural Pozzolan and Portland cement was almost 15.8 micron.

The used slag had a high specific gravity (2.87) as compared to natural Pozzolan (2.29 for the first phase and 2.33 for the second and third phases). The specific gravity of both slag and natural Pozzolan, however, was lower than that of Portland cement (3.15).

Table 3.3 Chemical composition of slag

Compound, %	Slag
Calcium oxide (CaO)	43.64
Silica (SiO_2)	31.0
Alumina (Al_2O_3)	11.5
Iron oxide (Fe_2O_3)	0.8
Magnesium oxide (Na_2O)	4.7
Potassium oxide (K_2O)	0.84
Sulfur trioxide (SO_3)	4.85
Titanium oxide	0.57

Table 3.4 Mechanical and physical properties of slag

Property	Allowable limit, ASTM C989	Slag results
7 day compressive strength, MPa	min, 75*	90
28 day compressive strength, MPa	min, 95*	107
Air content of mortar, %	max, 12	5.8
Specific gravity, g/cm^3	--	2.87
Loss on ignition, %	max, 10	0.3
Autoclave expansion, %	max, 0.5	0
specific surface, cm^2/g	--	5420
Remaining on sieve No. 325 (45 µm), %	max, 20	2.6
Sulfide sulfur, % as SO_3	max, 2.5	0.66
Sulfate Ion, % as SO_3	max, 4	3.2

* For Grade 100 slag based on ASTM C989

3.1.3. Portland cement

For preparation of reference mixtures, Type V Portland cement was used as it is a statewide cement in Nevada. This cement is generally used when there are special requirements in regards to sulfate resistance of concrete as it is in Nevada. The chemical and physical properties of the used cement are shown in Tables 3.5 and 3.6, respectively.

Table 3.5 Chemical requirements of Portland cement

Property	Specification limit	Test result
Chemical Composition (%)		
SiO_2	not applicable	20.42
Al_2O_3	max, 6.0	4.25
Fe_2O_3	max, 6.0	4.05
CaO	not applicable	63.31
MgO	max, 6.0	2
SO_3	expansion not exceed 0.02% at 14 days	2.98
Na_2O	not applicable	0.04
K_2O	not applicable	0.69
CO_2	not applicable	1.53
Loss on ignition	max, 3.0	2.5
Insoluble Residue	max, 0.75	0.44
Limestone	max, 5.0	3.7
Potential Compounds (%)		
C_3S	not applicable	53
C_2S	not applicable	18
C_3A	max, 5	4
C_4AF	not applicable	12
$C_4AF + 2(C_3A)$	max, 25.0	20
Optional Requirements		
$C_3S + C_3A$ (%)	limit not specified by purchaser	57
Equivalent alkalis (%)	0.6	0.49

Table 3.6 Physical properties of Portland cement

Property	Specification limit	Test result
Air content of mortar, %	max, 12	8
Fineness by air permeability, cm^2/g	min, 2600	4206
Autoclave expansion, %	max, 0.80	0.02
Specific gravity	--	3.15
Compressive Strength, psi		
1 Day	not applicable	2055
3 Days	min, 1160	3493
7 Days	min, 2180	4702
28 Days	min, 3050	not available
Time of setting (minutes)		
Initial: Not less than	45	99
Not more than	375	
Optional Requirements		
False set (%)	min, 50	82

3.1.4. Alkaline activator

As mentioned earlier, sodium hydroxide and sodium silicate solutions were selected as alkaline activators. Their properties are presented below:

3.1.4.1. Sodium hydroxide

Sodium hydroxide pellets, supplied by Duda Diesel LLC, were used to make sodium hydroxide solutions. The sodium hydroxide pellets were composed of 97.0 to 98.2% sodium hydroxide, up to 1.2% sodium chloride and 0.4 to 1.0% sodium carbonate.

In different stages of this dissertation, sodium hydroxide solutions were made with various concentrations including 0.5, 1, 1.5, 1.75, 2, 2.5, 3, 4, 5 and 7.5 mole (M). A liter of solution with these molarities were made by solving 20, 40, 60, 70, 80, 100, 120, 160, 200 and

300 g of sodium hydroxide powder in enough water to reach the volume of one liter, respectively.

3.1.4.2. Sodium silicate

Type D sodium silicate with modulus of 2 was selected for the purpose of this study. It was supplied by PQ Corporation. Type D sodium silicate was in liquid form composed of 55.97% water and 44.03% solid by weight. The solid part was a combination of sodium oxide and silicon dioxide with SiO_2-to-Na_2O ratio (modulus) of almost 2. Its properties are reported in Table 3.7.

This type of sodium silicate was selected after testing three different sodium silicates with modulus of 2, 2.58 and 3.22 (Type D, M and O, respectively). The performances of alkali-activated mortars made with these types of sodium silicates are documented in Table 3.8. Considering the compressive strength test results and observation of flow and setting time, type D was selected for this dissertation. Although Type O showed slightly higher compressive strength than Type D for ambient temperature-cured samples (comparison of mix D80 and O80), mortar mix O80 set fast in couple of minutes before allowing to cast all the samples.

Table 3.7 Properties of Type D sodium silicate

Characteristics	Lower limit	Upper limit	Test results
Alkali, %	14.55	14.85	14.8
SiO_2, %	27.93	30.87	29.23
Solids, %	42.48	45.72	44.03
Modulus	1.90	2.10	1.98
Specific gravity, g/cm^3	1.5268	1.5426	1.53
Viscosity SS	80.00	150.00	112
pH	--	--	12.9
Appearance	--	--	Thick liquid
Color	--	--	Clear to hazy white
Odor	--	--	Odorless
Solubility in water	--	--	Miscible

Table 3.8 Compressive strength of testing mortars prepared with use of different sodium silicates

Mix id	Type of sodium silicate	Binder		Activator		Compressive strength, psi			Observations
		Natural Pozzolan, %	Slag, %	Sodium hydroxide (7.5M), %	Sodium silicate, %	7 days, curing room	1 day, oven	7 days, oven	
D100	D	100	0	70	30	974	2125	2541	Long setting
M100	M	100	0			1031	2188	2475	Long setting
O100	O	100	0			1005	2217	2290	Long setting
D80	D	80	20			2704	4581	NM	Moderately fast set
M80	M	80	20			1774	4098	NM	Fast set
O80	O	80	20			2878	2108	NM	Very fast set (Flow was lost in couple minutes)

* fine aggregate-to-binder ratio was 2.
NM: Not measured

3.1.5. Aggregates

Aggregate selection is important in design of concrete as it occupies a large portion of concrete volume. For the purpose of this research, coarse and fine aggregates were obtained from a same quarry in Southern Nevada.

The gradation of fine aggregate is shown in Table 3.9. As can be seen, the used fine aggregate met the requirements set forth by ASTM C33. The fine aggregate's physical properties are reported in Table 3.10. The used fine aggregate had SSD specific gravity of 2.78 and absorption of 0.81%. It wasn't susceptible to ASR and didn't contain clay lumps and lightweight particles.

Tables 3.11 and 3.12 present the gradation and physical properties of coarse aggregates, respectively. The provided coarse aggregate was in the size range of #4 to 0.5 inch size (No.7 aggregates size based on ASTM C33). Its SSD specific gravity and absorption were 2.77 and 0.79%, respectively. These values were almost similar to those of fine aggregate. The coarse aggregate' impurities, clay lumps, lightweight particles, abrasion resistance and ASR potential were well below the standard maximum limits.

Samples were taken from different drums of provided aggregates to test their gradations. The gradation of the fine aggregate was found to be consistent for all samples. The gradation of the coarse aggregate varied for different tested samples, although they were still in acceptable range (between upper and lower limits of standard). To create consistent gradation of coarse aggregates, they were sieved out and stored into three size categories. The size designations were: 3/8 to ½ inch, No. 4 sieve (3/16 inch) to 3/8 inch, and smaller than No. 4 sieve. Both coarse and fine aggregates were dried to a uniform moisture content of less than 0.1%. This moisture content was also measured before each batching to ensure accurate proportioning.

Table 3.9 Gradation of fine aggregate

Sieve number	Percent passing	Allowable range
3/8 in	100	100
#4	100	95 to 100
#8	95	80 to 100
#16	65	50 to 85
#30	43	25 to 60
#50	24	5 to 30
#100	9	0 to 10
#200	2.7	0 to 3

Table 3.10 Physical properties of fine aggregate

Laboratory test	Results	Requirements
Relative density (specific gravity) oven-dry,	2.755	--
Relative density (specific gravity) saturated-surface dry	2.777	--
Apparent relative density (apparent specific gravity)	2.818	--
Absorption, %	0.81	--
Damp loose unit weight, pcf	85 pcf@1.5% moisture	--
Organic impurities	Less than Color Plate No.1	Not detrimental
Clay Lumps and Friable Particles, %	0	max, 3
Lightweight particles, %	0 Specific Gravity 2.0	max, 0.3
Soundness of Aggregates, %	Sodium Sulfate-1.7% Loss	max, 10
Sand equivalent value	93	NA
Potential Alkali-Reactivity of Aggregate (Mortar Bar Method), %	0.06	max, 0.1
Accelerated Detection of Potentially Deleterious Expansion of Mortar Bars Due to Alkali-Silica Reaction, %	0.03	max, 0.1

Table 3.11 Gradation of coarse aggregate

Sieve number	Percent passing	Allowable range
3/4 in	100	100
½ in	100	90 to 100
3/8 in	68	40 to 70
#4	4	0 to 15
#8	2	0 to 5
#50	1	-
#100	0.2	-
#200	0.2	0 to 1

Table 3.12 Physical properties of coarse aggregate

Laboratory Test	Results	Requirements
Relative Density (Specific Gravity) Oven-Dry	2.747	--
Relative Density (Specific Gravity) Saturated-Surface Dry	2.768	--
Apparent Relative Density (Apparent Specific Gravity)	2.801	--
Absorption, %	0.79	--
Dry-Rodded Unit Weight, pcf	98	--
Cleanness Value (C.V.) NDOT Test Method NEV. 228B	91	NA
Clay Lumps and Friable Particles, %	0	max, 3
Lightweight Particles, %	None Specific Gravity 2.0	max, 0.3
Soundness of Aggregates, %	Sodium Sulfate-1.4% Loss	max, 12
Resistance to Degradation Abrasion ASTM C 131, %	18% Loss	max, 50
Potential Alkali-Reactivity of Aggregate (Mortar Bar Method)	0.07	max, 0.1
Accelerated Detection of Potentially Deleterious Expansion of Mortar Bars Due to Alkali-Silica Reaction	0.03	max, 0.1

3.1.6. Water

Distilled water was used throughout this dissertation. It was used in different stages of this research for making sodium hydroxide and other solutions used for different experiments.

3.2. Mixing procedure and curing

Different mixing methods and mixing equipment were used for production of alkali-activated pastes, mortars, and concretes. Alkali-activated pastes were made in accordance with ASTM C305 and mixed in the mixer shown in Figure 3.2. Mortars and concretes were batched based on ASTM C305 and C192, respectively. The mortar and concrete mixers are shown in Figures 3.3 and 3.4, respectively. Figures 3.5 and 3.6 show the vibratory plate and curing room used in this research, respectively.

Figure 3.2 Paste mixer

Figure 3.3 Mortar mixer

Figure 3.4 Concrete mixer

Figure 3.5 Vibratory plate

Figure 3.6 Curing room

3.3. Testing methods

As specific standards have not been designed for alkali-activated binders, the developed ASTM standards for hydraulic cements were used. This section provides the testing methods utilized for each phase of this dissertation. Table 3.13 documents a summary of the evaluated properties of alkali-activated pastes. The designed experiments for alkali-activated mortars and concretes are reported in Tables 3.14 and 3.15, respectively.

Table 3.13 Test methods for fresh and hardened properties of alkali-activated pastes

Characteristics	Specification
Flow ability	ASTM C1437
Setting time	ASTM C191
Compressive strength	ASTM C109
Heat of hydration	Designed device
Drying shrinkage	ASTM C596
Absorption	ASTM C642 with modification
Density	ASTM C 642 with modification
Volume of permeable voids	ASTM C 642 with modification
Flexural strength	ASTM C78
XRD and SEM	No standard available

Table 3.14 Test methods for fresh and hardened properties of alkali-activated mortars

Characteristics	Specification
Flow ability	ASTM C1437
Setting time	ASTM C807
Compressive strength	ASTM C109
Tensile strength	ASTM C496
Absorption	ASTM C642 with modification
Density	ASTM C642 with modification
Volume of permeable voids	ASTM C642 with modification
Heat of hydration	Designed device
Rapid chloride penetration	ASTM C1202
Rapid chloride migration	NT BUILD 492/ AASHTO TP 64
Drying shrinkage	ASTM C157/C596
XRD	No standard available

Table 3.15 Test methods for fresh and hardened properties of alkali-activated concretes

Characteristics	Specification
Flow ability	ASTM C143
Setting time	ASTM C403
Compressive strength	ASTM C39
Modulus of elasticity	ASTM C469
Tensile strength	ASTM C496
Absorption	ASTM C642
Density	ASTM C642
Volume of permeable voids	ASTM C642
Rapid chloride penetration	ASTM C1202
Rapid chloride migration	NT BUILD 492/AASHTO TP 64
Drying shrinkage	ASTM C157
Freeze-thaw resistance	ASTM C672
Corrosion	FM 5-522
Acid resistance	No standard available
XRD	No standard available

3.3.1. Pastes

Flow of alkali-activated pastes was measured according to ASTM C807 upon batching. The flow table, used for this test, is show in Figure 3.7.

Figure 3.7 Flow Table

Setting times were also measured upon batching by use of Vicat needle. The device is shown in Figure 3.8. ASTM C191 was used for evaluation of initial and final setting times. The initial setting time was defined as the time that needle penetrated 25 mm (1 in) in the paste within 30 seconds. Final setting time was defined as the time that needle couldn’t penetrate visibly.

Upon batching, three samples were also cast in 50 by 100 mm disks (2 by 4 in) and were kept in isolated boxes for measurement of heat of hydration. The designed boxes are shown in Figure 3.9. The temperature of sample in isolated boxes was monitored till it reached the ambient temperatures (usually for 2 days).

Figure 3.8 Setting time test device

Figure 3.9 The designed boxes for measurement of heat of hydration

Compressive strength of alkali-activated pastes was measured according to ASTM C109 by breaking 50 by 100 mm (2 by 4 in) cylinders. This test was conducted on 3 samples for each mix and at different ages of 3, 7, 28 and 90 days. The compression hydraulic jack, used in different stages of this dissertation, is shown in Figure 3.10.

Figure 3.10 Compressive strength test setup

Drying shrinkage of alkali-activated pastes was measured according to ASTM C596 and by casting six 25×25×285 mm (1×1×11-1/4 in) prisms. For this test, samples were cured for 3 days before transferring to humidity chamber (50±5% relative humidity and ambient temperature). The humidity chamber (shrinkage room), drying shrinkage prismatic samples and dial gauge are presented in Figure 3.11.

Figure 3.11 Humidity chamber (shrinkage room), drying shrinkage samples and dial gauge

ASTM C642 was used as the basis for measuring absorption, density and volume of permeable voids of alkali-activated pastes. The temperature was, however, modified to 60℃ as the standard temperature of 105℃ was found excessive for the pastes, resulting in cracking of the samples. This test was conducted on 28-day cured pastes. Different equipment, used for this experiment, are shown in Figure 3.12.

Figure 3.12 Oven, boiling bowl and scale

The X-ray diffraction (XRD) and scanning electron microscope (SEM) were conducted using PANalytical X-ray Diffractometer (X’Pert Poro) and JEOL JSM Scanning Electron Microscope, respectively. The test devices for these tests are presented in Figures 3.13 and 3.14, respectively. XRD was conducted at different ages and on powders prepared from different pastes passing sieve #200 (75 micron). SEM was done in different ages and on small pieces of the produced pastes.

Figure 3.13 SEM

Figure 3.14 PANalytical X-ray diffractometer

A test setup was designed in accordance with ASTM C78 (four-point loading) to measure flexural strength of alkali-activated pastes. It is shown in Figure 3.15. This test was conducted on 50×50×200 mm samples (2×2×8 in) and at the age of 28 days.

Figure 3.15 Flexural strength test setup

3.3.2. Mortars

Flow of alkali-activated mortars was measured in accordance with ASTM C1437 and upon batching. The flow Table is shown in Figure 3.7.

Setting times of mortars were measured by Vicat and modified Vicat (ASTM C807) upon batching. Two types of needles were used having 1 and 2 mm diameters. The setting time is defined as the time that 1mm- and 2 mm-needles penetrate 25 and 10 mm in the mortar within 30 seconds, respectively.

Compressive strength of alkali-activated mortars was measured based on ASTM C109 and on 75 by 150 mm cylinders (3 by 6 in). The compressive strength was measured at different ages of 3, 7, 28 and 28 days. On each age, 3 samples were tested.

Tensile strength of alkali-activated mortars was measured according to ASTM C496 on the basis of Brazilian method (indirect tensile strength). The 28-day cylinders with dimension of 75 by 150 mm (3 by 6 in) were used for this test.

Drying shrinkage of alkali-activated mortars was measured in accordance with ASTM C157 and on 25×25×285 mm prisms (1×1×11-1/4 in). For the purpose of this test, samples were cured till the age of 7 days before moving to humidity chamber (50 ± 5% relative humidity).

Absorption, density and volume of permeable voids of the studied mortars were measured based on ASTM C642. The drying temperature was reduced to 80°C as 105°C could be excessive for mortars. This test was conducted on 28-day mortar disks having diameter of 100 mm (4 in) and height of 50 mm (2 in).

Heat of hydration of mortars was measured by use of the developed isolated boxes (See Figure 3.9). Three 100 by 100 mm (4 by 4 in) cylindrical samples were cast for this experiment.

Rapid chloride penetration test was measured in accordance with ASTM C1202. The device and cells used for this test are shown in Figure 3.16. This test was conducted on 28-day disks with diameter of 100 mm (4 in) and height of 50 mm (2 in).

Figure 3.16 RCPT test cell and device

Rapid chloride migration test was carried out based on NT BUILD 492 and on 28-day disks with diameter of 100 mm (4 in) and height of 50 mm (2 in). The device used for this test is shown in Figure 3.17.

Figure 3.17 RMT test setup

3.3.3. Concretes

The workability of alkali-activated concretes was measured upon batching and in accordance with ASTM C143. The slump cone used for measurement of flow is shown in Figure 3.18.

Figure 3.18 Slump flow

The setting times of the developed alkali-activated concretes were assessed in accordance with ASTM C403. The device for this test is shown in Figure 3.19. This test was conducted upon batching. The test was carried out on mortar part of concrete which was separated from coarse aggregate by passing concrete through sieve #4 (4.75 mm).

Figure 3.19 Setting time test device for concrete

ASTM C39 was used to evaluate compressive strength of alkali-activated concretes. This test was conducted on 100 by 200 mm (4 by 8 in) cylinders and at different ages of 1, 3, 7, 28 and 90 days. A minimum of 3 samples were used for each mixture. A sample of this experiment is shown in Figure 3.20.

Tensile strength of alkali-activated concretes was measured according to ASTM C496 on the basis of Brazilian method (Indirect tensile strength). The 28-day cylinders with dimension of 100 by 200 mm (4 by 8 in) were used for this test. This test setup is also shown in Figure 3.20.

ASTM C469 was used for measurement of elastic modulus. The extensometer used for this test is shown in Figure 3.21. This test was conducted on 100 by 200 mm (4 by 8 in) cylinders and at the age of 28 days.

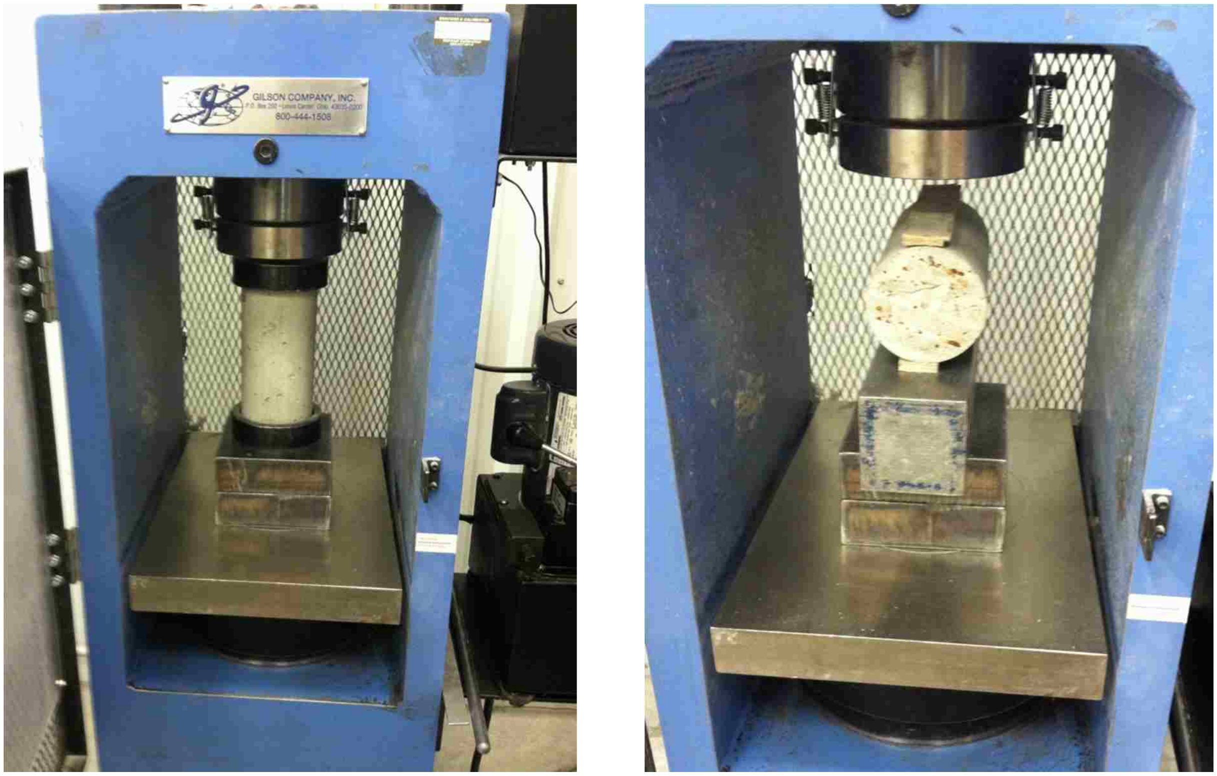


Figure 3.20 Compressive test (left) and indirect tensile test (right)

Figure 3.21 Extensometer used for deflection measurement

ASTM C642 was used for measurements of absorption, density and volume of permeable voids. This test was conducted on disks with diameter of 100 mm (4 in) and height of 50 mm (2 in) and at the ages of 28 and 90 days.

Rapid chloride penetration and rapid chloride migration tests were conducted according to ASTM C1202 and NT BUILD 492, respectively. These tests were conducted on 28-day cured samples. The test setups were similar to those used for mortars.

ASTM C157 was used for assessing drying shrinkage of alkali-activated concretes. This test was conducted on 75×75×285 mm (3×3×11-1/4 in) prisms which cured for 28 days before transferring to humidity chamber. The shrinkage samples and dial gauge are shown in Figure 3.22.

Figure 3.22 Shrinkage samples and dial gauge

An accelerated test method was designed based on FM 5-522 for measurement of reinforcement corrosion in concrete. In this test, the 28-day cured reinforced concrete samples, shown in Figure 3.23, were subjected to 5% saltwater and a voltage of 6 V (increased to 30 V for this dissertation). The passed current was monitored till sample fails. In this experiment, the failure (break) of sample happens with a considerable jump in the passed current due to cracking. The time between starting the test till failure was considered as time of failure.

Figure 3.23 Corrosion test setup

As there is not any standard yet for evaluating acid resistance of concrete, a test method was designed to assess performance of alkali-activated concretes against acid attack. This test method dealt with the immersion of samples in a diluted sulfuric acid solution (pH of below 1) for a total of 4 months. The pH of solution was measured weekly and balanced to below 1 by adding fresh acid to the solution. Figure 3.24 shows the cylindrical molds used as acid containers. At every week, samples were weighed and mass change was monitored. Samples were also tested for compressive strength at the end of 4 month immersion.

Figure 3.24 Acid containers

Freeze-thaw resistance of alkali-activated concretes were measured according to an accelerated method using 3% saltwater and freezing temperature of -20 ˚C (-4 ˚F). The 28-day cured samples were immersed in saltwater. Afterward, they were subjected to a total of 56 freezing and thawing cycles, where one cycle is defined as 24 hours in freezing at -20 ˚C (-4 ˚F) and 24 hours thawing at room temperature. The mass loss is measured at 5 or 7 cycle intervals. Figure 3.25 shows freezer and containers housing testing samples subjected to freezing and thawing cycles.

Figure 3.25 Freezer and samples in freezing and thawing cycle

CHAPTER 4- DEVELOPMENT OF ALKALI-ACTIVATED NATURAL POZZOLAN/SLAG PASTE

4.1. Introduction

The first phase of experimental program dealt with development of alkali-activated natural pozzolan/slag pastes with proper fresh and strength properties. To this aim, three major objectives were defined for this phase of study:

(1) **Providing adequate fresh properties**: Natural pozzolan-based alkali-activated binders set late, whereas slag-based alkali-activated binders have been known with their quick setting times. The preliminary experiments on natural pozzolan/slag-based alkali-activated binders, activated with combinations of sodium hydroxide and sodium silicate, showed quick setting time as a major concern for these binders as well. Therefore, prolonging the setting time to reasonable durations was the major goal of this phase. In addition to the setting time, flow spread of the alkali-activated natural pozzolan/slag pastes was measured to assure adequacy of workability. The proper fresh properties were defined as follows:

- Initial setting time of more than 1.5 hrs but less than 5 hrs.
- Final setting time of less than 10 hrs.
- Flow of 2 to 6 inches (5.08 to 15.24 cm). Although a suitable flow based on ASTM C109 for Portland cement mixtures is about 4.375 inches (11.11 cm) (4.25 to 4.675 inches (10.80 to 11.87 cm)), a flow of 4±2 inches (10.16±5.08 cm) was considered for this study. The reason for selection of this range was (1) the fact that alkali-activated binders have not shown bleeding for flow

spreads of 4.375 to 6 inches (11.11 to 15.24 cm) and can be easily compacted using a vibratory table for flow of above 2 inches (5.08 cm), and (2) to have more options for designing different mixtures and assessing influential parameters. Accordingly, the flow of below 2 inches (5.08 cm) was considered unacceptable.

(2) **Developing proper compressive strengths:** The second objective was to ensure that the selected mixture proportions could develop adequate strength. Two criteria were considered: (1) acceptable mixtures must have a minimum 28-day compressive strength of 20 MPa (almost 3000 psi) as required for structural materials, and (2) mixtures with delayed setting times and drastic reduction in strength are considered unacceptable.

(3) **Assessing the role of mixture proportioning on properties of alkali-activated natural pozzolan/slag pastes:** For the mixtures meeting the requirements of the first two goals (proper fresh and strength properties), effects of mixture proportioning on various properties were studied. The studied variables included binder combinations (slag and natural Pozzolan contents), alkaline activator combinations (sodium silicate and sodium hydroxide dosages), and sodium hydroxide concentrations. Evaluation of these parameters assisted in the selection of suitable combinations used for devising alkali-activated mortars and concretes.

4.2. Preliminary evaluation

As mentioned earlier, short setting has been one of the major concerns for slag-based alkali-activated binders. In order to demonstrate this concern, a comparison was made between alkali-activated and Portland cement pastes. Tables 4.1 and 4.2 report setting times of alkali-activated natural Pozzolan/slag and Portland cement pastes, respectively. These mixtures are referred as reference mixtures. The alkali-activated reference pastes contained 70% natural Pozzolan and 30% slag as binders, and 30% sodium silicate and 70% sodium hydroxide (5M) as alkaline activators. Ref I, Ref II and Ref III were designed with solution (alkaline activator solution)-to-binder ratios (S/B) of 0.55, 0.51 and 0.47, respectively. Ref IV-PC was the Portland cement paste made for comparison purposes.

It can be seen in Table 4.1 that all alkali-activated reference pastes set rapidly. Their initial and final setting times were averagely about 12 and 36 minutes, respectively. These values were almost 92 and 84% lower than those of Portland cement paste, respectively. This observation shows the importance of this phase of research for development of proper mixture combinations before proceeding with production of alkali-activated mortars and concretes.

Table 4.1 Mixture proportion and properties of reference alkali-activated natural pozzolan/slag pastes

Mix id.	S/B	Materials, g					Flow, cm	Initial set, min	Final set, min	Compressive strength, MPa	
		Natural Pozzolan	Slag	Sodium hydroxide	Sodium silicate	Admixture				7 days	28 days
Ref I	0.55	2450	1050	1347.5	577.5	0	15.24*	14:05	43:11	30.6	47.7
Ref II	0.51	2450	1050	1249.5	535.5	0	10.80	12:45	35:30	36.2	50.4
Ref III	0.47	2450	1050	1151.5	493.5	0	5.72	9:45	28:15	37.6	51.8

* 15.24 cm was achieved in 15 drops instead of 25 drops. It means that the flow was higher than 15.24 cm but the flow Table doesn't allow for further measurement.

Table 4.2 Mixture proportion and properties of reference Portland cement paste

Mix id.	Water-to-cement ratio (w/c)	Materials, g			Flow, cm	Initial set, min	Final set, min	Compressive strength, MPa	
		Portland cement	water	Admixture				7 days	28 days
Ref IV-PC	0.35	3500	1225	0	11.87	154	231	57.4	74.7

* The reason for high strength is that Portland cement Paste was made with a low w/c of 0.35.

4.3. Development of mixtures with adequate setting time

In order to mitigate the setting time concern, two strategies were considered:

(a) Use of different admixtures including well-known set retarders developed for Portland cement, different acids proven in the literature as set retarders for alkali-activated slags, and other compounds shown retarding capabilities for Portland cement. This strategy was considered as the first strategy. The admixtures included: commercial retarders, malic acid, phosphoric acid, sodium phosphate, sodium gluconate, lignosulfonate-based admixture, and gypsum.

(b) Reduction in alkaline concentration by decreasing molarity of sodium hydroxide solution. This strategy was considered as an alternative plan in case the first strategy failed.

4.3.1. First strategy (use of admixtures)

As the first strategy for prolonging the setting time, various commercial and non-commercial set-retarding admixtures were used including: commercial retarders developed for Portland cement, malic acid, phosphoric acid, sodium phosphate, sodium gluconate, lignosulfonic acid sodium salt, and gypsum. Effects of these admixtures on fresh and strength properties of alkali-activated natural pozzolan/slag pastes are discussed in following subsections:

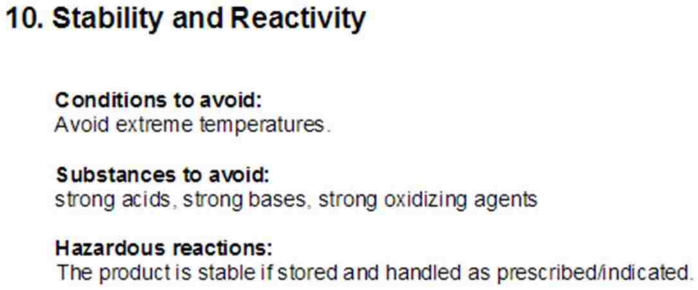
4.3.1.1. Commercial retarders and water reducers

One of the major difficulties for applications of alkali-activated binders has been unavailability of commercial admixtures for these binders. The majority of admixtures, modified for Portland cement, don't work for alkali-activated binders. They are not stable in the high alkaline environment of alkali-activated binders.

In this phase, datasheets and safety-sheets of various set retarders and water reducers of two major admixture companies (BASF and GRACE) were reviewed. The one common item in all the admixtures' datasheets was "to avoid strong bases", as shown in Figure 4.1. After consultation with the BASF representatives and their laboratory staff, one type of set-retarder known as Masterset Delvo (formerly Delvo Stabilizer) was selected. In addition, two types of water reducers were chosen to observe their influences on fresh properties of alkali-activated binders. These admixtures were MasterGlenium 3030 and MasterPozzolith 700 (formerly Pozzolith 700N).

A number of mixtures were made by addition of the above-mentioned admixtures to alkali-activated natural pozzolan/slag pastes. Their inclusion didn't show any specific effect on setting time or flow of alkali-activated natural pozzolan/slag pastes. As mentioned earlier, the reason for the observed behavior was instability of commercial admixtures with high alkaline environment of alkali-activated binders. These admixtures were disintegrated by alkalis, thus became ineffective.

Conclusion: Commercial admixture, which developed for Portland cements, can't be used for alkali-activated binders.



10. Stability and Reactivity

Conditions to avoid:
Avoid extreme temperatures.

Substances to avoid:
strong acids, strong bases, strong oxidizing agents

Hazardous reactions:
The product is stable if stored and handled as prescribed/indicated.

Figure 4.1 Commercial admixtures' datasheet

4.3.1.2. Malic acid

Malic acid is one of the few compounds which has shown retarding effect in the literature of alkali-activated slags (Brough et al. 2000). Accordingly, it was used in this phase of study. The first question, however, was how to add malic acid to the paste? Three options were considered:

(1) Introducing malic acid to the paste with other ingredients. As addition of acid to the alkaline environment generates heat, this option was not considered.

(2) Combining malic acid with sodium hydroxide before mixing. Figure 4.2 shows a mixture of malic acid with sodium hydroxide. Although this combination generated heat (temperature of solution increased from 76^{O}F to 107 and 132^{O}F when 4 and 10% malic acid was added to sodium hydroxide solution, respectively), the reaction product remained in liquid condition. Therefore, the product was cooled down and used for mixing.

(3) Combining malic acid with sodium silicate before mixing. Figure 4.2 also presents a reaction product of malic acid with sodium silicate solution. This combination not only generated heat (temperature of solution increased from 76^{O}F to 92^{O}F for addition of about 4% malic acid), but also changed the phase from liquid to solid. It wasn't even possible to add more than 4% malic acid to sodium silicate. Therefore, this combination wasn't considered.

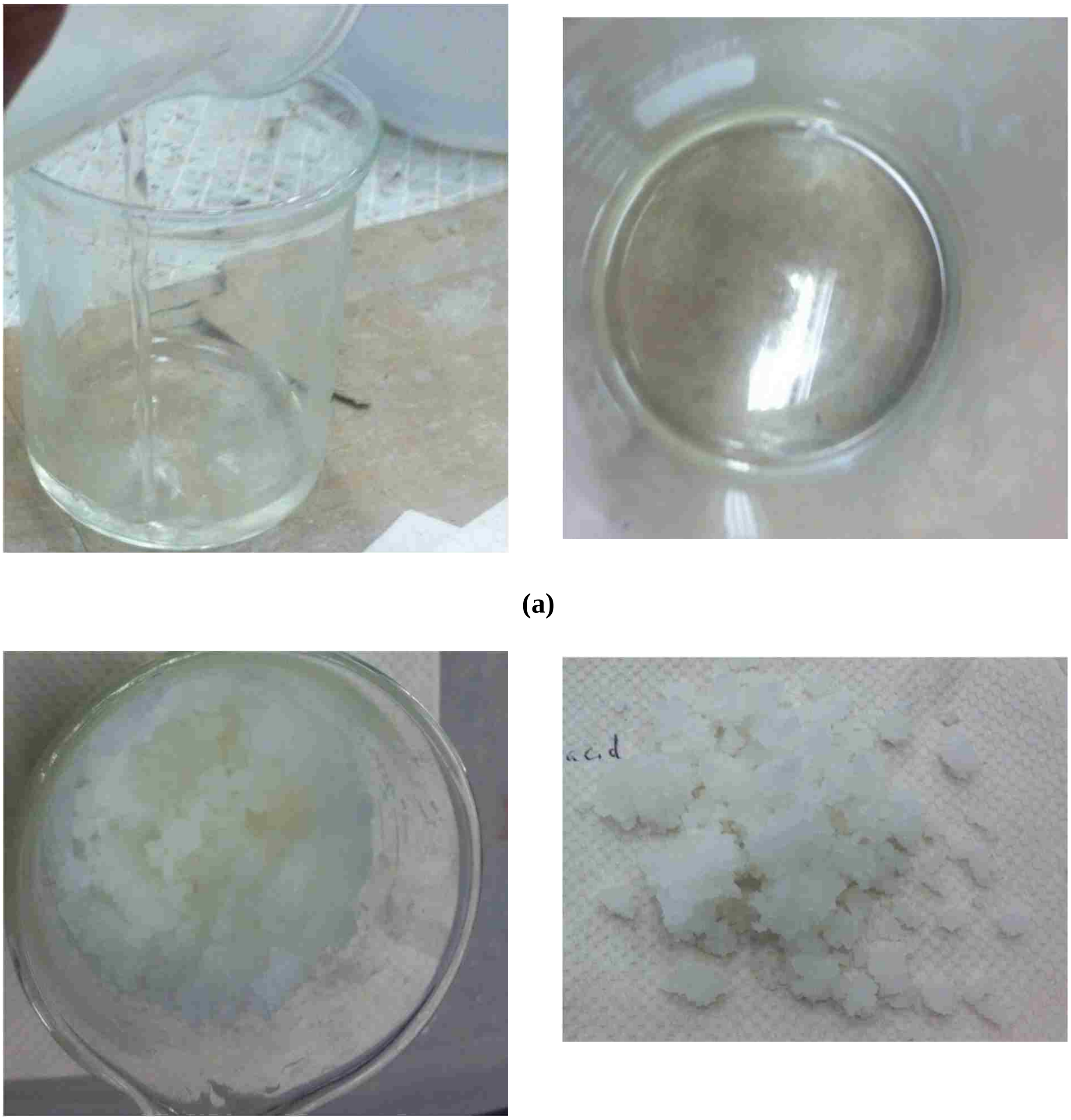
Accordingly, the second method was used for inclusion of malic acid to alkali-activated natural Pozzolan/slag pastes. Different percentages of malic acid were designed to be added including 2, 4, 6, 8 and 10% by weight of the total binder. Table 4.3 documents the mixture proportions of the designed pastes. The fresh and strength properties of malic acid contained alkali-activated pastes are reported in Table 4.4. It can be seen that:

(1) The setting times were considerably delayed using high dosages of malic acid (10%). While the increases in setting time were insignificant for 2 and 4% malic acid, the initial and final setting times were prolonged to about 1 and 2 days by addition of 10% malic acid, respectively. This observation was similar to the findings of the other researchers showing that a minimum amount of malic acid is needed to provide retarding effects (Chang et al. 2005).

(2) At small dosages, use of malic acid reduced the flow of the mixture, while inclusion of high dosage (10%) didn't affect the workability.

(3) Use of malic acid significantly reduced compressive strength of alkali-activated natural pozzolan/slag pastes. The 7-day compressive strength reduced by 18, 37 and 73% when 2, 4 and 10% malic acid was added to the paste, respectively. For the similar dosages of malic acid, the 28-day compressive strength decreased by 25, 28 and 57%, respectively. Due to this significant reduction in the strength, it was decided to not proceed with the use of 6 and 8% malic acid. The observed behavior could be related to the reactions of acid and basic solutions hindering alkali-activation of the binders.

__Conclusion:__ Although it was found that malic acid can delay setting time, its inclusion resulted in a drastic reduction of compressive strength. Due to the detrimental effect on the strength, malic acid wasn’t selected for further research.



(a)

(b)

Figure 4.2 Use of malic acid, (a) combination of sodium hydroxide with malic acid, (b) combination of sodium silicate with malic acid

Table 4.3 Mixture proportion of malic acid contained alkali-activated natural pozzolan/slag pastes

Mix id.	Mixture description	Materials, g				
		Natural Pozzolan	Slag	Sodium hydroxide	Sodium silicate	Malic acid
Ref II	Reference	2450	1050	1249.5	535.5	0
MA2	2% malic acid	2450	1050	1249.5	535.5	70
MA4	4% malic acid	2450	1050	1249.5	535.5	140
MA6	6% malic acid	2450	1050	1249.5	535.5	210
MA8	8% malic acid	2450	1050	1249.5	535.5	280
MA10	10% malic acid	2450	1050	1249.5	535.5	350

Table 4.4 Fresh and strength properties of malic acid contained alkali-activate natural pozzolan/slag pastes

Mix id.	Flow, cm	Initial set, min	Final set, min	Compressive strength, MPa	
				7 days	28 days
Ref II	10.80	12:45	35:30	36.2	50.4
MA2	7.62	13:37	42:03	29.9	37.6
MA4	2.54	18:40	63:40	22.7	36.1
MA6	Not proceed				
MA8	Not proceed				
MA10	10.80	23 hrs	48 hrs	9.7	21.4

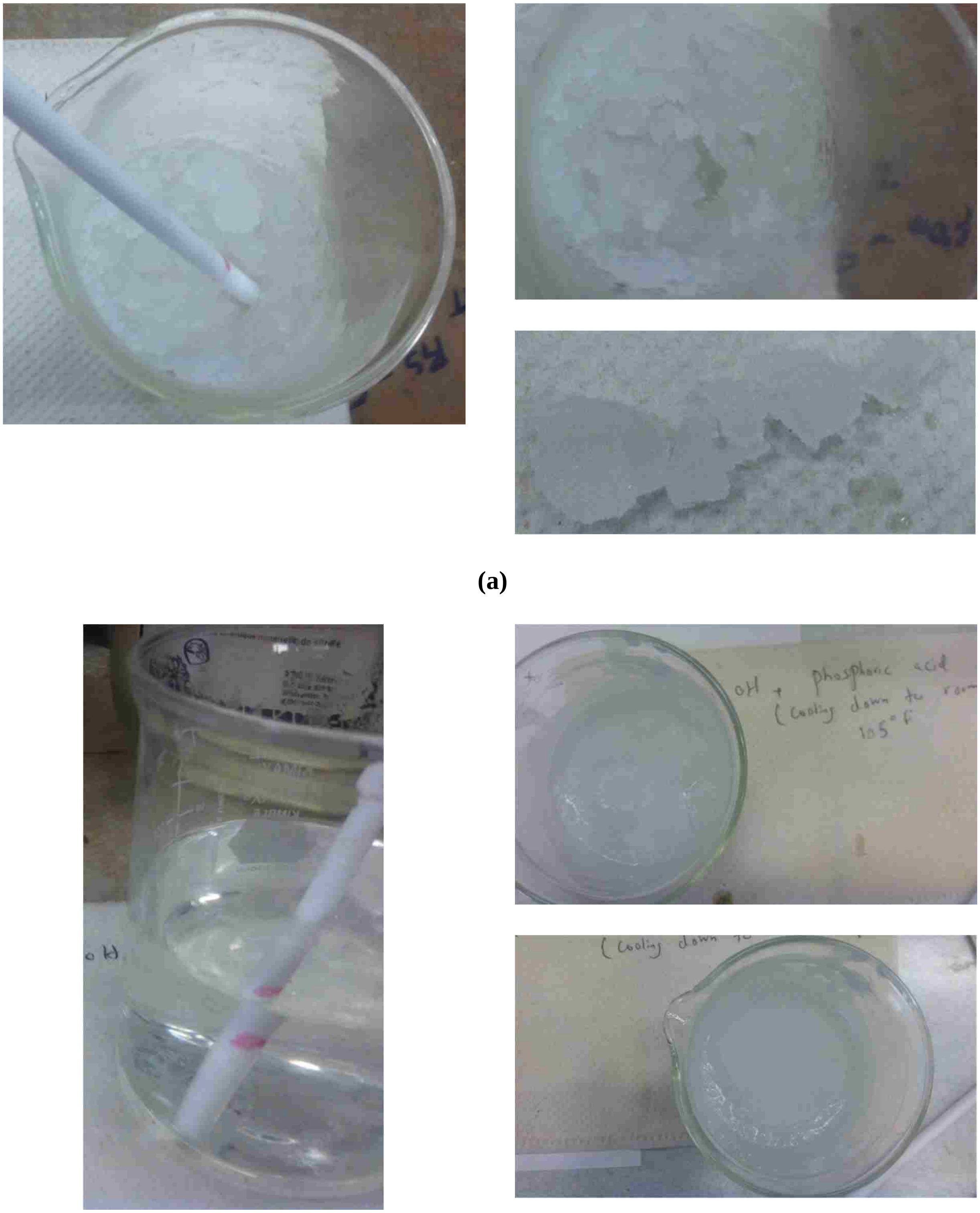
4.3.1.3. Phosphoric acid and sodium phosphate

Phosphoric acid and sodium phosphate have also shown retarding effects as reported in the literature of alkali-activated slags (Chang et al. 2005, Gong and Yang 2000). Similar to malic acid, sodium phosphate and phosphoric acid can’t be added during mixing as their inclusions generate heat. Therefore, combinations of these admixtures with sodium hydroxide and sodium silicate solutions were studied.

In the case of sodium silicate solution, combination with either of phosphoric acid or sodium phosphate changed the phase of solution from liquid to solid (crystals) as shown in Figures 4.3 (a) and 4.4 (a), respectively. The temperature of solution increased from 76^{O}F to 100 and 147^{O}F, when sodium silicate was combined with 6% sodium phosphate and 4% phosphoric acid, respectively.

When similar amount of phosphoric acid was combined with sodium hydroxide, the temperature raised to 154^{O}F. The solution was liquid at first, but crystallized as the solution cooled down. This observation is shown in Figure 4.3 (b). Figure 4.4 (b) shows the solution made by combination of sodium phosphate and sodium hydroxide. Almost 60^{O}F was generated when 6% sodium phosphate was added to sodium hydroxide. The resulting solution was very viscose. Due to the phase changes by addition of these admixtures, their application for alkali-activated pastes were impossible.

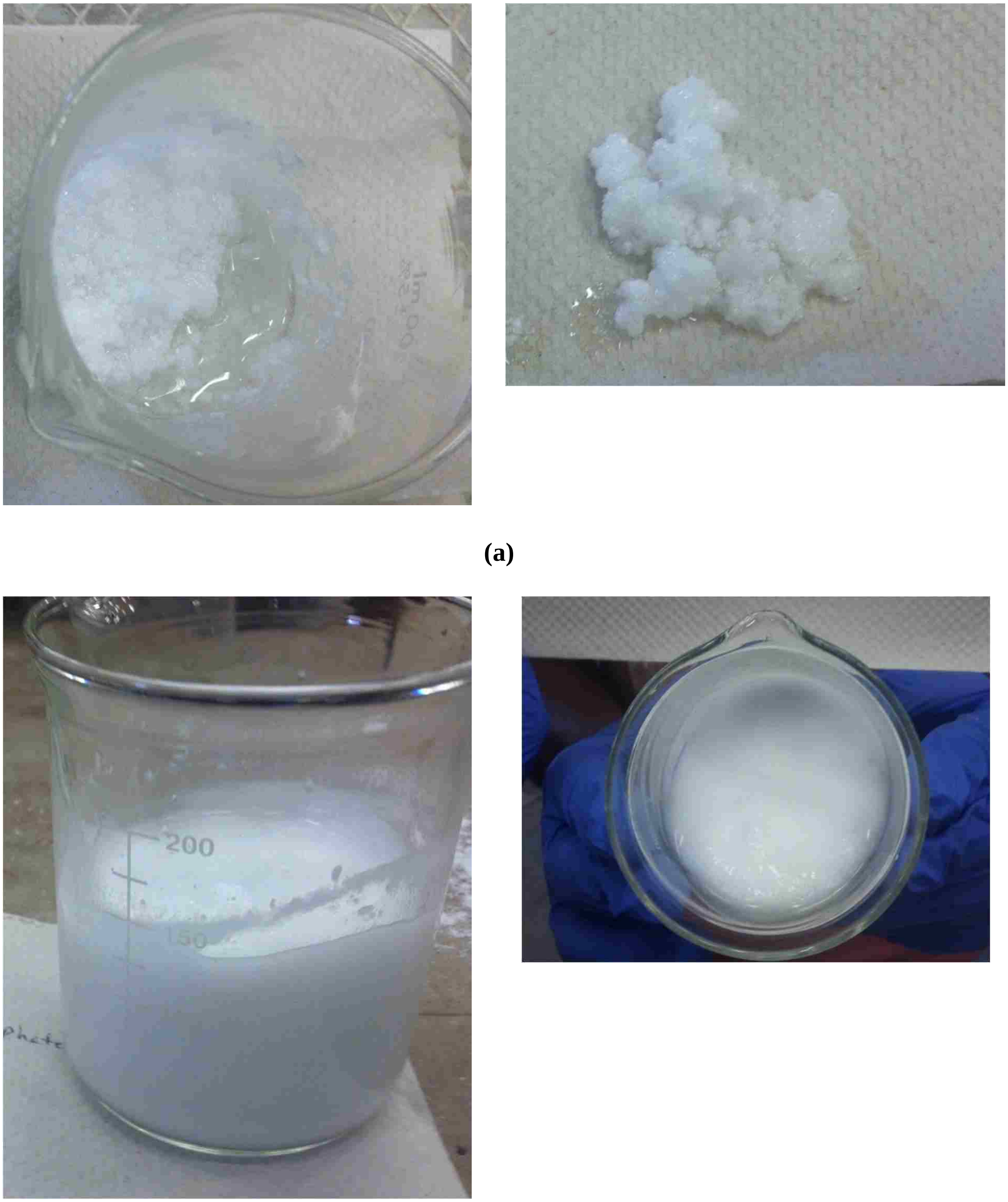
Conclusion: The observed phase changes to solid rendered utilization of these admixtures impossible. Therefore, it was decided to not proceed with phosphoric acid and sodium phosphate. Also, the strength reduction observed with weaker acid (malic acid) suggested that a similar or higher strength reduction could take place with these admixtures. It’s worth mentioning that Chang et al. (2005) also observed strength reduction when phosphoric acid was used as a retarder.



(a)

(b)

Figure 4.3 Use of phosphoric acid, (a) combination with sodium silicate, (b) combination with sodium hydroxide



(a)

(b)

Figure 4.4 Use of sodium phosphate, (a) combination with sodium silicate, (b) combination with sodium hydroxide

4.3.1.4. Lignosulfonic acid sodium salt

Lignosulfonate-based admixtures are known as strong retarders. Accordingly, lignosulfonic acid sodium salt was used as a trial set-retarding admixture. It was resolved in a sodium hydroxide solution prior to mixing as shown in Figure 4.5. There was no problem of heat release or phase change. The combined solution was used for production of alkali-activated natural pozzolan/slag pastes. Lignosulfonic acid sodium salt was added to the mixture in two different dosages of 3 and 6% of the total binder. Tables 4.5 and 4.6 document their mixture proportion, fresh properties and compressive strengths. It can be seen that:

(1) Use of lignosulfonate-based admixture increased the setting time. The initial and final setting times were almost 2.5 times of those of the reference paste. This increase, however, wasn’t sufficient. While the setting times were still below the targets, use of higher dosage of lignosulfonic acid sodium salt didn’t provide additional delay. The setting times of alkali-activated natural pozzolan/slag pastes containing 3 and 6% lignosulfonic acid sodium salt were almost similar.

(2) Use of lignosulfonate-based admixture considerably reduced the workability of the studied pastes. While the produced pastes were flowable upon batching, they lost their workability within a few minutes before completion of the flow test.

(3) Addition of lignosulfonic acid sodium salt resulted in almost 41 to 46% reduction in the 7-day compressive strength. An almost similar reduction was observed for the 28-day compressive strength.

Conclusion: Although lignosulfonate-based admixture showed increases in setting time of alkali-activated natural pozzolan/slag pastes, it couldn’t hinder the setting process to a reasonable time. In addition, its inclusion drastically reduced workability and strength. Consequently, it wasn’t considered for further research.

Figure 4.5 Use of lignosulfonic acid sodium salt, (a) combination with sodium hydroxide, (b) produced alkali-activated paste samples

Table 4.5 Mixture proportion of alkali-activated natural pozzolan/slag pastes containing lignosulfonic acid sodium salt

Mix id.	Mixture description	Materials, g				
		Natural Pozzolan	Slag	Sodium hydroxide	Sodium silicate	Admixture
Ref II	Reference	2450	1050	1249.5	535.5	0
SL3	3% lignosulfonate	2450	1050	1249.5	535.5	105
SL6	6% lignosulfonate	2450	1050	1249.5	535.5	210

Table 4.6 Fresh and strength properties of alkali-activated natural pozzolan/slag pastes containing lignosulfonic acid sodium salt

Mix id.	Flow, cm	Initial set, min	Final set, min	Compressive strength, MPa	
				7 days	28 days
Ref II	10.80	12:45	35:30	36.2	50.4
SL3	5.08*	31:10	95:25	19.7	25.7
SL6	4.45*	35:15	99:30	21.4	--

* The paste was super flowable at completion of mixing but lost the flow during the flow test

4.3.1.5. Sodium gluconate

In development of admixtures for Portland cement concrete, sodium gluconate has been found as an admixture that can increase workability and setting time. Therefore, it was considered for this phase of study as well. Sodium gluconate was solved in sodium hydroxide solution before mixing. It was easily solved without any sign of heat generation or phase change.

A number of mixtures were designed having different dosages of sodium gluconate, including 0.25, 0.5, 1, 2, and 4% by weight of the total binder. Tables 4.7 and 4.8 present mixture proportion, fresh properties and strength of alkali-activated natural pozzolan/slag pastes having sodium gluconate.

Table 4.7 Mixture proportion of sodium gluconate contained alkali-activated natural pozzolan/slag pastes

Mix id.	Mixture description	Materials, g				
		Natural Pozzolan	Slag	Sodium hydroxide	Sodium silicate	Sodium gluconate
Ref III	Reference	2450	1050	1151.5	493.5	0
SG0.25	0.25% sodium gluconate	2450	1050	1151.5	493.5	8.75
SG0.5	0.5% sodium gluconate	2450	1050	1151.5	493.5	17.5
SG1	1% sodium gluconate	2450	1050	1151.5	493.5	35
SG2	2% sodium gluconate	2450	1050	1151.5	493.5	70
SG4	4% sodium gluconate	2450	1050	1151.5	493.5	140

Table 4.8 Fresh and strength properties of sodium gluconate contained alkali-activated natural pozzolan/slag pastes

Mix id.	Flow, cm	Initial set, min	Final set, min	Compressive strength, MPa	
				7 days	28 days
Ref III	5.72	9:45	28:15	37.6	51.8
SG0.25	11.43	10:30	27:45	40.0	56.9
SG0.5	13.02	10:36	25:30	41.9	53.9
SG1	15.24	11:30	25:30	44.9	53.1
SG2	15.24*	12:45	25:10	36.6	53.0
SG4	15.24*	15:10	25:25	25.7	39.7

* 15.24 cm was achieved in 23 and 18 drops for SG2 and SG4 instead of 25 times, respectively. It means that the flow was higher than 15.24 cm but the flow table didn’t allow for further measurement.

It can be seen that:

(1) Addition of sodium gluconate didn’t increase the setting times. Initial and final setting times of pastes with and without sodium gluconate were almost similar.

(2) Use of sodium gluconate improved the workability of alkali activated natural pozzolan/slag pastes. It can be seen that the flow of alkali-activated pastes having 0.25,0.5 ,1, 2 and 4% sodium gluconate were 5.72, 7.30, 9.53, 9.53 and 9.53 cm higher than that of reference

paste without sodium gluconate, respectively. These differences could have been higher if the flow table allowed for flow measurements of more than 15.24 cm.

(3) Addition of sodium gluconate in small dosages improved the compressive strength. The compressive strength of alkali activated natural pozzolan/slag pastes increased by averagely 8.1, 7.8 and 11.0% when 0.25, 0.5 and 1% sodium gluconate was added, respectively. Higher dosages of sodium gluconate, however, resulted in strength reduction. While the strength of paste having 2% sodium gluconate was almost similar to that of the reference paste, strength of mixture with 4% sodium gluconate was averagely 27.5% lower than that of reference paste.

Conclusion: Although use of sodium gluconate improved workability and strength, it didn’t hinder the setting times. Therefore, it wasn’t selected for the next phases of this research.

4.3.1.6. Gypsum

Gypsum plays an important role in controlling the hardening rate of Portland cement. Without gypsum, Portland cement sets immediately after mixing with water leaving no time for concrete placing. Thus, gypsum was considered for this part of the study as well.

Tables 4.9 and 4.10 document mixture proportions and properties of various mixtures designed with adding different dosages of gypsum including 0.5, 1 and 2% by weight of total binder. As inclusion of gypsum significantly reduced the flow, it was used with either 1% sodium gluconate or higher solution-to-binder ratio. Accordingly gypsum was added to two different mixtures: (1) Ref I with S/B of 0.55, and (2) Ref III with S/B of 0.47 and by addition of 1% sodium gluconate as it was impossible to add gypsum to mixture Ref III without sodium gluconate. After several trials, it was also decided to add gypsum one minute after all the other components were mixed. Addition of gypsum with other ingredients was tried (mixtures G2-SG1* and G2-S/B0.55* shown in Tables 4.9 and 4.10), which resulted in significant reduction of flow.

Table 4.9 Mixture proportion of gypsum contained alkali-activated natural pozzolan/slag pastes

Mix id.	Mixture description	Materials, g					
		Natural Pozzolan	Slag	Sodium hydroxide	Sodium silicate	Gypsum	Sodium gluconate
Ref III	Reference	2450	1050	1151.5	493.5	0	0
G2	Similar to Ref III+ 2% gypsum	2450	1050	1151.5	493.5	70	0
G2-SG1*	Similar to Ref III+2% gypsum+1% sodium gluconate	2450	1050	1151.5	493.5	70	35
G2-SG1	Similar to Ref III+2% gypsum+1% sodium gluconate	2450	1050	1151.5	493.5	70	35
G1-SG1	Similar to Ref III+1% gypsum+1% sodium gluconate	2450	1050	1151.5	493.5	35	35
G0.5-SG1	Similar to Ref III+0.5% gypsum+1% sodium gluconate	2450	1050	1151.5	493.5	17.5	35
Ref I	Reference	2450	1050	1347.5	577.5	0	0
G2-S/B0.55*	Similar to Ref I+2% gypsum	2450	1050	1347.5	577.5	70	0
G2-S/B0.55	Similar to Ref I+2% gypsum	2450	1050	1347.5	577.5	70	0
G1-S/B0.55	Similar to Ref I+1% gypsum	2450	1050	1347.5	577.5	35	0
G0.5-S/B0.55	Similar to Ref I+0.5% gypsum	2450	1050	1347.5	577.5	17.5	0

* These mixtures were made by adding gypsum with other components. This method resulted in really low workability. Therefore, gypsum was added to the mixture a minute after mixing the other components

Table 4.10 Fresh and strength properties of gypsum contained alkali-activated natural pozzolan/slag pastes

Mix id.	Flow, cm	Initial set, min	Final set, min	Compressive strength, MPa	
				7 days	28 days
Ref III	5.72	9:45	28:15	37.6	51.8
G2	Impossible to cast				
G2-SG1*	2.54	7:20	17:25	41.1	--
G2-SG1	8.26	7:15	18:20	38.6	43.1
G1-SG1	11.43	8:35	20:10	38.7	46.4
G0.5-SG1	12.70	9:00	19:55	44.6	56.3
Ref I	15.24	14:05	43:11	30.6	47.7
G2-S/B0.55*	0.64*	14:35	44:25	17*	--
G2-S/B0.55	10.16	12:50	38:25	33.7	44.2
G1-S/B0.55	10.16	12:35	40:10	33.7	45.3
G0.5-S/B0.55	12.70	13:25	39:05	33.8	45.9

* The significantly low workability caused unsuitable compaction and thus low strength

Based on the results presented in Table 4.10, it can be concluded that:

(1) Use of gypsum wasn’t effective in hindering the setting process. In fact, its addition slightly reduced the setting times.

(2) The workability of studied pastes was significantly reduced by inclusion of gypsum.

(3) Addition of gypsum resulted in considerable strength reduction.

Conclusion: Use of gypsum not only didn’t improve setting time, but also reduced flow, setting time and strength. Therefore, it wasn’t selected for further research.

4.3.2. Second strategy (reduction of sodium hydroxide concentrations)

As the studied admixtures were either unable to hinder the setting process or delayed the setting times along with drastic reduction in compressive strength, the second option, i.e. reduction of sodium hydroxide concentration, was considered. Use of lower sodium silicate content was also studied, which has not been proceeded due to the considerable reduction in compressive strength.

A gradual reduction of sodium hydroxide concentration was designed for this phase of investigation. Table 4.11 shows the mixture proportions and properties of mixtures designed with lower sodium hydroxide molarity. The NaOH concentrations included 5, 3, 2, 1, 0.5 and 0 (water used instead of sodium hydroxide) M.

Table 4.11 Mixture proportions and properties of alkali-activated natural pozzolan/slag pastes having sodium hydroxide with different molarities

Mix id.	Molarity	Materials, g				Flow, cm	Initial set, min	Final set, min	Strength, MPa	
		Natural Pozzolan	Slag	Sodium hydroxide	Sodium silicate				7 days	28 days
Ref III-5	5	2450	1050	1151.5	493.5	5.72	9:45	28:15	37.6	51.8
Ref III-3	3	2450	1050	1151.5	493.5	6.35	66	123	42.7	59.0
Ref III-2	2	2450	1050	1151.5	493.5	10.16	115	195	40.6	55.5
Ref III-1	1	2450	1050	1151.5	493.5	10.80	165	305	39.0	52.7
Ref III-0.5	0.5	2450	1050	1151.5	493.5	11.43	320	440	38.7	52.1
Ref III-0*	0	2450	1050	1151.5*	493.5	6.35	245	500	26.1	50.3
Ref II-5	5	2450	1050	1249.5	535.5	10.80	12:45	35:30	36.2	50.4
Ref II-3	3	2450	1050	1249.5	535.5	11.43	85	145	34.0	53.7
Ref II-2	2	2450	1050	1249.5	535.5	12.70	110	270	31.5	50.0

* Sodium hydroxide was replaced with water for this mixture

It can be seen that:

(1) Reduction of sodium hydroxide molarity was effective in delaying the setting times. The initial setting time increased from almost 10 minutes for 5M mixture (Mix Ref III-5) to 66, 115, 165, and 320 minutes for 3, 2, 1 and 0.5M mixtures, respectively. Similarly, the final setting time of Ref III-3, Ref III-2, Ref III-1 and Ref III-0.5 with molarities of 3, 2, 1 and 0.5M was 95, 167, 277, and 412 minutes more than that of Ref III-5 with 5M sodium hydroxide, respectively. The setting times of mixtures with molarities of 0.5, 1 and 2M were in the acceptable range designed for this research.

(2) The reduction in compressive strength due to the reduction of molarity was insignificant. In fact, there was an optimum sodium hydroxide concentration (between 2 and 3M). The compressive strength slightly increased with increases in molarity for up to 3M, after which it reduced by increasing concentration of sodium hydroxide to 5M.

(3) Reduction of sodium hydroxide concentration improved the workability of alkali-activated natural pozzolan/slag pastes. The flow of alkali-activated pastes increased from 5.72 cm for 5M mixtures to 6.35, 10.16, 10.80, and 11.43 cm for 3, 2, 1 and 0.5M mixtures, respectively.

Conclusion: As reduction of sodium hydroxide concentration improved fresh properties (setting time and workability) and didn't show detrimental effect on the strength, this strategy was selected for further research. Mixtures with sodium hydroxide concentrations of 0.5, 1 and 2M satisfied all the established requirements, so these molarities were selected for the next phase of the study. Sodium hydroxide solution with concentration of 3M wasn't considered due to the following reasons:

- The fresh properties of 3M mixtures were in border line of the required fresh properties.
- Once higher slag content is used, the setting time is expected to reduce further, making 3M sodium hydroxide concentration an unacceptable activator.

4.4. Effects of mixture proportions on properties of alkali-activated natural Pozzolan/slag pastes

Upon identification of the most effective strategy for prolonging the setting time and before proceeding with production of alkali-activated mortars, influences of mixture proportioning on properties of alkali-activated natural pozzolan/slag pastes were studied. Results of this section were used in selection of proper proportions of natural Pozzolan and slag, and suitable combination of sodium hydroxide and sodium silicate for the next phases of this research. The following combinations were assessed in this phase:

1. The binder was consisted of natural Pozzolan and slag with natural Pozzolan-to-total binder ratios of 0.3, 0.4, 0.5, 0.6 and 0.7. These ratios correspond to slag-to-total binder ratios of 0.7, 0.6, 0.5, 0.4 and 0.3, respectively.
2. Alkaline activator was consisted of sodium hydroxide and sodium silicate solutions. Three different sodium silicate-to-total alkaline activator ratios of 0.2, 0.3 and 0.4 were selected. These ratios represent 80, 70 and 60% of alkaline activator was sodium hydroxide, respectively. There were two main reasons to not include higher dosages of sodium silicate; namely, (1) price of sodium silicate is considerably higher than

that of sodium hydroxide. A liter of sodium hydroxide (0.5 and 1M) costs close to the price of a liter of distilled water (less than a dollar), whereas sodium silicate is almost $7.5 per liter for laboratory purposes, and (2) use of higher dosages of sodium silicate results in reduction of workability which has to be compensated with additional alkaline activator (their effects on workability will be presented in this chapter).

3. Sodium hydroxide concentrations of 0.5, 1 and 2M were used. In order to provide a clear vision on effects of sodium hydroxide molarity, NaOH concentration of 3M and 0M (Pure water) was also designed for a couple of mixtures.

The setting time, flow, compressive strength, drying shrinkage, absorption and heat of hydration of these mixtures were measured to assess their performances and influences of mixture proportioning.

4.4.1. Mixture proportions

Table 4.12 documents the mixture proportions of designed alkali activated natural Pozzolan/slag pastes. As mentioned earlier, these mixtures were made with sodium hydroxide concentrations of 0, 0.5, 1, 2, and 3M, natural Pozzolan-to-total binder ratios of 0.3, 0.4, 0.5, 0.6, and 0.7 (slag-to-total binder ratios of 0.7, 0.6, 0.5, 0.4 and 0.3, respectively), and sodium silicate-to-total alkaline activator ratios of 0.2, 0.3 and 0.4 (sodium hydroxide-to-total alkaline activator ratios of 0.8, 0.7 and 0.6, respectively). A solution-to-binder ratio (S/B) of 0.47 was kept for all the mixtures.

In this Table, mixture id. XM-SLY-SSZ means that the used sodium hydroxide was X mole, Y% of the total binder was slag ((100-Y)% was natural Pozzolan), and Z% of the total activator was sodium silicate ((100-Z)% was sodium hydroxide).

Table 4.12 Mixture proportions of alkali activated natural Pozzolan/slag pastes

Mix id.	Mixture description	Materials, g			
		Natural Pozzolan	Slag	Sodium hydroxide	Sodium silicate
2M-SL30-SS30	30% slag, 70% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (2M)	2450	1050	1151.5	493.5
2M-SL40-SS30	40% slag, 60% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (2M)	2100	1400	1151.5	493.5
2M-SL50-SS30	50% slag, 50% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (2M)	1750	1750	1151.5	493.5
2M-SL60-SS30	60% slag, 40% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (2M)	1400	2100	1151.5	493.5
2M-SL70-SS30	70% slag, 30% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (2M)	1050	2450	1151.5	493.5
1M-SL30-SS30	30% slag, 70% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M)	2450	1050	1151.5	493.5
1M-SL40-SS30	40% slag, 60% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M)	2100	1400	1151.5	493.5
1M-SL50-SS30	50% slag, 50% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M)	1750	1750	1151.5	493.5
1M-SL60-SS30	60% slag, 40% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M)	1400	2100	1151.5	493.5
1M-SL70-SS30	70% slag, 30% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M)	1050	2450	1151.5	493.5
0.5M-SL30-SS30	30% slag, 70% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (0.5M)	2450	1050	1151.5	493.5
0.5M-SL40-SS30	40% slag, 60% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (0.5M)	2100	1400	1151.5	493.5
0.5M-SL50-SS30	50% slag, 50% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (0.5M)	1750	1750	1151.5	493.5
0.5M-SL60-SS30	60% slag, 40% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (0.5M)	1400	2100	1151.5	493.5
0.5M-SL70-SS30	70% slag, 30% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (0.5M)	1050	2450	1151.5	493.5
2M-SL50-SS40	50% slag, 50% Pozzolan, 40% sodium silicate, 60% sodium hydroxide (2M)	1750	1750	987	658
2M-SL50-SS20	50% slag, 50% Pozzolan, 20% sodium silicate, 80% sodium hydroxide (2M)	1750	1750	1316	329
1M-SL50-SS40	50% slag, 50% Pozzolan, 40% sodium silicate, 60% sodium hydroxide (1M)	1750	1750	987	658
1M-SL50-SS20	50% slag, 50% Pozzolan, 20% sodium silicate, 80% sodium hydroxide (1M)	1750	1750	1316	329
0.5M-SL50-SS40	50% slag, 50% Pozzolan, 40% sodium silicate, 60% sodium hydroxide (0.5M)	1750	1750	987	658
0.5M-SL50-SS20	50% slag, 50% Pozzolan, 20% sodium silicate, 80% sodium hydroxide (0.5M)	1750	1750	1316	329

Table 4.12 Mixture proportions of alkali activated natural Pozzolan/slag pastes (continued)

Mix id.	Mixture description	Materials, g			
		Natural Pozzolan	Slag	Sodium hydroxide	Sodium silicate
3M-SL30-SS30	30% slag, 70% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (3M)	2450	1050	1151.5	493.5
3M-SL50-SS30	50% slag, 50% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (3M)	1750	1750	1151.5	493.5
0M-SL30-SS30	30% slag, 70% Pozzolan, 30% sodium silicate, 70% water	2450	1050	1151.5	493.5
0M-SL50-SS30	50% slag, 50% Pozzolan, 30% sodium silicate, 70% water	1750	1750	1151.5	493.5

4.4.2. Results and discussion

Table 4.13 reports the fresh and strength properties of alkali-activated natural Pozzolan/slag pastes. It can be seen that except for mixture 2M-SL50-SS40 having 40% sodium silicate, the flow spreads of all designed mixtures were in the range of 5.72 to 15.24 cm. The setting time of 0.5, 1 and 2M mixtures were in acceptable range defined in section 4.1. The setting times of 3M pastes were not in the target range. The 7-day and 28–day compressive strengths were in the ranges of 15 to 50 MPa and 19 to 70 MPa, respectively.

Effects of mixture proportions and sodium hydroxide concentrations on properties of alkali-activated natural pozzolan/slag pastes are discussed in details in the following subsections.

Table 4.13 Fresh and strength properties of alkali-activated pastes having different combinations of slag and natural Pozzolan

Mix id.	Flow, cm	Initial set, min	Final set, min	Compressive strength, MPa	
				7 days	28 days
2M-SL30-SS30	10.16	125	200	40.6	55.5
2M-SL40-SS30	11.11	120	200	44.2	62.3
2M-SL50-SS30	11.43	110	195	46.8	65.1
2M-SL60-SS30	12.70	120	195	48.0	59.2
2M-SL70-SS30	12.70	120	175	40.4	41.9
1M-SL30-SS30	10.80	170	310	39.0	52.7
1M-SL40-SS30	12.07	170	310	41.4	54.1
1M-SL50-SS30	12.70	160	263	41.6	53.1
1M-SL60-SS30	13.65	165	260	40.7	49.3
1M-SL70-SS30	13.34	145	210	37.4	41.2
0.5M-SL30-SS30	11.43	320	440	38.7	52.1
0.5M-SL40-SS30	12.70	280	420	41.3	52.1
0.5M-SL50-SS30	13.65	230	340	39.1	50.7
0.5M -SL60-SS30	14.41	225	305	36.0	49.8
0.5M -SL70-SS30	13.97	185	255	34.0	41.2
2M-SL50-SS40	1.27	48	112	48.9	49.4
2M-SL50-SS20	13.97	95	145	25.6	36.8
1M-SL50-SS40	5.72	90	230	51.9	64.9
1M-SL50-SS20	15.24	110	150	17.1	24.1
0.5M-SL50-SS40	8.26	140	370	49.4	70.0
0.5M-SL50-SS20	15.24	110	155	15.0	19.8
3M-SL30-SS30	6.35	66	123	42.7	59.0
3M-SL50-SS30	6.35	85	135	56.1	68.3
0M-SL30-SS30	6.35	360	500	26.1	50.3
0M-SL50-SS30	8.89	350	445	33.8	46.8

4.4.2.1. Effect of binder combinations (natural Pozzolan and slag contents)

Figure 4.6 shows the effects of binder combinations on the workability of alkali-activated natural Pozzolan/slag pastes. Overall, increases in slag contents improved the workability of alkali-activated pastes. On average, the flow increased by 1.2, 0.6, and 1 cm when slag content was increased from 30 to 40, 40 to 50, and 50 to 60% of the total binder, respectively. The flow of pastes with slag contents of 60 and 70% was nearly similar. The observed increases can be related to the high water demand of the used natural Pozzolan. The natural Pozzolan used in this phase had a water demand of 103%.

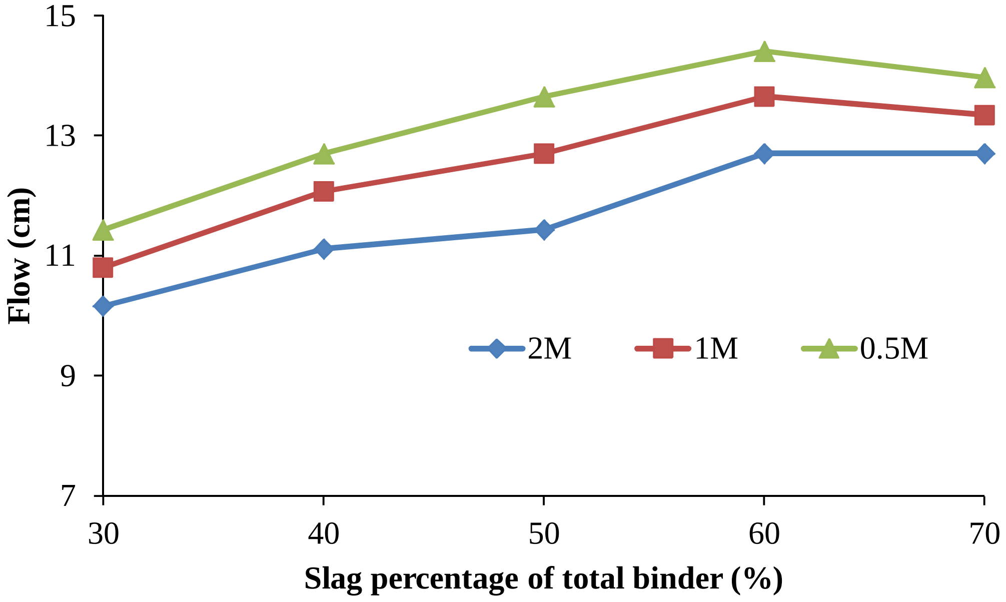


Figure 4.6 Effects of binder combination on the flow of alkali-activated natural pozzolan/slag pastes

Figures 4.7 and 4.8 present the initial and final setting times of alkali-activated pastes having different amounts of slag and natural Pozzolan. These results are also reported in Table 4.13. In general, increases in slag content (reduction of natural Pozzolan dosage) resulted in faster setting times. The reductions in setting times were more significant in case of mixtures with low sodium hydroxide concentrations (0.5M). The reductions were negligible when higher NaOH molarities were used, in particular 2M.

For 0.5M mixtures, the initial setting time was reduced by 12.5, 17.9, 2.2 and 17.8% when slag content was increased from 30 to 40, 40 to 50, 50 to 60, and 60 to 70%, respectively. For similar changes in slag contents, the final setting times decreased by 4.5, 19, 10.3 and 16.4%, respectively. In case of pastes with molarities of 1 and 2M, while the setting times slightly reduced with increases in the dosage of slag in the mixtures, the setting times were almost in the same ranges. Increases in the molarity of sodium hydroxide to 3M resulted in an almost opposite trend. The 3M paste with 30% slag content (mixture 3M-SL30-SS30) had slightly higher setting time than similar paste having 50% slag (mixture 3M-SL50-SS30).

The observed reductions in setting time by increasing slag content can be related to the higher reactivity of slag in comparison with that of natural Pozzolan. The higher alkalinity, however, was able to increase the initial reactivity of natural Pozzolans. This can be clearly seen in the results of hydration heat shown in Figures 4.9 to 4.12.

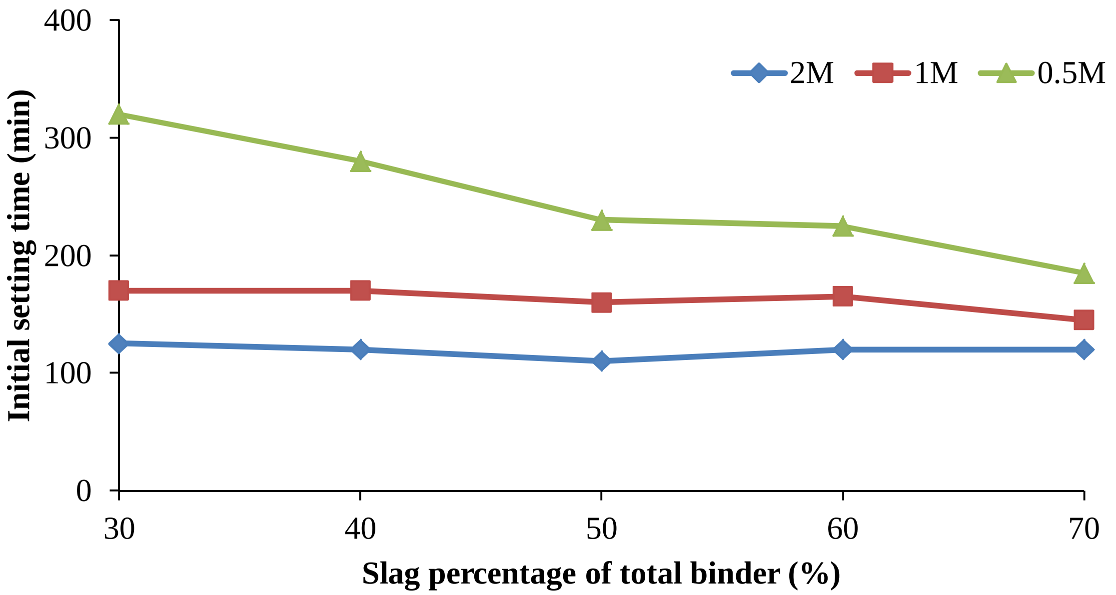


Figure 4.7 Effects of binder combination on the initial setting time of alkali-activated natural pozzolan/slag pastes

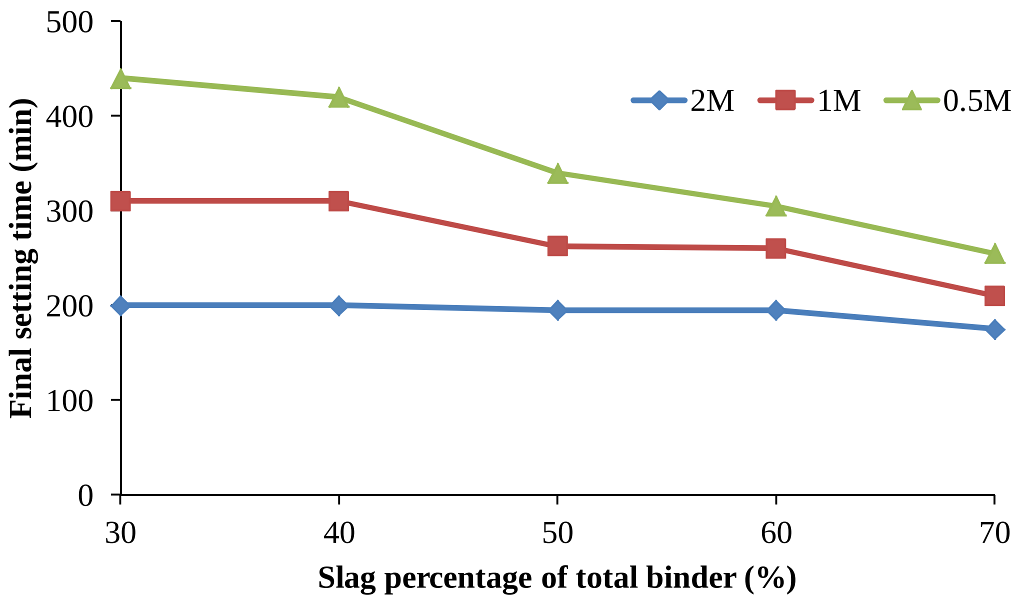


Figure 4.8 Effects of binder combination on the final setting time of alkali-activated natural pozzolan/slag pastes

Heat of hydration of a group of mixtures was also measured. The temperatures of alkali-activated natural pozzolan/slag pastes for a duration of 2 days are shown in Figures 4.9 and 4.10 for 2 and 0.5M mixtures, respectively. The peak temperature and time of reach the peak are presented in Figures 4.11 and 4.12, respectively. It can be seen in Figures 4.9 and 4.10 that the peak temperature shifted to the up and left side of the plots with increases in slag content. This observation shows that use of higher slag contents led to generation of more heat and acceleration of chemical reactions.

For 2M alkali activated natural pozzolan/slag pastes, the maximum temperature occurred at 8.33, 5.97 and 4.97 hr for mixtures having 30, 50 and 70% slag, respectively. For similar slag contents, these peaks happened at 23.63, 11.01 and 7.23 hr for 0.5M mixtures, respectively. These observations proved that the reactions were accelerated by increases in slag content which coincided with the results obtained for setting times. It can also be seen that while there was an almost 16 hr difference between 0.5M mixtures having 30 and 70% slag to reach their peak temperature, this difference was narrowed to almost 3 hr for 2M alkali-activated natural pozzolan/slag pastes.

In addition, it was observed that the peak temperature increased by increasing slag content and reducing natural Pozzolan content. There was a significant increase in peak temperature when slag content increased from 30 to 50%. For this increase, the maximum temperature increased by almost 9 and 5.5°C for 2 and 0.5M mixtures, respectively. The increase in peak temperature was insignificant when slag content was increased from 50 to 70%. On average, the maximum temperature of alkali-activated pastes having 70% slag was 1.3°C more than that of pastes having 50% slag.

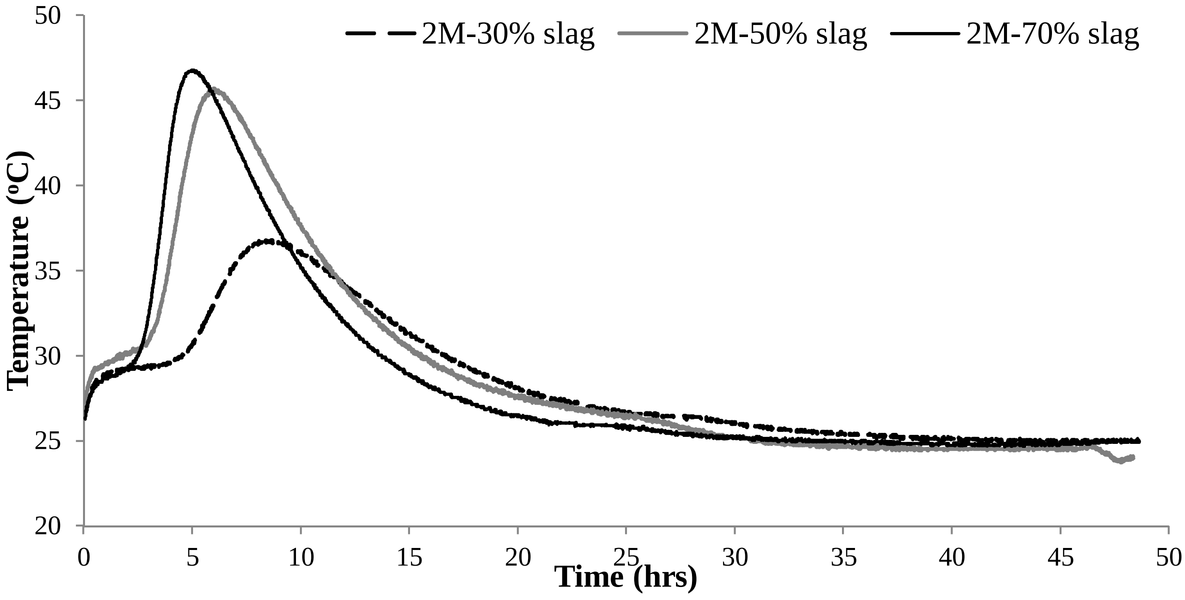


Figure 4.9 The heat of hydration of alkali-activated natural Pozzolan/slag pastes having different binder combinations and sodium hydroxide concentration of 2M

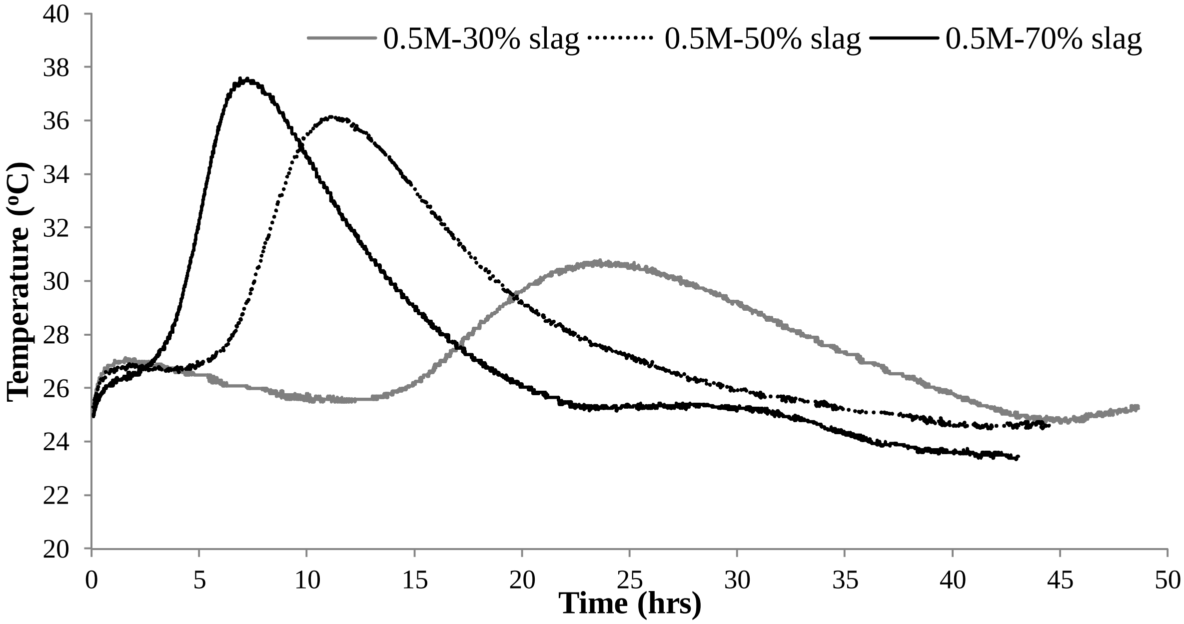


Figure 4.10 The heat of hydration of alkali-activated natural Pozzolan/slag pastes having different binder combinations and sodium hydroxide concentration of 0.5M

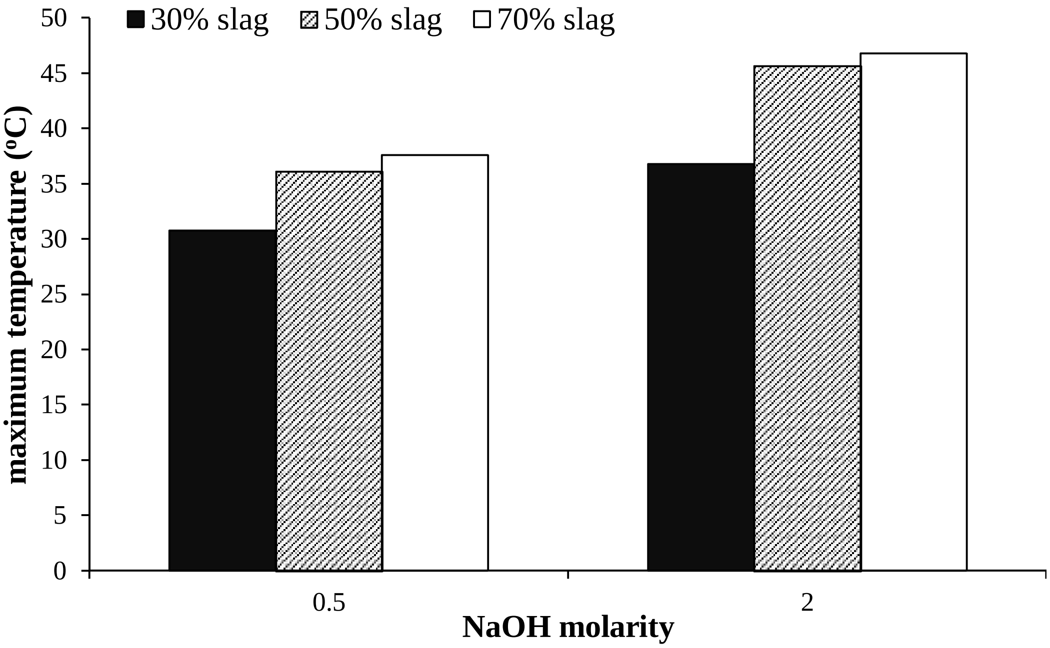


Figure 4.11 The peak temperature for alkali-activated natural pozzolan/slag pastes having different slag contents

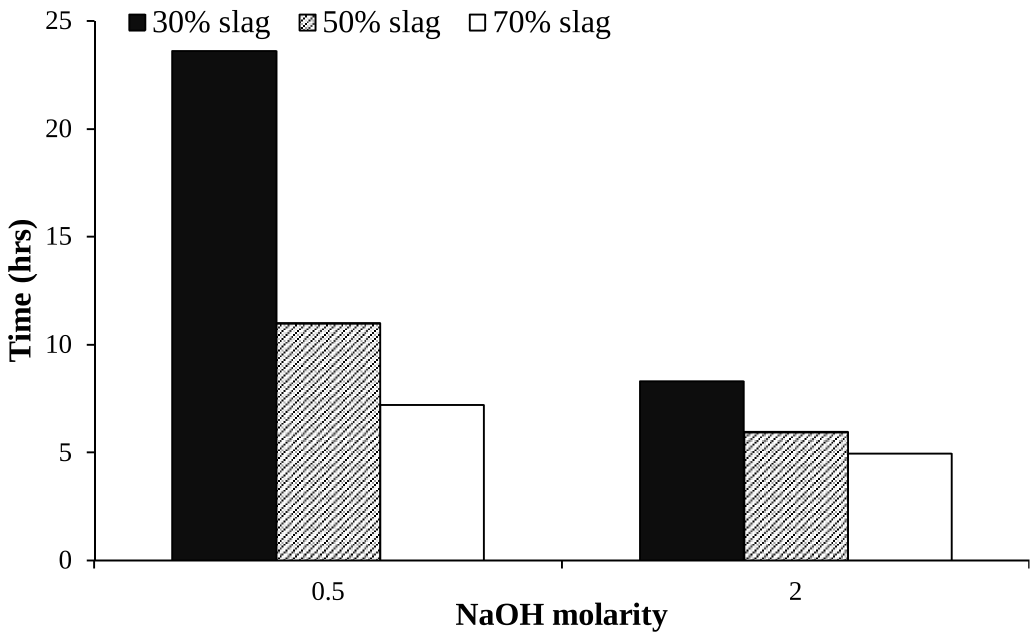


Figure 4.12 Time to reach peak temperature for alkali-activated natural pozzolan/slag pastes with different slag contents

Figures 4.13 and 4.14 show the 7- and 28-day compressive strengths of alkali-activated natural pozzolan/slag pastes having different slag contents, respectively. It can be seen that there was an optimum combination of slag and natural Pozzolan which was dependent on the molarity of sodium hydroxide solution; the optimum slag content increased with increases in sodium hydroxide concentration.

In case of pastes with sodium hydroxide concentration of 0.5M, the optimum amounts of slag was around 40% (60% natural Pozzolan). The 7-day compressive strength of 0.5M mixtures increased 6.7%, when slag content was increased from 30 to 40%, after which it reduced by 5.3, 8.0 and 5.5% when slag content was increased from 40 to 50, 50 to 60 and 60 to 70%, respectively. It’s not doable to find the exact optimum percentage (mathematically optimum content), but it can be inferred that the optimum dosage of slag was about 40% of the total binder. Similarly, there was reduction in the 28-day compressive strengths of 0.5M mixtures when slag content was beyond 40%.

When sodium hydroxide concentration was increased to 1 and 2M, the optimum slag percentage increased to the range of 40 to 60%. For these molarities, the compressive strength increased when slag content was increased from 30 to 40%. The compressive strengths for slag contents of 40, 50 and 60% were almost similar. It, however, considerably decreased by increasing slag content to 70%.

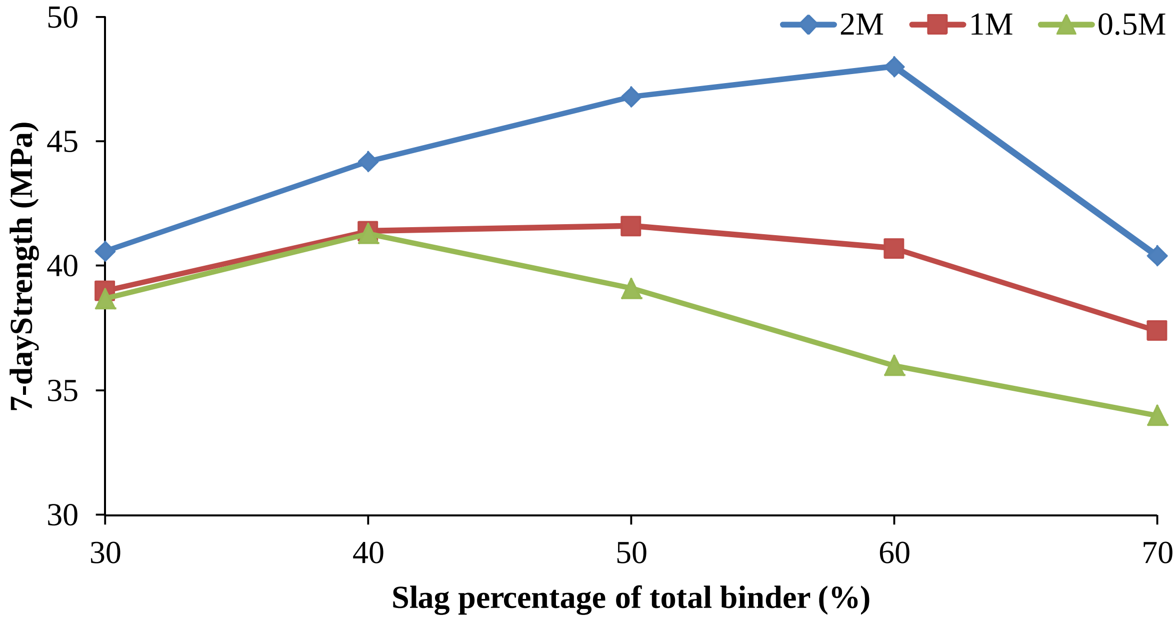


Figure 4.13 The 7-day compressive strength of alkali-activated natural pozzolan/slag pastes having different binder combinations

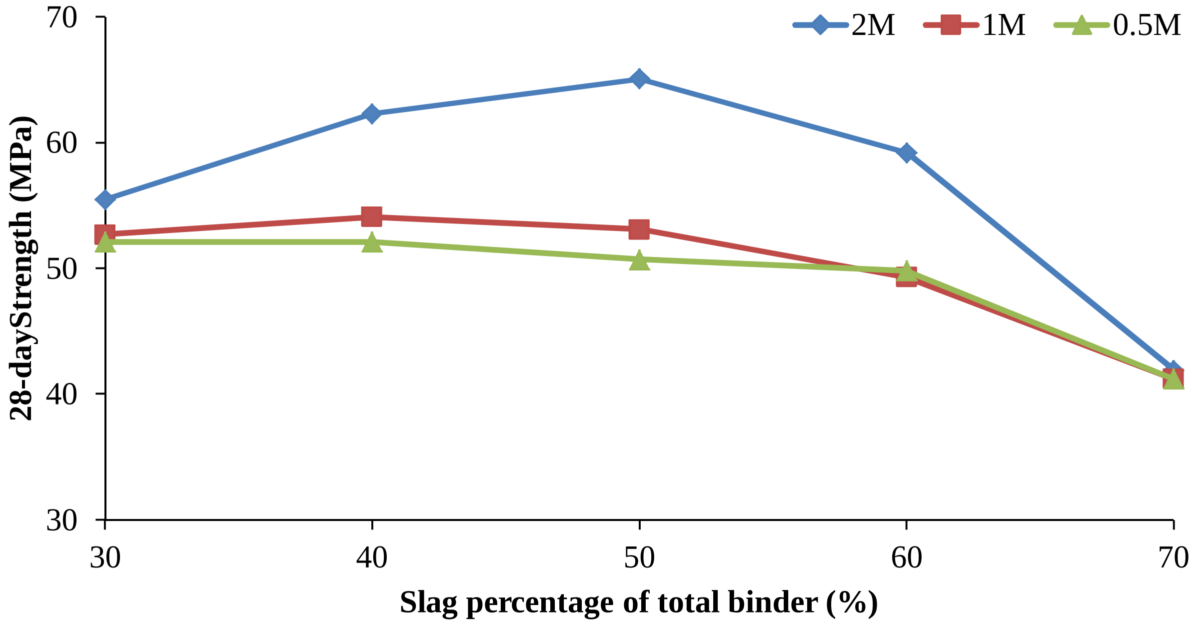


Figure 4.14 The 28-day compressive strength of alkali-activated natural pozzolan/slag pastes having different binder combinations

Absorption and drying shrinkage tests were also conducted on a group of mixtures with different slag and natural Pozzolan contents. Table 4.14 documents the results of absorption test. While the absorption and volume of permeable voids were almost similar for mixtures having 30 and 50% slag, these values considerably increased by increasing the slag content to 70%. This observation was more significant for 0.5M mixtures. The close performance of pastes having 30 and 50% slag and the worst performance of pastes having 70% slag matched with the results of compressive strength.

The density of alkali-activated natural pozzolan/slag pastes also increased with increases in slag contents. This increase can be related to the higher specific gravity of slag (2.87) in comparison with that of natural Pozzolan (2.29).

Table 4.14 Results of absorption test for alkali-activated natural pozzolan/slag pastes

Measured property	Ref IV-PC	0.5 M			2M		
		Slag content, %					
		30	50	70	30	50	70
Absorption after immersion, %	15.43	19.54	19.86	22.09	17.88	18.33	19.06
Absorption after immersion and boiling, %	15.73	20.36	20.72	22.85	19.34	19.10	19.91
Bulk density, dry	1.79	1.51	1.54	1.53	1.55	1.58	1.59
Bulk density after immersion	2.07	1.81	1.85	1.87	1.82	1.87	1.90
Bulk density after immersion and boiling	2.07	1.82	1.86	1.88	1.84	1.89	1.91
Apparent density	2.49	2.19	2.26	2.36	2.20	2.27	2.33
Volume of permeable voids, %	28.14	30.81	31.92	35.05	29.89	30.26	31.74

Figure 4.15 shows the results of drying shrinkage test for alkali-activated natural pozzolan/slag pastes. It can be seen that increases in slag content significantly reduced the drying shrinkage. For mixtures with NaOH concentration of 2M, the ultimate drying shrinkage of

mixtures having 50 and 70% slag was almost 27 and 37% lower than that of paste with 30% slag content, respectively. Similarly, the ultimate drying shrinkage of 0.5M mixtures containing 50 and 70% slag was 38 and 53% lower than that of mixture having 30% slag, respectively. It was also observed that alkali-activated natural pozzolan/slag pastes having 30% slag (70% natural Pozzolan) reached their ultimate shrinkage in almost a month, whereas the shrinkage happened gradually for mixtures having 50 and 70% slag.

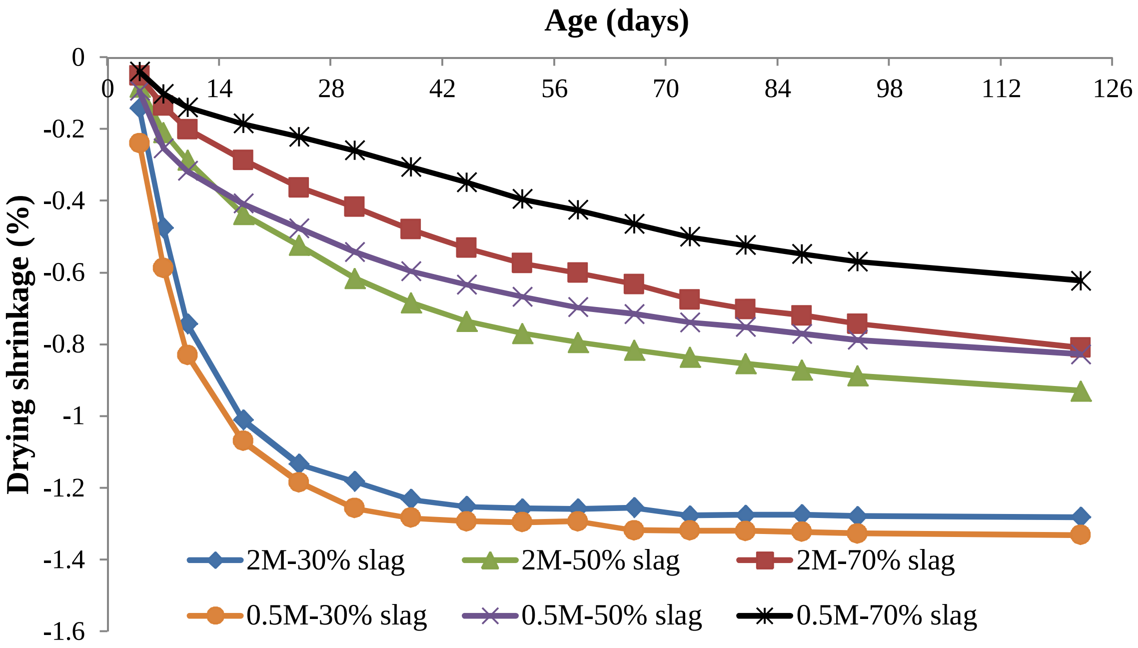


Figure 4.15 The drying shrinkage of alkali-activated natural pozzolan/slag pastes

4.4.2.2. Effect of sodium hydroxide concentration

The influences of sodium hydroxide molarity on properties of alkali-activated natural pozzolan/slag pastes are presented in this section. The selected NaOH concentrations were 0.5, 1, 2 and 3M for two groups of mixtures with slag-to-binder ratios of 0.3 and 0.5.

Figure 4.16 shows effects of sodium hydroxide concentration on the workability of alkali-activated natural Pozzolan/slag pastes. It can be seen that the flow of pastes activated with sodium hydroxide and sodium silicate was higher than those activated with water and sodium silicate; meaning that use of sodium hydroxide increased the workability. However, the workability reduced when sodium hydroxide molarity increased. The increase in flow by inclusion of sodium hydroxide was also observed for Portland cement and alkali-activated mixtures by different researchers (Jolicoeur et al. 1992, Smaoui et al. 2005, Li et al. 2016) which will be discussed in next chapter. The reduction in flow due to the increases in molarity of sodium hydroxide can be related to the amount of alkaline and water in the prepared solution. An increase in the sodium hydroxide concentration allowed for more sodium hydroxide pellets and less free water for a given volume, resulting in the reduction of flow.

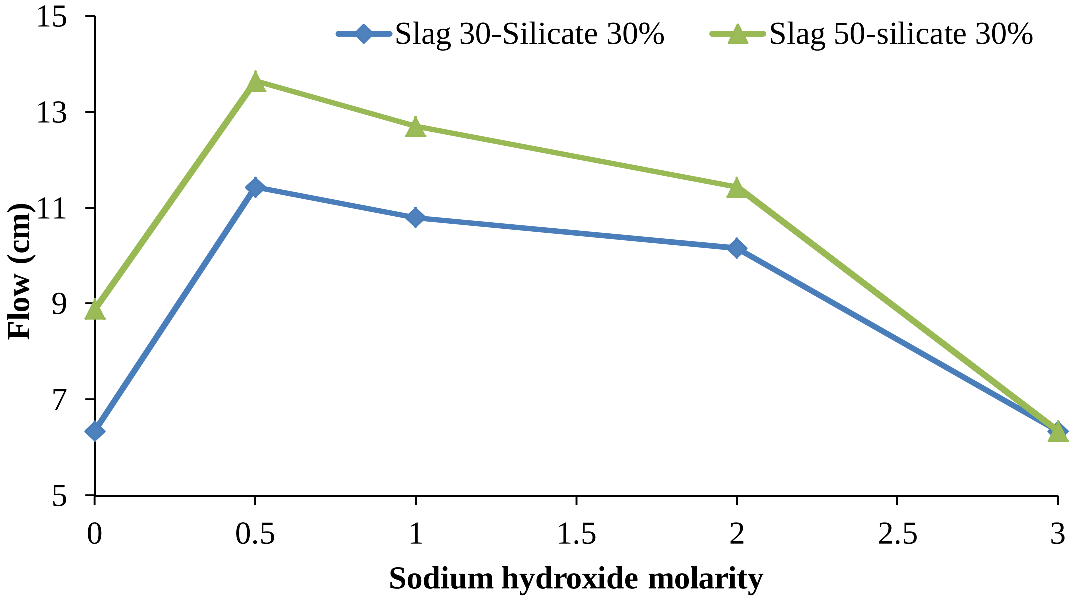


Figure 4.16 The flow of alkali-activated natural pozzolan/slag pastes having different NaOH molarities

The initial and final setting times of alkali-activated natural pozzolan/slag pastes with different sodium hydroxide concentrations are presented in Figures 4.17 and 4.18, respectively. The initial setting times reduced by averagely 22.7, 38.7, 28.9 and 35.0%, when NaOH molarity was increased from 0 to 0.5, 0.5 to 1, 1 to 2 and 2 to 3, respectively. For similar increases in molarity, the final setting times reduced by averagely 17.8, 26.1, 30.7 and 34.6%, respectively. As presented earlier, when sodium hydroxide concentration was increased from 3 to 5M, the initial and final setting times decreased by 85.1 and 76.3%, respectively. The reason for the observed reductions is acceleration of reaction process due to the higher alkaline environment. The accelerated initial activity by increasing NaOH concentration can be corroborated from the results of hydration heat presented in Figure 4.19.

Figure 4.19 shows the heat of hydration of 0.5, 2, 3 and 5M pastes having slag-to-total binder ratio of 0.3. The acceleration trend through inclusion of NaOH with higher concentrations can be clearly detected in this figure. As NaOH molarity was increased, the reactions happened faster, thus generating more heat and quicker setting times. Figures 4.9 through 4.12 also showed the heat of hydration of alkali-activated natural pozzolan/slag pastes having 0.5 and 2M sodium hydroxide concentrations for different binder combinations. It can be seen that the peak temperature increased and accelerated when NaOH molarity was increased from 0.5 to 2M for all different slag and natural Pozzolan contents. For alkali-activated pastes with slag contents of 30, 50 and 70%, the maximum temperature of 2M mixtures were 6.0, 9.6 and 9.2°C higher than those of 0.5M, respectively. For similar slag contents, the time to reach peak temperature reduced from 23.625 to 8.325, 11.008 to 5.967, and 7.225 to 4.967 hr when sodium hydroxide concentration was increased from 0.5 to 2M, respectively.

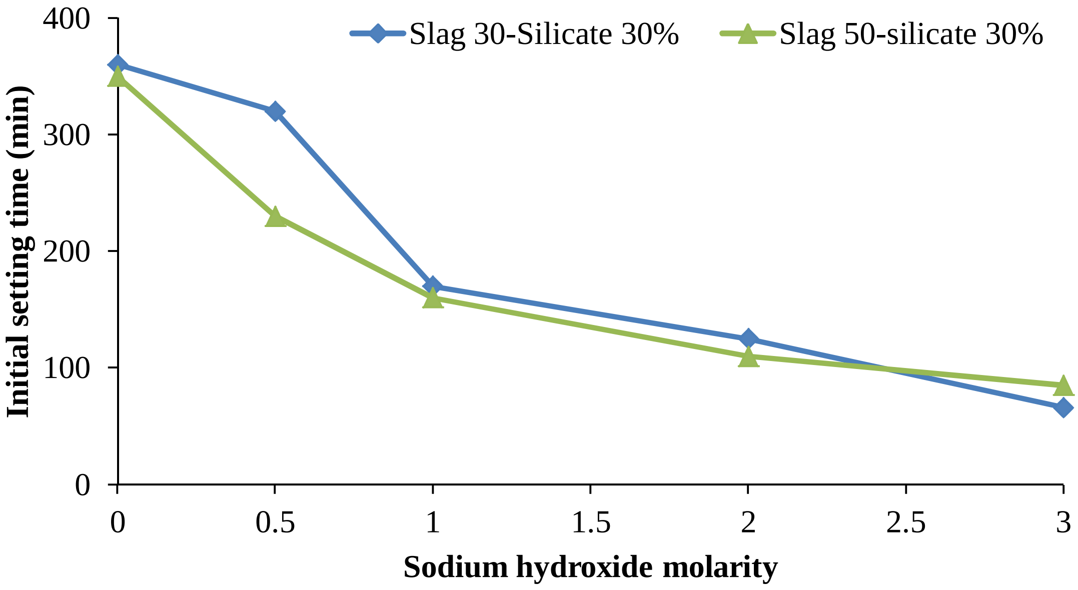


Figure 4.17 The initial setting time of alkali-activated natural pozzolan/slag pastes having different NaOH molarities

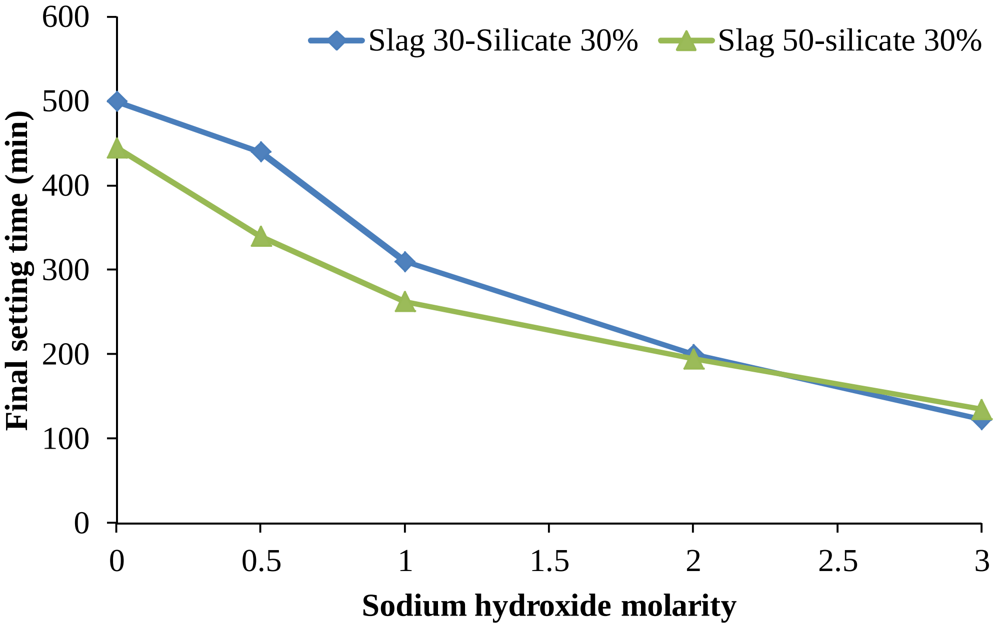


Figure 4.18 The final setting time of alkali-activated natural pozzolan/slag pastes having different NaOH molarities

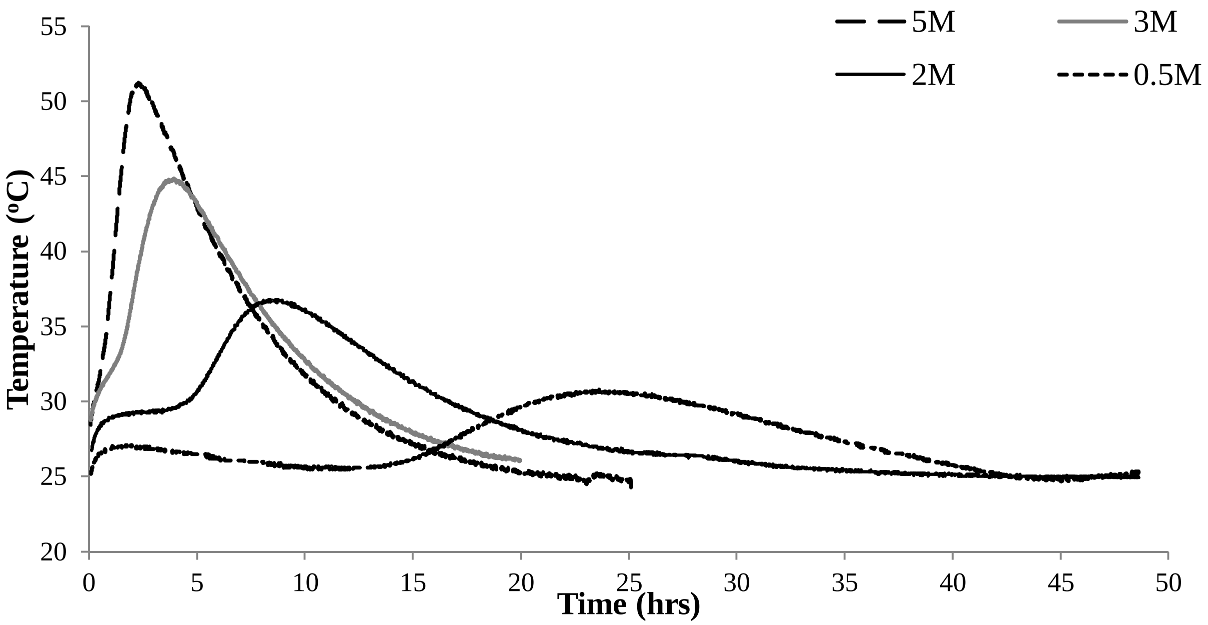


Figure 4.19 The effects of NaOH concentration on the heat of hydration

Figures 4.20 and 4.21 present the 7- and 28-day compressive strengths of alkali-activated natural pozzolan/slag pastes having different NaOH concentrations, respectively. It can be seen that increases of sodium hydroxide concentrations led to slight increases in compressive strengths of pastes having 30% slag (and 70% natural Pozzolan). For these mixtures, the 7-day compressive strength of alkali-activated natural pozzolan/slag pastes increased by averagely 48.0, 0.7, 4.2 and 5.1%, when sodium hydroxide concentration was increased from 0 to 0.5, 0.5 to 1, 1 to 2, and 2 to 3M, respectively. For similar increases, the 28-day compressive strength increased by averagely 3.6, 1.3, 5.2 and 6.3%, respectively. In these figures and Figures 4.14 and 4.15, it can be seen that increases in molarity of sodium hydroxide was more effective in strength development of mixtures having higher slag contents. The compressive strengths of pastes having 50% slag increased by averagely 12.2, 5.5, 17.5, and 12.5% when sodium hydroxide concentration was increased from 0 to 0.5, 0.5 to 1, 1 to 2, and 2 to 3M, respectively. The observed increases can be related to availability of more alkaline for activation processes.

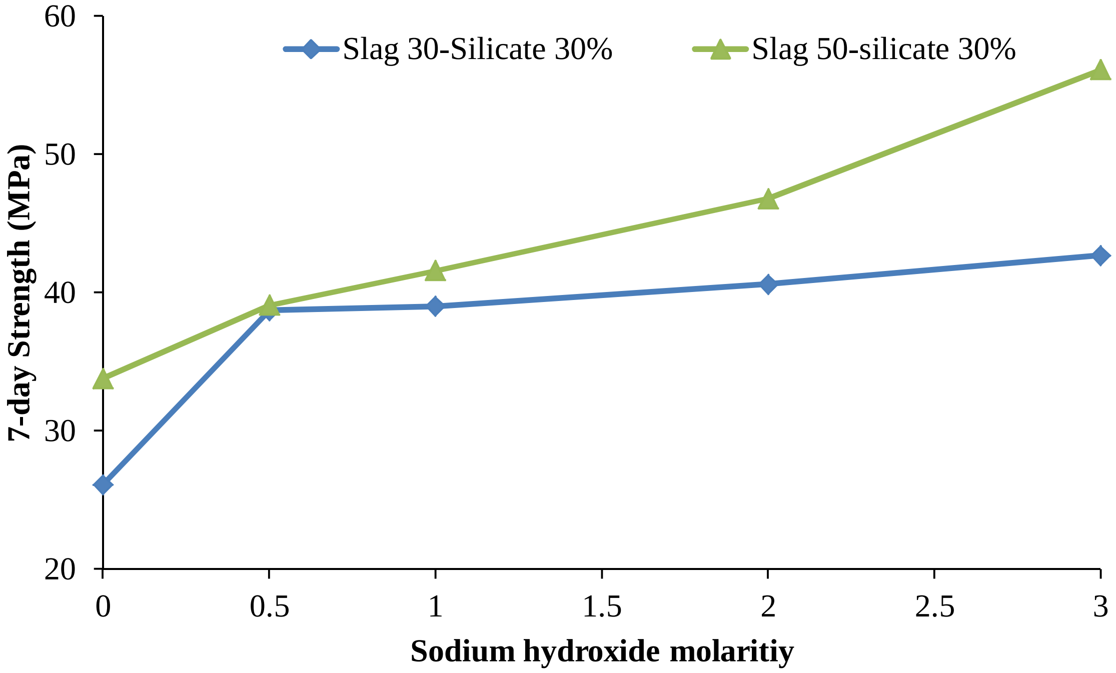


Figure 4.20 The 7-day compressive strength of alkali-activated natural pozzolan/slag pastes having different sodium hydroxide concentrations

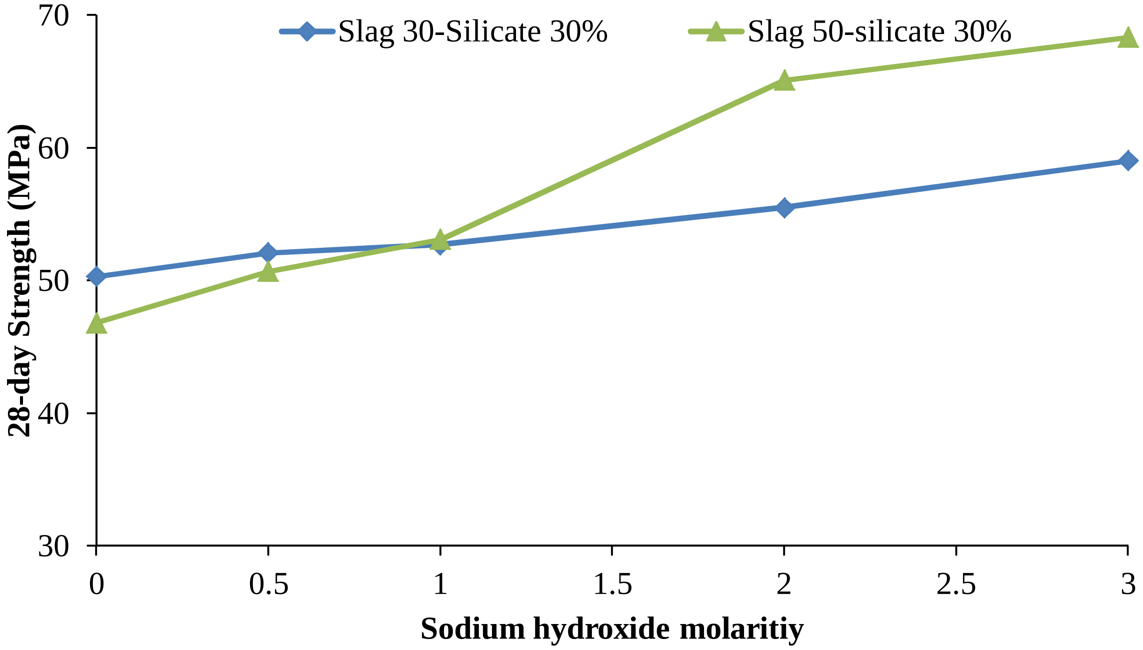


Figure 4.21 The 28-day compressive strength of alkali-activated natural pozzolan/slag pastes having different sodium hydroxide concentrations

The results of absorption test are shown in Table 4.14 for a group of mixtures having different sodium hydroxide concentrations. It can be seen that while the results of 0.5 and 2M pastes were close, 2M mixtures had slightly lower absorption and volume of permeable voids than those of 0.5M mixtures. These reductions were more significant for mixtures with higher slag contents. From these observations and the compressive strength results, it can be inferred that sodium hydroxide affected slag more than natural Pozzolan.

The shrinkage of alkali-activated natural pozzolan/slag pastes having sodium hydroxide concentrations of 0.5 and 2M are presented in Figure 4.15. In general, the drying shrinkages of alkali-activated natural pozzolan/slag pastes were close for these molarities. However, mixtures having 0.5M had slightly lower drying shrinkage than 2M mixtures.

4.4.2.3. Effect of alkaline activator combinations (sodium hydroxide and sodium silicate contents)

The effects of alkaline activator combinations on properties of alkali-activated natural pozzolan/slag pastes are presented in this section. For this purpose, the sodium silicate contents of 20, 30 and 40% were used; these dosages corresponded to sodium hydroxide contents of 80, 70 and 60%, respectively.

Figure 4.22 shows effects of sodium silicate and sodium hydroxide contents on the workability of alkali-activated natural pozzolan/slag pastes. It can be seen that the flow reduced as sodium silicate dosage was increased. The reduction was more significant when sodium silicate content was increased from 30 to 40% than when it was increased from 20 to 30%. The flow of alkali-activated natural pozzolan/slag pastes reduced by 1.6, 2.5 and 2.5 cm when sodium silicate content increased from 20 to 30% for mixtures having 0.5, 1 and 2M sodium hydroxide, respectively. For pastes with similar sodium hydroxide concentrations, these reductions were 5.4, 7 and 10.2 cm when sodium silicate content increased from 30 to 40%, respectively.

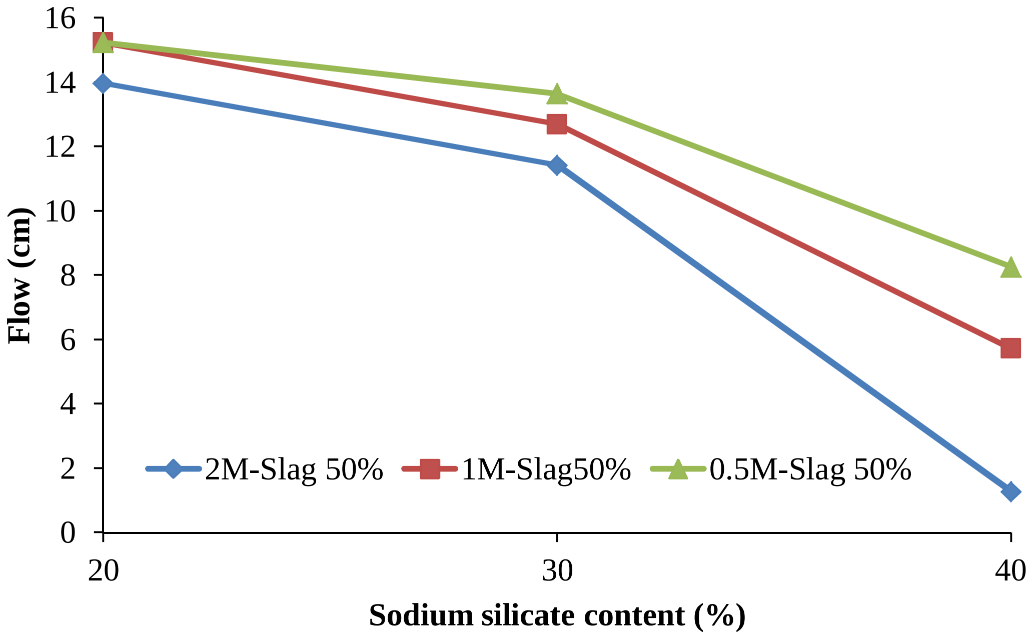


Figure 4.22 Effects of sodium silicate and sodium hydroxide contents on the workability

The results of initial and final setting times are presented in Figures 4.23 and 4.24, respectively. Overall, alkali-activated natural pozzolan/slag pastes with 30% sodium silicate content had higher setting times than those having 20 and 40% sodium silicate. The trend was also dependent on sodium hydroxide concentration. As molarity of sodium hydroxide increased, the observed differences between setting times of mixtures with 30% sodium silicate and mixtures having 20 and 40% sodium silicate were narrowed.

The initial setting time of 0.5M mixtures was almost tripled when sodium silicate dosage was increased from 20 to 30%. Further increases in sodium silicate content from 30 to 40% reduced the initial setting time of 0.5M mixtures by 39%. In case of 1 and 2M mixtures, the initial setting time of pastes with 30% sodium silicate were 45.5 and 15.8% higher than those of mixtures having 20% sodium silicate, respectively. Increases in sodium silicate content from 30 to 40% resulted in 56.3 and 43.8% reduction in initial setting time of 1 and 2M mixtures, respectively.

Similarly, the final setting times increased by increases in sodium silicate dosage from 20 to 30%. The final setting time increased by 119.3, 75.3 and 34.5% for 0.5, 1 and 2M mixtures, when the sodium silicate to total activator ratio increased from 0.2 to 0.3, respectively. Further increases of sodium silicate content (from 30 to 40%) reduced the final setting time. The reduction was 12.5 and 42.5% for 1 and 2M, respectively. In case of 0.5M, however, the difference was insignificant between mixtures having 30 and 40% sodium silicate.

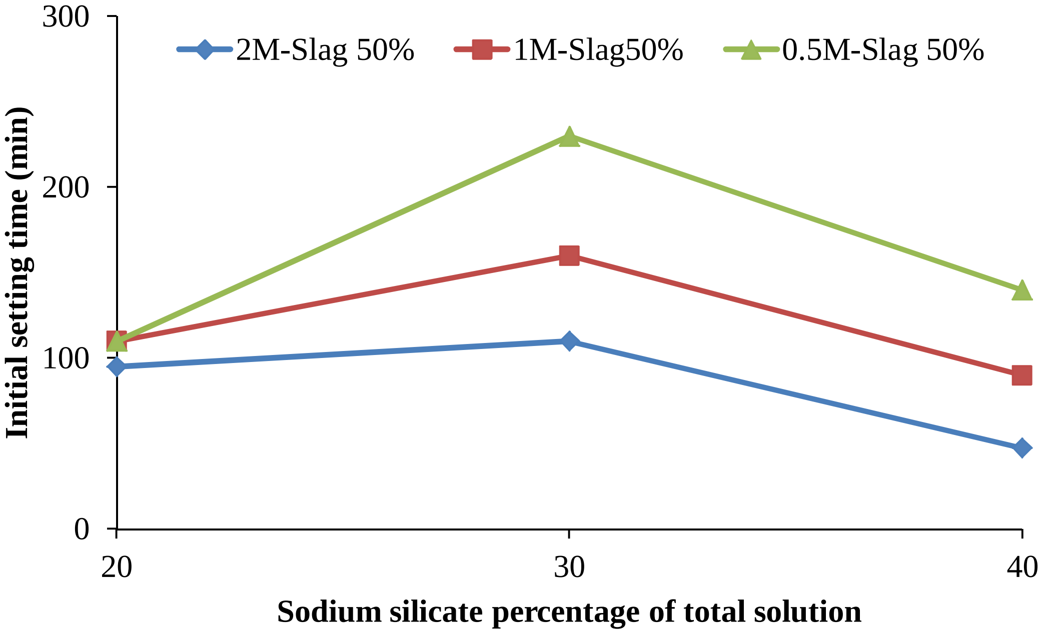


Figure 4.23 Effects of sodium silicate and sodium hydroxide contents on the initial setting time

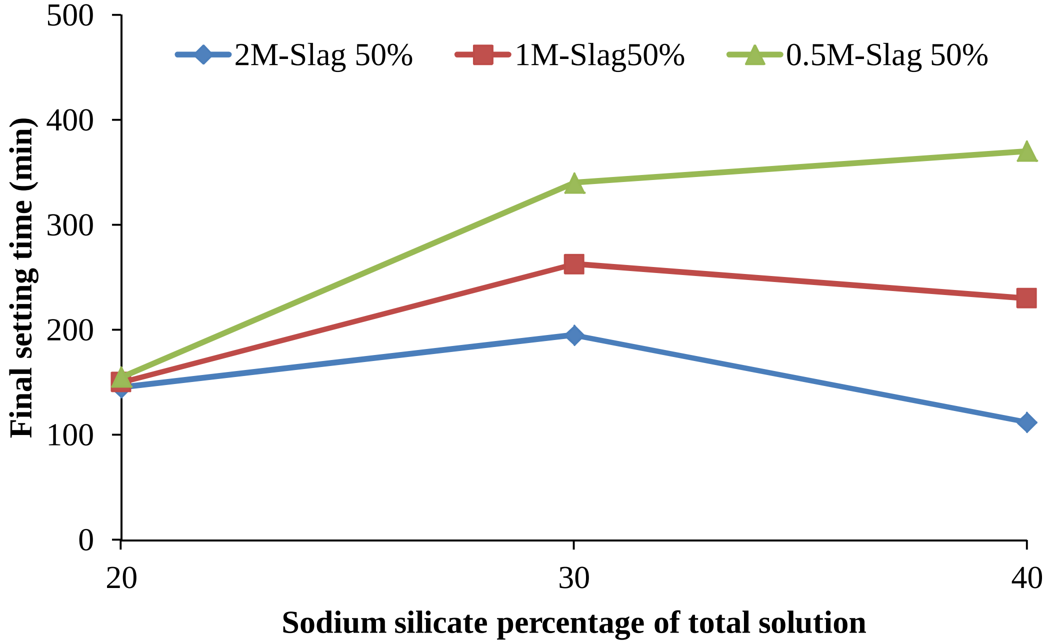


Figure 4.24 Effects of sodium silicate and sodium hydroxide contents on the final setting time

Figures 4.25 and 4.26 show the 7- and 28-day compressive strengths of alkali-activated natural pozzolan/slag pastes having different sodium silicate contents, respectively. In general, increases in sodium silicate content led to significant strength improvements. The compressive strength of 0.5, 1 and 2M mixtures increased by averagely 158.6, 132.3 and 80.0%, when sodium silicate content was increased from 20 to 30%, respectively. These increases led the 28-day compressive strength to rise from 19.8, 24.1 and 36.8 MPa to 50.7, 53.1 and 65.1 MPa for NaOH concentrations of 0.5, 1 and 2M, respectively.

The increases in sodium silicate contents from 30 to 40% resulted in averagely 32.1 and 23.5% increases in compressive strength of 0.5 and 1M mixtures, respectively. For 2M mixtures, however, this increase of sodium silicate content resulted in strength reduction which was due to the loss of flow and insufficient compaction. The flow of 2M mixtures having 40% sodium silicate (2M-SL50-SS40) was around 1.27 cm which made the compaction difficult. Due to the low workability, the samples didn't compact properly, which in turn resulted in varied strengths within the samples. However, it was clear that if sufficient flow could have been provided, the strength of 40% sodium silicate contained pastes could be higher than that of 30% sodium silicate contained pastes.

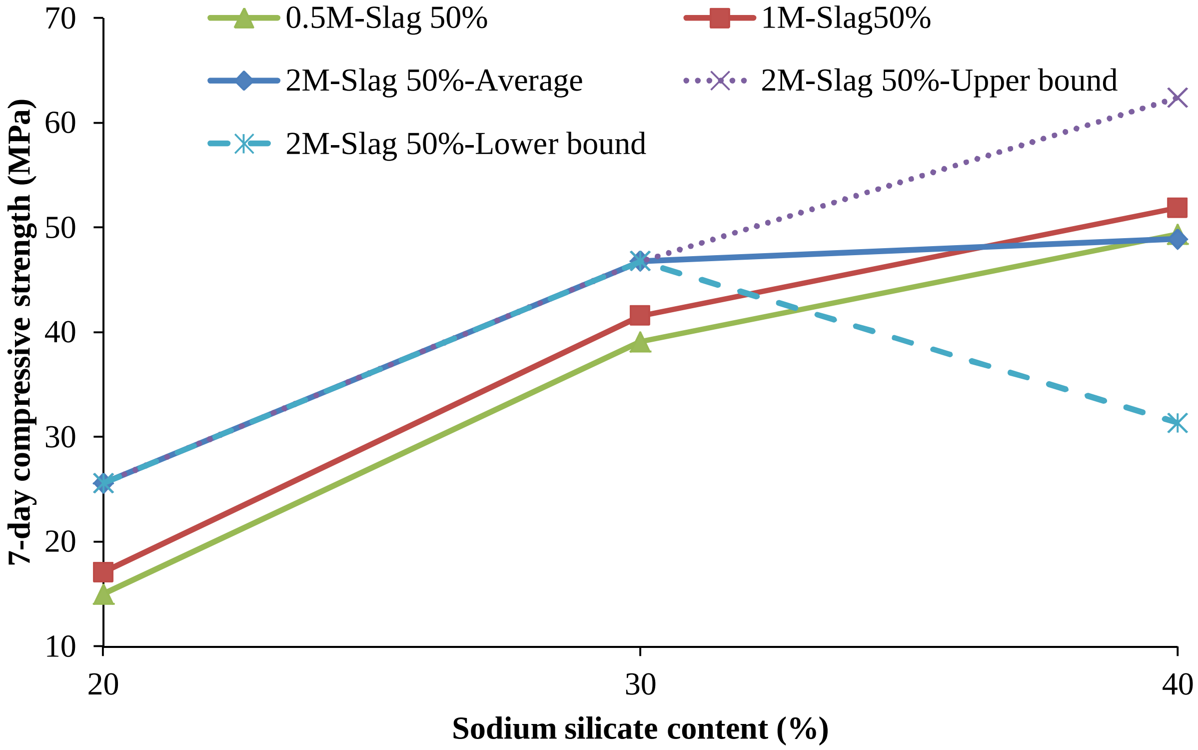


Figure 4.25 Effect of activator combination on the 7-day compressive strength

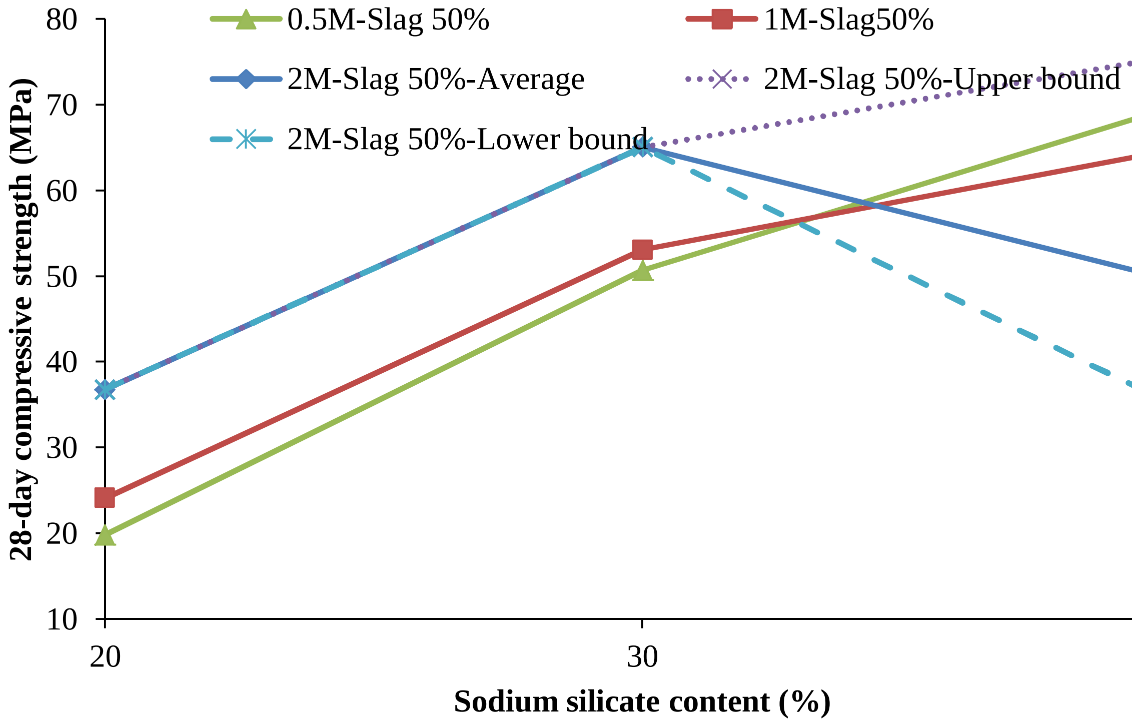


Figure 4.26 Effect of activator combination on the 28-day compressive strength

4.5. Comparison with Portland cement pastes

As mentioned earlier, the flow of 0.5, 1 and 2M alkali-activated natural pozzolan/slag pastes with 20 and 30% sodium silicate was in the range of 10.16 to 15.24 cm. Their initial and final setting times were in the ranges of 215±105 and 307.5±132.5 minutes, respectively. The flow, initial setting time and final setting times for reference Portland cement paste (shown in Table 4.2) were 11.87 cm, 154 minutes and 231 minutes, respectively. From these results, it can be deduced that the designed alkali-activated natural pozzolan/slag pastes had flow and setting times in the same ranges of those of Portland cement paste.

The 28–day compressive strengths of alkali-activated natural pozzolan/slag pastes were in the ranges of 19 to 70 MPa, whereas this value was about 75 MPa for Portland cement paste. Although the Portland cement paste had high strength due to its low w/c, there were a number of alkali-activated natural pozzolan/slag pastes producing nearly similar strengths using S/B of 0.47. It’s obvious that higher strengths can be developed with reduction of S/B (through use of sodium gluconate or development of high range water reducers for alkali-activated binders) which wasn’t within the scope of this research. Also, it’s worth mentioning that if Portland cement paste was designed with a higher w/c (closer to S/B of alkali-activated natural pozzolan/slag pastes), it would most likely develop lower strengths.

The heat of hydration of Portland cement paste was also measured and the results are presented in Figure 4.27. It can be seen that the peak temperature of Portland cement paste (almost 80°C) was significantly higher than that of alkali-activated natural pozzolan/slag pastes (30 to 50°C). The peak temperature of Portland cement paste occurred at almost 6.93 hr which was close to that of 2M alkali-activated paste.

The results of absorption test for Portland cement paste are reported in Table 4.14. It can be seen that the volume of permeable voids of Portland cement paste was averagely 7% lower than that of 2M mixtures. The density of Portland cement paste was also 10 to 15% higher than that of alkali-activated natural pozzolan/slag pastes.

The drying shrinkage of Portland cement paste was also measured. Its ultimate drying shrinkage is presented in Figure 4.28 along with those of alkali-activated natural pozzolan/slag pastes. It was seen that alkali-activated pastes having 30, 50 and 70% slag shrank averagely 4, 2.7 and 2.2 times of the reference Portland cement paste, respectively.

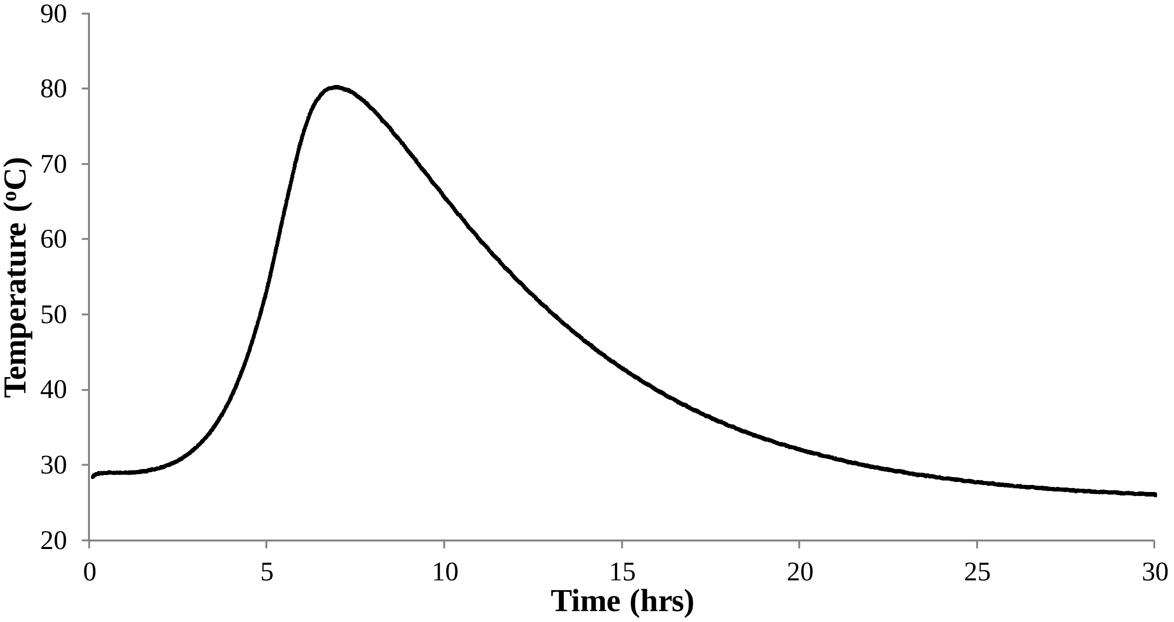


Figure 4.27 The heat of hydration of Portland cement paste

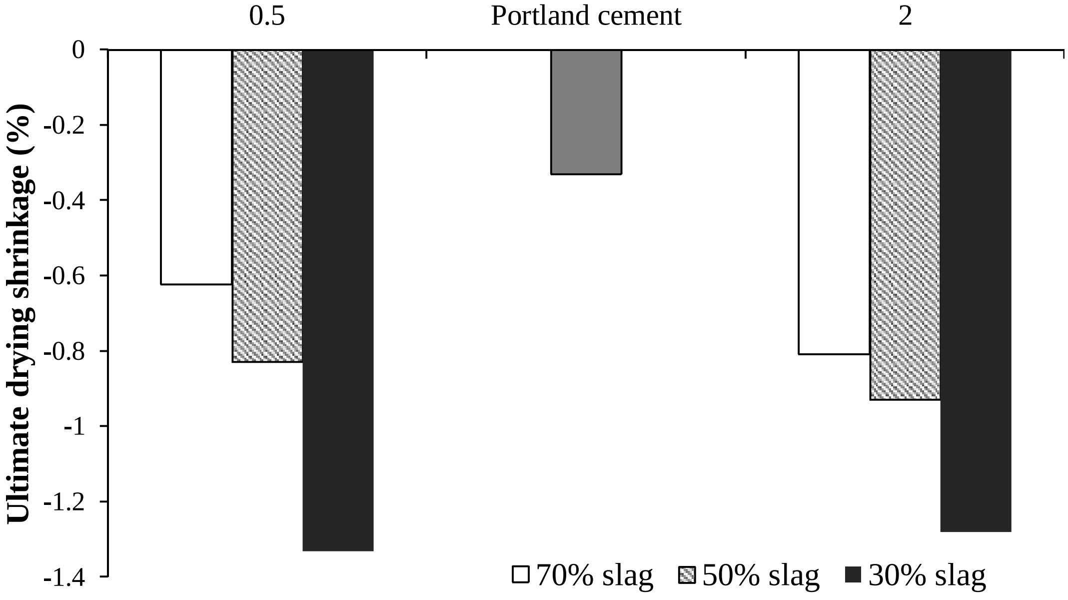


Figure 4.28 The ultimate drying shrinkage of Portland cement and alkali-activated natural pozzolan/slag pastes

CHAPTER 5- ALKALI-ACTIVATED NATURAL POZZOLAN/SLAG MORTARS

5.1. Introduction

The second phase of this study dealt with development and evaluation of alkali-activated natural Pozzolan/slag mortars. To this end, different dominant parameters were considered and several mixture proportions were designed based on (1) the findings of the first phase of investigation on alkali-activated pastes, and (2) preliminary assessment on the influence of sodium silicate contents, alkaline activator solution-to-binder ratios, sodium hydroxide concentrations, and fine aggregate-to-binder ratios on early properties of alkali-activated natural Pozzolan/slag mortars. Followings are a list of factors that were studied in this phase:

- *Binder combination (slag and natural Pozzolan contents):*

  Three different slag-to-total binder ratios of 0.3, 0.5 and 0.7 were selected. These ratios corresponded to natural Pozzolan-to-total binder ratios of 0.7, 0.5 and 0.3, respectively.

- *Sodium hydroxide concentration:*

  Based on the results of first phase of the study, three sodium hydroxide concentrations of 0.5, 1 and 2M were chosen.

- *Activator combination (sodium silicate and sodium hydroxide contents):*

  In order to assess the influence of activator combinations, three sodium silicate-to-alkaline activator ratios of 0.2, 0.25 and 0.3 were considered for a group of alkali-activated natural Pozzolan/slag mortars having sodium hydroxide concentration of 1M. Higher dosages of sodium silicate were not used due to their adverse effects on flow, setting time, and mixture economy.

- *Alkaline activator solution-to-binder ratio (S/B):*

In order to observe effects of alkaline activator solution-to-binder ratio, three different S/B of 0.52, 0.56 and 0.6 were considered for a group of alkali-activated natural Pozzolan/slag mortars having sodium hydroxide concentration of 1M. Lower S/B wasn't selected as it would result in insufficient workability and lack of proper compaction.

A comprehensive experimental program was used to assess the performance of alkali-activated natural Pozzolan/slag mortars which included flow spread, setting time, compressive strength, drying shrinkage, absorption, rapid chloride penetration, rapid chloride migration, and heat of hydration. Portland cement mortars (control) were also made for comparison purposes.

5.2. Mixtures proportions

Table 5.1 documents the mixture proportions of alkali-activated natural Pozzolan/slag mortars. As mentioned earlier, these mixtures were designed with slag contents of 30, 50 and 70% (natural Pozzolan contents of 70, 50 and 30%, respectively); sodium hydroxide concentrations of 0.5, 1 and 2M; sodium silicate contents of 20, 25 and 30% (sodium hydroxide contents of 80, 75 and 70%, respectively); and alkaline activator solution-to-blinder ratios (S/B) of 0.52, 0.56 and 0.60. A constant fine aggregate-to-binder ratio of 2 was used for all alkali-activated natural Pozzolan/slag mortars which was selected from a preliminary research on different ratios of 1.5, 2, 2.5 and 3. In this Table, mixture id. XM-SLY-SSZ-W represents that sodium hydroxide had X mole, slag was Y% of the total binder ((100-Y)% was for natural Pozzolan), sodium silicate constituted Z% of the total activator ((100-Z)% was sodium hydroxide), and W was used for solution-to-binder ratio.

Table 5.2 shows the mixture proportions of Portland cement mortars (control mortars). These mixtures were designed with fine aggregate-to-binder ratios of 2.75 (standard mortar) and 2 (similar to the alkali-activated natural Pozzolan/slag mortars). A water-to-cement ratio of 0.485 was used for Portland cement mortars in accordance with ASTM C109.

Table 5.1 Mixture proportions of alkali-activated natural Pozzolan/slag mortars

Mix id.	Mixture description	Materials, g			
		Slag	Natural Pozzolan	Sodium hydroxide	Sodium silicate
2M-SL30-SS30-0.60	30% slag, 70% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (2M), S/B=0.60	1583	3694	2217	950
2M-SL50-SS30-0.60	50% slag, 50% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (2M), S/B=0.60	2639	2639	2217	950
2M-SL70-SS30-0.60	70% slag, 30% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (2M), S/B=0.60	3694	1583	2217	950
1M-SL30-SS30-0.60	30% slag, 70% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M), S/B=0.60	1583	3694	2217	950
1M-SL50-SS30-0.60	50% slag, 50% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M), S/B=0.60	2639	2639	2217	950
1M-SL70-SS30-0.60	70% slag, 30% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M), S/B=0.60	3694	1583	2217	950
0.5M-SL30-SS30-0.60	30% slag, 70% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (0.5M), S/B=0.60	1583	3694	2217	950
0.5M-SL50-SS30-0.60	50% slag, 50% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (0.5M), S/B=0.60	2639	2639	2217	950

* Fine aggregate was 10556g for all the mixtures

Table 5.1 Mixture proportions of alkali-activated natural Pozzolan/slag mortars (continued)

Mix id.	Mixture description	Materials, g			
		Slag	Natural Pozzolan	Sodium hydroxide	Sodium silicate
0.5M-SL70-SS30-0.60	70% slag, 30% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (0.5M), S/B=0.60	3694	1583	2217	950
1M-SL30-SS30-0.56	30% slag, 70% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M), S/B=0.56	1583	3694	2069	887
1M-SL50-SS30-0.56	50% slag, 50% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M), S/B=0.56	2639	2639	2069	887
1M-SL70-SS30-0.56	70% slag, 30% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M), S/B=0.56	3694	1583	2069	887
1M-SL30-SS30-0.52	30% slag, 70% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M), S/B=0.52	1583	3694	1921	823
1M-SL50-SS30-0.52	50% slag, 50% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M), S/B=0.52	2639	2639	1921	823
1M-SL70-SS30-0.52	70% slag, 30% Pozzolan, 30% sodium silicate, 70% sodium hydroxide (1M), S/B=0.52	3694	1583	1921	823
1M-SL30-SS20-0.60	30% slag, 70% Pozzolan, 20% sodium silicate, 70% sodium hydroxide (1M), S/B=0.60	1583	3694	2533	633
1M-SL50-SS20-0.60	50% slag, 50% Pozzolan, 20% sodium silicate, 70% sodium hydroxide (1M), S/B=0.60	2639	2639	2533	633
1M-SL70-SS20-0.60	70% slag, 30% Pozzolan, 20% sodium silicate, 70% sodium hydroxide (1M), S/B=0.60	3694	1583	2533	633
1M-SL30-SS25-0.60	30% slag, 70% Pozzolan, 25% sodium silicate, 70% sodium hydroxide (1M), S/B=0.60	1583	3694	2375	792
1M-SL50-SS25-0.60	50% slag, 50% Pozzolan, 25% sodium silicate, 70% sodium hydroxide (1M), S/B=0.60	2639	2639	2375	792
1M-SL70-SS25-0.60	70% slag, 30% Pozzolan, 25% sodium silicate, 70% sodium hydroxide (1M), S/B=0.60	3694	1583	2375	792

* Fine aggregate was 10556g for all the mixtures

Table 5.2 Mixture proportions of Portland cement mortars

Mix id.	Fine aggregate-to-cement ratio	Water-to-cement ratio	Materials, g		
			Portland cement	Water	Fine aggregate
Control 1	2.75	0.485	4486	2176	12338
Control 2	2		5278	2560	10556

5.3. Results and discussions

Influence of binder combination, activator combination, sodium hydroxide concentration, and S/B on properties of alkali-activated mortars are discussed in the following subsections.

5.3.1. Workability

Table 5.3 reports the flow spread of alkali-activated natural Pozzolan/slag mortars. Figures 5.1 and 5.2 show overall effects of different variables on the workability of the studied mortars. The influence of each variable is discussed below.

Table 5.3 Fresh properties and hydration heat of alkali-activated natural Pozzolan/slag mortars

Mix id.	Flow (cm)	Setting times (minutes)		Heat of hydration	
		Initial	Final	Peak temperature (°C)	Time to reach peak temperature (hr)
2M-SL30-SS30-0.60	11.11	146.3	220	30.5	10.517
2M-SL50-SS30-0.60	11.11	121.25	168.75	36.05	8.292
2M-SL70-SS30-0.60	11.11	108.75	141.25	38.6	6.017
1M-SL30-SS30-0.60	14.40	245	402.5	28.45	20.400
1M-SL50-SS30-0.60	12.38	230	312.5	33.05	10.092
1M-SL70-SS30-0.60	8.57	128.8	180	36.3	6.800
0.5M-SL30-SS30-0.60	12.70	325	523.3	28.85	25.617
0.5M-SL50-SS30-0.60	8.89	263.75	348.75	31.5	11.058
0.5M-SL70-SS30-0.60	6.67	150	210	34.25	7.358
1M-SL30-SS30-0.56	11.58	150	256.25	29.3	17.31
1M-SL50-SS30-0.56	9.53	167.5	243.75	33.1	8.82
1M-SL70-SS30-0.56	7.62	98.75	135	36.85	6.13
1M-SL30-SS30-0.52	10.16	117.5	218.75	29.65	14.10
1M-SL50-SS30-0.52	7.94	103.75	177.5	34.1	8.33
1M-SL70-SS30-0.52	4.13	57.5	97.5	37.05	5.74
1M-SL30-SS20-0.60	15.24	293.3	325	29.85	13.458
1M-SL50-SS20-0.60	15.24	137.5	192.5	33.35	6.833
1M-SL70-SS20-0.60	15.09	72.5	97.5	34.6	5.008
1M-SL30-SS25-0.60	15.24	270	425	29.4	18.200
1M-SL50-SS25-0.60	15.24	200	285	33.4	9.408
1M-SL70-SS25-0.60	13.02	117.5	150	35.75	6.025

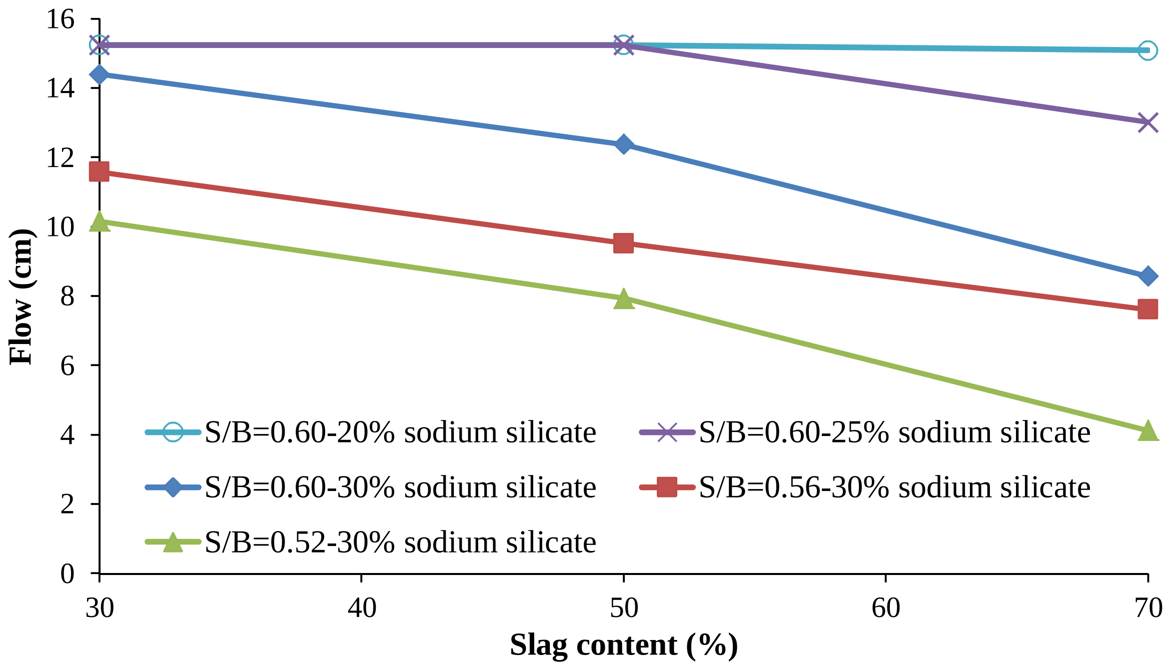


Figure 5.1 Effects of slag contents, sodium silicate contents and S/B on the flow of mixtures having sodium hydroxide concentration of 1M

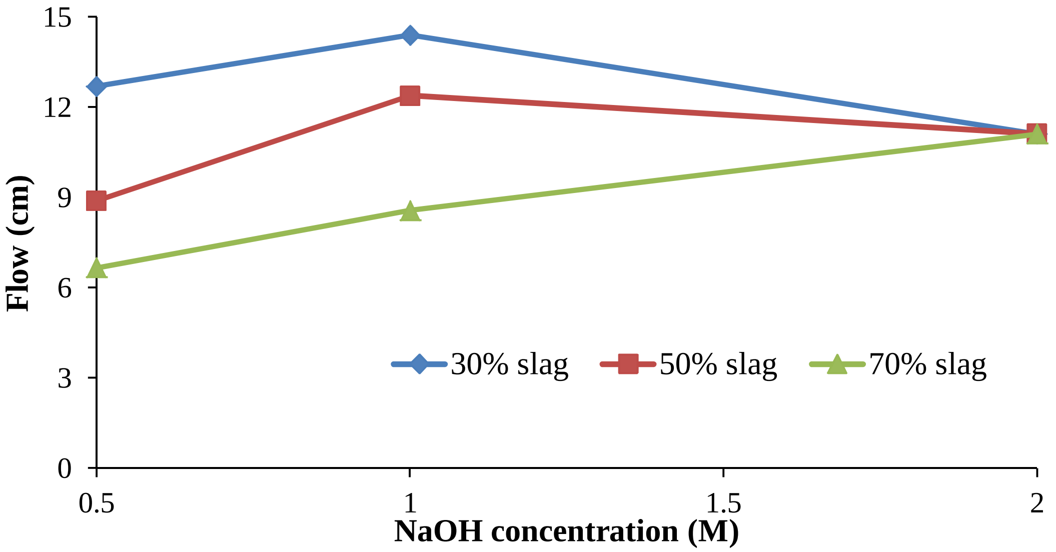


Figure 5.2 Flow of alkali-activated natural Pozzolan/slag mortars having different NaOH concentrations and binder combinations

5.3.1.1. Effects of binder combination

The influence of binder combination (slag and natural Pozzolan contents) on the flow of alkali-activated natural Pozzolan/slag mortars having different NaOH concentrations, activator combinations, and solution-to-binder ratios (S/B) are shown in Figures 5.1 and 5.2. In general, increases in slag content (reduction of natural Pozzolan dosage) resulted in lower workability.

On average, there was about 18 and 33% reduction in the flow of mixtures having S/B of 0.52, 0.56 and 0.60 when slag content was increased from 30 to 50 and 50 to 70%, respectively. The average reductions were about 24, 20 and 0% for each 20% increase in slag content of mortars having sodium hydroxide concentrations of 0.5, 1 and 2M, respectively.

This observation can be related to the finer particle size distribution of the used slag in comparison with that of the used natural Pozzolan (see Figure 3.1 of Chapter 3). The observed behavior was opposite of the trend found in the first phase for alkali-activated pastes. The reason can be the difference in physical properties of natural Pozzolans used in phases I and II. While natural Pozzolans were provided from the same source with almost similar chemical properties, their physical properties were different. The natural Pozzolan used in the second phase had a water demand of 98%, whereas the one used for the first phase had a water requirement of 103%.

5.3.1.2. Effects of activator combination

The flow spread of alkali-activated natural Pozzolan/slag mortars having different sodium silicate and sodium hydroxide dosages are shown in Figure 5.1. It was found that increases in sodium silicate content (decreases in sodium hydroxide dosage) reduced the workability of the studied mixtures. The flow reduced by averagely 11% for each 5% increases in sodium silicate content. It should, however, be noted that the flow table limited measurement of above 15.24 cm, which in turn, didn't allow for exact comparisons. It's also worth mentioning that the average reduction can't be extrapolated to sodium silicate contents of above 30%. In the first phase on alkali-activated pastes, it was seen that the flow significantly reduced when sodium silicate increased from 30 to 40%. To confirm findings of the first phase, two additional mixtures were made with 35 and 40% sodium silicate contents (having slag dosage of 30%). Their flow spreads were 14 and 81% lower than that of 30% sodium silicate contained mortar, respectively. The reduction in flow increased drastically for sodium silicate content of above 35%.

The reduction in workability of alkali-activated natural Pozzolan/slag mortars by use of higher dosages of sodium silicate can be attributed to higher solid-to-liquid ratio of sodium silicate in comparison with that of sodium hydroxide. The solid-to-liquid ratio was 44.03/55.97 = 0.787 for sodium silicate solution, whereas it was about 0.02, 0.04 and 0.08 for sodium hydroxide solutions with concentrations of 0.5, 1 and 2M, respectively.

5.3.1.3. Effects of alkaline activator solution-to-binder ratio

Figure 5.1 also shows the workability of alkali-activated natural Pozzolan/slag mortars having different solution-to-binder ratios. It was seen that the workability reduced with decreases in S/B. The flow reduced by averagely 18 and 25% when S/B decreased from 0.60 to 0.56 and 0.56 to 0.52, respectively. This trend was similar to the typical behavior of Portland cement. "As the mixtures with higher S/B contained more water, they became more plastic and workable, allowing for ease of mixing and placement" (Ghafoori et al. 2016).

5.3.1.4. Effects of sodium hydroxide concentrations

Figure 5.2 shows the flow spreads of alkali-activated natural Pozzolan/slag mortars with different NaOH concentrations. It can be seen that the workability increased as sodium hydroxide molarity increased from 0.5 to 1M, after which, it reduced with increasing molarity from 1 to 2M. When NaOH molarity increased from 0.5 to 1M, the flow of the studied mortars increased by 1.7, 3.5 and 1.9 cm for mortars having slag contents of 30, 50 and 70%, respectively. For 70% slag contained mortars, the increases in molarity from 1 to 2M resulted in 2.5 cm further increases in the flow. By increasing the molarity from 1 to 2M, the flow reduced by 3.3 and 1.3 cm for mixtures with slag contents of 30 and 50%, respectively. The observed behavior was similar to the observations of the first phase on alkali-activated pastes where overall use of higher sodium hydroxide reduced the workability but mixtures activated with 0.5M sodium hydroxide and sodium silicate had higher workability than mixtures activated with water and sodium silicate.

These trends were close to the observations of Jolicoeur et al. (1992) presented in the literature where using 0.5, 1 and 2% Na_2O in the system of pastes resulted in quicker slump loss (lower workability) than inclusion of 4% Na_2O. It was also observed by Smaoui et al. (2005) that addition of NaOH to Portland cement concrete resulted in increases in workability. In addition, it was seen by Li et al. (2016) that the flow of high performance cementitious mortars increased with increasing alkaline content to an optimum level, after which it significantly reduced for higher alkaline dosages. Therefore, it can be inferred that a certain amount of alkalis may increase the workability, after which increasing sodium hydroxide concentration results in reduction of flow due to the reduction of water content. For a given volume, increases in sodium hydroxide concentration reduces the water portion of the activator solution.

5.3.2. Heat of hydration

The hydration heat of alkali-activated natural Pozzolan/slag mortars was measured by monitoring their temperatures for about 48 hr in isolated thermal boxes. In order to avoid presentation of several figures for various mixtures or different influential factors, the maximum temperature (peak) and elapsed time to reach the peak temperature are reported in Table 5.3 for all alkali-activated natural Pozzolan/slag mortars. In addition, Figures 5.3 through 5.6 show the typical effects of binder combination, activator combination, S/B, and sodium hydroxide concentration on hydration heat of alkali-activated natural Pozzolan/slag mortars recorded during 48 hr after mixing, respectively. The results are discussed below.

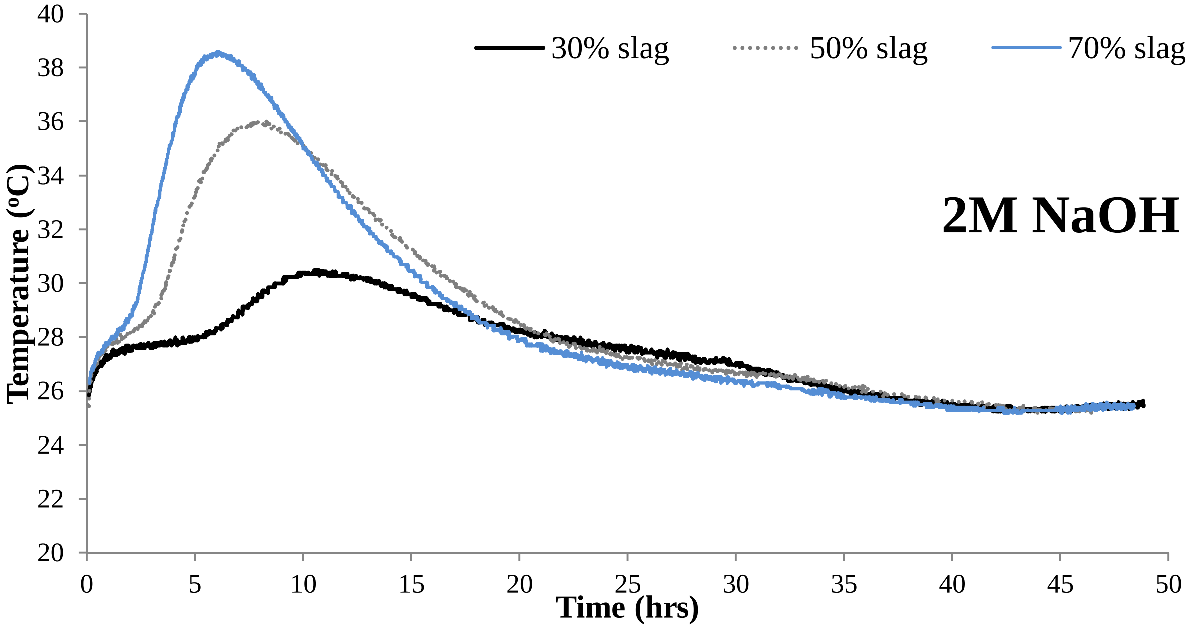


Figure 5.3 Heat of hydration of alkali-activated natural Pozzolan/slag mortars with different slag contents and NaOH concentration of 2M

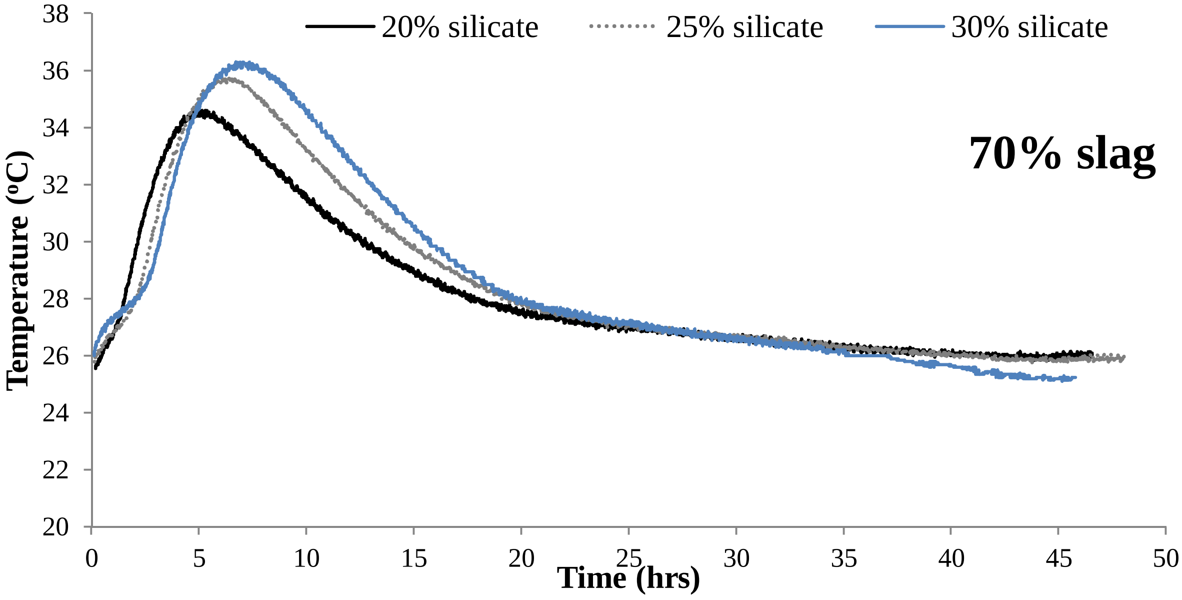


Figure 5.4 Hydration heat of alkali-activated natural Pozzolan/slag mortars having different sodium silicate contents and slag content of 70%

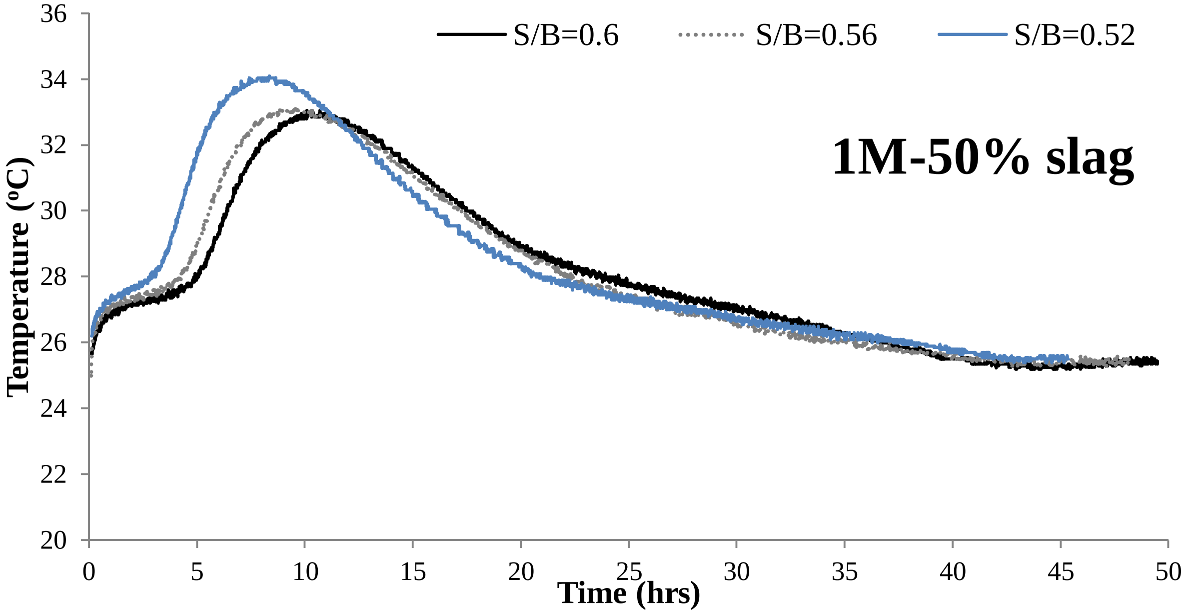


Figure 5.5 Hydration heat of alkali-activated natural Pozzolan/slag mortars having different S/B and slag content of 50%

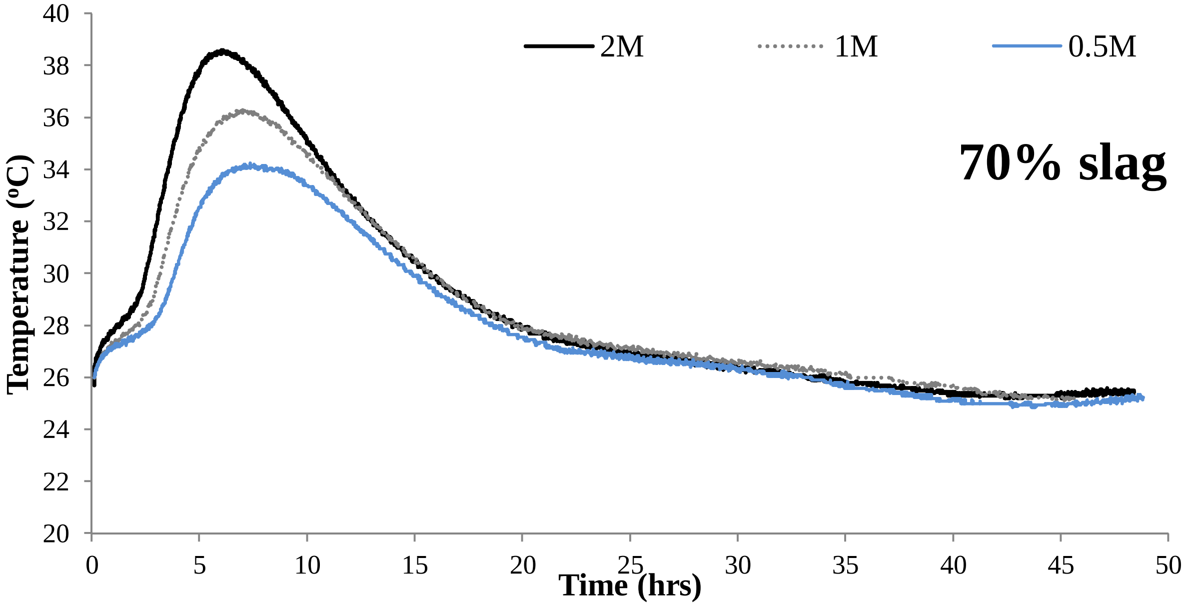


Figure 5.6 Heat of hydration of alkali-activated natural Pozzolan/slag mortars having different NaOH concentrations and slag content of 70%

5.3.2.1. Effects of binder combination

Figure 5.3 shows heat of hydration of alkali-activated natural Pozzolan/slag mortars having different binder combinations (slag and natural Pozzolan contents) for NaOH molarity of 2M, sodium silicate content of 30% and S/B of 0.6. Table 5.3 reports the maximum temperature and time to reach the peak temperature for mortars having different slag and natural Pozzolan contents.

It can be seen that similar to the results of phase I on alkali-activated pastes, the peak temperature increased and time of its occurrence reduced as slag content was increased. When slag content was increased from 30 to 50 and 50 to 70%, the maximum temperature increased by 2.65 and 2.75°C for 0.5M mixtures, 4.60 and 3.25°C for 1M mixtures, and 5.55 and 2.55°C in case of 2M mortars, respectively. For similar increases in slag content, the time to reach peak temperature reduced by 14.56 and 3.70 hr for 0.5M mixtures, 10.31 and 3.29 hr for 1M mixtures, and 2.23 and 2.28 hr for 2M mixtures, respectively.

Variation of binder combination resulted in similar changes for mixtures with different sodium silicate contents; increases in slag content led to acceleration of reactions and generation of more heat. For mortars having sodium silicate contents of 20, 25 and 30%, the peak temperature increased by averagely 2.38, 3.18 and 3.93°C and time of peak shortened by averagely 4.23, 6.09 and 6.80 hr for each 20% increases in slag contents, respectively. Similarly, increases in slag contents led to higher heat generation and accelerated reactions for S/B of 0.52, 0.56 and 0.60. On average, each 20% increases in slag content resulted in 3.70, 3.78 and 3.93°C increases in peak temperature of mortars having S/B of 0.52, 0.56 and 0.60, respectively. For similar solution-to-binder ratios, the time of peak temperature decreased by averagely 4.18, 5.59 and 6.80 hr for each 20% increase in slag content, respectively.

This observation can be related to the increases in the CaO content which is the main chemical component of slag. It was proven in different studies that higher lime content accelerated the hydration reaction of the mixture (Lee and Lee 2013, Yip 2004). It should also be noted that while available lime in slag could react with water, sodium hydroxide and sodium silicate, the reactions of natural Pozzolan only occur with strong alkaline solutions and with a slower reactivity rate (longer reaction times). The higher reactivity of slag than natural Pozzolan can also be easily concluded from comparison between behavior of alkali-activated slag and alkali-activated natural Pozzolan mixtures which was discussed in Chapter 2. It was shown that while alkali-activated slag systems set quickly as a sign of fast reactions, natural Pozzolan based geopolymers set late without use of elevated temperatures.

5.3.2.2. Effects of activator combination

The influence of sodium silicate and sodium hydroxide contents on the hydration heat of alkali-activated natural Pozzolan/slag mortars are shown in Figure 5.4. It can be seen that as sodium silicate content was increased, the peak temperature shifted to the right of the plots; indicating delays in initial reactivity. Figure 5.7 also highlights this observation by documenting the time that peak temperature took place. For the mixtures having 30% slag, the maximum temperature happened 4.74 and 2.20 hr later as sodium silicate was increased from 20 to 25% and 25 to 30%, respectively. In case of mortars having 50 and 70% slag, the peak temperature delayed by 2.58 and 1.02 hr when sodium silicate content was increased from 20 to 25%, and retarded by 0.68 and 0.78 hr when silicate content was increased from 25 to 30%, respectively.

These observations indicated that for the studied mixture proportions and at the initial stages of reactions (within the first few hours), sodium hydroxide was more involved in the reaction process than sodium silicate. This finding can be supported by the observations of Shi and Day (1996b) presented as Figure 2.6 of Chapter 2. It can be seen in this figure that the maximum heat of hydration reached considerably faster for sodium hydroxide-activated slag than sodium silicate-activated slag.

These observations can be related to the effects of initial pH on early hydration. In a number of publications, it was stated that the early hydration of slag was accelerated as the pH of activator increased (Yuan et al. 1987, Roy et al. 1992, Song et al. 2000). The main reason for this explanation was the effect of pH on dissolution of slag. It was shown that percentage of soluble silica from slag almost doubled when pH increased from 13 to 14 (Fernandez Jimenez 2000, Pacheco-Torgal et al. 2015). Similarly, increases of pH increases silica dissolution of aluminosilicates (Pacheco-Torgal et al. 2015). For a given amount of Na_2O, sodium hydroxide has higher pH than any other sodium-containing compounds, thus NaOH-activated slag showed the shortest induction period than slag activated with any other sodium-containing compounds such as sodium silicate and sodium carbonate. In case of this study, the used sodium silicate had pH of 12.9, whereas the pH of sodium hydroxide solution was about 14. Therefore, the accelerated reactions with increases in sodium hydroxide portion of activator can be related to the increases in the pH of the whole activator.

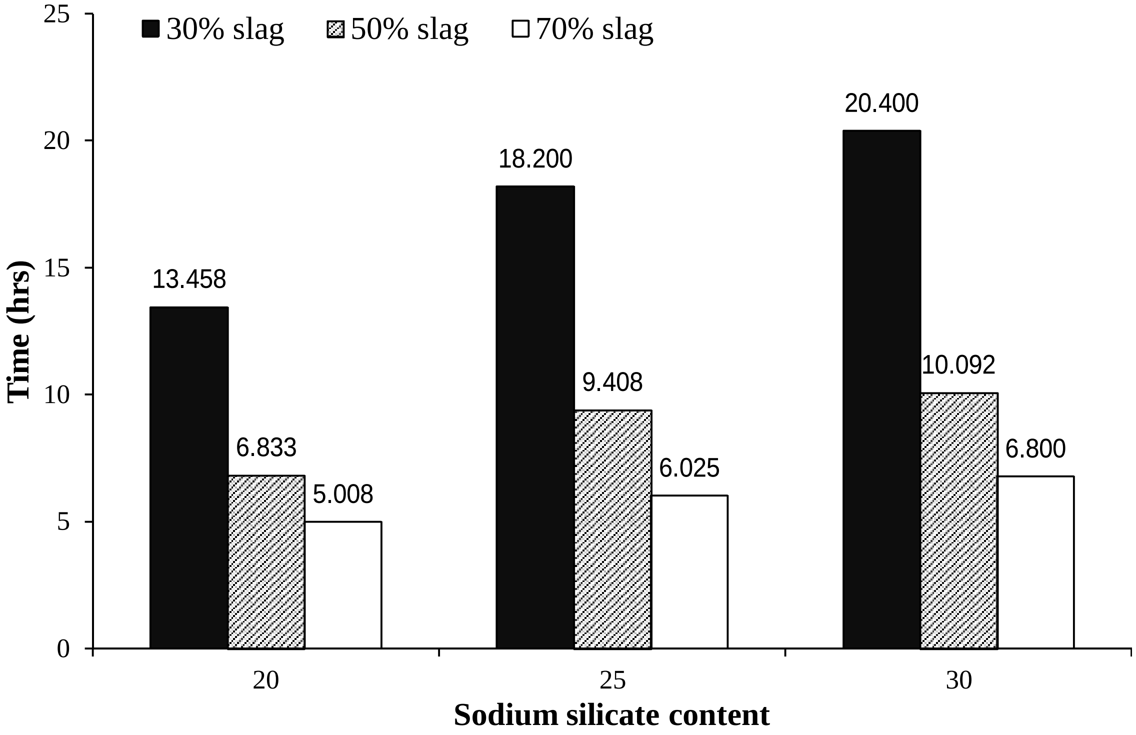


Figure 5.7 Time to reach peak temperature for alkali-activated natural Pozzolan/slag mortars with different sodium silicate dosages

Figure 5.8 shows effect of activator combination on the peak temperature. It can be seen that the maximum temperatures of mixtures having 20, 25 and 30% sodium silicate were not much different for mortars with 30 and 50% slag content. There were, however, slight increases in maximum temperature with increases in sodium hydroxide content of these mixtures which can be related to the earlier discussion on effect of pH in dissolubility of silica and thus early hydration. On the other hand, the peak temperature reduced by increases in sodium hydroxide portion of activator (reduction of sodium silicate content) for mortars having 70% slag. This observation can be due to the reason discussed below:

Unlike silica and alumina, calcium becomes less soluble with increases in pH. Therefore, as slag content of mixture was increased, a reduction in sodium hydroxide and an increase of sodium silicate dosages became more favorable for initial reaction resulting in higher heat evolution. It should be mentioned that the observed behavior could change using other combinations of sodium hydroxide and sodium silicate.

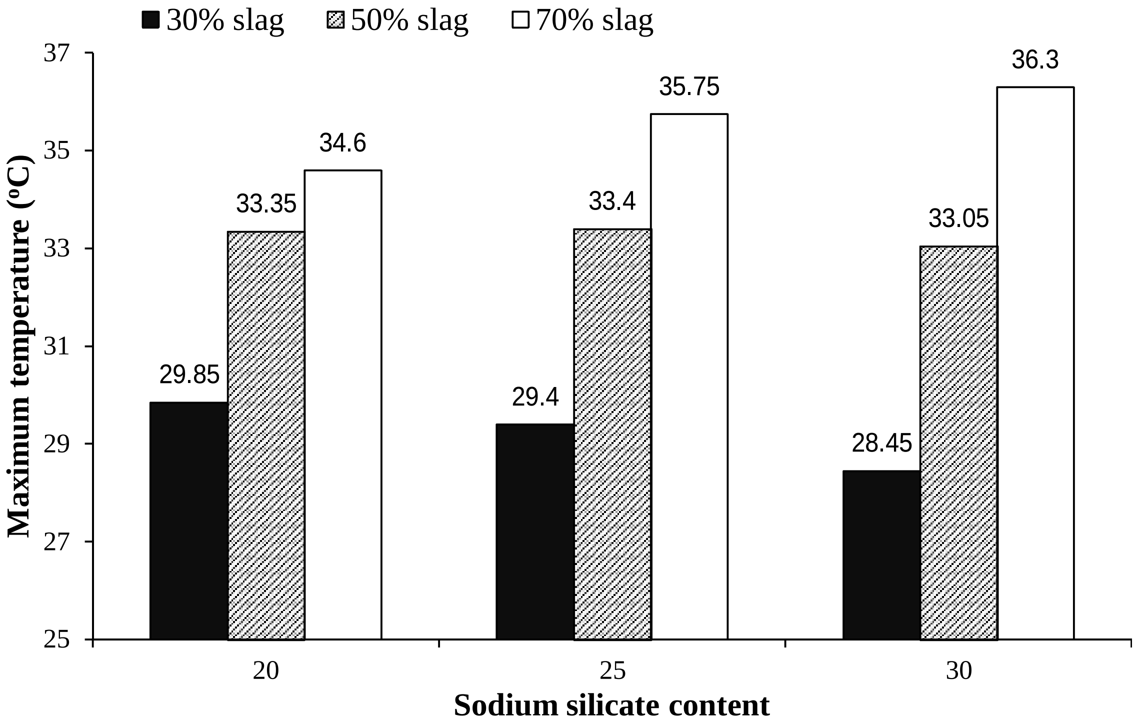


Figure 5.8 Maximum temperature of alkali-activated natural Pozzolan/slag mortars with different sodium silicate dosages

5.3.2.3. Effects of alkaline activator solution-to-binder ratio

The hydration heat of alkali-activated natural Pozzolan/slag mortars having different S/B is shown in Figure 5.5. As can be seen, there were increases in peak temperature with reductions in solution-to-binder ratio. As S/B was reduced from 0.60 to 0.56, the peak temperature increased by 0.85, 0.05 and 0.55°C for mortars having 30, 50 and 70% slag contents, respectively. For similar slag contents, the reduction of S/B from 0.56 to 0.52 led to 0.35, 1.00 and 0.20°C increases in peak temperature, respectively. As S/B was reduced, the reaction processes accelerated which, in turn, reduced the time to reach peak temperature. In case of mortars having 30% slag, time to reach peak temperature reduced by averagely 3.15 hr for each 0.04 reduction in S/B. Similar trend was observed for mortars with slag contents of 50 and 70%. The difference, however, was less than that of mixtures with slag contents of 30%. For mortars with slag content of 50%, the peak of temperature happened 1.27 and 0.49 hr earlier when S/B was reduced from 0.60 to 0.56 and 0.56 to 0.52, respectively. For mortars with 70% slag (and 30% natural Pozzolan), the peak temperature reached faster by averagely 0.53 hr for each 0.04 reduction in S/B.

It can be deduced from these observations that increasing S/B delayed the reaction activities which were also observed by Shi and Day (1996b) when water-to-slag ratio of alkali-activated slag pastes increased. The delayed reactivity, specially seen for mixtures having high natural Pozzolan content, are likely due to the delay in geopolymerization stage and product formation by increasing water content of the mixture.

5.3.2.4. Effects of sodium hydroxide concentrations

Figure 5.6 presents the influence of sodium hydroxide concentration on the hydration heat of alkali-activated natural Pozzolan/slag mortars. It can be seen that increases in molarity of sodium hydroxide led to higher reaction rates. In case of mortars with 30% slag, increases in sodium hydroxide concentration from 0.5 to 2M increased the peak temperature by 1.65°C and accelerated the reactions by 15.1 hr. For 50% slag contained mixtures, similar increases in molarities led to 4.55°C increase in peak temperature and 2.77 hr faster reaction processes. When slag content increased to 70%, the same increases in sodium hydroxide concentrations resulted in 4.35°C increase in peak temperature. This increase accelerated the reaction process by 1.34 hr.

A similar behavior was observed by Shi and Day (1996b) and Song et al. (2000) reporting an increased cumulative hydration heat by increasing NaOH dosage of alkali-activated slag pastes. In particular, Song et al. (2000) found a linear relationship between dq/dt_{max} (heat evolution) and NaOH concentration and an inverse relationship between t_{max} (time to reach peak temperature) and NaOH concentration. This observation was related to faster hydration of slag in higher NaOH concentrations. A similar outcome took place for natural Pozzolan as dissolution of silica increased with an increase in NaOH molarity (Bondar et al. 2011a).

5.3.3. Setting time

Table 5.3 also reports setting times of alkali-activated natural Pozzolan/slag mortars. Figures 5.9 through 5.12 show effects of different parameters on the initial and final setting times of alkali-activated natural Pozzolan/slag mortars.

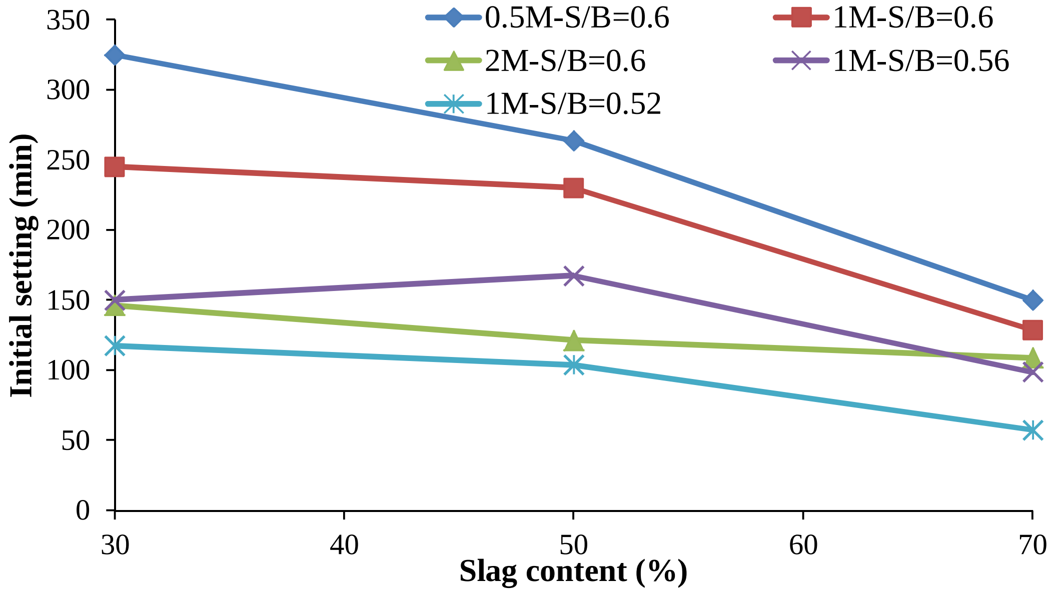


Figure 5.9 Effects of slag content, molarity and S/B on the initial setting time of alkali-activated natural Pozzolan/slag mortars

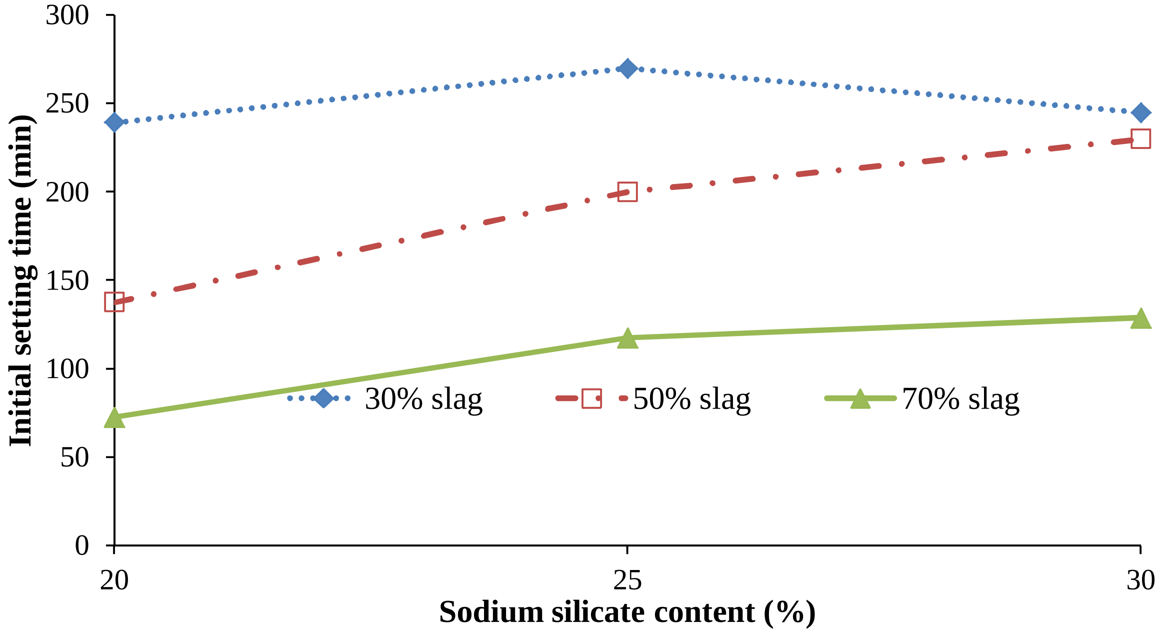


Figure 5.10 Initial setting time of alkali-activated natural Pozzolan/slag mortars having different sodium silicate contents

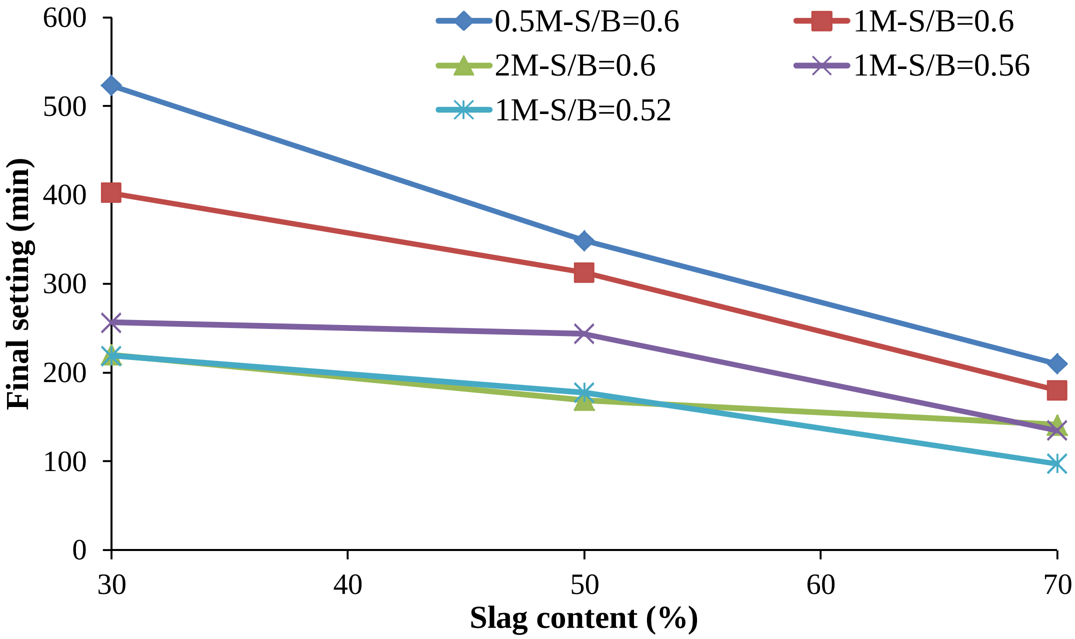


Figure 5.11 Effects of slag content, molarity and S/B on the final setting time of alkali-activated natural Pozzolan/slag mortars

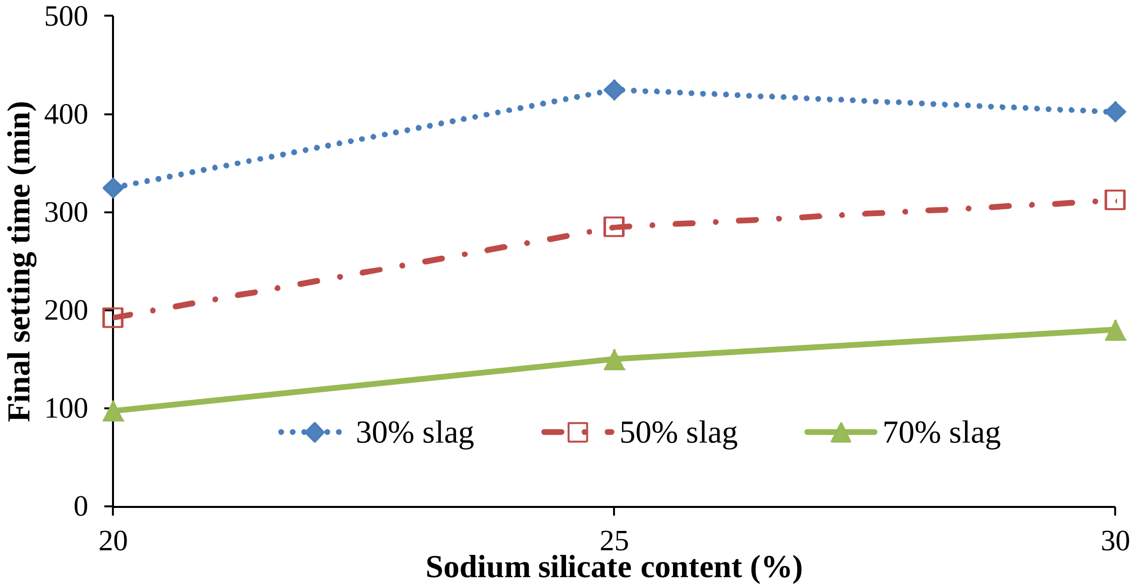


Figure 5.12 Final setting time of alkali-activated natural Pozzolan/slag mortars having different sodium silicate contents

5.3.3.1. Effects of binder combination

The influence of binder combination on the initial and final setting times of alkali-activated natural Pozzolan/slag mortars can be seen in Table 5.3 and Figures 5.9 through 5.12. The results of this phase confirmed observations of the first phase that, overall, the setting times reduced with reduction of natural Pozzolan contents (increases in slag-to-total binder ratio). In case of alkali-activated natural Pozzolan/slag mortars having S/B of 0.6, an increase in slag content from 30 to 50% resulted in 61, 15 and 25 min reduction in the initial setting time and 175, 90 and 51 min reduction in the final setting time for sodium hydroxide concentrations of 0.5, 1 and 2M, respectively. When slag content was increased from 50 to 70%, the initial setting times decreased by 114, 101 and 13 min, and final setting time reduced by 139, 133 and 28 min for similar NaOH molarities, respectively.

Similarly, Figures 5.10 and 5.12 show an overall reduction in the setting times with increases in slag content for mortars having different sodium silicate contents. For sodium silicate contents of 20, 25 and 30%, the setting times of mortars having 70% natural Pozzolan (30% slag) were averagely 30.2 and 61.5% higher than those of mortars containing 50 and 30% natural Pozzolan (50 and 70% slag), respectively.

Influence of slag contents on the setting time of mortars with different S/B can be seen in Figures 5.9 and 5.11. Similarly, it can be seen that use of higher slag dosage in these mixtures led to lower setting times. For mixtures with S/B of 0.52, 0.56 and 0.60, when slag content was increased from 30 to 50 and 50 to 70%, the setting times reduced by averagely 9 and 44%, respectively.

The observed behaviors can be related to the higher reactivity of slag in comparison with natural Pozzolan which was confirmed with the results of hydration heat. It was seen in Figure 5.4 that by increasing the slag dosage, alkali-activated natural Pozzolan/slag mortars generated more heat and reached maximum temperature in a shorter period of time which points to their faster reactivity. Figures 5.13 and 5.14 show the maximum generated temperatures and their occurrence time for mixtures having different slag contents and sodium hydroxide concentrations. These figures confirm the abovementioned conclusion for all the studied mortars. It can be seen that for 0.5M mortars, the time to reach maximum temperature reduced from 25.6 to 7.4 hr (71% reduction) when slag content was increased from 30 to 70%. This gap was 13.6 hr (from 20.4 to 6.8 hr with 67% reduction) in case of 1M mortars, and 4.5 hr (from 10.5 to 6 hr with 43% reduction) for 2M mortars. These observations follow a similar trend reported for setting times of the studied mortars (Figures 5.9 and 5.11) indicating that as molarity of sodium hydroxide solution was increased, the differences between setting times of mixtures having different slag contents narrowed.

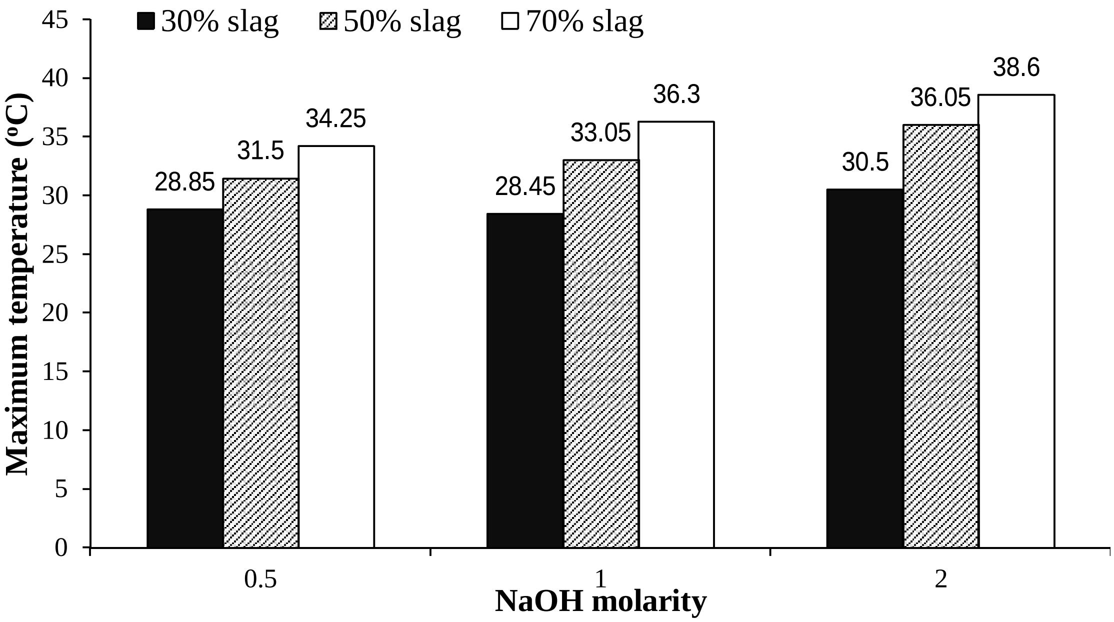


Figure 5.13 Peak temperature of alkali-activated natural Pozzolan/slag mortars with different slag contents and sodium hydroxide concentrations

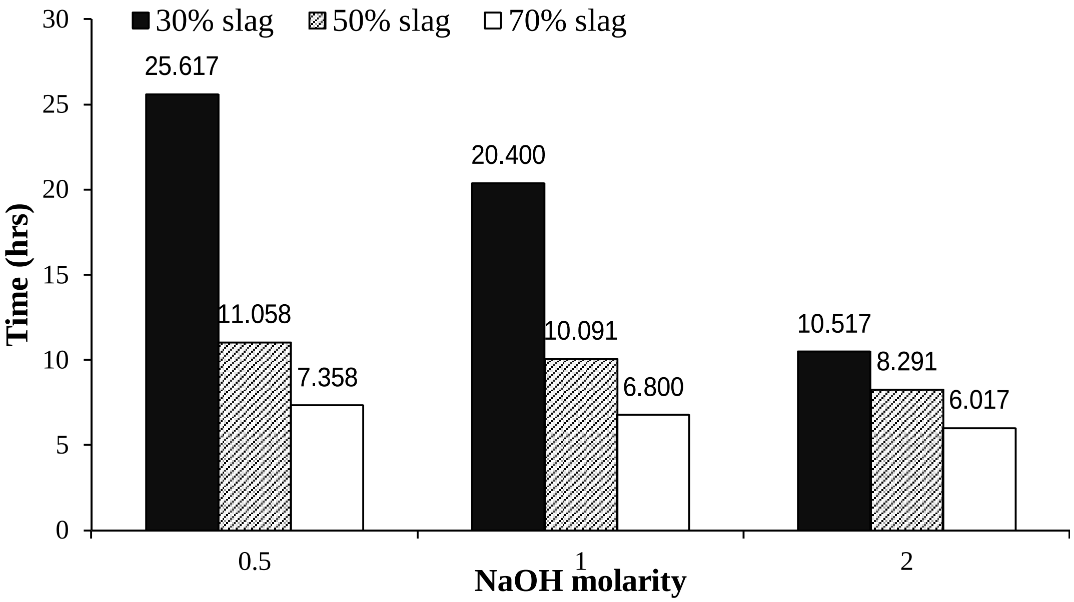


Figure 5.14 Time to reach peak temperature for alkali-activated natural Pozzolan/slag mortars with different slag contents and sodium hydroxide concentrations

5.3.3.2. Effects of activator combination

The initial and final setting times of alkali-activated natural Pozzolan/slag mortars having different sodium silicate contents are presented in Figures 5.10 and 5.12, respectively. It can be seen that overall, increases in sodium silicate content in the range of 20 to 30% delayed the setting times of alkali-activated natural Pozzolan/slag mortars.

The initial and final setting times increased by averagely 33 and 44% when sodium silicate content was increased from 20 to 25%, respectively. Further increases in sodium silicate from 25 to 30% resulted in averagely 5 and 8% increases in the initial and final setting times, respectively. In first phase of this study, it was also seen that the setting time increased when sodium silicate content increased from 20 to 30%. It was, however, observed in the first phase that further increases in sodium silicate dosage (from 30 to 40%) led to shorter setting times. To confirm this finding, the setting times of mortars having 35 and 40% sodium silicate were measured for 30% slag contained mixtures. Use of 35 and 40% sodium silicate significantly reduced the setting times. The setting times of mortars containing 35 and 40% sodium silicate were averagely 62 and 80% lower than those of mortars having 30% sodium silicate, respectively. Their setting times were well below the acceptable ranges. Therefore, the conclusion of delaying setting times through increases in sodium silicate content was only valid for sodium silicate contents of 20 and 30%. Further increases in sodium silicate content showed reversing trends for both alkali-activated natural Pozzolan/slag pastes and mortars.

These results are well supported with the findings of hydration heat. Figure 5.7 shows the time that mixtures with different sodium silicate contents reached their peak temperature. It can be seen that similar to the setting time results, as sodium silicate content was increased, it took longer time for alkali-activated natural Pozzolan/slag mortars to reach their maximum temperature. It can also be seen in Figure 5.4 that the heat generation happened sooner for mixtures with lower sodium silicate contents (higher sodium hydroxide dosages). As discussed earlier, this observation can be related to the pH of alkaline activator which is the dominant factor for early hydration. Subsequently, mortars having higher sodium hydroxide concentration had faster early reactions, which in turn, reduced their setting times. A similar trend was also documented by Shi and Day (1996b) on slag activated with only sodium hydroxide or sodium silicate (see Figure 2.6 of literature chapter).

5.3.3.3. Effects of alkaline activator solution-to-binder ratio

The influence of solution-to-binder ratio on the initial and final setting times of alkali-activated natural Pozzolan/slag mortars are presented in Figures 5.9 and 5.11, respectively. It was found that the setting times reduced as S/B decreased.

For each 0.04 reduction in S/B, the initial setting time reduced by averagely 26.0, 27.4 and 27.7% for mixtures having slag contents of 30, 50 and 70%, respectively. For similar slag dosages, the final setting time shortened by averagely 22.8, 21.6 and 22.9% for each 0.04 reduction in S/B, respectively. This behavior was similar to the typical trend seen for Portland cement. This observation is also in line with the results of hydration heat (time to reach the maximum temperature) presented in Figure 5.5. As the mixtures with a higher S/B contained more water, evaporation of the extra water took longer time, resulting in slower hardening of the mortars.

5.3.3.4. Effects of sodium hydroxide concentrations

The influences of sodium hydroxide concentration on the initial and final setting times of alkali-activated natural Pozzolan/slag mortars are presented in Figures 5.9 and 5.11, respectively. It can be seen that increases in molarity of NaOH solution reduced the setting times. Similar to the results of first presented for alkali-activated pastes, the observed reduction narrowed as slag content was increased.

The setting times of alkali-activated natural Pozzolan/slag mortars having 30% slag contents reduced by averagely 23.8 and 42.8% when sodium hydroxide concentrations increased from 0.5 to 1 and 1 to 2M, respectively. Similar increases in molarity of sodium hydroxide reduced the setting times by averagely 11.6 and 46.6% for mortars having 50% slag, and 14.2 and 18.5% for mortars containing 70% slag, respectively. This observation can be related to the accelerated activation by increasing the alkaline concentration as dissolution of aluminosilicates occurred faster with increases in alkaline concentrations, leading to accelerated reactions.

Figure 5.14 also presents the time to reach peak temperature for alkali-activated natural Pozzolan/slag mortars having different sodium hydroxide molarities. The results shown in Figure 5.14 are in line with the observations reported for setting time. For mixtures with slag contents of 30, 50 and 70%, the final setting times of 0.5M mixtures were 2.38, 2.07 and 1.49 times of that of 2M mixtures, respectively. For similar slag contents, time to reach the peak temperature for 0.5M mixtures were 2.44, 1.33 and 1.22 times more than those obtained for 2M mixtures, respectively.

As discussed earlier, the reaction process including dissolution of silica accelerates when sodium hydroxide concentration increases due to increases in alkalinity of activator. The accelerated reactions result in faster setting times.

5.3.4. Compressive strength

The compressive strengths of alkali-activated natural Pozzolan/slag mortars were measured at the ages of 1, 3, 7, 28 and 90 days, and their results are presented in Table 5.4. Overall, the 28-day compressive strengths of alkali-activated natural Pozzolan/slag mortars were in a broad range of 20 to 47 MPa depending on the binder combination, activator combination, sodium hydroxide concentration, and S/B. The influence of these factors is discussed in the sections to follow.

Table 5.4 Compressive strength of alkali-activated natural Pozzolan/slag mortars (MPa)

Mix id.	1 day	3 days	7 days	28 days	90 days
2M-SL30-SS30-0.60	9.2	17.2	22.0	34.3	38.8
2M-SL50-SS30-0.60	20.1	26.1	32.5	40.0	51.7
2M-SL70-SS30-0.60	25.7	31.5	37.1	46.5	56.4
1M-SL30-SS30-0.60	5.6	15.9	25.5	38.2	43.2
1M-SL50-SS30-0.60	19.7	27.4	33.1	43.1	53.1
1M-SL70-SS30-0.60	23.0	28.7	31.7	40.0	48.3
0.5M-SL30-SS30-0.60	3.8	14.0	22.6	35.5	43.5
0.5M-SL50-SS30-0.60	18.1	25.2	31.4	41.0	48.5
0.5M-SL70-SS30-0.60	21.2	24.8	28.9	36.8	45.7
1M-SL30-SS30-0.56	7.1	18.4	28.1	39.7	46.2
1M-SL50-SS30-0.56	21.2	28.4	33.7	43.2	53.6
1M-SL70-SS30-0.56	24.9	29.9	35.1	43.5	51.9
1M-SL30-SS30-0.52	11.8	22.2	30.9	41.9	47.9
1M-SL50-SS30-0.52	22.8	28.5	34.0	43.2	53.0
1M-SL70-SS30-0.52	25.4	29.4	34.7	42.2	49.3
1M-SL30-SS20-0.60	8.5	13.4	16.3	21.1	25.5
1M-SL50-SS20-0.60	10.7	14.2	16.4	20.9	25.9
1M-SL70-SS20-0.60	11.2	12.9	15.1	20.4	26.4
1M-SL30-SS25-0.60	6.1	16.4	23.0	29.2	33.1
1M-SL50-SS25-0.60	16.9	22.6	25.7	35.1	40.9
1M-SL70-SS25-0.60	17.3	21.2	25.3	30.5	34.9

5.3.4.1. Effects of binder combination

Influences of binder combination (slag and natural Pozzolan contents) on the compressive strength of mortars made with sodium hydroxide concentrations of 0.5, 1 and 2M are shown in Figure 5.15.

At early age of curing (1 and 3 days), increases in slag dosage showed a positive influence on the compressive strength. At these ages, the studied mortars with 70% slag developed higher strength than mortars having 50 and 30% slag with the latter gained the lowest compressive strengths. The 1-day compressive strengths of mixtures with 70% slag were 5.58, 4.11 and 2.79 times of those of mixtures having 30% slag, and 1.17, 1.17 and 1.28 times of those of 50% slag contained mixtures for molarities of 0.5, 1 and 2M, respectively. For similar molarities, the 3-day compressive strengths of mortars having 70% slag were 1.77, 1.81, and 1.83 times of those of mortars containing 30% slag, and 0.98, 1.05 and 1.21 times of those of 50% slag contained mixtures, respectively. This observation can be related to the higher reactivity of slag than natural Pozzolan at early ages as seen with the results reported for hydration heat and setting time in Subsections 5.3.2.1 and 5.3.3.1, respectively. This finding also correlates well with the results of Lloyd et al. (2009) who showed from a micro-analysis that the calcium within the alkali-activated fly ash/slag binder is essential to the high early strength development.

As the curing age was extended, the reaction rate of natural Pozzolan increased. The compressive strength of mixtures with higher Pozzolan contents increased at a higher rate than mixtures with lower natural Pozzolan dosages which narrowed the large gap observed at early ages between mixtures having different slag contents. The ratios of 7-, 28- and 90-day compressive strengths of mortars with 70% slag to those of mixtures with 30% slag were 1.28, 1.04 and 1.05 for 0.5M mixtures; 1.24, 1.05 and 1.12 for 1M mixtures; and 1.69, 1.36 and 1.45 for 2M mixtures, respectively.

The 7-, 28- and 90-day compressive strengths of mortars with 70% slag were 8, 10 and 6% lower than those of mortars with 50% slag for sodium hydroxide concentration of 0.5M, respectively. In case of 1M, 70% slag contained mixtures had 4, 7 and 9% lower 7-, 28- and 90-day compressive strengths than 50% slag contained mixtures, respectively. At similar ages, the compressive strengths of 70% slag mortars were averagely about 13% higher than those of 50% slag mortars for sodium hydroxide concentration of 2M. From these observations, it can be concluded that, similar to the results of phase I on alkali-activated pastes, the optimum slag content increased with increases in sodium hydroxide concentration. It increased from about 50% for sodium hydroxide concentration of 0.5 and 1M to 70% for 2M mixtures.

Similar trend was observed for mixtures with different slag contents of 30, 50 and 70%, sodium hydroxide concentration of 1M, and S/B of 0.6, 0.56 and 0.52. At early ages (1 and 3 days), the compressive strengths of 70% slag contained mortars were higher than those of mortars with 30 and 50% slag. For the late ages, the 50% slag contained mortars developed the highest compressive strengths. The same behavior was seen for mixtures with different sodium silicate contents as mortars with slag content of 50% developed higher compressive strengths than mortars having slag contents of 30 and 70%.

The overall increases in compressive strength through increases in slag content can be related to the presence of CaO which improved the strength of the geopolymer by forming an amorphously structured Ca–Al–Si gel (Lee and Lee 2013), resulting in denser microstructure. This was also reported in a previous study by Yip (2004). Kumar et al. (2010) also suggested that the increase in the compressive strength with the addition of slag could result from the formation of gel phases (C–S–H and A–S–H) and compactness of the microstructure.

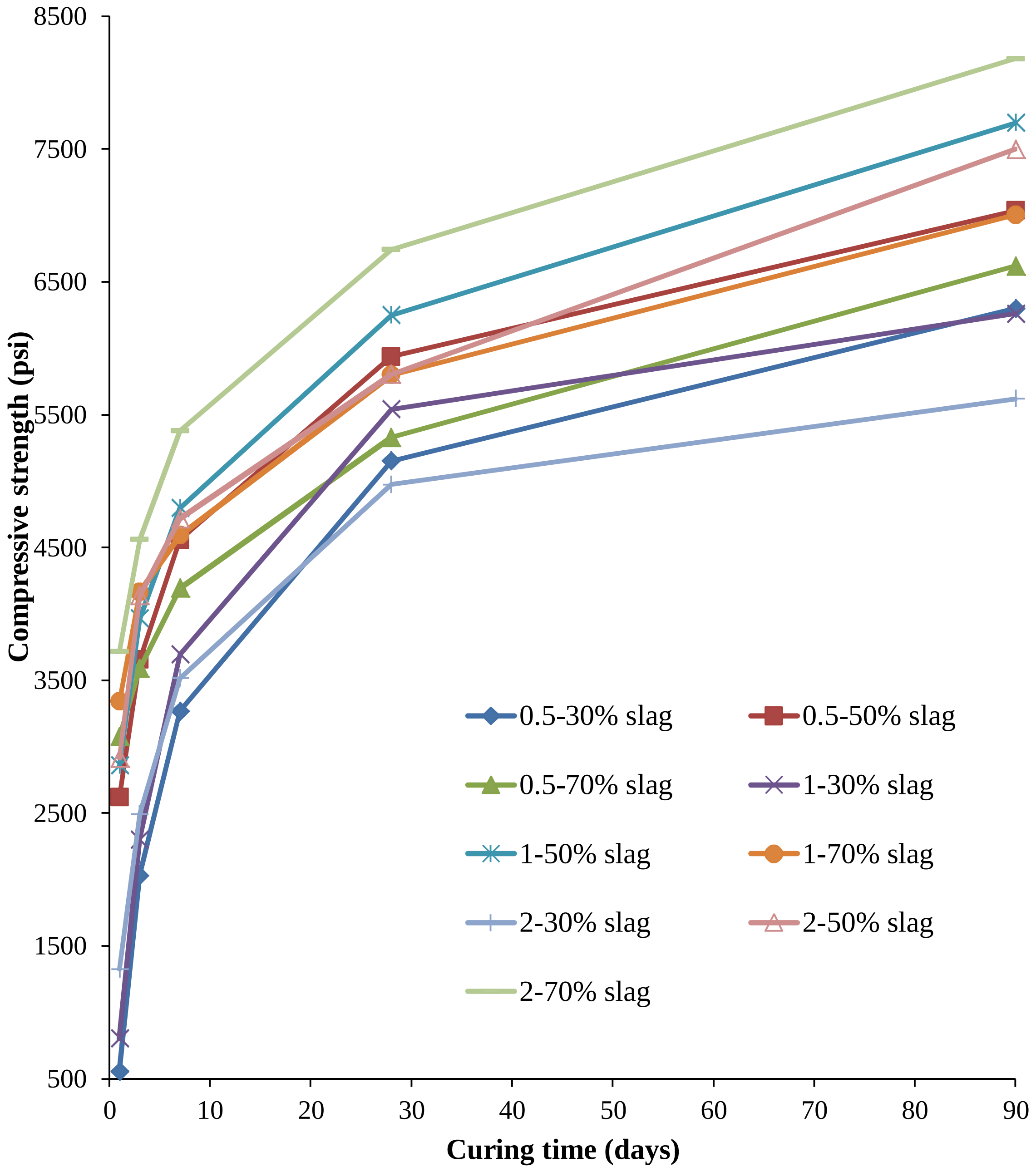


Figure 5.15 Compressive of alkali-activated natural Pozzolan/slag mortars with different slag contents (1 psi = 0.00689476 MPa, 1 MPa = 145.038 psi)

5.3.4.2. Effects of activator combination

Figure 5.16 presents the influence of activator combination on the compressive strength of alkali-activated natural Pozzolan/slag mortars. It can be seen that increases in sodium silicate dosage considerably improved the compressive strength of alkali-activated natural Pozzolan/slag mortars. The 1-, 3-, 7-, 28- and 90-day compressive strengths increased by averagely 28.1, 48.6, 55.1, 51.9 and 40.0% when sodium silicate content was increased from 20 to 25%, respectively. At the same curing ages, increases in sodium silicate content from 25 to 30% led to 13.8, 17.9, 21.7, 28.3 and 32.9% improvements, respectively.

This observation can be related to the reactions of sodium silicate with calcium oxide of slag. The onions of sodium silicate react with Ca^{2+} dissolving from the surface of the slag grains and form the primary C–S–H (Qureshi and Ghosh 2014). As more sodium silicate content becomes available, the increased onion of sodium silicate elevates C-S-H formation. These observations can be confirmed with the findings of different studies presented in the literature. Atis et al. (2009) and Shi and Li (1989) observed that in all their studied cases, sodium silicate-activated slags developed higher strengths than sodium hydroxide-activated slags which indicate more positive effects of sodium silicate than sodium hydroxide. Also, in various studies on low calcium binders, it was observed that activation of fly ash and natural Pozzolan was more effective by combination of sodium silicate and sodium hydroxide than when only sodium hydroxide was used (Bondar et al. 2011a, Sierra 2015). Lloyd et al. (2009) also found from microstructural observations that geopolymer activated with a silicate-based solution showed a more homogeneous microstructure than that activated with a NaOH-based solution, which may improve the compressive strength. In addition to improvement of microstructure, Aydin and

Baradan (2014) related the strength improvement to the decreases in Ca/Si ratio of C–S–H with increases in silicate content of activator which improved the binding ability of C–S–H.

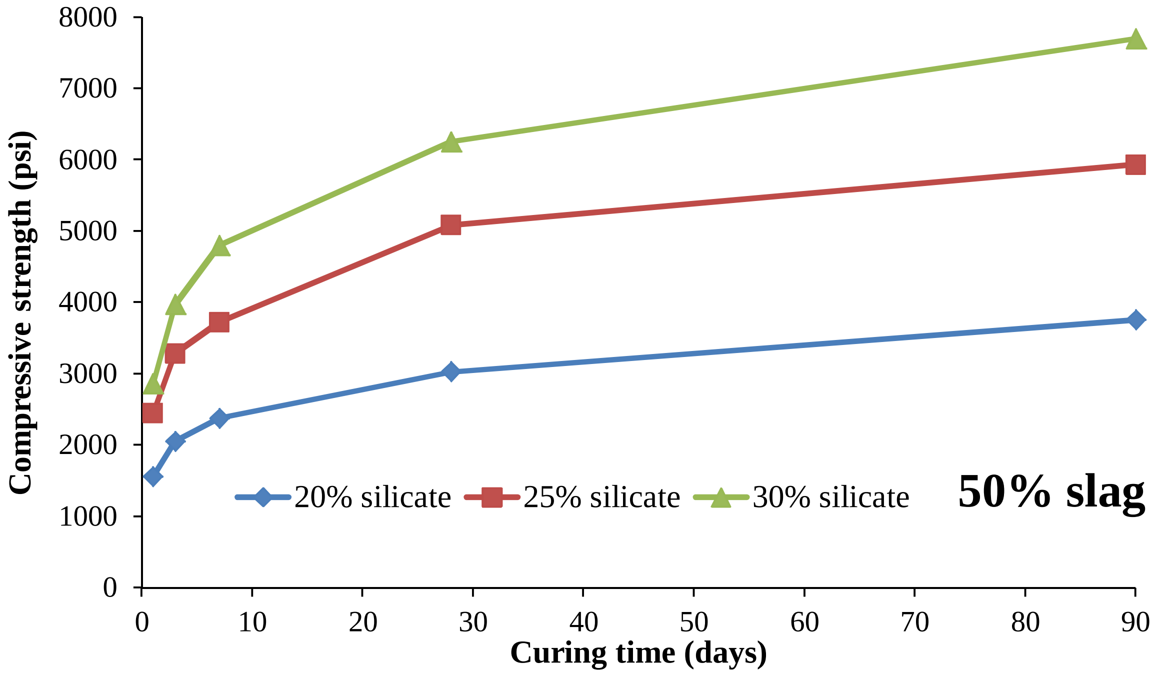


Figure 5.16 The compressive strength of alkali-activated natural Pozzolan/slag mortars having different sodium silicate contents and slag content of 50% (1 psi = 0.00689476 MPa, 1 MPa = 145.038 psi)

5.3.4.3. Effects of alkaline activator solution-to-binder ratio

The influence of solution-to-binder ratio on the compressive strength was also studied and its typical trend is presented in Figure 5.17 for slag content of 30%. In general, the compressive strength slightly improved with reduction of S/B, displaying a similar behavior to that of Portland cement mixtures. The improvements, however, reduced as the curing age was increased. The 1-, 3-, 7-, 28- and 90-day compressive strengths of alkali-activated natural

Pozzolan/slag mortars increased by averagely 14.2, 7.9, 7.6, 4.3 and 5.1% when S/B reduced from 0.60 to 0.56, respectively. Further reduction in S/B from 0.56 to 0.52 led to 25.3, 6.4, 3.2, 0.9 and -0.8% increases in 1-, 3-, 7-, 28- and 90-day compressive strengths, respectively.

It was also observed that the improvements were more significant for mortars with lower slag contents (higher natural Pozzolan contents); in particular when S/B was changed from 0.56 to 0.52. This observation could be related to the lower workability of Mixtures 1M-SL70-SS30-0.52 (70% slag and S/B of 0.52) and 1M-SL50-SS30-0.52 (50% slag and S/B of 0.52) which could have caused insufficient densification.

Ravikumar (2012) found a reliable relationship between porosity, compressive strength and activator-to-binder ratio. He stated that an increase in activator-to-binder ratio increases the porosity of alkali-activated mixture, which in turn, reduces the compressive strength. It can be said that as solution-to-binder ratio increases, the amount of evaporable water in the paste also increases. As evaporable water moves towards surface, it vacates capillary pores. The higher amounts of pores results in higher porosity and lower strength and mechanical properties. The results presented in this study also validate this process as documented by the results of volume of voids which increased with increases in solution-to-binder ratio (see Section 5.3.5).

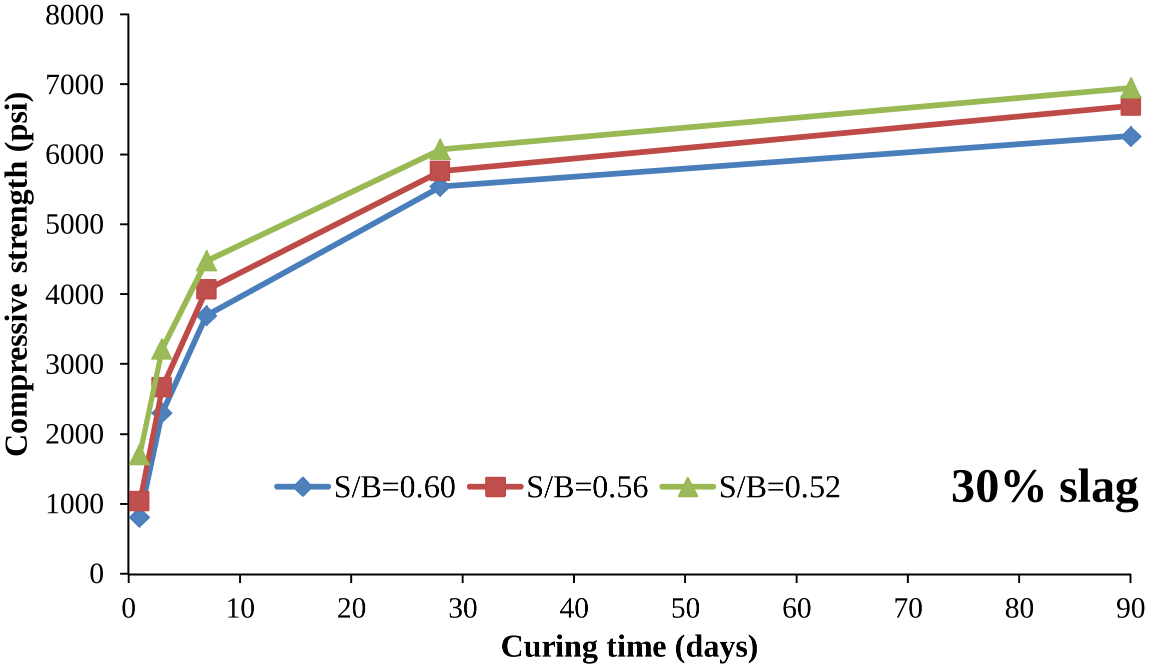


Figure 5.17 Compressive strength of alkali-activated natural Pozzolan/slag mortars having different S/B and slag content of 30% (1 psi = 0.00689476 MPa, 1 MPa = 145.038 psi)

5.3.4.4. Effects of sodium hydroxide concentrations

Figure 5.15 presents the results of compressive strength for alkali-activated natural Pozzolan/slag mortars with different sodium hydroxide concentrations. It can be seen that the influences of NaOH molarity on the compressive strength was dependent on slag content of the mixture as the optimum sodium hydroxide concentration increased with increases in slag content of the studied mixtures.

In case of alkali-activated natural Pozzolan/slag mortars having 30% slag, the late-age compressive strengths (28 and 90 days) increased as molarity of solution was increased from 0.5 to 1M, after which they reduced by further increases in NaOH concentration. For these mixtures, the 28-day and 90-day compressive strengths increased by averagely 3.5% when NaOH molarity was increased from 0.5 to 1M, and reduced by 10.2% when it was increased from 1 to 2M. In fact, 2M mortars developed lower strengths than 0.5M mortars. The higher molarity only resulted in higher strengths at early ages. The 1- and 3-day compressive strengths of 2M mixtures (with 30% slag) were 64.3 and 8.2% higher than those of 1M mixtures; and 142.1 and 22.9% higher than those of 0.5M mixtures, respectively.

Similar trend was observed for mixtures having 50% slag and 50% natural Pozzolan; the late-age compressive strength increased as sodium hydroxide concentration increased from 0.5 to 1M and reduced by further increases in NaOH molarity. The 2M mixtures, however, developed higher compressive strengths than 0.5M mixtures. For these mixtures, the 90-day compressive strengths of 1M mixtures were 2.7 and 9.5% higher than those of 2 and 0.5M mixtures, respectively.

A different trend was observed for mixtures containing 70% slag and 30% natural Pozzolan; the higher molarity led to higher strengths for these mixtures. The 1-day, 3-day, 7-day, 28-day and 90-day compressive strengths of 2M mixtures were 11.7, 9.8, 17.0, 16.3 and 16.8% higher than those of 1M mixtures; and 21.2, 27.0, 28.4, 26.4 and 23.4% higher than those of 0.5M mixtures, respectively.

While increases in compressive strength of 70% slag contained mixtures can be correlated to the increases in solubility of the binders, the strength reduction for mixture having high natural Pozzolan content (and low slag content) can be justified via explanations given by different researchers who studied the effects of NaOH concentration on the strength of alkali-activated fly ash and metakaolin (aluminosilicates). Palomo et al. (1999), Memon et al. (2013)

and Alonso and Palomo (2001) observed that an excess of OH^- concentration in the system of aluminosilicate-based binders caused strength reductions. It was stated by Memon et al. (2013) that excessive hydroxyl ions led to aluminosilicate gel precipitation at the early stages, hindering subsequent geopolymerization to result in lower strength. Alonso and Palomo (2001) related the strength reduction to the delay in formation of alkaline polymer as a result of (1) “the stability of ion species: polymerization is favored when dissolved components are in their molecular form, and an increase of pH provokes higher stability of ion species”, and (2) “ion mobility: a higher sodium hydroxide concentration provokes an increase in the dissolved species amount, and a greater difficulty in the species diffusion in the aqueous phase.” Because of the similarity in chemical compositions amongst fly ash, metakaolin, and natural Pozzolan; the above explanations are equally valid for the studied alkali-activated mixtures having high amounts of natural Pozzolan.

5.3.5. Absorption

Table 5.5 reports the results of absorption test for all the studied alkali-activated natural Pozzolan/slag mortars. The effects of different variables on absorption results are presented below.

Table 5.5 Results of absorption test for alkali-activated natural Pozzolan/slag mortars

Mix id.	Absorption after immersion (%)	Absorption after immersion and boiling (%)	Volume of permeable voids (%)
2M-SL30-SS30-0.60	9.27	9.79	19.73
2M-SL50-SS30-0.60	8.58	9.25	18.95
2M-SL70-SS30-0.60	8.71	9.57	19.75
1M-SL30-SS30-0.60	10.40	10.88	21.74
1M-SL50-SS30-0.60	8.74	9.37	19.06
1M-SL70-SS30-0.60	8.92	9.93	20.19
0.5M-SL30-SS30-0.60	10.80	11.55	22.77
0.5M-SL50-SS30-0.60	8.95	9.72	19.63
0.5M-SL70-SS30-0.60	9.74	10.97	22.00
1M-SL30-SS30-0.56	8.74	9.24	18.80
1M-SL50-SS30-0.56	8.22	8.89	18.24
1M-SL70-SS30-0.56	8.15	9.14	18.81
1M-SL30-SS30-0.52	7.75	8.38	17.20
1M-SL50-SS30-0.52	7.26	7.93	16.44
1M-SL70-SS30-0.52	8.05	8.84	18.37
1M-SL30-SS20-0.60	10.39	10.66	21.23
1M-SL50-SS20-0.60	8.90	9.19	18.62
1M-SL70-SS20-0.60	10.84	11.27	22.55
1M-SL30-SS25-0.60	10.09	10.41	20.73
1M-SL50-SS25-0.60	8.98	9.34	19.00
1M-SL70-SS25-0.60	9.65	10.24	20.69

5.3.5.1. Effects of binder combinations

Figures 5.18 and 5.19 present the influences of binder combination on the absorption and volume of permeable voids of alkali-activated natural Pozzolan/slag mortars having different sodium hydroxide concentrations, respectively. It can be seen that the absorption and permeable voids of mortars having 50% slag were lower than those of mortars containing 30 and 70% slag. While the absorption results of mortars with 30 and 70% slag contents were fairly similar to one another, the 70% slag contained mortars displayed slightly lower absorption than that of 30% slag contained mortars. The void contents of mortars with 50 and 70% slag were lower than those of mortars having 30% slag by 13.8 and 3.4% for 0.5M mixtures; 12.3 and 7.1% for 1M mixtures; and 4.0 and 0% for 2M mixtures, respectively.

The effects of slag content on the absorption properties of mixtures with different sodium silicate content and S/B are reported in Table 5.5. These results can also be seen in Figures 5.20 through 5.23. Similarly, alkali-activated mortars having 50% slag and 50% natural Pozzolan showed the lowest absorption and volume of permeable voids. The performances of mortars containing 30 and 70% slag were almost at the same levels.

The observed trend was similar to the trend found for compressive strength. For majority of the mixtures, mortars having 50% slag performed superior to mortars with 30 and 70% slag in both absorption and compressive strength tests. Also, for both properties, the differences in performance of mixtures with different slag contents narrowed as NaOH molarity was increased.

These observations are close to the findings of Ismail et al. (2013a) on 28-day absorption of slag/fly ash activated mortars. At this age of curing, the performance of their studied mortars was in order of 50/50 – 75/25 – 25/75 slag/fly ash combination. A similar trend was observed by Chi and Huang (2013) where they produced slag/fly ash activated mortars with different combinations of fly ash and slag. In case of their studied mortars, the absorption of 50/50 combination of slag/fly ash was slightly superior to 75/25 combination; both were significantly better than 25/75 and 0/100 combinations. They related this behavior to the difference of the formed gels and finer particle size of slag in comparison with fly ash. “The slag-rich systems predominantly form a C–(A)–S–H gel with a significant bound water content, while the fly ash-rich systems form N–A–S–(H) with a lower bound water content.” Therefore, fly ash-rich systems (having more N-A-S-H gels) absorbed more water. Furthermore, their used slag had a much finer particle size which could fill the pore resulting in lower water absorption. Due to similarity between the binder used in this study and that used in the study reported by Ismail et al. (2013a), both of the above explanations are also valid for the studied alkali-activated natural Pozzolan/slag mortars.

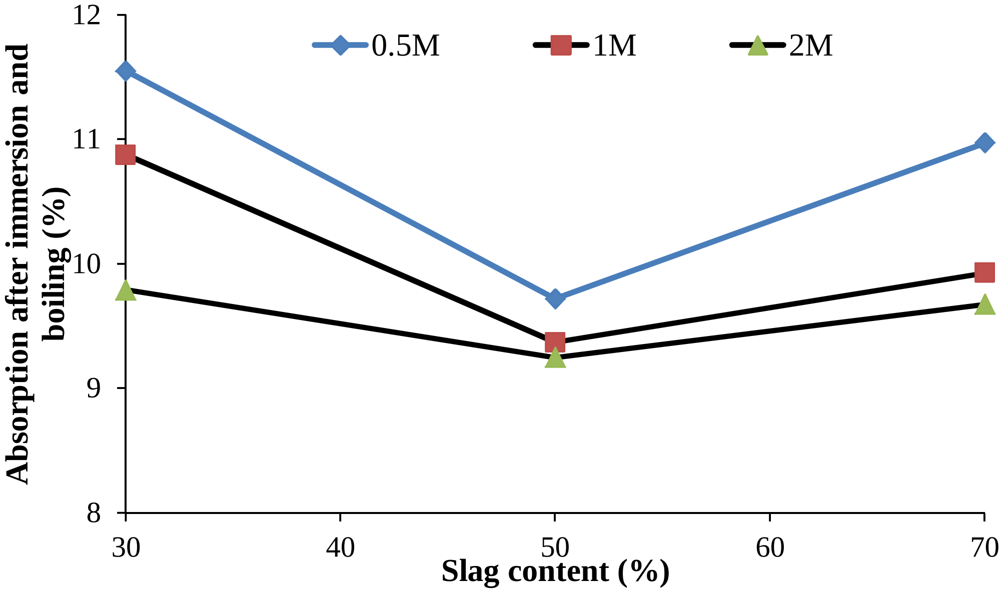


Figure 5.18 Absorption of alkali-activated natural Pozzolan/slag mortars with different slag content and sodium hydroxide concentration

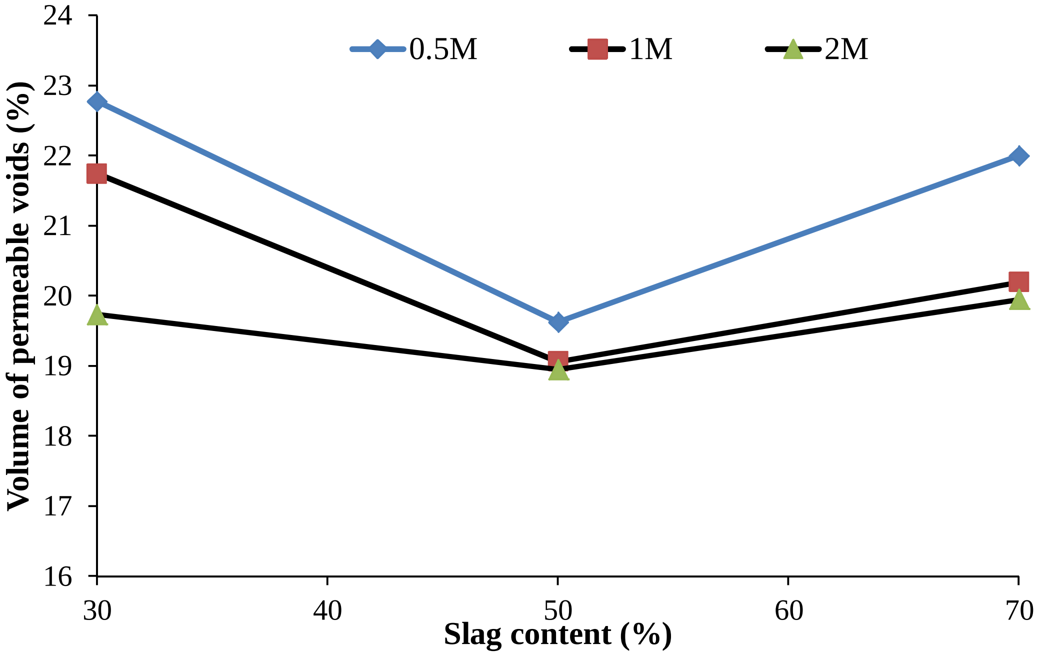


Figure 5.19 Volume of permeable voids of alkali-activated natural Pozzolan/slag mortars with different slag contents and sodium hydroxide concentrations

5.3.5.2. Effects of activator combination

The influence of sodium silicate contents on the absorption and volume of permeable voids of alkali-activated natural Pozzolan/slag mortars are presented in Figures 5.20 and 5.21, respectively. As can be seen, while the absorption results were in the same ranges for majority of the studied natural Pozzolan/slag mortars, the influence of sodium silicate content on absorption was dependent on the slag content of the mixture. In case of mortars with 30% slag, absorption of mortars having 20 and 25% sodium silicate content was almost similar. For this slag dosage, increases in sodium silicate content from 25 to 30% resulted in slight increases in absorption and volume of permeable voids. For mortars having 50% slag, the absorption of mixtures were almost the same. For these mixtures, absorption increased slightly as sodium silicate content increased. An opposite trend was observed for mixtures having 70% slag. For these mixtures, there were obvious improvements in absorption due to increases in sodium silicate contents. This observation can be attributed to the modification of C-S-H gel in the mixtures having high slag dosage through increases in silicate content. As alluded to in the Section 5.3.4 describing the results for compressive strength, use of higher sodium silicate in the mortars containing high amounts of slag improved microstructure and binding capacity of C-S-H gel through reduction of Ca/Si ratio.

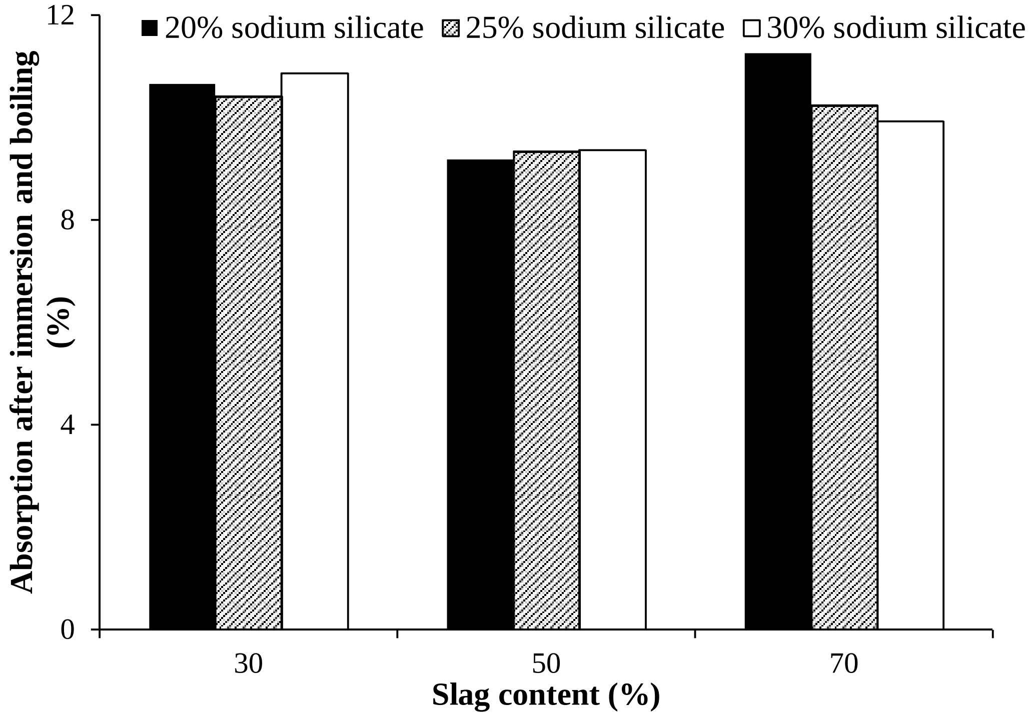


Figure 5.20 Absorption of alkali-activated natural Pozzolan/slag mortars having different sodium silicate contents

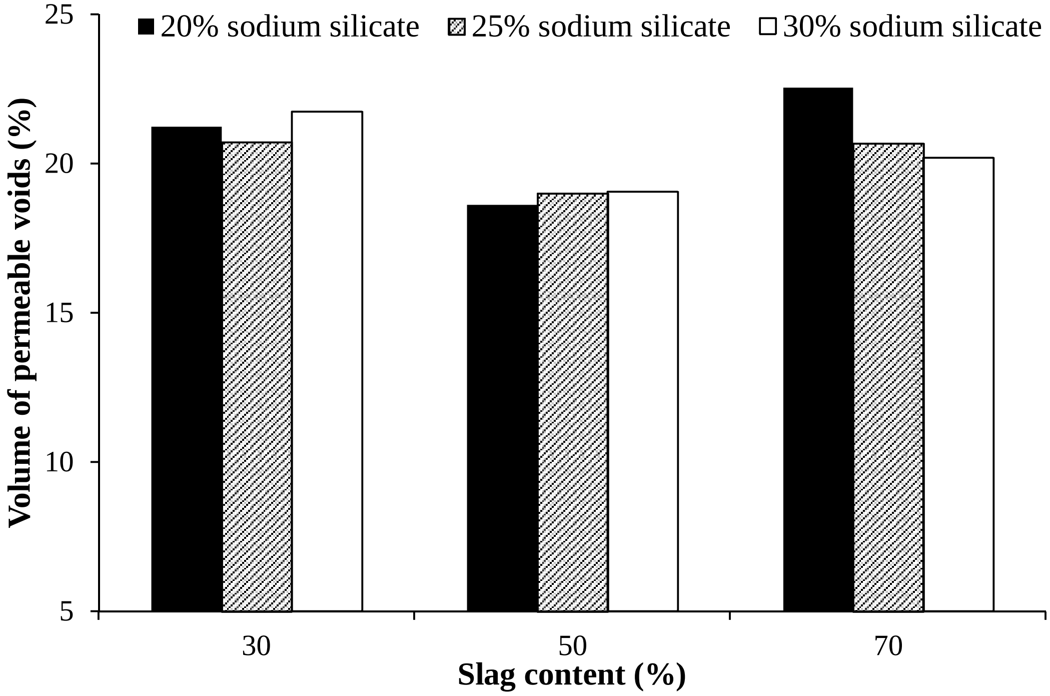


Figure 5.21 Volume of permeable voids of alkali-activated natural Pozzolan/slag mortars having different sodium silicate contents

5.3.5.3. Effects of alkaline activator solution-to-binder ratio

Figures 5.22 and 5.23 show the results of absorption test for alkali-activated natural Pozzolan/slag mortars having different solution-to-binder ratios. As expected, reduction of S/B improved absorption properties. On average, each 0.04 reduction in S/B resulted in 11.5, 7.7 and 5.5% reduction in absorption of mortars having 30, 50 and 70% slag, respectively. For similar slag contents, volume of permeable voids reduced by averagely 10.4, 6.9 and 4.5% for each 0.04 reduction in S/B, respectively.

This behavior is consistent with the results reported for compressive strength (Section 5.3.4) and is similar to the behavior seen in Portland cement mortars. The observed behavior can be related to entrapment of more water within the alkali-activated paste which allowed for additional capillary voids and more porous microstructure upon evaporation of migrated pore water to the surface of the studied specimens.

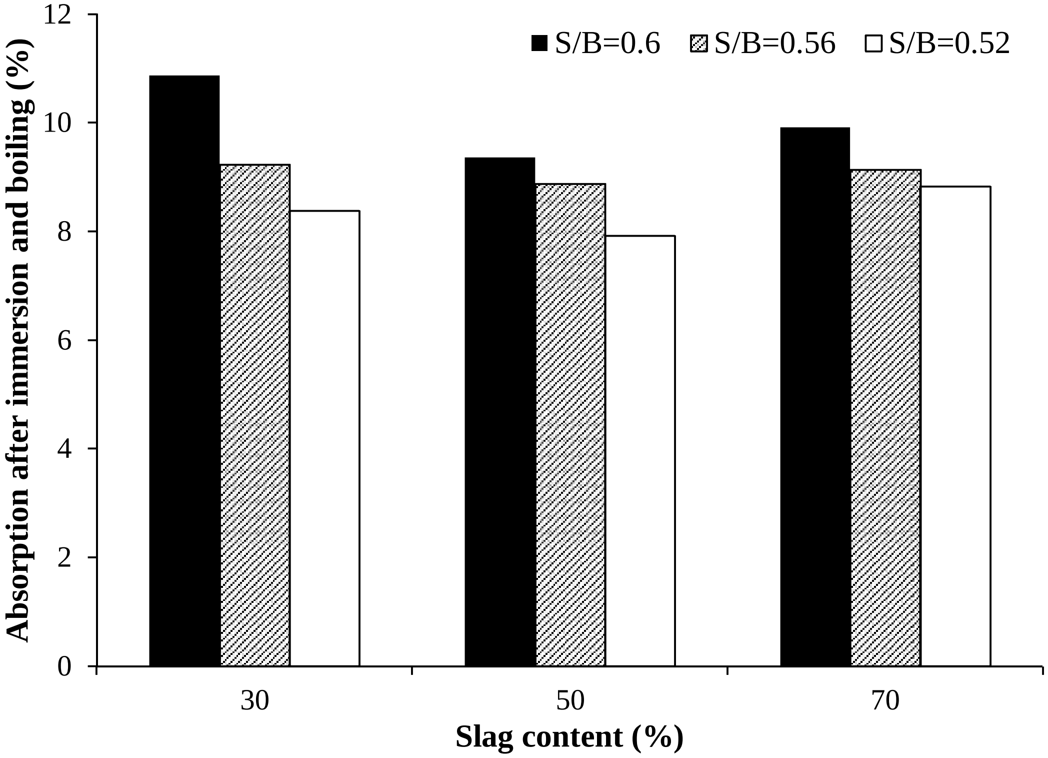


Figure 5.22 Absorption of alkali-activated natural Pozzolan/slag mortars having different S/B

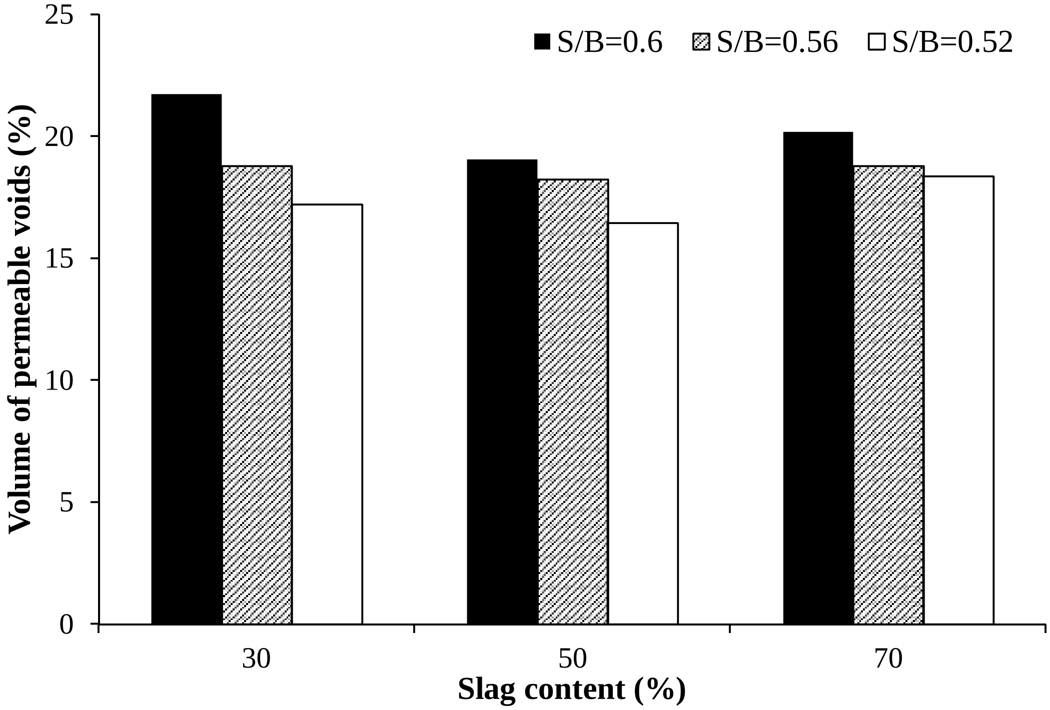


Figure 5.23 Volume of permeable voids of alkali-activated natural Pozzolan/slag mortars having different S/B

5.3.5.4. Effects of sodium hydroxide concentration

The results of absorption test for alkali-activated natural Pozzolan/slag mortars having different sodium hydroxide concentrations are shown in Figures 5.24 and 5.25. It can be seen that absorption of alkali-activated natural Pozzolan/slag mortars reduced as the molarity of NaOH was increased. The absorption properties (absorption and volume of permeable voids) of 30% slag contained mortars reduced by averagely 4.7 and 10.0% when the NaOH concentration was increased from 0.5 to 1 and 1 to 2M, respectively. These improvements were 3.0 and 1.2% for 50% slag contained mortars, and 8.7 and 2.7% for 70% slag contained mortars, respectively. These findings follow the observations made by Melo Neto et al. (2008) and Chi and Huang

(2013) where reduction in porosity of alkali-activated slag systems with increases in Na_2O content were reported.

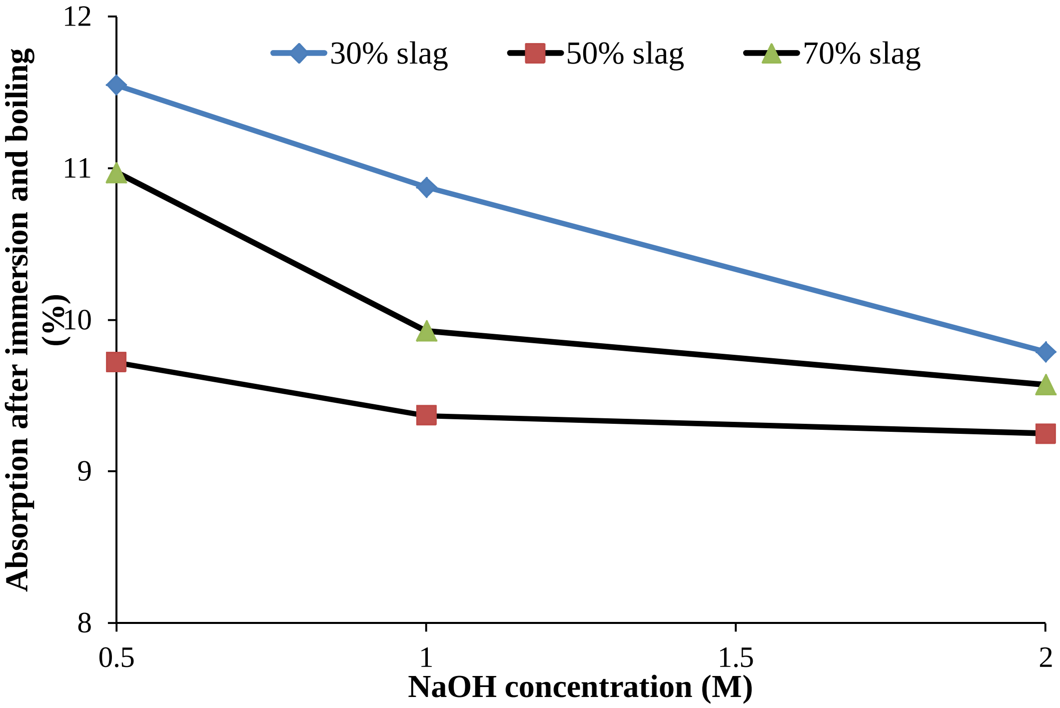


Figure 5.24 Absorption of alkali-activated natural Pozzolan/slag mortars having different NaOH concentrations

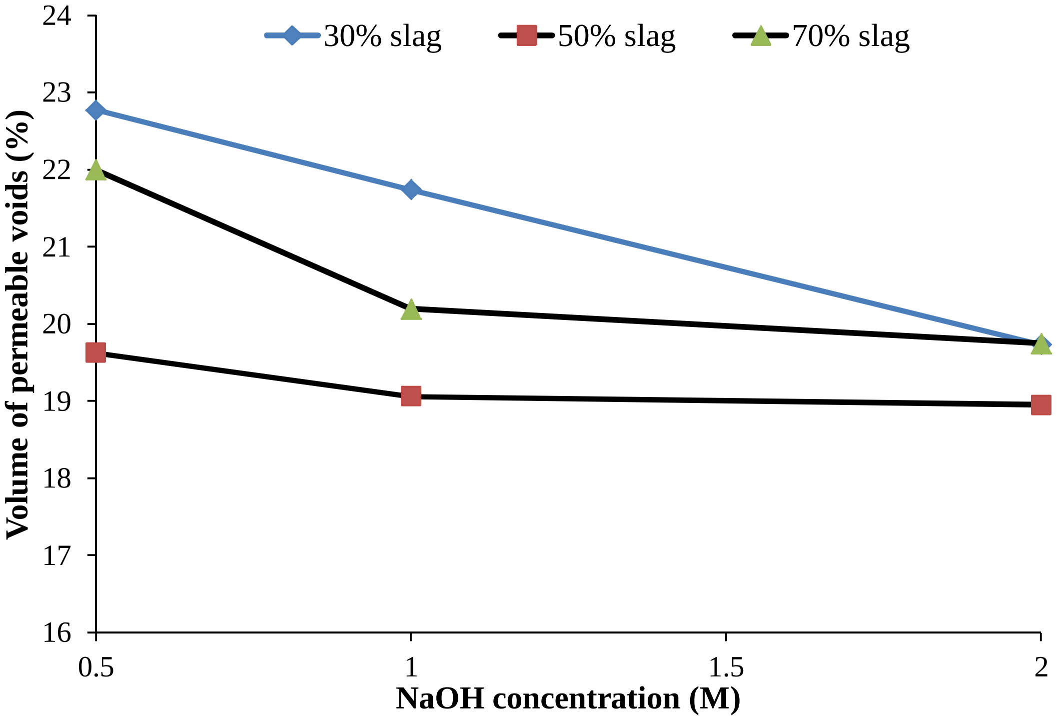


Figure 5.25 Volume of permeable voids of alkali-activated natural Pozzolan/slag mortars having different NaOH concentrations

5.3.6. Rapid chloride penetration test

Table 5.6 documents the results of rapid chloride penetration test (RCPT). The general trend for effects of binder combination, activator combination, sodium hydroxide concentration and S/B are presented in Figures 5.26 through 5.28.

Table 5.6 Results of RCPT and RMT for alkali-activated natural Pozzolan/slag mortars

Mix id.	Rapid chloride penetration test (Coulombs)	Rapid chloride migration test (mm)
2M-SL30-SS30-0.60	6613	18.68
2M-SL50-SS30-0.60	1522	4.64
2M-SL70-SS30-0.60	1108	3.15
1M-SL30-SS30-0.60	4958	11.97
1M-SL50-SS30-0.60	944	3.79
1M-SL70-SS30-0.60	743	3.23
0.5M-SL30-SS30-0.60	3511	9.90
0.5M-SL50-SS30-0.60	791	4.09
0.5M-SL70-SS30-0.60	656	2.91
1M-SL30-SS30-0.56	2915	8.51
1M-SL50-SS30-0.56	762	2.76
1M-SL70-SS30-0.56	518	2.43
1M-SL30-SS30-0.52	1601	6.99
1M-SL50-SS30-0.52	516	2.43
1M-SL70-SS30-0.52	467	1.93
1M-SL30-SS20-0.60	652	5.37
1M-SL50-SS20-0.60	443	3.30
1M-SL70-SS20-0.60	448	3.01
1M-SL30-SS25-0.60	1727	6.49
1M-SL50-SS25-0.60	514	3.74
1M-SL70-SS25-0.60	482	3.00

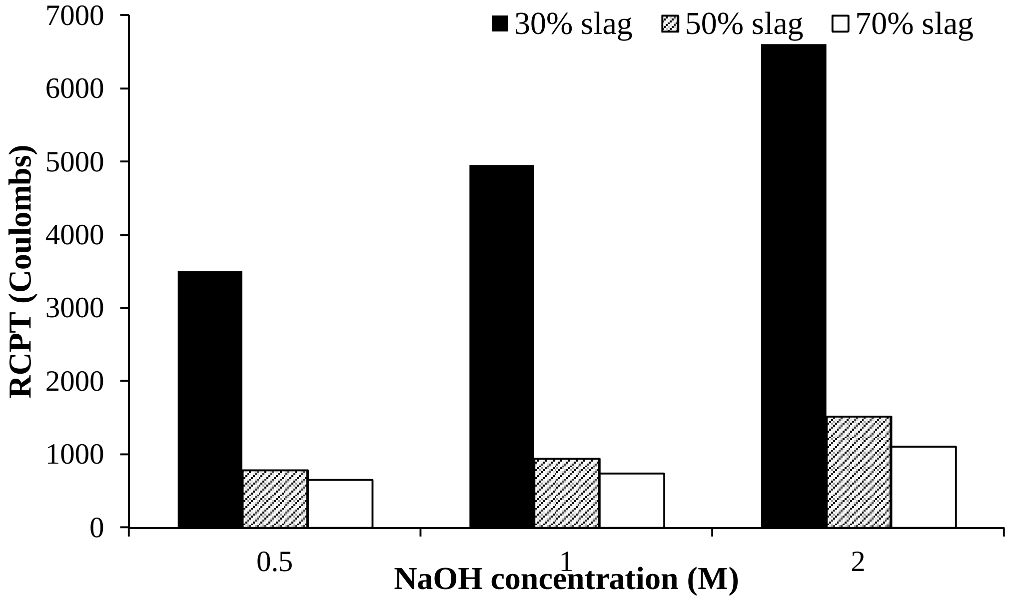


Figure 5.26 RCPT results of alkali-activated natural Pozzolan/slag mortars with different slag contents and sodium hydroxide concentrations

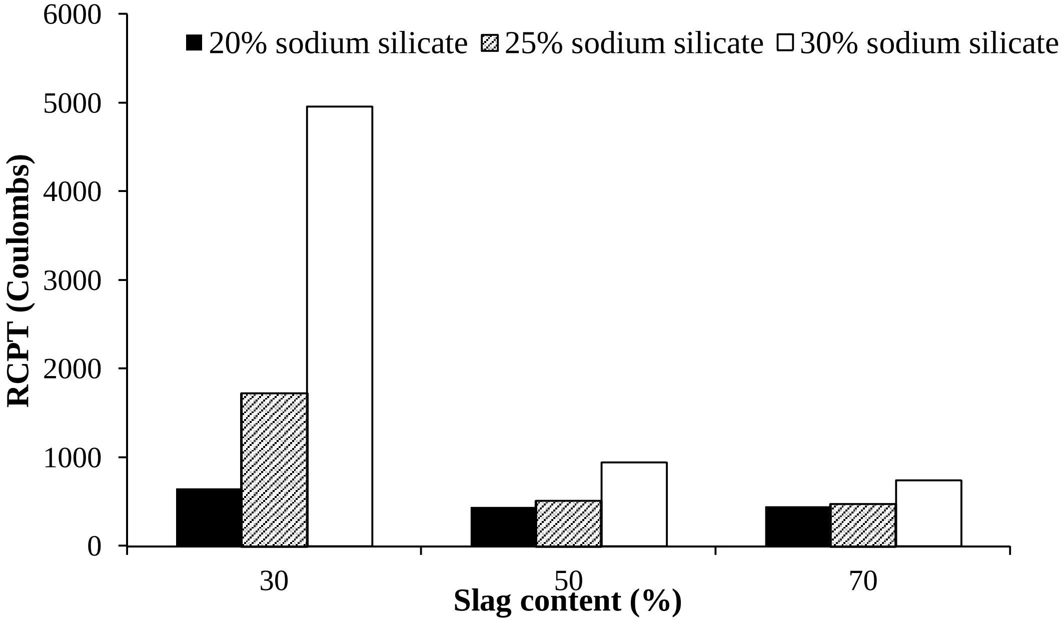


Figure 5.27 RCPT results of alkali-activated natural Pozzolan/slag mortars having different sodium silicate contents

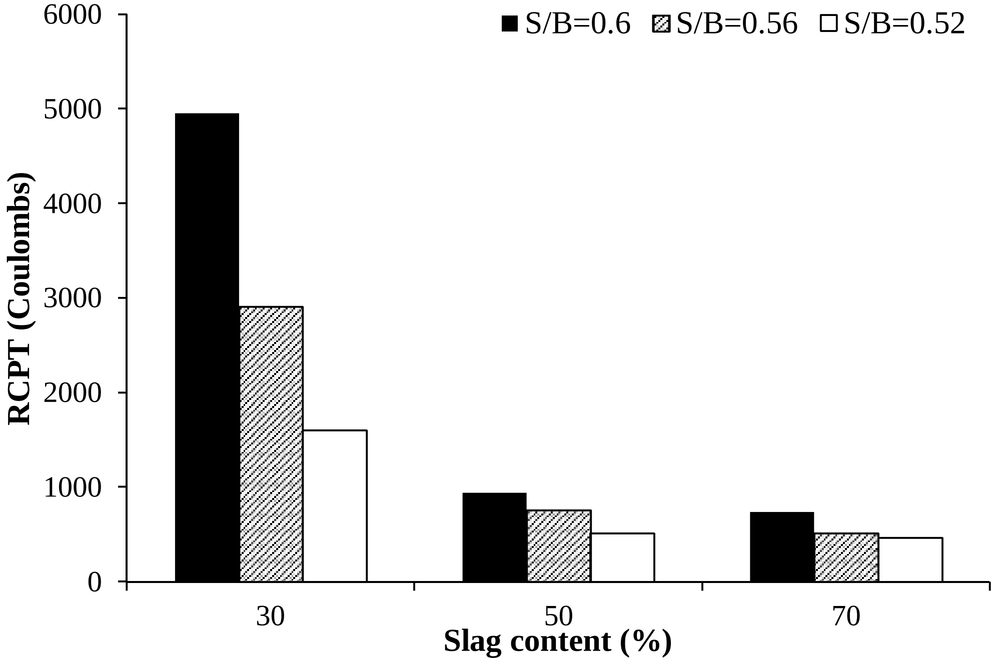


Figure 5.28 RCPT results of alkali-activated natural Pozzolan/slag mortars having different S/B

5.3.6.1. Effects of binder combination

The influence of binder combination on rapid chloride penetration of alkali-activated natural Pozzolan/slag mortars are shown in Figures 5.26, 5.27 and 5.28 for mixtures having different NaOH molarities, sodium silicate contents and S/B, respectively. It can be seen that increases in slag content resulted in reduction of passing charges.

There was a significant reduction in the passing charge, when slag content was increased from 30 to 50%. For mixtures with NaOH concentrations of 0.5, 1 and 2M, this increase in slag content led to 77.5, 81.0 and 77.0% reduction in RCPT passing charges, respectively. For sodium silicate contents of 20, 25 and 30%, the RCPT results of mortars having 50% slag were 32.1, 70.2 and 81.0% lower than those of mortars containing 30% slag, respectively. Similarly, increases in slag content from 30 to 50% resulted in 81.0, 73.9 and 67.8% reductions in the passing charge of mortars with S/B of 0.6, 0.56 and 0.52, respectively. On average, the passing charges of mortars with 70% slag were 16% lower than those of mortars having 50% slag.

As the amounts of hydroxide ions in pore solution has been known as a major factor contributing to the charges passing in rapid chloride penetration test, it can be inferred from these observations that there were more free hydroxyls available in mixtures with lower slag dosages. While chloride permeability improved through increases in slag content, a considerable portion of the observed reductions could be due to the higher availability of hydroxyls in the mixtures having lower slag contents. This observations is consistent with the results of compressive strength where increases in NaOH concentration was ineffective for mixtures made with 30% slag, whereas use of higher NaOH molarity considerably improved the strength of mixtures having 70% slag. It's possible that sodium hydroxide solution reacted more efficiently with slag in comparison with natural Pozzolan, thus more hydroxyl ions left in the mortars containing high amount of natural Pozzolan (i.e. 70% by weight of total binder).

5.3.6.2. Effects of activator combination

Figure 5.27 shows the effect of sodium silicate contents on the results of rapid chloride penetration test. It can be seen that the passing charges increased with increases in sodium silicate content. As sodium silicate was increased from 20 to 25%, the passing charges increased by almost 165, 16 and 7% for mortars having slag contents of 30, 50 and 70%, respectively. For the similar slag contents, increases in sodium silicate dosage from 25 to 30% resulted in 187, 84 and 54% increases in the passing charges, respectively.

The increases in the RCPT values through increases in sodium silicate content, which was along with reduction of sodium hydroxide solution, can be related to the higher alkalis content of sodium silicate in comparison with that of sodium hydroxide. While 14.8% of sodium silicate was alkalis, sodium hydroxide solutions were prepared by dissolving 20 (almost 2% alkalis), 40 (almost 4% alkalis) and 80g (almost 8% alkalis) NaOH pellets in nearly a liter of water for concentrations of 0.5, 1 and 2M, respectively. Douglas et al. (1992) also observed increases in RCPT passing charges by increasing sodium silicate-to-slag ratio of alkali-activated slag concretes.

5.3.6.3. Effects of alkaline activator solution-to-binder ratio

The results of RCPT for alkali-activated natural Pozzolan/slag mortars with different solution-to-binder ratios are shown in Figure 5.28. Considerable reductions in the passing charges were observed through reduction of S/B. For slag content of 30%, the passing charges of mortars with S/B of 0.52 were 45.1 and 67.7% lower than those having S/B of 0.56 and 0.6, respectively. These improvements reduced to 32.3 and 45.3% for slag content of 50%; and 9.8 and 37.1% for slag content of 70%, respectively.

The observed improvements by use of lower S/B can be related to the improvement in pore structure (reported for the results of absorption and compressive strength) as well as reduction of free hydroxyl ions through reduction of alkaline solution content.

5.3.6.4. Effects of sodium hydroxide concentrations

The influence of sodium hydroxide concentrations on the RCPT charges is presented in Figure 5.26. It can be seen that the passing charges increased as sodium hydroxide concentration was increased. Increases in NaOH molarity from 0.5 to 1M caused 1477, 153 and 187 coulombs increases in the passing charges of mortars having 30, 50 and 70% slag, respectively. For similar slag contents, the increases in NaOH concentration from 1 to 2M resulted in 1655, 578 and 365 coulombs increases in the passing charges, respectively.

The observed increases can be related to the increases in hydroxyl ions (OH^-). As the molarity of sodium hydroxide increased, the hydroxyl ions increased, resulting in increased passing charges.

5.3.7. Rapid chloride migration test

Table 5.6 also reports the results of rapid chloride migration test (RMT) for all alkali-activated natural Pozzolan/slag mortars. The influence of different factors on the results of RMT is discussed below.

5.3.7.1. Effects of binder combination

Figures 5.29, 5.30 and 5.31 show effects of slag and natural Pozzolan contents on the chloride penetration depth of alkali-activated natural Pozzolan/slag mortars with different NaOH concentrations, sodium silicate contents and S/B, respectively.

Similar to the RCPT results, the higher slag contents led to lower chloride penetration. The chloride penetration depth of alkali-activated natural Pozzolan/slag mortars considerably reduced when slag content was increased from 30 to 50%. The penetration depths of mortars having 50% slag were 58.7, 68.3 and 75.2% lower than those of mortars having 30% slag for NaOH molarities of 0.5, 1 and 2M, respectively. Increases in slag content from 30 to 50% resulted in 38.5, 42.4 and 68.3% improvements in the chloride penetration depths of mortars having sodium silicate contents of 20, 25 and 30%; and 68.3, 67.6 and 65.2% reduction in penetration depth of mixtures with S/B of 0.6, 0.56 and 0.52, respectively.

However, further increases in slag content did not result in considerable improvement in the chloride penetration depths. It can be seen that the penetration depths reduced by averagely 19.5%, when slag contents increased from 50 to 70%.

Ismail et al. (2013a) observed a similar trend in their RMT studies using fly ash/slag alkali-activated concretes. They stated that the degree of penetration increased with the inclusion of higher fly ash in the binder. They attributed their findings to “the change of the microstructure of the system from a dense C-A-S-H binding gel to a more porous hybrid (C-N)-A-S-H type gel” (Ismail et al. 2013). Similarly, Yang et al. (2014) reported that “the incorporation of slag as a secondary precursor in fly-ash-based geopolymers contributed to the refinement of pore structure and thus restricted the movement of chloride ions in the paste.” Due to the similarity in binder chemical compositions, it can be deduced that the studied alkali-activated natural Pozzolan/slag mortars also behaved similarly once the natural Pozzolan content of the binder increased.

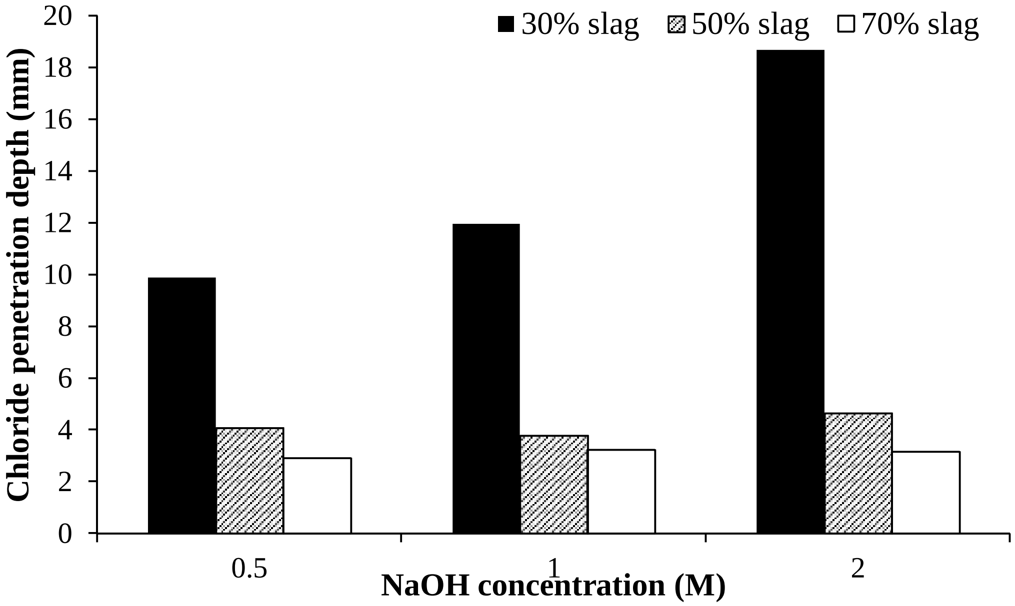


Figure 5.29 Chloride penetration depth of alkali-activated natural Pozzolan/slag mortars with different slag contents and sodium hydroxide concentrations

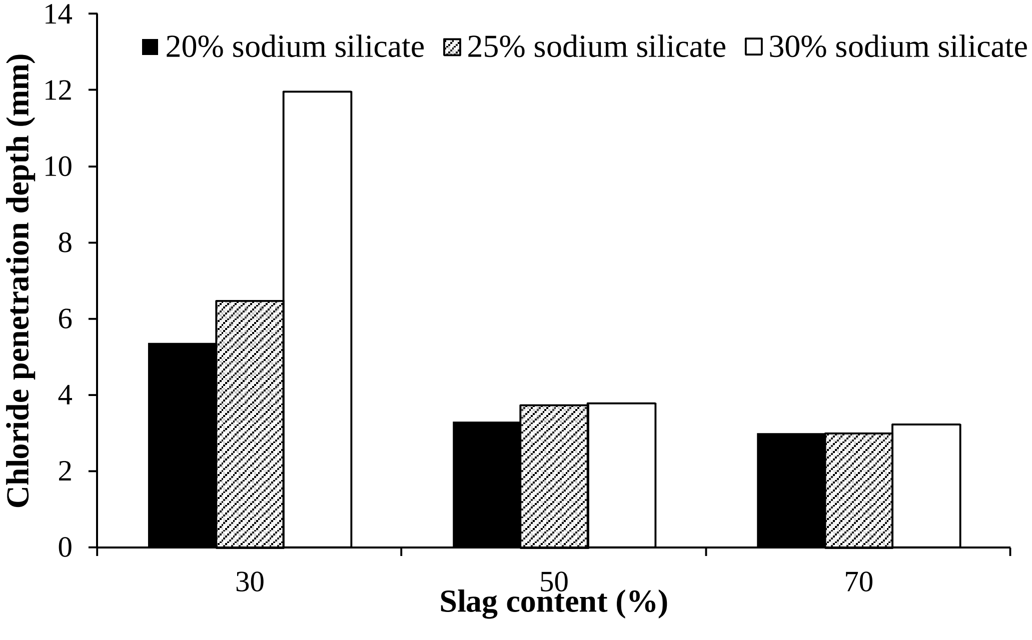


Figure 5.30 Chloride penetration depth of alkali-activated natural Pozzolan/slag mortars with different sodium silicate contents

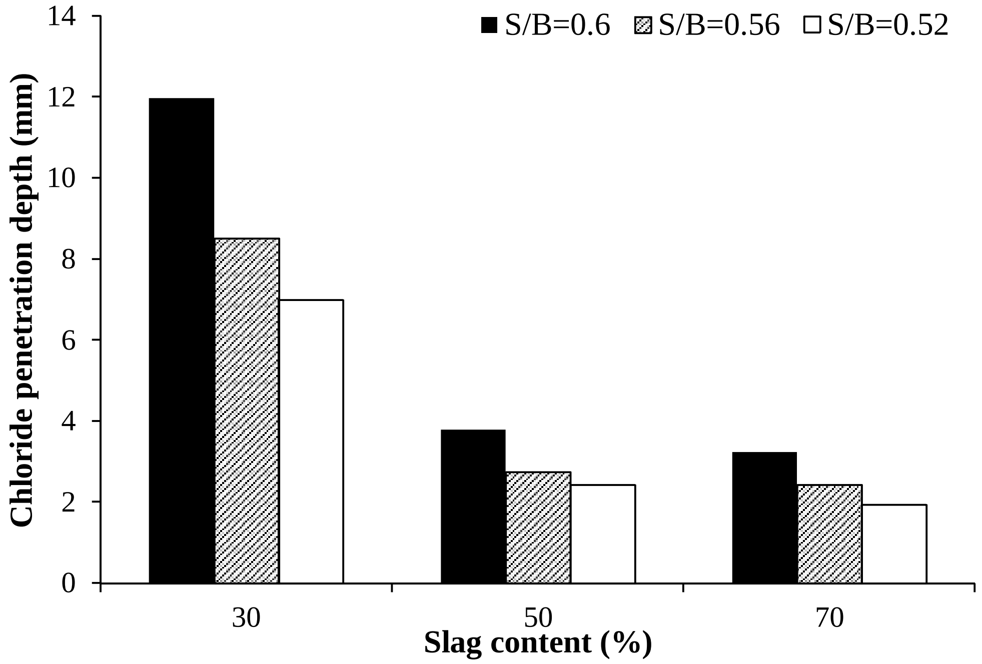


Figure 5.31 Chloride penetration depth of alkali-activated natural Pozzolan/slag mortars having different S/B

5.3.7.2. Effects of activator combination

Figure 5.30 presents the results of rapid chloride migration test for alkali-activated natural Pozzolan/slag mortars having different sodium silicate contents. It can be seen that similar to the results of rapid chloride penetration test, the chloride penetration depth increased with increases in sodium silicate content. Increases in sodium silicate content from 20 to 25% and 25 to 30% resulted in 20.9 and 84.4% increases in chloride penetration depth of mortars having slag contents of 30%, respectively. The increases were not as considerable for mixtures with slag contents of 50 and 70%. Similar increases in sodium silicate content reduced the chloride penetration depth by 13.3 and 1.3% for 50% slag contained mixtures; and -0.3 and 7.7% for 70% slag contained mixtures, respectively.

The significant increases in chloride penetration depth of 30% slag contained mixtures can be explained through reviewing the results obtained for absorption and RCPT of the studied natural Pozzolan/slag mortars. The increases in the results of these two tests with increases in sodium silicate content suggested that the pore structure of 30% slag contained mortars were weakened with the higher sodium silicate content. This, in turn, allowed for higher penetration of chloride ions.

5.3.7.3. Effects of alkaline activator solution-to-binder ratio

Figure 5.31 shows the chloride penetration depths of alkali-activated natural Pozzolan/slag mortars having different solution-to-binder ratios. Similar to the RCPT, reduction of S/B led to considerable improvements in the depth of penetration. As S/B was reduced from 0.6 to 0.56, the penetration depth decreased by 14.0, 32.5 and 16.5% for mortars containing 30, 50 and 70% slag, respectively. For similar slag contents, the reduction of S/B from 0.56 to 0.52 led to 17.9, 12.0 and 20.6% improvements in penetration depths, respectively. The higher amounts of capillary pores as a result of higher solution-to-binder ratio resulted in easier movement of chloride ions through the studied mortars.

5.3.7.4. Effects of sodium hydroxide concentrations

Table 5.6 and Figure 5.29 present the results of rapid chloride migration test for alkali-activated natural Pozzolan/slag mortars having sodium hydroxide concentrations of 0.5, 1 and 2M. Overall, increases in the sodium hydroxide concentrations increased the chloride penetration depth of alkali-activated natural Pozzolan/slag mortars. This was particularly seen in mortars having 30% slag and 70% natural Pozzolan. The chloride penetration depths of 30% slag contained mortars activated with 2M sodium hydroxide were 8.8 and 6.7mm higher than those having 0.5 and 1M NaOH, respectively. In case of mortars having 50 and 70% slag, there was a slight difference between penetration depths of mixtures having different sodium hydroxide concentrations. For these slag contents, the penetration depths of 2M mixtures were averagely 0.75 and 0.05mm more than those of mixtures with lower NaOH concentrations of 0.5 and 1M, respectively.

The observed increases in penetration depth by increasing NaOH concentration from 0.5 (and 1) to 2M for 30% slag contained mixtures may be related to its microstructure which also produced lower compressive strength.

5.3.8. Drying shrinkage

The alkali-activated natural Pozzolan/slag mortars were transferred to the shrinkage room (with relative humidity of 50±5% and a temperature of 24°C) after 7 days of curing in the moist-curing room. The drying shrinkage of samples was measured for a period of about 5 months. In order to avoid presentation of several figures for each mixture or for different factors, their ultimate drying shrinkages are reported in Table 5.7. Figures 5.32 through 5.35 show the typical trends for different studied variables affecting drying shrinkage of the studied alkali-activated natural Pozzolan/slag mortars.

Table 5.7 Ultimate drying shrinkage of alkali-activated natural Pozzolan/slag mortars

Mix id.	Ultimate shrinkage (%)
2M-SL30-SS30-0.60	-0.4423
2M-SL50-SS30-0.60	-0.3542
2M-SL70-SS30-0.60	-0.3458
1M-SL30-SS30-0.60	-0.4069
1M-SL50-SS30-0.60	-0.3075
1M-SL70-SS30-0.60	-0.3042
0.5M-SL30-SS30-0.60	-0.3984
0.5M-SL50-SS30-0.60	-0.3329
0.5M-SL70-SS30-0.60	-0.3185
1M-SL30-SS30-0.56	-0.3806
1M-SL50-SS30-0.56	-0.3078
1M-SL70-SS30-0.56	-0.3014
1M-SL30-SS30-0.52	-0.3320
1M-SL50-SS30-0.52	-0.2824
1M-SL70-SS30-0.52	-0.2727
1M-SL30-SS20-0.60	-0.2297
1M-SL50-SS20-0.60	-0.1982
1M-SL70-SS20-0.60	-0.1947
1M-SL30-SS25-0.60	-0.3068
1M-SL50-SS25-0.60	-0.2449
1M-SL70-SS25-0.60	-0.2480

5.3.8.1. Effects of binder combination

The typical influence of binder combination on the drying shrinkage of alkali-activated natural Pozzolan/slag mortars is presented in Figure 5.32 for mixtures with sodium hydroxide concentration of 2M. It can be seen that the drying shrinkage reduced with increases in slag content. The reduction, however, was more significant when slag content was increased from 30 to 50% in comparison with when it was increased from 50 to 70%. The ultimate drying shrinkages of 0.5M mortars having 50 and 70% slag were 16.4 and 20.1% lower than those of mortars containing 30% slag, respectively. In case of 1 and 2M mortars, the mortars containing

50% slag shrank 24.4 and 19.9% lower than mortars having 30% slag, respectively. Similar to the 0.5M mortars, 1M and 2M mortars having 50 and 70% slag shrank at almost the same levels.

The influence of slag contents on the ultimate drying shrinkage of mixtures with sodium silicate contents of 20, 25 and 30% are also reported in Table 5.7. Similarly, it can be seen that use of higher slag dosage led to lower drying shrinkages. The ultimate shrinkages of mortars with 50 and 70% slag, however, were almost the same. On average, the ultimate drying shrinkages of 30% slag contained mortars were 19.4 and 19.9% higher than those of mortars having 50 and 70% slag, respectively. The observed differences, however, narrowed as sodium silicate content was reduced. Alkali-activated natural Pozzolan/slag mortars having 30% slag shrank averagely 24.8, 19.7 and 14.5% more than those having higher slag contents (50 and 70% slag) for sodium silicate contents of 30, 25 and 20%, respectively.

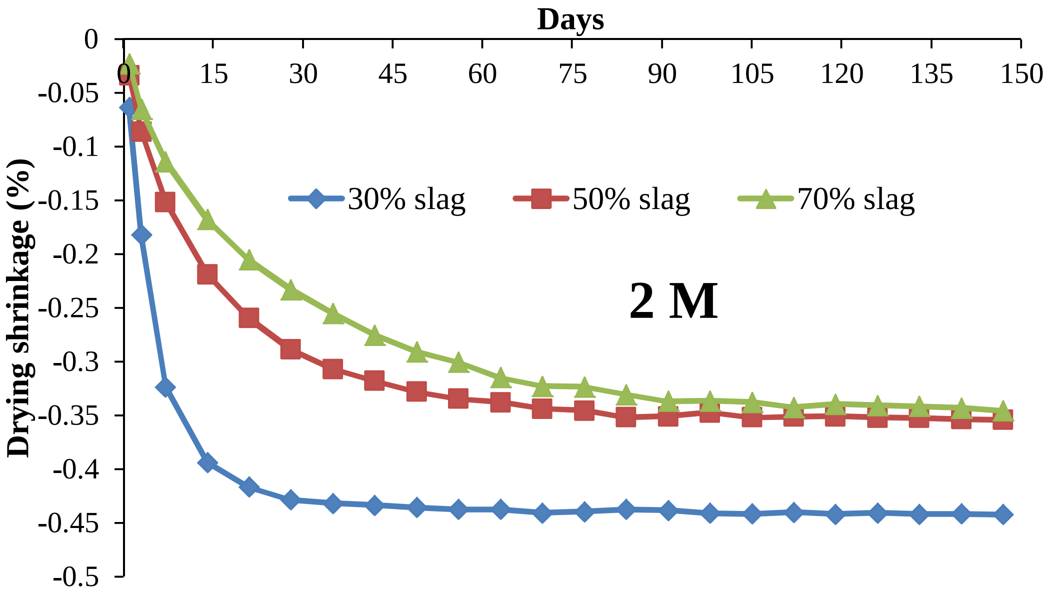


Figure 5.32 The drying shrinkage of alkali-activated natural Pozzolan/slag mortars having different slag contents and sodium hydroxide concentration of 2M

The effects of slag contents on the ultimate drying shrinkage are also documented in Table 5.7 for mixtures with S/B of 0.6, 0.56 and 0.52. Overall, the ultimate drying shrinkage reduced as slag content of alkali-activated natural Pozzolan/slag mortar was increased. For S/B of 0.60, 0.56 and 0.52, the ultimate drying shrinkage improved by 24.4, 19.1 and 14.9%, when slag content was increased from 30 to 50%, respectively. For similar S/B, the increases in slag content from 50 to 70% led to only 1.1, 2.1 and 3.4% reduction in the ultimate drying shrinkage, respectively.

It can also be seen in Figures 5.32 (2M mixtures) that 30% slag contained mortar reached its ultimate shrinkage within a month. In case of mixture containing 50% slag, it took almost 2 to 2.5 months to reach the ultimate shrinkage. This time was between 2.5 and 3 months for 70%

slag contained mixture. This trend was also seen for mixtures with sodium hydroxide concentrations of 0.5 and 1M.

The reduced shrinkage due to increases in slag content was opposite of the trend found by Rashad (2013), Chi and Huang (2013), Chi et al. (2015), and Deb et al. (2015) on fly ash/slag based mixtures who observed higher shrinkage through increases in slag portion of the binder. In these studies, two reasons were used to explain this observation. (1) Chi et al. (2015) related shrinkage increases to chemical shrinkage (reduction in volume resulting from the chemical reaction between the reagent and water) of the produced gels. The main reaction products of alkali-activated binders having high slag content are hydrotalcite and C-S-H gel with high chemical shrinkage, which lead to an increase in the total amount of shrinkage, (2) Rashad (2013) attributed the reduction in drying shrinkage of alkali-activated fly ash/slag mortars by increasing fly ash portion of binder to the spherical shape of fly ash particles which acted as micro-aggregate increasing volume stability of the mixture. From this point of view, unlike fly ash, natural Pozzolan has angular shape particles.

There were also two studies showing a nearly similar trend to the observations of this investigation. In the study conducted by Marjanovic et al. (2015a), drying shrinkage of mortar with 25/75 combination of fly ash/slag was almost similar or slightly more than that of 0/100 combination. Yusuf et al. (2014) observed that the drying shrinkage of ground steel slag/ultrafine palm ash pastes and mortars reduced by increasing slag portion of the binder. They related the significant improvement in shrinkage by increasing slag content to preventing the internal micro-cracks and enhancing pore-filling and pore refinement. The reason was that hydration of slag generated additional C-S-H that changed the macrospores into the mesopores through pore filling or pore refinement. This consequently reduced the shrinkage of the mortars and corroborated the pore filling capability of steel slag. The role of Ca^{2+} as a pore filler and a network modifier was also reported by Yip et al. (2008), which eventually reduce drying shrinkage. Due to similarity in trend, coupled with the results of mercury intrusion porosimetry (porosity) presented in Chapter 6, it is reasonable to assume the explanations given by Yusuf et al. (2014) are also valid for the studied alkali-activated natural Pozzolan/slag mortars.

5.3.8.2. Effects of activator combination

The typical trend for effects of activator combination on the drying shrinkage of alkali-activated natural Pozzolan/slag mortars is shown in Figure 5.33. It was seen that the drying shrinkage increased with increases in sodium silicate dosages (decreases in sodium hydroxide contents). In case of 30% slag content, the mortars with 30% sodium silicate shrank 77.1 and 32.6% more than mortars containing 20 and 25% sodium silicate, respectively. The ultimate drying shrinkage of mortars having 50 and 70% slag increased by 23.6 and 27.4% when sodium silicate was increased from 20 to 25%; and by 25.6 and 22.7% as sodium silicate content was increased from 25 to 30%, respectively.

A similar trend was observed by Atis et al. (2009) studying alkali-activated pastes. They observed higher drying shrinkage by increasing the sodium silicate content. Cincotto et al. (2003) also observed a similar trend for autogenous shrinkage. Similarly, Deb et al. (2015) found increases in drying shrinkage of fly ash/slag based mixtures by increasing sodium silicate content. Aydin and Baradan (2014) observed increases in drying shrinkage by increasing silica-to-Na_2O ratio of activator (modulus of sodium silicate). They related the increases in drying shrinkage by increasing silicate content of activator to the change in microstructure of mortars.

They stated that "shrinkage under various conditions depends on the loss of water from the mesopores (pore diameter between 2.5 and 50 nm) and also the size of the macropores (pore diameter between 50 and 10,000 nm), which determines easiness of evaporation of water from the mesopores" (Aydin and Baradan 2014). They attributed the increases of shrinkage by increasing the silicate content to the observed increases in volume of mesopores. A similar process can be expected in this investigation as an increase in sodium silicate content and decrease in sodium hydroxide concentration increased silica-to-Na_2O ratio, leading to increases in mesopores volume and subsequent increases in the drying shrinkage of the studied alkali-activated natural Pozzolan/slag mortars.

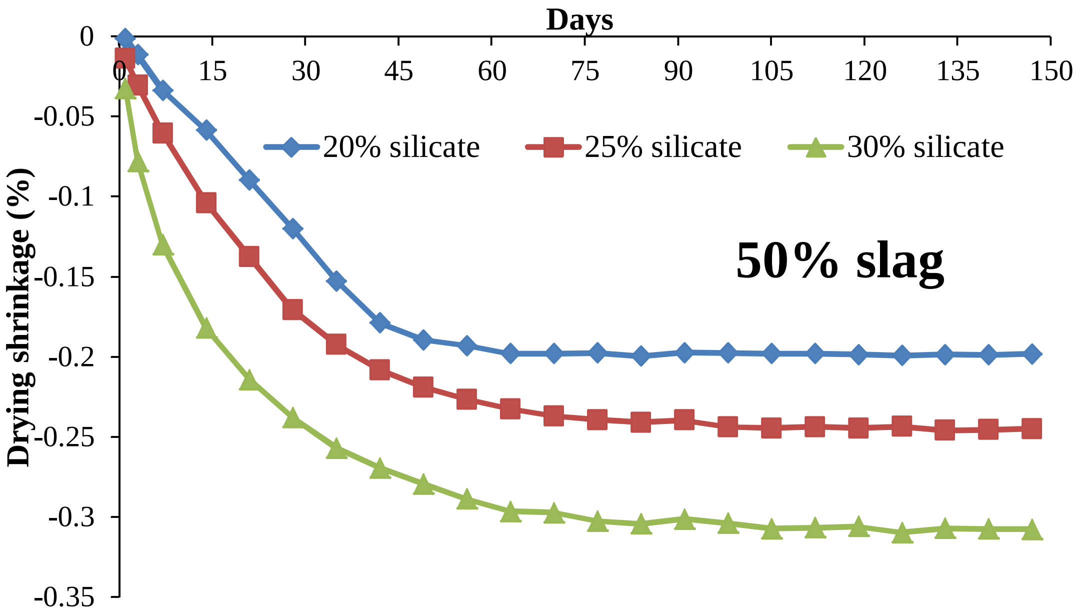


Figure 5.33 Drying shrinkage of alkali-activated natural Pozzolan/slag mortars having different sodium silicate contents and slag content of 50%

5.3.8.3. Effects of alkaline activator solution-to-binder ratio

Influence of solution-to-binder ratio on the drying shrinkage of alkali-activated natural Pozzolan/slag mortars is shown in Figure 5.34. As expected, the drying shrinkage reduced with decreases in S/B. The ultimate drying shrinkage of mortars with S/B of 0.52 was 12.8 and 18.4% lower than that of mortars having S/B of 0.56 and 0.60 for slag content of 30%, respectively. These improvements reduced to 8.3 and 8.2% for 50% slag content; and 9.5 and 10.4% for 70% slag content, respectively.

The increases in drying shrinkage, due to increases in solution-to-binder ratio, can be related to the weakened paste microstructure and higher availability of evaporable moisture which is responsible for volume instability. Chi et al. (2012) also observed a similar trend with increases in liquid-to-slag ratio.

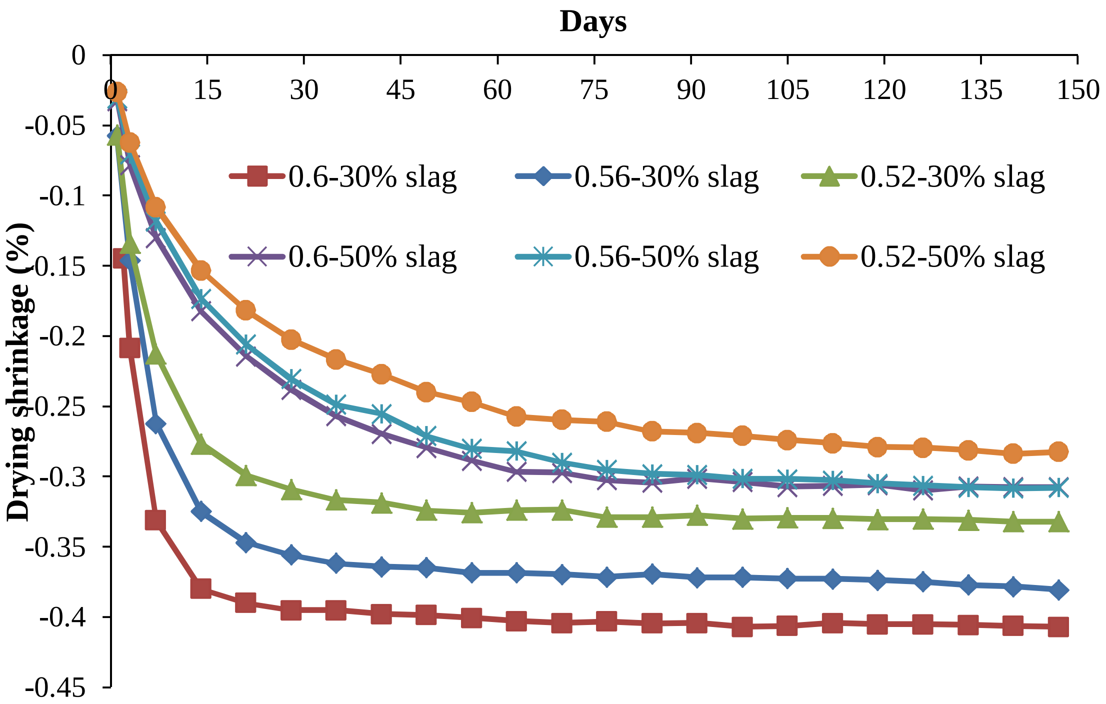


Figure 5.34 Drying shrinkage of alkali-activated natural Pozzolan/slag mortars having different S/B and slag content of 30% and 50%

5.3.8.4. Effects of sodium hydroxide concentrations

Influence of sodium hydroxide concentrations on the drying shrinkage of alkali-activated natural Pozzolan/slag mortars are shown in Figure 5.35. Overall, the drying shrinkages of 2M mixtures were higher than those of 0.5 and 1M mixtures. The 1M mixtures shrank almost similar to that of 0.5M mixtures.

The ultimate drying shrinkage of 2M mixtures were 8.0, 13.2 and 12.0% higher than that of 1M mixtures for slag contents of 30, 50 and 70%, respectively. For the same amounts of slag, 1M mixtures shrank averagely 3.6% less than 0.5M mixtures, respectively.

A similar trend was observed by Atis el al. (2009) where drying shrinkage of alkali-activated slag mortars increased by increasing sodium hydroxide concentrations. Aydin and Baradan (2014) also observed increases in drying shrinkage with an increase in Na_2O content of activator. Similar to the results of this study, they found the effect of Na_2O content on drying shrinkage to be less significant as compared to the influence of silicate-to-Na_2O content (silicate content of activator) on drying shrinkage of alkali-activated mortars.

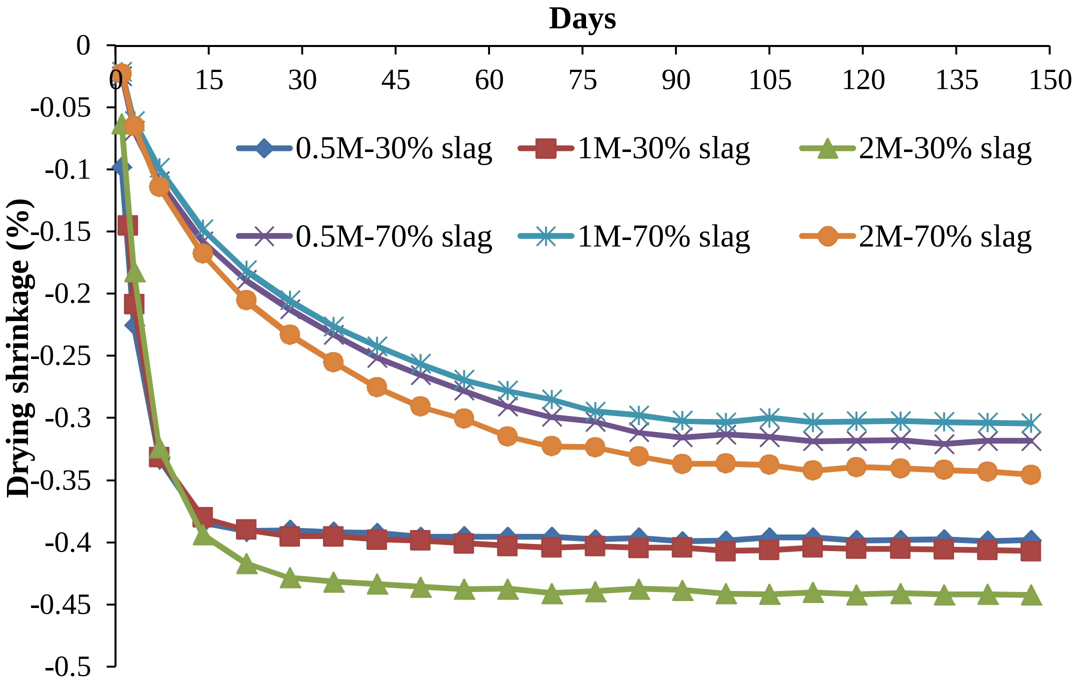


Figure 5.35 Drying shrinkage of alkali-activated natural Pozzolan/slag mortars having different NaOH concentrations

5.4. Comparison with Portland cement mortars

For the purpose of comparison, two reference mixtures were designed using Portland cement as the sole binder. Their mixture proportions are reported in Table 5.2. Mixture Control 1 was designed according to ASTM C109 with water-to-cement ratio of 0.485 and fine aggregate-to-cement ratio of 2.75. Mixture Control 2 was made with similar water-to-cement ratio, but fine aggregate-to-cement ratio of 2. This ratio was similar to that of alkali-activated natural Pozzolan/slag mortars.

Table 5.8 documents the fresh properties of Portland cement mortars. Their flow was 15.24 cm, thus they were compacted and casted easily. No sign of bleeding was observed. Their initial and final setting times were in the ranges of 155 to 176 and 242 to 255 minutes, respectively. Compared to the Portland cement mortars, the alkali-activated natural Pozzolan/slag mortars had a wider range of setting times which were dependent on combinations of binders and activators used.

Table 5.8 Fresh properties of Portland cement mortars

Mix id.	Fine aggregate-to-cement ratio	Flow, cm	Initial set, min	Final set, min
Control 1	2.75	15.24	155	242.5
Control 2	2	15.24*	176	255

* This flow was achieved in 18 drops instead of 25 times. In fact, the flow was higher than 15.24 cm but the flow Table didn’t allow for further measurement.

Figure 5.36 shows the heat of hydration of Portland cement mortars. Control 2 with lower amounts of fine aggregate had higher peak temperature, which was due to its higher amounts of cement for a given volume. The lowest and highest peak temperatures for alkali-activated and Portland cement mortars are shown in Figure 5.37. It can be seen that Portland cement mortars generated more heat of hydration than alkali-activated natural Pozzolan/slag mortars. The minimum and maximum peak temperatures of Portland cement mortars were 52 and 24% higher than those of alkali-activated natural Pozzolan/slag mortars, respectively. Lower heat of hydration can offer a great benefit for use of alkali-activated natural Pozzolan/slag mortars in mass concrete production. Figure 5.38 presents time to reach peak temperature for alkali-activated and Portland cement mortars. There was a considerably wider range (5 to 26 hr) for alkali-activated natural Pozzolan/slag mortars, as compared to that of Portland cement mortars (10 to 10.6 hr).

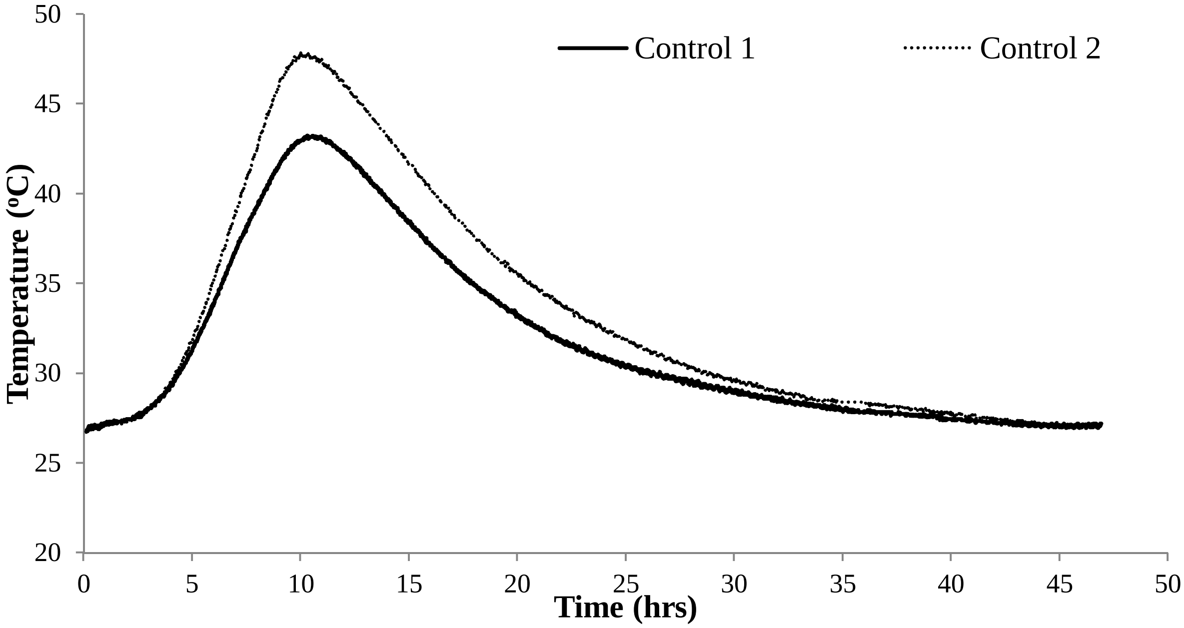


Figure 5.36 Heat of hydration of Portland cement mortars

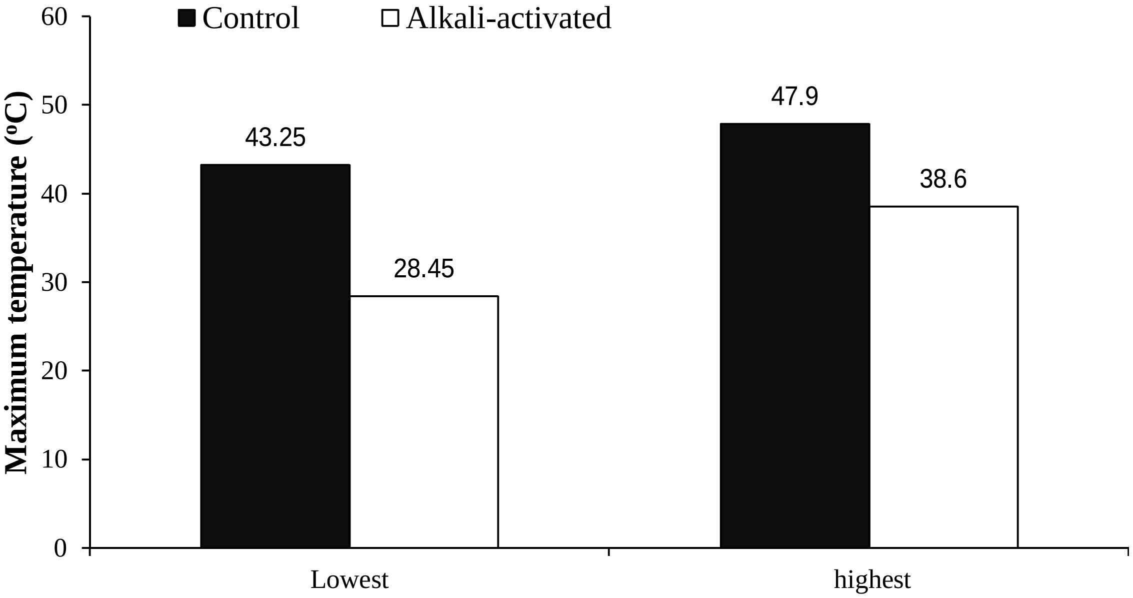


Figure 5.37 Minimum and maximum peak temperature of Portland cement and alkali-activated natural Pozzolan/slag mortars

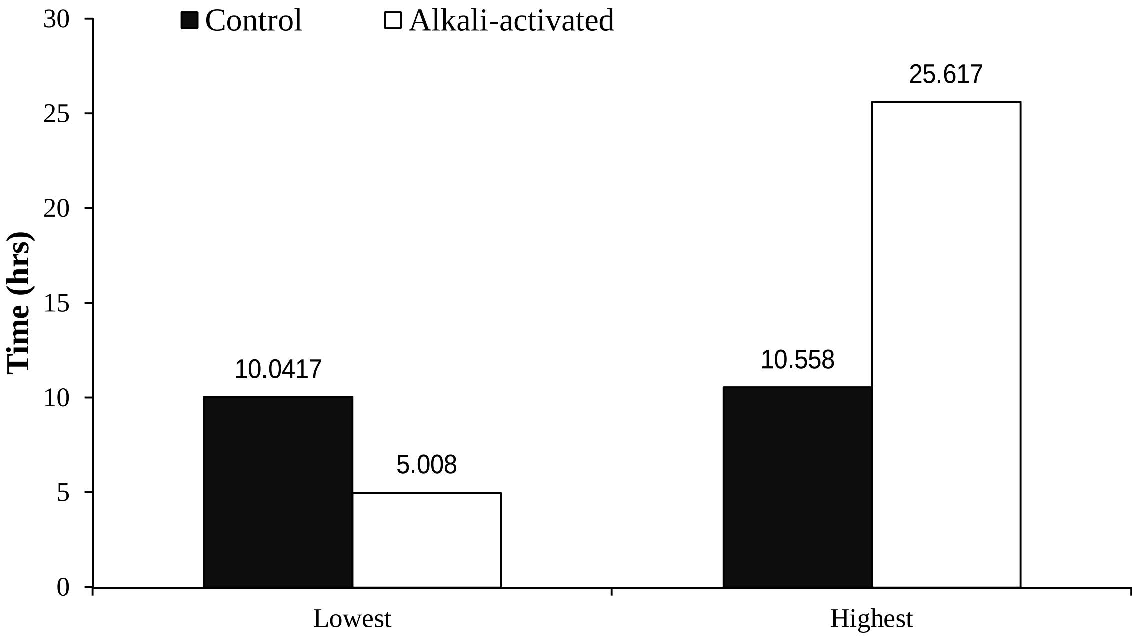


Figure 5.38 Minimum and maximum time to reach peak temperature for Portland cement and alkali-activated natural Pozzolan/slag mortars

The compressive strengths of Portland cement mortars are shown in Figure 5.39. The reference mortars Control 1 and Control 2 developed 28-day compressive strengths of 56 and 72 MPa, respectively. These strengths were higher than those of alkali-activated natural Pozzolan/slag mortars ranging between 20 and 47 MPa. It should be noted that higher strengths (more than the abovementioned range) could be produced with alkali-activated natural Pozzolan/slag mortars. As an example, only increases of sodium silicate to 35% were tried for 1M mixtures having 50 to 70% slag which increased the strength to about 55 MPa.

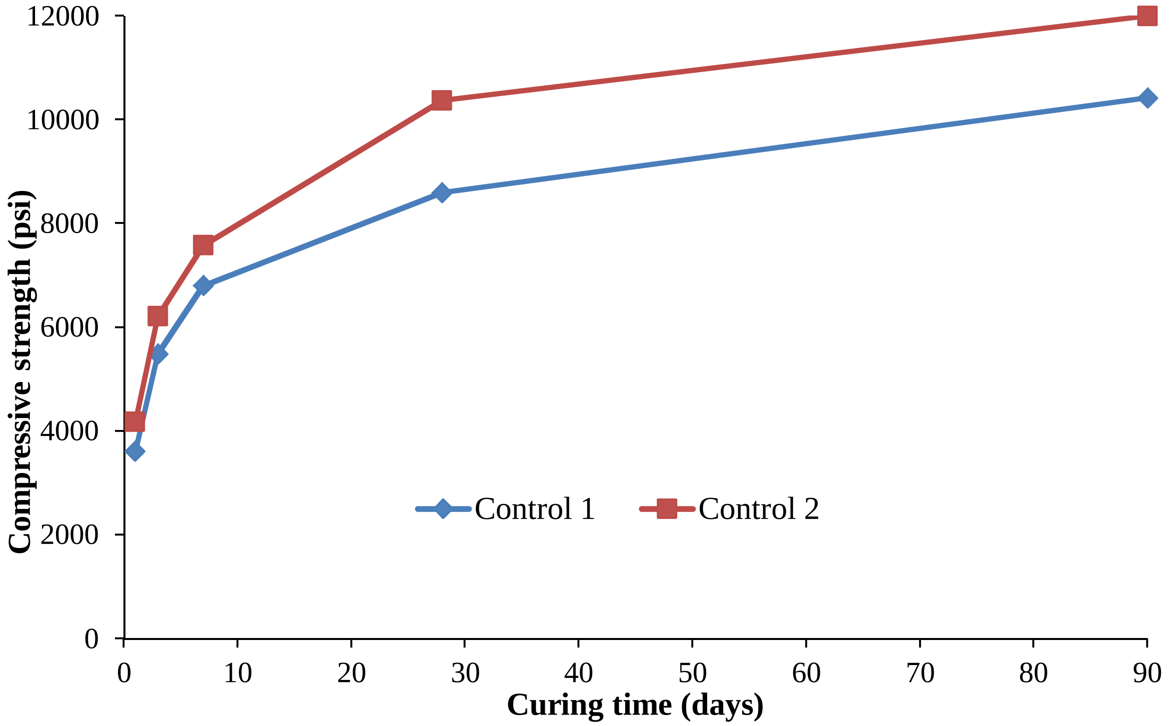


Figure 5.39 Compressive strength of Portland cement mortars (1 psi = 0.00689476 MPa, 1 MPa = 145.038 psi)

The results of rapid chloride penetration, rapid chloride migration and absorption tests are documented in Table 5.9 for Portland cement mortars. The absorption (after boiling), volume of permeable voids, passing charge and chloride penetration depth of Portland cement mortars were averagely 7.74%, 16.71%, 10113 coulombs and 33.5 mm, respectively. Figure 5.40 shows the ranges of passing charge of Portland cement and alkali-activated natural Pozzolan/slag mortars. Unlike alkali-activated mortars, Portland cement mortars showed a very high passing charge. The average charges passed through alkali-activated natural Pozzolan/slag mortars were almost 80% lower than those of the studied Portland cement mortars. Similarly, the chloride penetration depths of alkali-activated natural Pozzolan/slag mortars were considerably lower than those of

Portland cement mortars. The lowest penetration depth was for alkali-activated mortar 1M-SL70-SS30-0.52 (1.93 mm) which was 94% lower than that of Portland cement mortars. The average chloride penetration depth for alkali-activated natural Pozzolan/slag mortars was 15% of that of Portland cement mortars. These observations are also shown in Figure 5.41.

A comparison was also made between volume of permeable voids of alkali-activated and Portland cement mortars which is shown in Figure 5.42. The minimum and average total pores of alkali-activated natural Pozzolan/slag mortars were slightly higher than those of Portland cement mortars. It should, however, be noted that a number of studied alkali-activated natural Pozzolan/slag mortars had values similar to those of Portland cement mortars.

The different trend observed in absorption and chloride penetration and migration tests was related by Ismail et al. (2013a) to the poor reliability of the absorption and sorptivity tests for alkali-activated materials when the specimens are severely pre-dried before testing. Similar to the results of this study, Ismail et al. (2013) observed that while the migration coefficients (chloride penetration) of Portland cement concrete were 10 times higher than those alkali activated slag/fly ash concretes, their absorption and sorptivity results suggested that Portland cement concrete specimens had a lower water uptake.

Table 5.9 Results of transport properties tests for Portland cement mortars

Mix id.	Absorption after immersion (%)	Absorption after immersion and boiling (%)	Volume of permeable voids (%)	RCPT (Coulombs)	RMT (mm)
Control 1	6.87	7.15	15.66	9689	32.95
Control 2	8.16	8.33	17.76	10536	34.04

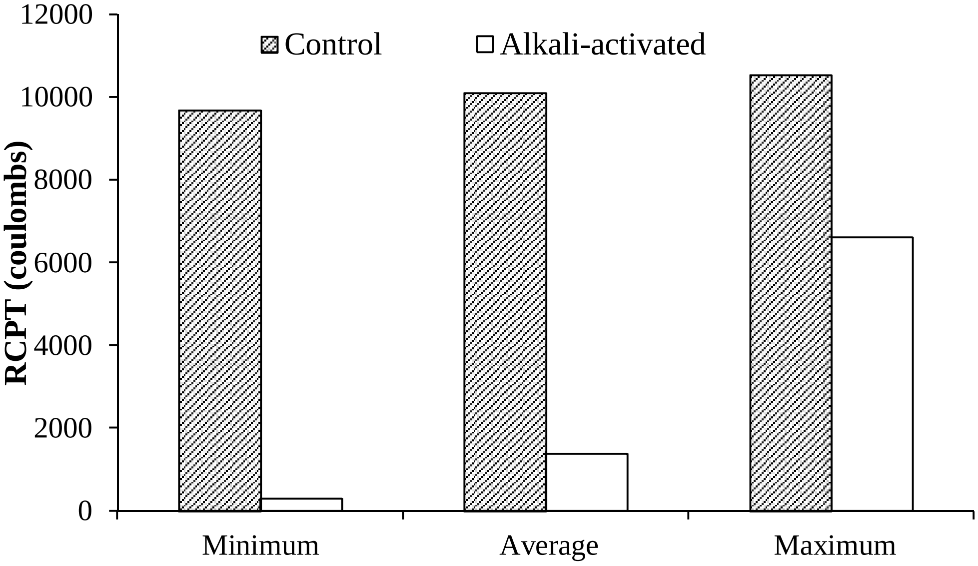


Figure 5.40 Minimum, average and maximum RCPT passing charge of Portland cement and alkali-activated natural Pozzolan/slag mortars

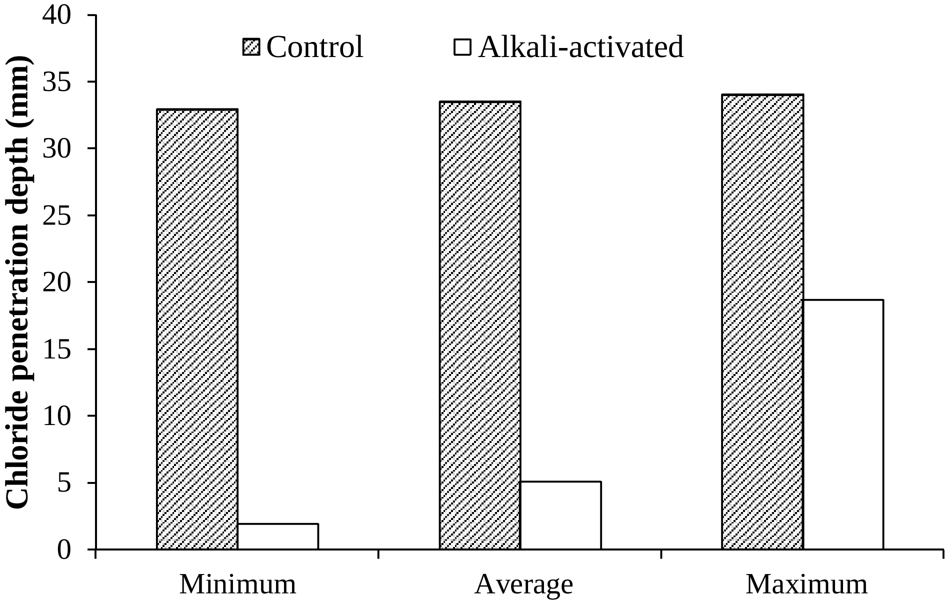


Figure 5.41 Minimum, average and maximum chloride penetration depth of Portland cement and alkali-activated natural Pozzolan/slag mortars

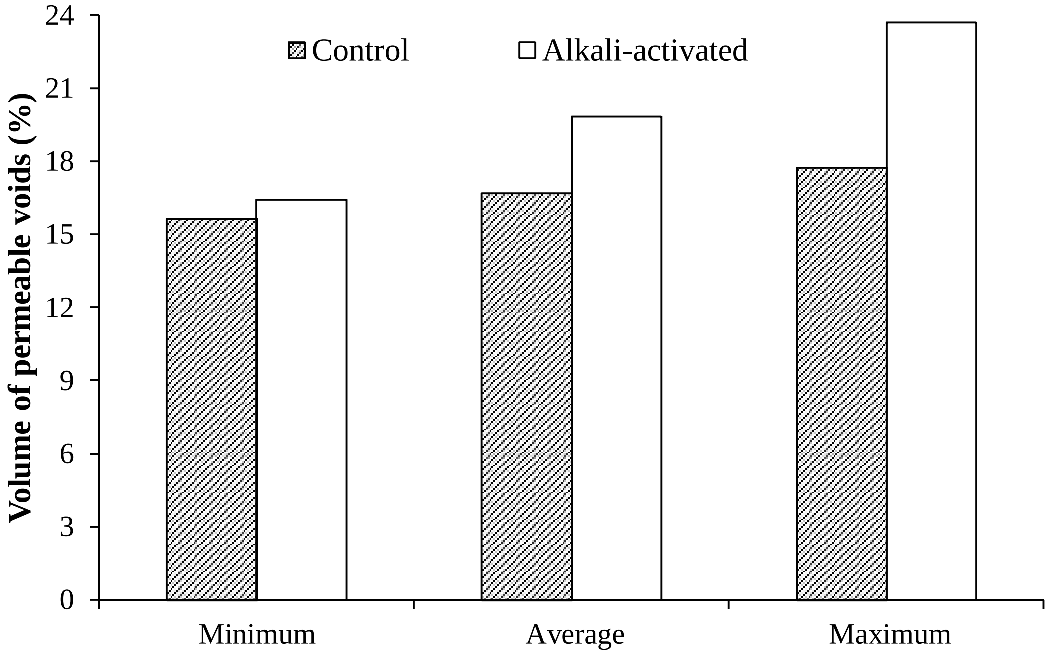


Figure 5.42 Minimum, average and maximum volume of permeable voids of Portland cement and alkali-activated natural Pozzolan/slag mortars

The drying shrinkages of Portland cement mortars are shown in Figure 5.43. A comparison of their ultimate drying shrinkage with those of alkali-activated natural Pozzolan/slag mortars is presented in Figure 5.44. It can be seen that the alkali-activated natural Pozzolan/slag mortars shrank considerably higher than those of Portland cement mortars. The minimum, average and maximum shrinkage observed in different alkali-activated natural Pozzolan/slag mortars were almost 1.7, 3 and 4 times of those of Portland cement mortars, respectively. The drying shrinkage could become a major problem which needs a solution for. It should, however, be noted that (1) there were some alkali-activated natural Pozzolan/slag mortars performing closer to Portland cement mortars, and (2) as coarse aggregates serves to constrain volume changes due to drying shrinkage, the gap in drying shrinkage between Portland cement and alkali-activated concretes are expected to be narrowed.

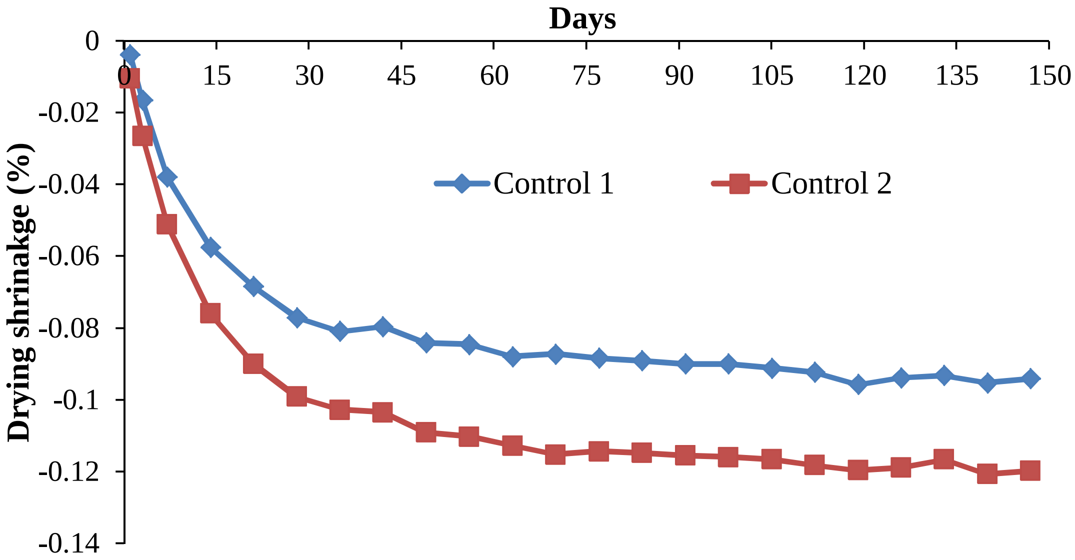


Figure 5.43 The drying shrinkage of Portland cement mortars

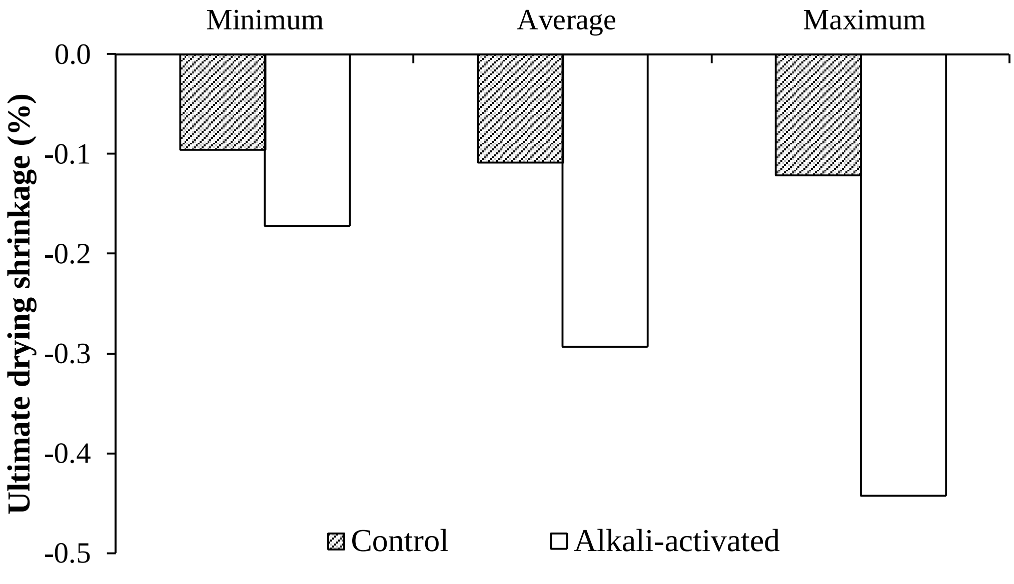


Figure 5.44 Minimum, average and maximum ultimate drying shrinkages of Portland cement and alkali-activated natural Pozzolan/slag mortars

CHAPTER 6- ALKALI-ACTIVATED NATURAL POZZOLAN/SLAG CONCRETES

6.1. Introduction

The third phase of this study dealt with development and evaluation of alkali-activated natural Pozzolan/slag concretes. To this end, different dominant parameters were considered and several mixture proportions were designed based on the findings of the first and second phases of investigation conducted on alkali-activated pastes and mortars, respectively. The following factors were considered:

- *Effects of binder combination:*

  Similar to the second phase of this study, three different slag-to-total binder ratios of 0.3, 0.5 and 0.7 were used.

- *Effects of sodium hydroxide concentration:*

  Based on the results of the first and second phases, sodium hydroxide concentrations of 0.5, 1 and 2M were initially chosen. However, as unreasonable setting times (long) were found for 0.5M alkali-activated natural Pozzolan/slag concretes, the selected sodium hydroxide concentrations were changed to 1, 1.75 and 2.5M.

- *Influences of activator combination:*

  In order to assess the effect of activator combination, different sodium silicate-to-alkaline activator ratios of 0.2, 0.25 and 0.3 were considered. Similar to the second phase on alkali-activated mortars, higher silicate contents were not chosen due to their adverse effects on slump flow, setting time and mixture economy.

After testing a number of trial batches, an alkaline activator solution-to-binder ratio (S/B) of 0.54 was chosen for all selected alkali-activated natural Pozzolan/slag concretes. This ratio was sufficient to achieve proper flow to ensure adequate compaction with no bleeding. Use of lower S/B would result in low workability for some of alkali-activated mixtures which, in turn, would reduce their compressive strengths. Increases in S/B would also result in strength reduction as it was observed in Chapter 5.

A comprehensive experimental program was devised to assess performance of alkali-activated natural Pozzolan/slag concretes to include fresh properties (slump flow and setting times), unit weights (fresh, demolded and oven-dry), mechanical properties (compressive and tensile strengths, and modulus of elasticity), transport properties (absorption, rapid chloride penetration, and rapid chloride migration), durability (frost resistance, chloride induced corrosion, and resistance to sulfuric acid attack), and dimension stability (drying shrinkage).

A Portland cement concrete with a water-to-cement ratio of 0.54 was also made for the purpose of comparison (reference concrete). This ratio was used due to three main reasons: (1) it was considered that using Portland cement and alkali-activated natural Pozzolan/slag concretes with almost similar ranges of compressive strength rationalize comparison between their other studied properties. Therefore, the reference Portland cement concrete was designed using the target 28-day compressive strength of 6000 psi (almost 40 MPa) which was nearly the average compressive strength of the main group of alkali-activated natural Pozzolan/slag concretes. Designing for this 28-day compressive strength, water-to-cement ratio was found in design handbooks to be about 0.54 (Kosmatka et al. 2002), (2) this ratio was similar to S/B of studied alkali-activated natural Pozzolan/slag concretes which made the comparison more reliable, and (3) using this water-to-cement ratio did not require any water reducer/ superplasticizer as it was also the case for studied alkali-activated natural Pozzolan/slag concretes.

6.2. Mixtures proportions

Table 6.1 documents the mixture proportions of studied alkali-activated natural Pozzolan/slag concretes. As mentioned earlier, these mixtures were designed with natural Pozzolan/slag combinations of 30/70, 50/50 and 70/30; sodium silicate contents of 20, 25 and 30% (sodium hydroxide dosages of 80, 75 and 70%, respectively); sodium hydroxide concentrations of 1, 1.75 and 2.5M; and S/B of 0.54. In this Table, mixture id. XM-SLY-SSZ represents that sodium hydroxide had X mole, slag was Y% of the total binder ((100-Y)% was for natural Pozzolan), and sodium silicate constituted Z% of the total activator ((100-Z)% was sodium hydroxide). Table 6.2 shows the mixture constituents and proportions for the selected alkali-activated natural Pozzolan/slag concretes per batch.

From herein, SLAG-Y% represents alkali-activated natural Pozzolan/slag concretes made with binders having Y% slag and (100-Y)% natural Pozzolan. SILICATE-Z% denotes that the used activator consisted of Z% sodium silicate and (100-Z)% sodium hydroxide.

Table 6.1 Mixture proportions of alkali-activated natural Pozzolan/slag concretes (kg/m^3)

Mix no.	Mixture Id.	Mixture description	Slag/ Pozzolan	Silicate/ hydroxide	Alkaline solution	Total binder	Coarse aggregate	Fine aggregate
1	0.5M-SL30-SS30	30% slag-30% silicate-0.5M	30/70	30/70	228.0	422.2	877.7	794.3
2	0.5M-SL50-SS30	50% slag-30% silicate-0.5M	50/50	30/70	228.0	422.2	877.7	815.5
3	0.5M-SL70-SS30	70% slag-30% silicate-0.5M	70/30	30/70	228.0	422.2	877.7	835.0
4	1M-SL30-SS30	30% slag-30% silicate-1M	30/70	30/70	228.0	422.2	877.7	794.3
5	1M-SL50-SS30	50% slag-30% silicate-1M	50/50	30/70	228.0	422.2	877.7	815.5
6	1M-SL70-SS30	70% slag-30% silicate-1M	70/30	30/70	228.0	422.2	877.7	835.0
7	1M-SL30-SS25	30% slag-25% silicate-1M	30/70	25/75	228.0	422.2	877.7	781.5
8	1M-SL50-SS25	50% slag-25% silicate-1M	50/50	25/75	228.0	422.2	877.7	802.8
9	1M-SL70-SS25	70% slag-25% silicate-1M	70/30	25/75	228.0	422.2	877.7	822.2
10	1M-SL30-SS20	30% slag-20% silicate-1M	30/70	20/80	228.0	422.2	877.7	768.2
11	1M-SL50-SS20	50% slag-20% silicate-1M	50/50	20/80	228.0	422.2	877.7	789.5
12	1M-SL70-SS20	70% slag-20% silicate-1M	70/30	20/80	228.0	422.2	877.7	808.9
13	1.75M-SL30-SS30	30% slag-30% silicate-1.75M	30/70	30/70	228.0	422.2	877.7	794.3
14	1.75M-SL50-SS30	50% slag-30% silicate-1.75M	50/50	30/70	228.0	422.2	877.7	815.5
15	1.75M-SL70-SS30	70% slag-30% silicate-1.75M	70/30	30/70	228.0	422.2	877.7	835.0

Table 6.1 Mixture proportions of alkali-activated natural Pozzolan/slag concretes (continued)

Mix no.	Mixture Id.	Mixture description	Slag/ Pozzolan	Silicate/ hydroxide	Alkaline solution	Total binder	Coarse aggregate	Fine aggregate
16	1.75M-SL30-SS25	30% slag-25% silicate-1.75M	30/70	25/75	228.0	422.2	877.7	781.5
17	1.75M-SL50-SS25	50% slag-25% silicate-1.75M	50/50	25/75	228.0	422.2	877.7	802.8
18	1.75M-SL70-SS25	70% slag-25% silicate-1.75M	70/30	25/75	228.0	422.2	877.7	822.2
19	1.75M-SL30-SS20	30% slag-20% silicate-1.75M	30/70	20/80	228.0	422.2	877.7	768.2
20	1.75M-SL50-SS20	50% slag-20% silicate-1.75M	50/50	20/80	228.0	422.2	877.7	789.5
21	1.75M-SL70-SS20	70% slag-20% silicate-1.75M	70/30	20/80	228.0	422.2	877.7	808.9
22	2.5M-SL30-SS30	30% slag-30% silicate-2.5M	30/70	30/70	228.0	422.2	877.7	794.3
23	2.5M-SL50-SS30	50% slag-30% silicate-2.5M	50/50	30/70	228.0	422.2	877.7	815.5
24	2.5M-SL70-SS30	70% slag-30% silicate-2.5M	70/30	30/70	228.0	422.2	877.7	835.0
25	2.5M-SL30-SS25	30% slag-25% silicate-2.5M	30/70	25/75	228.0	422.2	877.7	781.5
26	2.5M-SL50-SS25	50% slag-25% silicate-2.5M	50/50	25/75	228.0	422.2	877.7	802.8
27	2.5M-SL70-SS25	70% slag-25% silicate-2.5M	70/30	25/75	228.0	422.2	877.7	822.2
28	2.5M-SL30-SS20	30% slag-20% silicate-2.5M	30/70	20/80	228.0	422.2	877.7	768.2
29	2.5M-SL50-SS20	50% slag-20% silicate-2.5M	50/50	20/80	228.0	422.2	877.7	789.5
30	2.5M-SL70-SS20	70% slag-20% silicate-2.5M	70/30	20/80	228.0	422.2	877.7	808.9

Table 6.2 Mixture proportions of alkali-activated natural Pozzolan/slag concretes per batch (g)

Mixture No.	Sodium hydroxide	Sodium silicate	Slag	Natural Pozzolan	Fine aggregate	Coarse aggregate (No.4 to 3/8)	Coarse aggregate (3/8 to 1/2)
1, 4, 13, 22	2983.8	1278.8	2368.1	5525.6	14849.1	9024.6	7383.8
2, 5, 14, 23	2983.8	1278.8	3946.9	3946.9	15246.6	9024.6	7383.8
3, 6, 15, 24	2983.8	1278.8	5525.6	2368.1	15610.0	9024.6	7383.8
7, 16, 25	3197.0	1065.7	2368.1	5525.6	14611.6	9024.6	7383.8
8, 17, 26	3197.0	1065.7	3946.9	3946.9	15009.1	9024.6	7383.8
9, 18, 27	3197.0	1065.7	5525.6	2368.1	15372.5	9024.6	7383.8
10, 19, 28	3410.1	852.5	2368.1	5525.6	14362.7	9024.6	7383.8
11, 20, 29	3410.1	852.5	3946.9	3946.9	14760.2	9024.6	7383.8
12, 21, 30	3410.1	852.5	5525.6	2368.1	15123.5	9024.6	7383.8

6.3. Results and discussion

6.3.1. Workability

The workability of alkali-activated natural Pozzolan/slag concretes was measured using slump flow cone and the results are reported in Table 6.3. Typical effects of different variables; i.e. binder combination, activator combination, and sodium hydroxide concentration; on the slump flow of alkali-activated natural Pozzolan/slag concretes are shown in Figures 6.1 through 6.3. Their influences are discussed below.

Table 6.3 Fresh properties of alkali-activated natural Pozzolan/slag concretes

Property	Sodium silicate content (%)	Sodium hydroxide concentration (M)								
		1			1.75			2.5		
		Slag content (%)			Slag content (%)			Slag content (%)		
		30	50	70	30	50	70	30	50	70
Slump flow (cm)	20	26.0	23.5	15.2	24.1	22.9	21.6	24.1	23.5	22.9
	25	22.9	19.7	9.8	23.5	23.5	21.0	22.9	21.0	20.3
	30	21.3	15.2	3.8	20.3	19.7	11.1	11.4	10.2	8.6
Initial setting (min)	20	420	180	95	255	160	100	175	135	97
	25	680	300	140	360	210	130	210	160	115
	30	705	375	165	375	240	150	210	165	120
Final setting (min)	20	630	245	143	355	227	140	260	190	130
	25	990	385	195	550	290	180	350	230	150
	30	1050	500	235	585	340	205	365	233	170

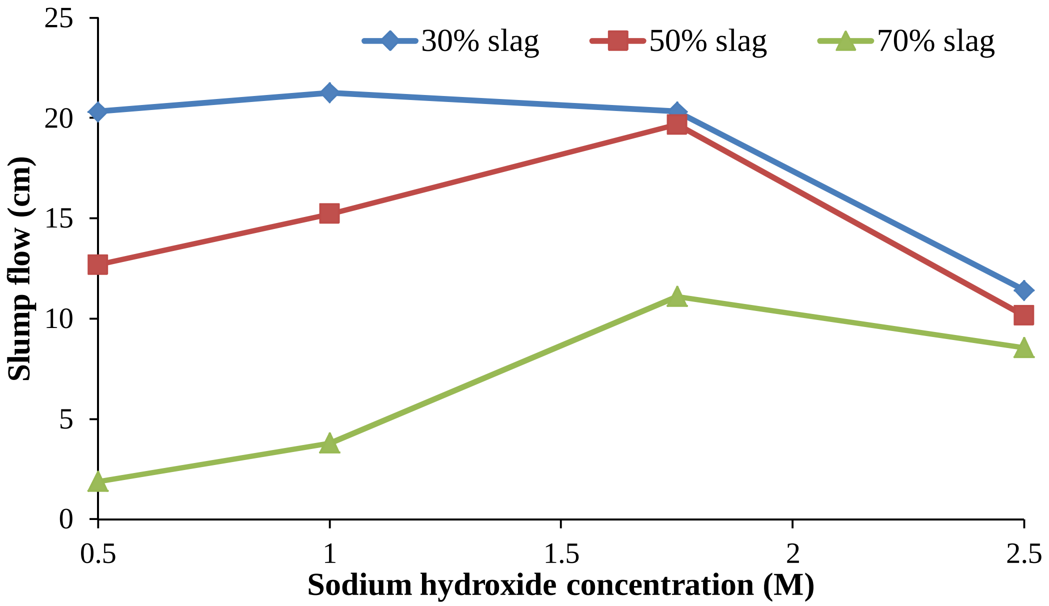


Figure 6.1 The slump flow of SILICATE-30% alkali-activated natural Pozzolan/slag concretes having different binder combinations and sodium hydroxide molarities

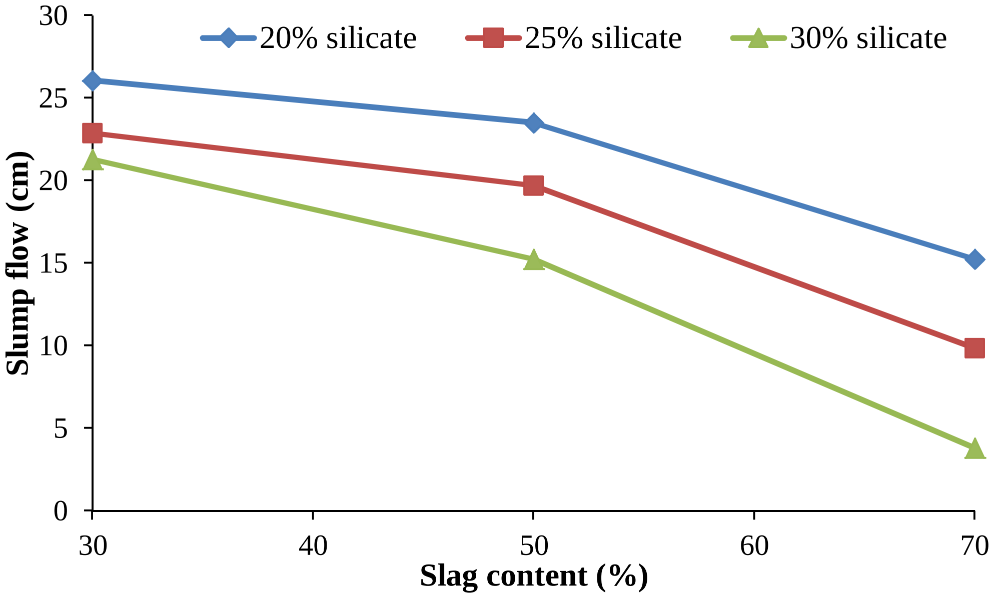


Figure 6.2 The slump flow of 1M alkali-activated natural Pozzolan/slag concretes having different binder and activator combinations

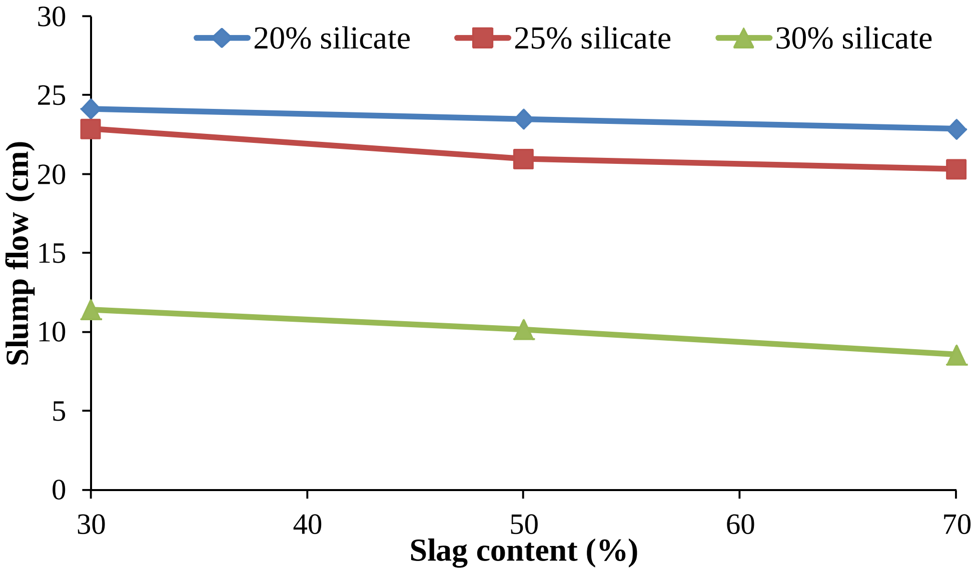


Figure 6.3 The slump flow of 2.5M alkali-activated natural Pozzolan/slag concretes having different binder and activator combinations

6.3.1.1. Effects of binder combination

Table 6.3 and Figures 6.1 through 6.3 show the influence of binder combination on the slump flow of alkali-activated natural Pozzolan/slag concretes. It can be seen that similar to the results of second phase on alkali-activated mortars, the workability of alkali-activated natural Pozzolan/slag concretes reduced with increases in slag content (decreases in natural Pozzolan dosage). This reduction was more significant for concretes having lower NaOH concentration.

On average, the slump flow of alkali-activated natural Pozzolan/slag concretes having sodium hydroxide concentrations of 0.5, 1, 1.75 and 2.5M reduced by 37.5, 17.3, 2.8 and 7.4% when slag content of binder was increased from 30 to 50%, respectively. For similar NaOH molarities, further increase in slag content from 50 to 70% led to averagely 85.0, 53.4, 20.0 and 7.1% reduction in the workability of alkali-activated natural Pozzolan/slag concretes, respectively.

As discussed before, the observed slump flow reduction by increasing slag portion of binder and workability increase by use of higher natural Pozzolan content can be related to the low water demand of natural Pozzolan used in this phase (98%) and its coarser particle size in comparison with that of the used slag.

6.3.1.2. Influences of activator combination

Figures 6.2 and 6.3 show the effect of activator combination (sodium silicate and sodium hydroxide dosages) on the workability of alkali-activated natural Pozzolan/slag concretes. It can be seen that the slump flow reduced as sodium silicate content was increased.

On average, the slump flow of SILICATE-30% concretes (activated with alkaline activator having 30% sodium silicate) were lower than those of SILICATE-25% and SILICATE-20% concretes by 30.3 and 42.8% for 1M mixtures; 25.6 and 26.1% for 1.75M mixtures; and 53.1 and 57.3% for 2.5M mixtures, respectively. When slag constituted 30, 50 and 70% of binder, increases in sodium silicate content from 20 to 25% resulted in averagely 6.7, 8.1 and 16.5% reduction in the workability of alkali-activated natural Pozzolan/slag concretes, respectively. For similar slag contents, the slump flow reduced by averagely 23.5, 30.1 and 55.4% when sodium silicate content was increased from 25 to 30%, respectively.

These observations were similar to the trends found in the first and second phases of this study on alkali-activated pastes and mortars. Similarly, this finding can be attributed to the higher solid-to-liquid ratio of sodium silicate solution (0.787) in comparison with that of sodium hydroxide solutions (almost 0.04, 0.07 and 0.10 for NaOH concentrations of 1, 1.75 and 2.5M, respectively).

6.3.1.3. Effects of sodium hydroxide concentration

Figure 6.1 also shows the typical influence of sodium hydroxide concentration on the workability of alkali-activated natural Pozzolan/slag concretes. Overall, the workability of alkali-activated natural Pozzolan/slag concretes increased when sodium hydroxide concentration was increased to an optimum level, after which, it reduced with increasing NaOH molarity.

It can be seen in Figure 6.1 that for SLAG-30% concretes, the slump flow of mixtures having different sodium hydroxide concentrations were almost similar (except for mixture 2.5M-SL30-SS30 which had a significantly lower workability than the other mixtures made with binders having 30% slag and activators containing 30% sodium silicate). In case of mixtures with natural Pozzolan/slag combination of 50/50, the slump flow increased as NaOH molarity was increased to up to 1.75M, after which it reduced when NaOH concentration was increased to 2.5M. A similar trend was observed for concretes made with binders having 70% slag and 30% natural Pozzolan (SLAG-70% concretes). For these mixtures, however, the optimum sodium hydroxide concentration was between 1.75 and 2.5M.

These observations were similar to the trends observed for alkali-activated pastes and mortars indicating that sodium hydroxide inclusion up to an optimum level improved workability, after which further increases caused loss of workability. As mentioned in Chapters 4 and 5, this was also seen by Jolicouer et al. (1992), Smaoui et al. (2005) and Li et al. (2016) for Portland cement and alkali-activated slag concretes.

6.3.2. Setting time

Table 6.3 also reports the initial and final setting times of alkali-activated natural Pozzolan/slag concretes. Figures 6.4 through 6.7 present the effects of dominant parameters on the setting times of alkali-activated natural Pozzolan/slag concretes which are discussed in the subsections to follow.

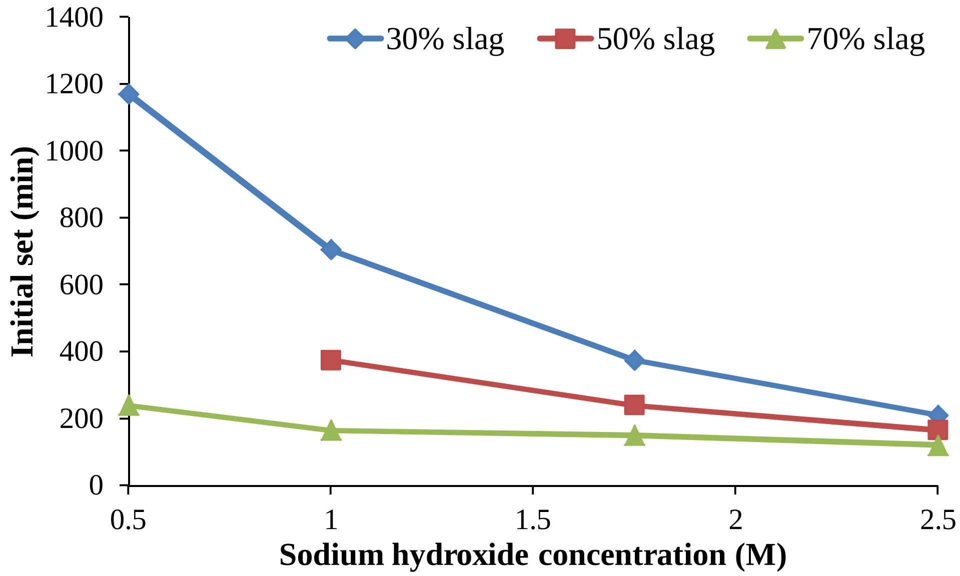


Figure 6.4 The initial setting time of SILICATE-30% alkali-activated natural Pozzolan/slag concretes having different binder combination and sodium hydroxide molarities

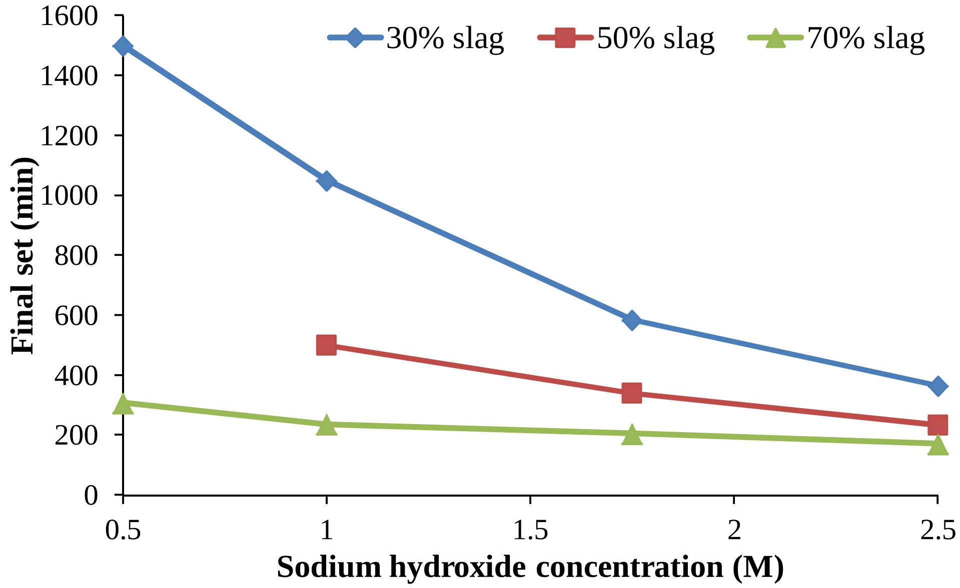


Figure 6.5 The final setting time of SILICATE-30% alkali-activated natural Pozzolan/slag concretes having different binder combinations and sodium hydroxide molarities

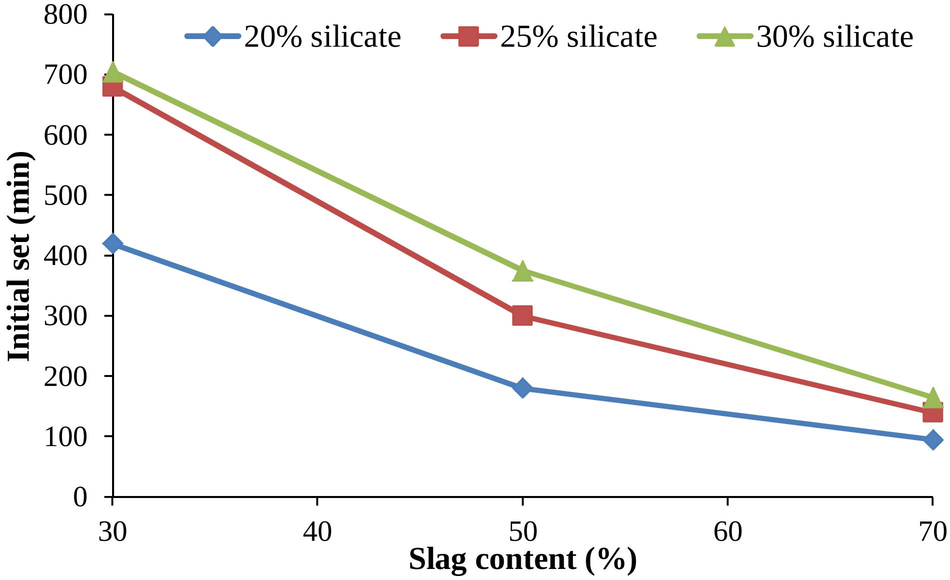


Figure 6.6 The initial setting time of 1M alkali-activated natural Pozzolan/slag concretes having different binder and activator combinations

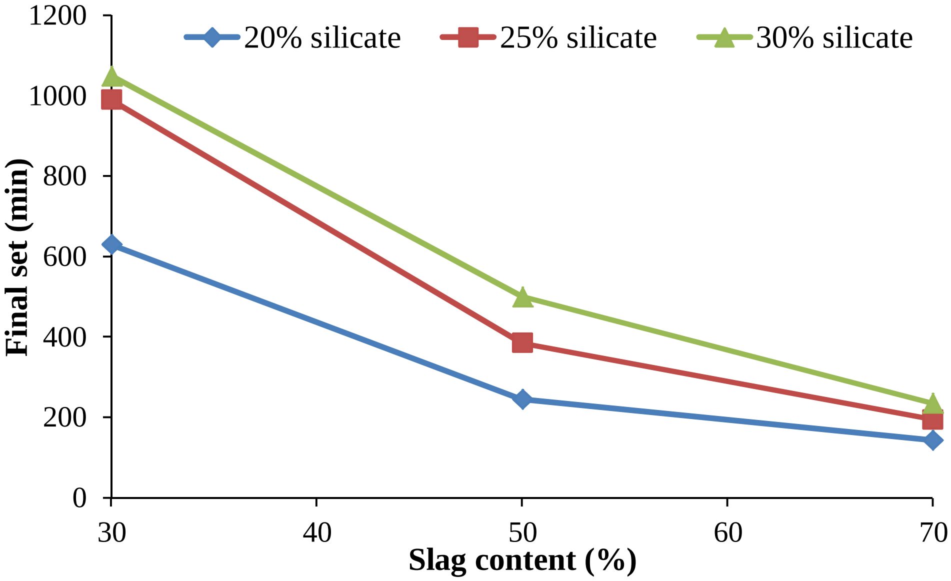


Figure 6.7 The final setting time of 1M alkali-activated natural Pozzolan/slag concretes having different binder and activator combinations

6.3.2.1. Effects of binder combination

Figures 6.4 through 6.7 show the influence of binder combination (slag and natural Pozzolan contents) on the initial and final setting times of alkali-activated natural Pozzolan/slag concretes. It can be seen that the setting times reduced as slag content was increased.

For mixtures with NaOH concentrations of 1, 1.75 and 2.5M, the setting times reduced by averagely 55.7, 40.0 and 27.6% when slag content of binder was increased from 30 to 50%, respectively. For similar sodium hydroxide concentrations, further increases in slag content from 50 to 70% led to averagely 50.1, 38.2 and 29.5% reduction in their setting times, respectively.

A similar trend was observed for mixtures having different sodium silicate contents. For SILICATE-20%, SILICATE-25% and SILICATE-30% concretes, mixtures made with binders having 70% slag (SLAG-70% mixtures) set 37.4, 40.3 and 40.1% faster than SLAG-50% mixtures; and 61.8, 65.5 and 62.6% earlier than SLAG-30% mixtures, respectively.

These observations, which support the findings of the two earlier phases of this investigation on alkali-activated pastes and mortars, can be related to the higher initial reactivity of slag in comparison with that of natural Pozzolan.

6.3.2.2. Influences of activator combination

The influences of alkaline activator combination (sodium silicate and sodium hydroxide dosages) on the initial and final setting times are presented in Figures 6.6 and 6.7, respectively. Overall, increasing sodium silicate content in the range of 20 to 30% of the total alkaline activator delayed the setting times of alkali-activated natural Pozzolan/slag concretes.

For mixtures with sodium hydroxide concentrations of 1, 1.75 and 2.5M, the setting times delayed by averagely 54.4, 35.6 and 21.4% when sodium silicate content of activator was increased from 20 to 25%, respectively. There were less significant increases in the setting times when sodium silicate portion of activator was increased from 25 to 30%. This increase in sodium silicate content resulted in averagely 17.2, 11.9 and 4.4% increases in the setting times of concretes having NaOH concentrations of 1, 1.75 and 2.5M, respectively.

A similar trend was observed for mixtures having different binder combinations. In case of concretes made with binders having 30, 50 and 70% slag, the setting times of SILICATE-30% mixtures were averagely 4.1, 15.1 and 14.2% more than those of SILICATE-25% mixtures; and 51.1, 59.5 and 48.2% more than those of SILICATE-20% mixtures, respectively.

This finding, which was in line with the observations on alkali-activated pastes and mortars, can be related to the effect of pH on early hydration of alkali-activated natural Pozzolan/slag concretes. As increases in pH of activator accelerated the early hydration and because sodium hydroxide had higher pH than sodium silicate, an increase in sodium hydroxide dosage (reducing sodium silicate content) resulted in faster early reactions which shortened setting times. Similar to the phases I and II (Chapters 4 and 5), the conclusion for increases in the setting times due to increases in sodium silicate content is only valid for the studied range of 20 to 30% and can’t be extrapolated for higher dosages.

6.3.2.3. Effects of sodium hydroxide concentration

Figures 6.4 and 6.5 show the influence of sodium hydroxide concentration on the initial and final setting times of alkali-activated natural Pozzolan/slag concretes, respectively. As can be seen, the setting times shortened as molarity of sodium hydroxide solution was increased. The reduction of setting time due to increases in NaOH concentration was significant for mixtures with slag content of 30% and it became less influential as slag portion of binder was increased.

The setting times of concretes having binders made with 30% slag (SLAG-30% concretes) reduced by averagely 44.3 and 36.3% when sodium hydroxide concentration was increased from 1 to 1.75 and 1.75 to 2.5M, respectively. Similar increases in NaOH molarity shortened the setting times by averagely 23.5 and 23.2% for SLAG-50% concretes; and 5.6 and 12.6% for concretes made with binders having 70% slag (SLAG-70% concretes), respectively.

These observations, which support the findings of first and second phases of this study on alkali-activated pastes and mortars, can be related to the acceleration of reactions through faster dissolution of silica due to increases in alkaline concentration.

6.3.3. Unit weight

Table 6.4 reports the unit weight of alkali-activated natural Pozzolan/slag concretes at their fresh, demolded and oven-dry states. It can be seen that depending on binder combination, activator combination and sodium hydroxide concentration, the fresh, demolded and oven-dry unit weights of alkali-activated natural Pozzolan/slag concretes were in the ranges of 2377 to 2437, 2370 to 2434 and 2246 to 2336 Kg/m^3, respectively. The unit weight of alkali-activated natural Pozzolan/slag concretes increased slightly with increases in slag content, sodium silicate dosage and sodium hydroxide concentration.

The fresh unit weight increased by averagely 0.51 and 0.36% when slag content of binder was increased from 30 to 50 and 50 to 70%, respectively. For similar increases in slag content, the demolded unit weight increased by averagely 0.55 and 0.37%, and the oven-dry density increased by averagely 1.11 and 0.47%, respectively. The observed increases can be related to the higher specific gravity of slag (2.87) in comparison with that of natural Pozzolan (2.33).

The fresh unit weight increased by averagely 0.41 and 0.22% when sodium silicate dosage of activator was increased from 20 to 25 and 25 to 30%, respectively. Similar increases in sodium silicate dosage increased the demolded unit weight by 0.31 and 0.23%, and the oven-dry density by 0.59 and 0.48%, respectively. This finding can be related to the higher specific gravity of sodium silicate solution (1.53) compared to that of sodium hydroxide solution (almost 1).

The unit weights also increased with increases in sodium hydroxide concentration. The unit weights (fresh and demolded) of 2.5M concretes were averagely 0.80 and 0.45% higher than those of concretes having NaOH concentration of 1 and 1.75M, respectively. Similarly, the oven-dry density of 2.5M concretes were averagely 1.19 and 0.56% more than those of 1 and 1.75M concretes, respectively. These marginal increases can be related to the slight increases in the unit weight of sodium hydroxide by increasing its molarity. The observed increases can also be attributed to the overall reduction of total porosity by increasing NaOH concentration (which will be presented in Section 6.3.7. volume of permeable voids).

Table 6.4 Unit weights of alkali-activated natural Pozzolan/slag concretes (Kg/m^3)

Property	Sodium silicate content (%)	Sodium hydroxide concentration (M)								
		1			1.75			2.5		
		Slag content (%)			Slag content (%)			Slag content (%)		
		30	50	70	30	50	70	30	50	70
Fresh unit weight	20	2377.6	2380.7	2396.1	2390.7	2402.3	2416.0	2398.6	2415.2	2420.1
	25	2390.8	2405.4	2409.0	2392.6	2403.9	2415.2	2400.7	2417.7	2423.1
	30	2397.3	2407.8	2409.2	2402.2	2406.1	2416.1	2402.9	2424.4	2436.6
Demolded unit weight	20	2370.1	2376.9	2393.0	2384.6	2398.7	2412.0	2394.7	2413.7	2417.4
	25	2386.7	2400.4	2406.0	2389.2	2400.9	2412.1	2398.1	2414.9	2420.2
	30	2394.0	2405.0	2407.0	2398.7	2403.3	2414.3	2401.0	2422.3	2433.6
Oven-dry unit weight	20	2246.9	2270.6	2270.4	2273.0	2283.5	2287.4	2279.0	2292.8	2321.1
	25	2260.2	2290.8	2300.0	2279.7	2307.1	2295.1	2273.6	2312.6	2326.4
	30	2266.9	2293.4	2315.0	2277.0	2304.0	2336.3	2298.3	2327.1	2327.2

6.3.4. Compressive strength

Table 6.5 presents the results of compressive strength for the studied alkali-activated natural Pozzolan/slag concretes. It can be seen that the compressive strength of alkali-activated natural Pozzolan/slag concretes was affected by the amounts of slag and natural Pozzolan, sodium hydroxide and sodium silicate contents, and sodium hydroxide concentrations. In general, similar to the two earlier phases of this study, the optimum amount of slag and natural Pozzolan was dependent on the molarity of sodium hydroxide solution. The influence of sodium hydroxide concentration was also dependent on the binder combination. Use of higher sodium silicate solution (also associated with reduction of sodium hydroxide solution) improved the compressive strengths. Effects of these variables on the compressive strength of alkali-activated natural Pozzolan/slag concretes are discussed in the following subsections.

Table 6.5 Compressive strengths of alkali-activated natural Pozzolan/slag concretes (MPa)

Age (days)	Sodium silicate content (%)	Sodium hydroxide concentration (M)								
		1			1.75			2.5		
		Slag content (%)			Slag content (%)			Slag content (%)		
		30	50	70	30	50	70	30	50	70
1	20	6.3	9.6	9.4	8.0	11.3	11.6	8.4	12.9	14.0
	25	3.7	14.2	15.0	7.4	14.8	18.2	8.2	16.3	19.0
	30	4.2	17.3	20.1	7.2	19.3	21.9	9.5	19.1	24.7
3	20	13.1	12.8	11.7	12.6	16.1	15.0	12.5	17.5	17.8
	25	13.6	20.0	19.2	15.1	21.4	21.9	14.7	24.1	24.6
	30	13.9	25.6	25.8	16.6	26.0	31.5	16.7	27.5	31.0
7	20	17.3	16.2	13.9	16.3	18.8	17.8	16.6	20.9	20.6
	25	22.2	25.2	24.1	20.4	26.5	24.8	20.3	28.2	30.9
	30	23.2	31.9	31.1	23.1	31.9	34.7	23.3	34.9	37.3
28	20	24.0	21.1	18.1	23.2	25.2	24.4	22.8	27.0	26.3
	25	32.8	34.0	28.6	29.9	34.5	33.2	28.2	35.5	39.9
	30	38.6	42.4	41.3	35.8	42.0	41.2	33.9	45.5	47.6
90	20	29.5	24.5	20.3	--	--	--	27.0	32.6	32.9
	25	37.0	39.7	34.9	--	--	--	33.8	43.8	45.9
	30	42.3	50.0	43.0	39.3	50.1	47.7	39.4	53.3	52.8

--: Not available

6.3.4.1. Effects of binder combination

Figures 6.8, 6.9 and 6.10 show the effect of binder combination on the compressive strength of alkali-activated natural Pozzolan/slag concretes made with sodium hydroxide concentrations of 1, 1.75 and 2.5M, respectively. In general, there were optimum combinations of natural pozzolan and slag which was dependent on NaOH molarity and sodium silicate content. The increases in slag content became more effective as sodium hydroxide concentration was increased. A similar trend was seen as sodium silicate content was increased. An increase in slag portion of binder was also useful to accelerate reactions, leading to increased early-age strengths.

At early age of curing (1 and 3 days), increases in slag dosage had a positive influence on the compressive strength. At these ages, concretes having binders made with 70% slag (SLAG-70% concretes) developed higher compressive strength than concretes made with binders having 50 and 30% slag with the latter gained the lowest compressive strengths. The 1-day compressive strengths of SLAG-70% concretes were averagely 3.44, 2.32 and 2.19 times of those of SLAG-30% concretes, and 1.07, 1.13 and 1.18 times of those of SLAG-50% concretes for NaOH molarities of 1, 1.75 and 2.5M, respectively. For similar sodium hydroxide concentrations, the 3-day compressive strengths of SLAG-70% concretes were 1.39, 1.51, and 1.65 times of those of SLAG-30% concretes, and 0.96, 1.06 and 1.06 times of those of SLAG-50% concretes, respectively. This observation can be related to the higher reactivity of slag than natural Pozzolan at early ages which was also seen in Chapters 4 and 5 on alkali-activated pastes and mortars, respectively. As mentioned in Chapter 5, this observation was in line with the results of the study made by Lloyd et al. (2009) who proved that presence of calcium in binder is essential to the early strength development.

As the curing age was extended, the reaction rate of natural Pozzolan increased. The compressive strength of concretes with higher natural Pozzolan contents increased at a higher rate than concretes with lower natural Pozzolan dosages which narrowed the large gap observed at early ages between mixtures having different slag contents. The ratios of 7-, 28- and 90-day compressive strengths of SLAG-70% concretes to those of concretes made with binders containing 30% slag (SLAG-30% concretes) were 1.08, 0.90 and 0.88 for 1M mixtures; 1.27, 1.10 and 1.21 for 1.75M mixtures; and 1.45, 1.32 and 1.31 for 2.5M mixtures, respectively. At these ages, the concretes made with binders having 50 and 70% slag had nearly similar compressive strengths. The ratios of 7-, 28- and 90-day compressive strengths of SLAG-70%

concretes to those of SLAG-50% concretes were 0.93, 0.89 and 0.86 for 1M mixtures; 0.99, 0.97 and 0.95 for 1.75M mixtures; and 1.05, 1.05 and 1.02 for 2.5M mixtures, respectively.

In order to highlight the effects of binder combination, Figure 6.11 shows the 28-day compressive strength of all studied alkali-activated natural Pozzolan/slag concretes. Table 6.6 documents the ranking of slag/natural Pozzolan combination in producing 28-day compressive strengths. It can be seen that for 1M mixtures, the highest 28-day compressive strengths were produced by concretes made with binders having 30, 50 and 50% slag for sodium silicate contents of 20, 25 and 30%, respectively. For 1.75M mixtures, an equal combination of slag and natural Pozzolan (50/50) produced the highest 28-day compressive strengths for all sodium silicate contents. For all 1.75M mixtures, the order of slag/natural Pozzolan combination in producing higher 28-day compressive strengths were 50/50, 70/30 and 30/70. For all 2.5M alkali-activated natural Pozzolan/slag concretes, the highest 28-day compressive strengths were in ascending order of 30/70, 50/50 and 70/30 combination of slag/natural Pozzolan indicating increases in strength with increases in slag content of binder.

As mentioned in Chapter 5, the overall improvement of compressive strength, with an increase in slag content, can be attributed to the higher availability of CaO which improved the strength of the geopolymer by forming an amorphously structured Ca–Al–Si gel, resulting in a denser microstructure (Lee and Lee 2013, Yip 2004, Kumar et al. 2010).

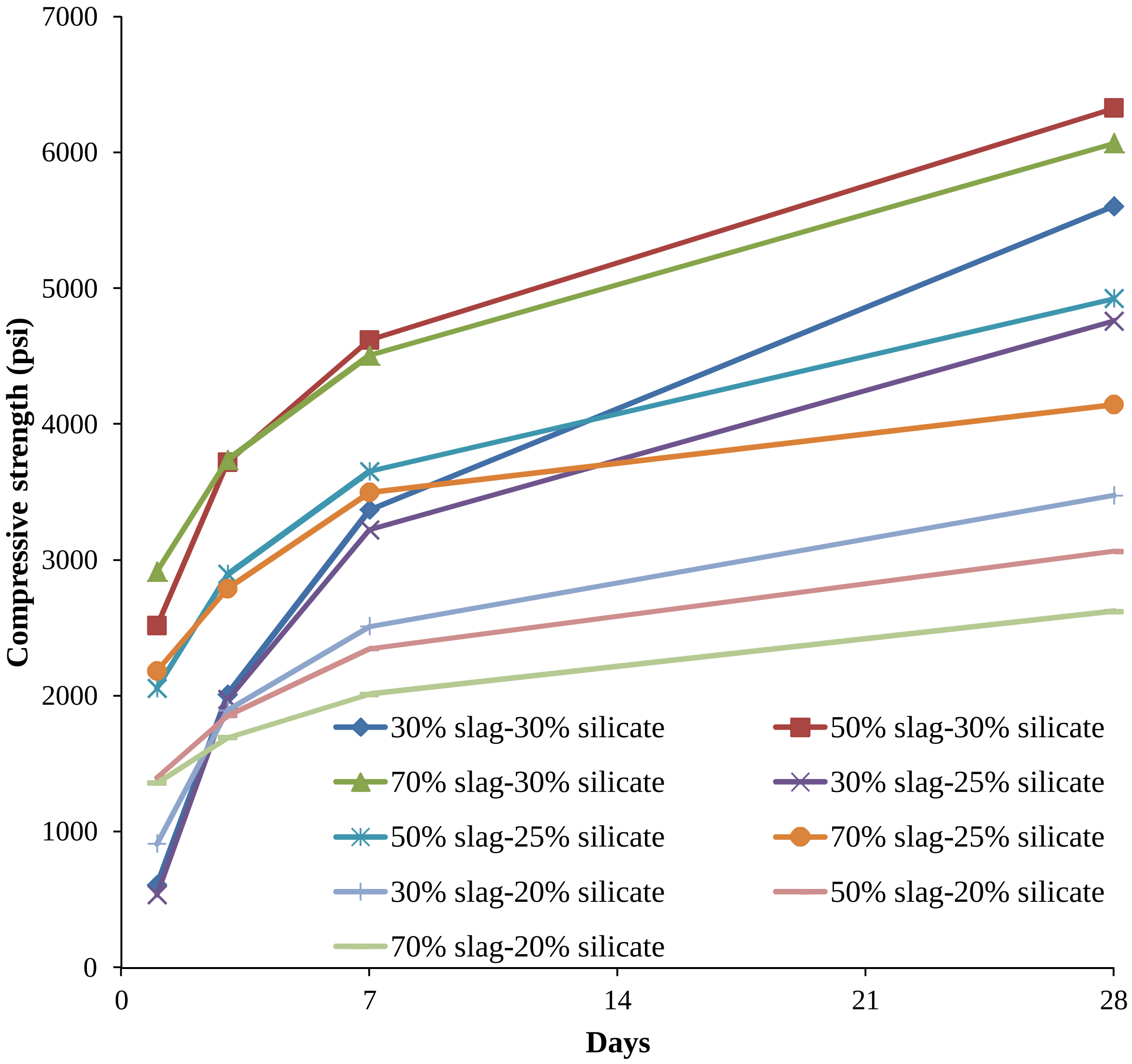


Figure 6.8 The compressive strength of 1M alkali-activated natural Pozzolan/slag concretes having different binder and activator combinations (1 psi = 0.00689476 MPa, 1 MPa = 145.038 psi)

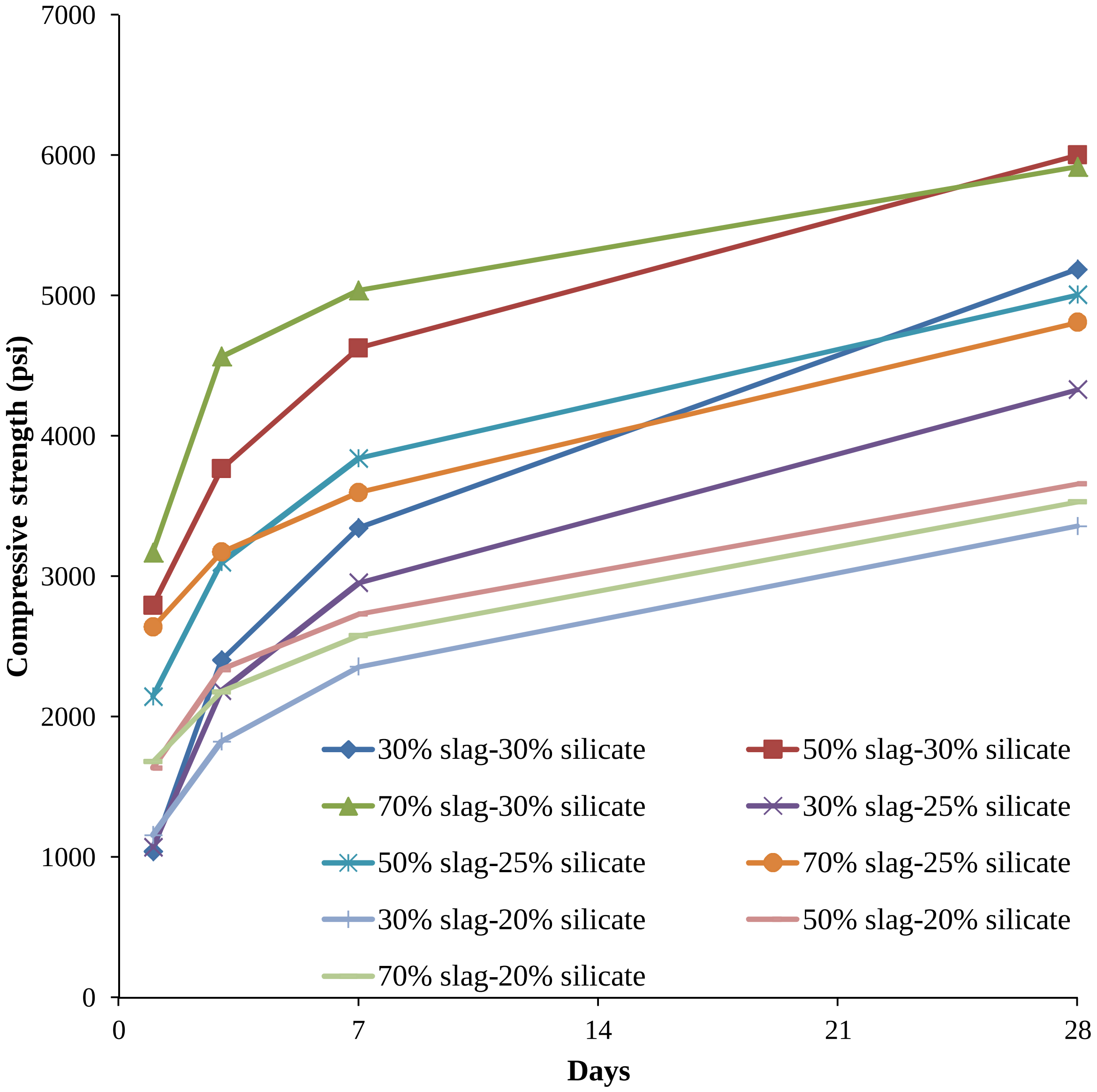


Figure 6.9 The compressive strength of 1.75M alkali-activated natural Pozzolan/slag concretes having different binder and activator combinations (1 psi = 0.00689476 MPa, 1 MPa = 145.038 psi)

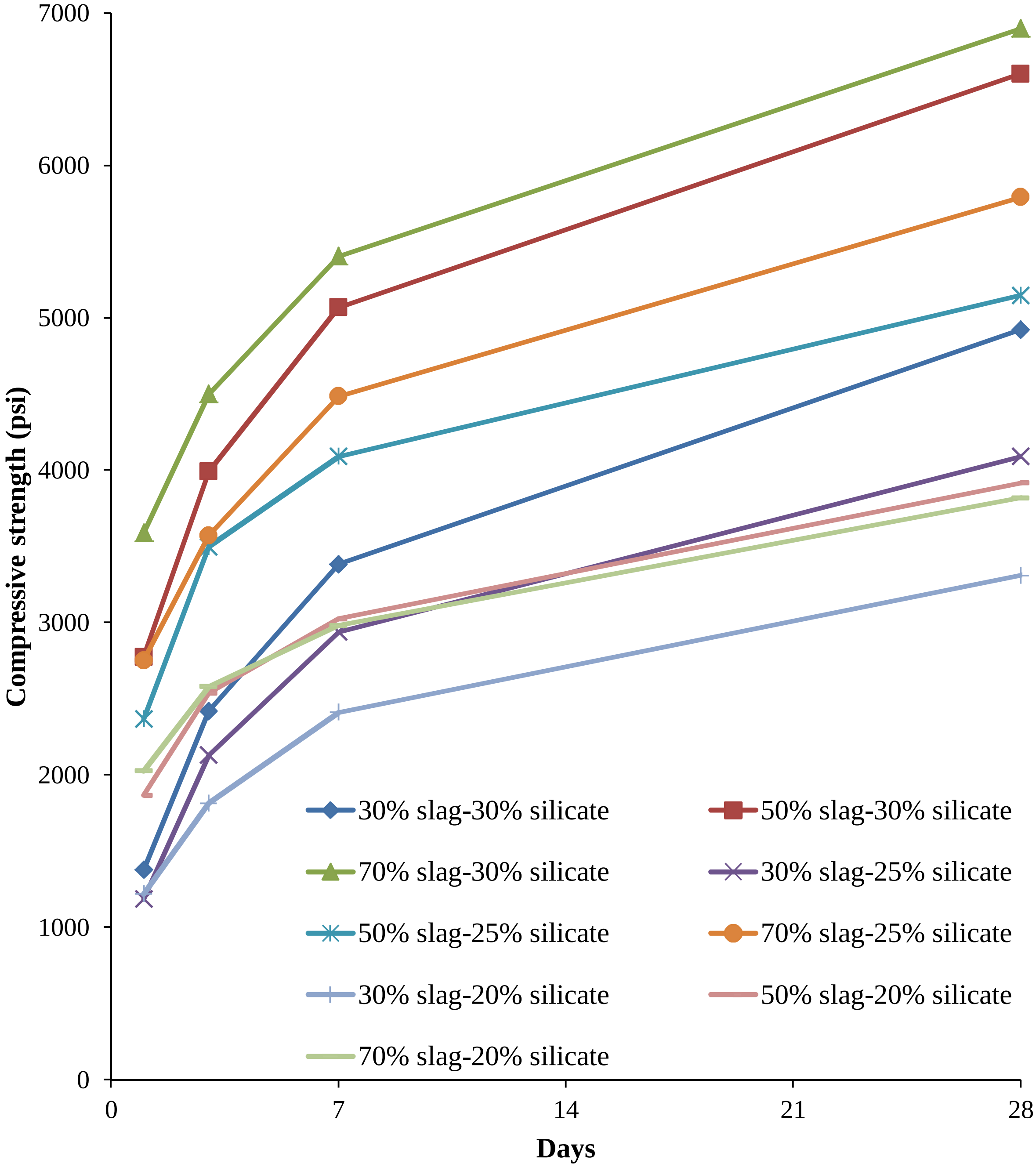


Figure 6.10 The compressive strength of 2.5M alkali-activated natural Pozzolan/slag concretes having different binder and activator combinations (1 psi = 0.00689476 MPa, 1 MPa = 145.038 psi)

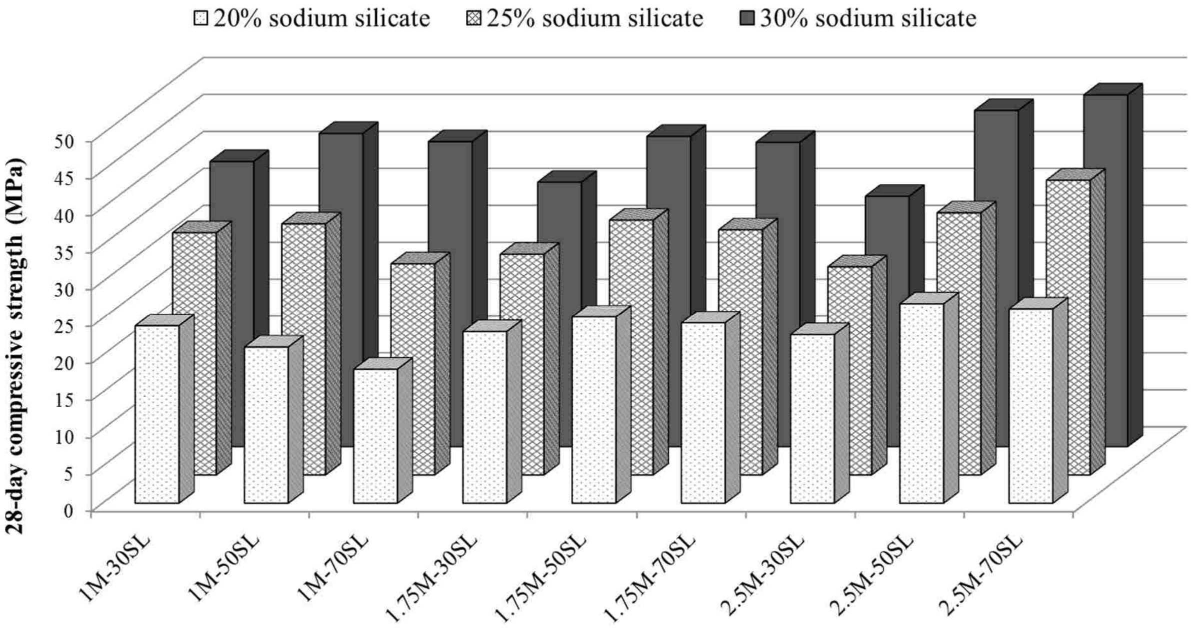


Figure 6.11 The 28-day compressive strength of alkali-activated natural Pozzolan/slag concretes organized based on slag contents

Table 6.6 Ranking of slag/natural Pozzolan combination in producing 28-day compressive strength

Sodium silicate content (%)	Sodium hydroxide concentration (M)		
	1	1.75	2.5
20	30/70-50/50-70/30	50/50-70/30-30/70	70/30-50/50-30/70
25	50/50-30/70-70/30	50/50-70/30-30/70	70/30-50/50-30/70
30	50/50-70/30-30/70	50/50-70/30-30/70	70/30-50/50-30/70

6.3.4.2. Effects of activator combination

The influence of activator combination on the compressive strength of alkali-activated natural Pozzolan/slag concretes is presented in Figures 6.8 through 6.11. It can be seen that the compressive strength improved with increases in sodium silicate content. In case of 1, 1.75 and 2.5M alkali-activated natural Pozzolan/slag concretes, the 28-day compressive strength increased by averagely 51.9, 33.9 and 35.6% when sodium silicate content was increased from 20 to 25%, respectively. For similar sodium hydroxide concentrations, further increases in sodium silicate content from 25 to 30% led to averagely 28.9, 21.5 and 22.6% improvements in the 28-day compressive strength, respectively.

As discussed in Chapter 5, the observed improvements by use of higher sodium silicate can be related to the enhancement of paste microstructure (developing a more homogenous microstructure) and improving the binding ability of C-S-H gel through reduction of its Ca/Si ratio.

6.3.4.3. Effects of sodium hydroxide concentration

Figure 6.12 shows the effect of sodium hydroxide concentration on the 28-day compressive strength of alkali-activated natural Pozzolan/slag concretes. Depending on the binder combination, sodium hydroxide molarity showed different influence on the compressive strength. In case of concretes made with binders having 50 and 70% slag, increases in sodium hydroxide concentration led to increases in compressive strengths. An opposite trend was observed for concretes made with binders having 30% slag.

On average, increases in molarity of sodium hydroxide solution from 1 to 1.75 and 1.75 to 2.5M improved the 28-day compressive strength by 6.7 and 6.1% for SLAG-50% concretes; and 16.9 and 14.5% for SLAG-70% concretes, respectively. Similar increases in sodium hydroxide concentration resulted in averagely 6.5 and 4.2% reduction in the 28-day compressive strength of concretes made with binders having 30% slag (SLAG-30% concretes), respectively.

As discussed in Chapter 5, while increasing NaOH molarity increased the solubility of binders, its increases were not always beneficial for polymerization of aluminosilicate. Similar observations were found by other researchers who studied the effects of NaOH concentration on the strength of alkali-activated fly ash and metakaolin (aluminosilicates). They showed that an excess of OH^- concentration in the system of aluminosilicate-based binders caused strength reductions. Memon et al. (2013) stated that excessive hydroxyl ions led to aluminosilicate gel precipitation at the early stages, hindering subsequent geopolymerization to result in lower strength. The strength reduction was related by Alonso and Palomo (2001) to the delay in formation of alkaline polymer as a result of (1) “the stability of ion species: polymerization is favored when dissolved components are in their molecular form, and an increase of pH provokes higher stability of ion species”, and (2) “ion mobility: a higher sodium hydroxide concentration provokes an increase in the dissolved species amount, and a greater difficulty in the species diffusion in the aqueous phase.” Due to the similarity in chemical compositions of fly ash, metakaolin, and natural Pozzolan, the above explanations are also valid for the studied alkali-activated natural Pozzolan/slag concretes containing high amounts of natural Pozzolan. Accordingly, concretes with high natural Pozzolan contents experienced strength reduction with increasing molarity of sodium hydroxide solution.

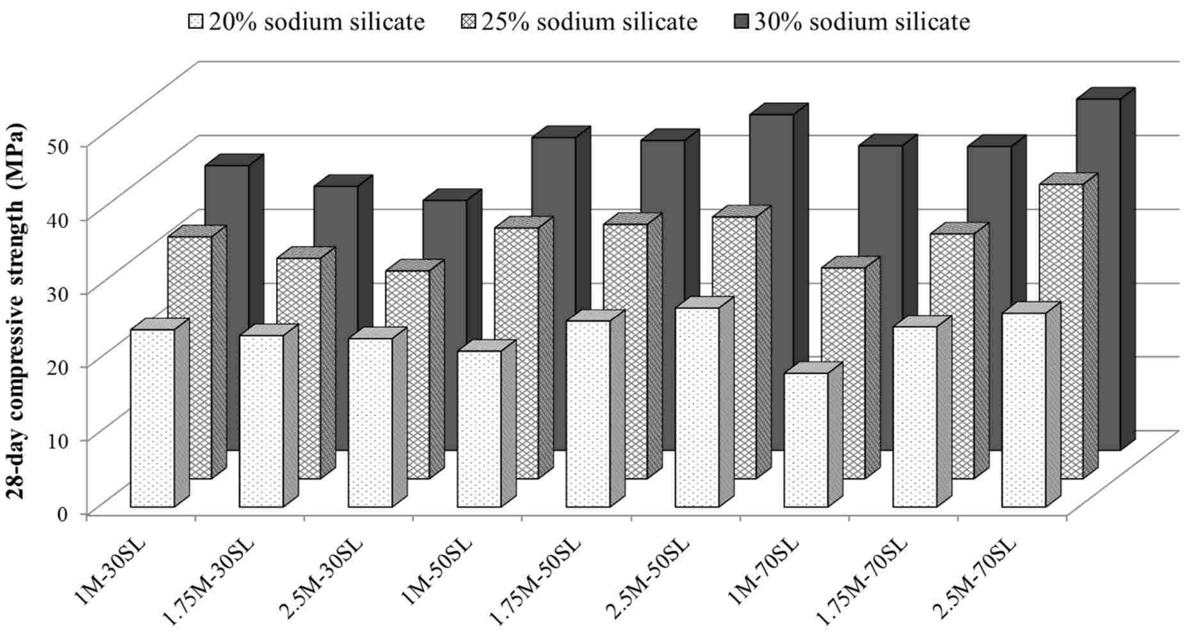


Figure 6.12 The 28-day compressive strength of alkali-activated natural Pozzolan/slag concretes organized based on sodium hydroxide concentration

6.3.5. Modulus of elasticity

The modulus of elasticity of alkali-activated natural Pozzolan/slag concretes was measured on 28-days cured samples and the results are presented in Table 6.7. It can be seen that the elastic modulus of alkali-activated natural Pozzolan/slag concretes were in the rage of 25 to 42 GPa which is similar to the typical range seen for Portland cement concrete. Effects of binder combination, activator combination and sodium hydroxide concentration on the elastic modulus were almost the same as those found for the compressive strength.

Similar to the compressive strength results, slag content of 30 to 50% was found to be the optimum range of binder's slag portion for 1 and 1.75M concretes. When molarity of NaOH solution was increased to 2.5M, this optimum altered to binders containing 50 to 70% slag. The optimum slag content of the binder was on the lower boundary of these ranges for sodium silicate content of 20%, whereas an opposite trend was seen for sodium silicate dosage of 30%.

Modulus of elasticity increased with increases in sodium silicate portion of the activator. The elastic modulus of SILICATE-30% concretes were higher than those of SILICATE-20% and SILICATE-25% concretes by 27.6 and 13.3% for 1M mixtures; 22.5 and 8.0% for 1.75M mixtures; and 31.4 and 2.3% for 2.5M mixtures, respectively.

Similar to the compressive strength results, increasing sodium hydroxide concentration wasn't beneficial for elastic modulus of SLAG-30% concretes. An increase in NaOH concentration from 1 to 2.5M caused an average reduction of 11.6% in elastic modulus of SLAG-30% concretes. On the other hand, modulus of elasticity of concretes made with binders having 50 and 70% slag increased with increases in sodium hydroxide molarity. A similar increase in sodium hydroxide concentration from 1 to 2.5M led to averagely 4.0 and 9.4% improvements in elastic modulus of SLAG-50% and SLAG-70% concretes, respectively.

Table 6.7 Modulus of elasticity of alkali-activated natural Pozzolan/slag concretes (GPa)

Sodium silicate content (%)	Sodium hydroxide concentration (M)								
	1			1.75			2.5		
	Slag content (%)			Slag content (%)			Slag content (%)		
	30	50	70	30	50	70	30	50	70
20	32.21	29.12	28.85	31.67	31.40	28.99	25.50	31.82	28.18
25	34.51	34.72	31.98	32.78	37.57	33.93	32.21	37.96	39.25
30	34.89	41.46	38.13	34.65	39.25	38.60	32.35	38.69	41.06

6.3.6. Tensile strength

Table 6.8 shows the results of indirect tensile strength measured on 28-day cured cylinders. It can be seen that the tensile strength of alkali-activated natural Pozzolan/slag concretes were in the range of 2.5 to 5.4 MPa which is similar to the typical range reported for Portland cement concretes. The tensile strength-to-compressive strength ratio of alkali-activated natural Pozzolan/slag concretes was in the range of 0.10 to 0.14 which is also similar to the typical ratio seen in Portland cement concretes. The behavior of alkali-activated natural Pozzolan/slag concretes in tensile strength was almost the same as that found for the compressive strength.

Except for mixtures with low NaOH concentration (1M) and sodium silicate content (20 and 25%), increasing slag content of binder improved the tensile strength. Increases in slag content from 30 to 50 and 50 to 70% reduced tensile strength of 1M concretes by averagely 1.1 and 4.0%, and improved tensile strength of 2.5M concretes by averagely 17.5 and 0.9%, respectively.

Similar to the compressive strength, the tensile strengths increased with increases in sodium silicate content. On average, the tensile strengths improved by 29.1 and 17.4% when sodium silicate content was increased from 20 to 25 and 25 to 30%, respectively.

In addition, an increase of sodium hydroxide concentration had a positive effect on the tensile strength of concretes made with binders having 50 and 70% slag. The tensile strengths of SLAG-30%, SLAG-50% and SLAG-70% concretes improved by averagely 1.9, 21.0 and 27.6% when sodium hydroxide concentration was increased from 1 to 2.5M, respectively.

Table 6.8 28-day tensile strength of alkali-activated natural Pozzolan/slag concretes (MPa)

Sodium silicate content (%)	Sodium hydroxide concentration (M)								
	1			1.75			2.5		
	Slag content (%)			Slag content (%)			Slag content (%)		
	30	50	70	30	50	70	30	50	70
20	3.05	2.88	2.46	--	--	--	3.17	3.29	3.39
25	3.81	3.49	3.54	--	--	--	3.74	4.42	4.49
30	3.98	4.40	4.44	4.03	4.54	4.46	4.11	5.36	5.27

--: Not available

6.3.7. Volume of permeable voids

The results of absorption test for alkali-activated natural Pozzolan/slag concretes are presented in Table 6.9. Effects of different variables on the volume of permeable voids are discussed below.

Table 6.9 Results of Absorption test for alkali-activated natural Pozzolan/slag concretes

Age (days)	Sodium silicate content (%)	Sodium hydroxide concentration (M)								
		1			1.75			2.5		
		Slag content (%)			Slag content (%)			Slag content (%)		
		30	50	70	30	50	70	30	50	70
Absorption (%)	20	5.58	5.79	6.32	5.44	5.67	5.73	5.48	5.49	5.41
	25	5.63	4.91	5.5	5.85	5.12	5.5	5.57	5.07	5.05
	30	6.09	4.94	5.04	5.9	5.16	4.64	5.63	4.49	5.1
Volume of permeable voids (%)	20	12.54	13.15	14.33	12.36	12.95	13.11	12.49	12.6	12.57
	25	12.72	11.25	12.65	13.3	11.82	12.62	12.63	11.71	11.74
	30	13.81	11.34	11.66	13.42	11.82	10.83	12.84	10.47	11.85

6.3.7.1. Effects of binder combination

The influence of binder combination on the volume of permeable voids of alkali-activated natural Pozzolan/slag concretes can be seen in Table 6.9. Similar to the results of second phase of this study, concretes with natural Pozzolan/slag combination of 50/50 (optimum level) usually had the lowest volume of permeable voids. Concretes having binders with 30/70 combination of natural Pozzolan/slag had lower voids volumes than those having binders with 70/30 combination (except for mixtures made with activators having sodium silicate content of 20%).

As discussed in Chapter 5, increases in slag content of binder led to increases in the amount of C-A-S-H gel which had higher bound water contents than N-A-S-H gel formed as a reaction product of aluminosilicates. This, in turn, resulted in lower water uptake. However, increasing more than an optimum level (50/50 combination of slag and natural Pozzolan) changed the structure of C-A-S-H gel to a less binding gel with increasing Ca/Si ratio, which could be the reason for the adverse effect of slag inclusion for more than the optimum level.

6.3.7.2. Effects of activator combination

Table 6.9 also shows the influence of activator combination on the volume of permeable voids of alkali-activated natural Pozzolan/slag concretes. Similar to the observations of the second phase of this study on alkali-activated mortars, an increase in sodium silicate content increased volume of permeable voids of SLAG-30% concretes, whereas contrary was found for concretes made with binders having slag contents of 50 and 70%.

On average, an increase in sodium silicate content from 20 to 25 and 25 to 30% increased voids volume of SLAG-30% concretes by 3.4 and 3.7%, respectively. Similar increases in sodium silicate dosage reduced the voids volume by averagely 10.1 and 3.3% for SLAG-50% concretes; and 7.4 and 7.0% for SLAG-70% concretes, respectively.

As also noted in Section 5.3.5.2, for high slag contained binders (50 and 70%), the results can be explained through modification of C-S-H gel (or C-A-S-H gel) through increases in silicate content. Use of higher sodium silicate can enhance paste microstructure and improve binding ability of C-S-H gel through reduction of Ca/Si ratio.

6.3.7.3. Influences of sodium hydroxide concentration

The effect of sodium hydroxide concentration on the voids volumes of alkali-activated natural Pozzolan/slag concretes can be seen in Table 6.9. Overall, there was a slight reduction in the volume of permeable voids of alkali-activated natural Pozzolan/slag concretes with increases in molarity of sodium hydroxide solution.

On average, the total voids volume of 2.5M concretes were lower than those of 1M concretes by 2.7, 2.6 and 5.9% for slag contents of 30, 50 and 70%, respectively. For sodium silicate contents of 20, 25 and 30%, the voids volumes improved (reduced) by averagely 5.6, 1.3 and 4.4% when sodium hydroxide concentration was increased from 1 to 2.5M, respectively.

These findings follow the observations made by Melo Neto et al. (2008) and Chi and Huang (2013) where reduction in porosity of alkali-activated slag systems with increases in Na_2O content were reported.

6.3.8. Rapid chloride penetration test

The results of rapid chloride penetration test (RCPT) for alkali activated natural Pozzolan/slag concretes are documented in Table 6.10. The effects of binder combination, activator combination and sodium hydroxide concentration on the passing charges are discussed below.

Table 6.10 Results of RCPT and RMT for alkali-activated natural Pozzolan/slag concretes

Property	Sodium silicate content (%)	Sodium hydroxide concentration (M)								
		1			1.75			2.5		
		Slag content (%)			Slag content (%)			Slag content (%)		
		30	50	70	30	50	70	30	50	70
RCPT (Coulombs)	20	607	354	367	--	--	--	1356	466	404
	25	1715	349	316	--	--	--	2172	527	421
	30	2390	447	314	3683	633	465	4111	691	418
RMT (mm)	20	5.44	4.2	4.25	--	--	--	9.15	4.57	3.8
	25	9.66	4.2	3.8	--	--	--	12.73	4.95	3.81
	30	15.53	4.83	3.18	17.49	4.17	3.95	20.15	5.06	4.04

--: Not available

6.3.8.1. Effects of binder combination

Figures 6.13 and 6.14 show the effect of binder combination on the passing charges of alkali-activated natural Pozzolan/slag concretes. Similar to the results of second phase (Chapter 5), the passing charges reduced as slag portion of binder was increased; particularly when slag content was increased from 30 to 50% (natural Pozzolan dosage was reduced from 70 to 50%). The reduction was not as significant when slag content was increased from 50 to 70%.

In case of mixtures having NaOH concentration of 1, 1.75 and 2.5M, increases in slag content from 30 to 50% led to averagely 67.5, 82.8, and 74.9% reduction in the passing charges of the studied alkali-activated natural Pozzolan/slag concretes, respectively. For similar NaOH molarities, concretes made with binders having 70% slag (SLAG-70%) had 11.8, 26.5, and 24.3% lower RCPT values than SLAG-50% concretes, respectively.

For concretes made with activators having sodium silicate content of 20, 25 and 30%, increases in slag content from 30 to 50% led to averagely 53.7, 77.7, and 82.4% reduction in the passing charges of the studied alkali-activated natural Pozzolan/slag concretes, respectively. Further increases in slag content (from 50 to 70%) reduced the passing charges by averagely 4.8, 14.8 and 31.9%, respectively.

Similar to the second phase of this study, as the strength of SLAG-30% concretes wasn't affected by increasing sodium hydroxide concentration, it can be inferred that there were significantly more free hydroxyls available in the concretes made with binders having lower slag contents. Higher availability of free hydroxyls resulted in higher passing charges.

6.3.8.2. Influences of activator combination

Figure 6.14 shows the effect of activator combination on the passing charges. Overall, increases in sodium silicate contents, accompanied with decreases in sodium hydroxide dosages, resulted in increases in the charges passed through the studied alkali-activated natural Pozzolan/slag concretes. These increases were far more significant for concretes whose binder had 70% natural Pozzolan dosage (30% slag).

In case of mixtures made with binders having slag content of 30, 50 and 70%, increases in sodium silicate content from 20 to 25% led to averagely 121.4, 5.8 and -4.8% increases in the passing charges, respectively. For similar slag dosages, the passing charges increased by 64.3, 29.6 and -0.7% when sodium silicate content was increased from 25 to 30%, respectively.

These observations, which are similar to the findings of alkali activated natural Pozzolan/slag mortars (Section 5.3.6.2), can be related to the higher alkaline content of sodium silicate solution in comparison with that of sodium hydroxide solution.

6.3.8.3. Effects of sodium hydroxide concentration

Figure 6.13 also shows the results of rapid chloride penetration test for concretes with different NaOH concentrations. It can be seen that as sodium hydroxide molarity was increased, the passing charges increased.

On average, the passing charges of 2.5M concretes were 74.0, 45.7 and 25.5% higher than those of 1M concretes for slag contents of 30, 50 and 70%, respectively. Similarly, when NaOH concentration was increased from 1 to 2.5M, the passing charges increased by 55.0, 37.0 and 53.2% for sodium silicate contents of 20, 25 and 30%, respectively.

The observed increases in ions transfer can be related to the increases in the amounts of free hydroxyl ions with increases in molarity of alkaline activator which resulted in higher ion movement.

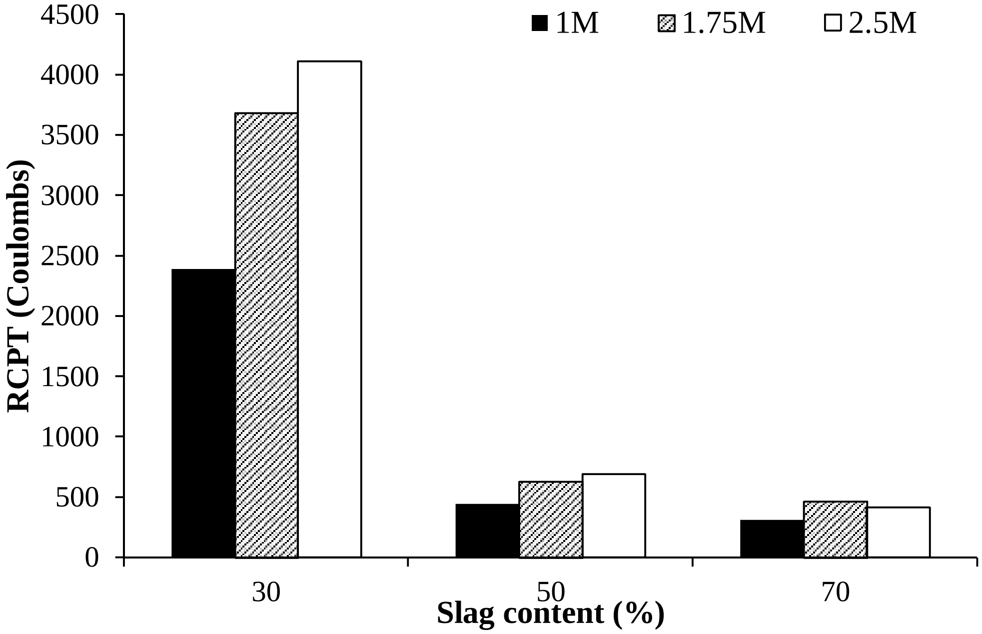


Figure 6.13 RCPT of SILICATE-30% alkali-activated natural Pozzolan/slag concretes having different binder combination and NaOH concentration

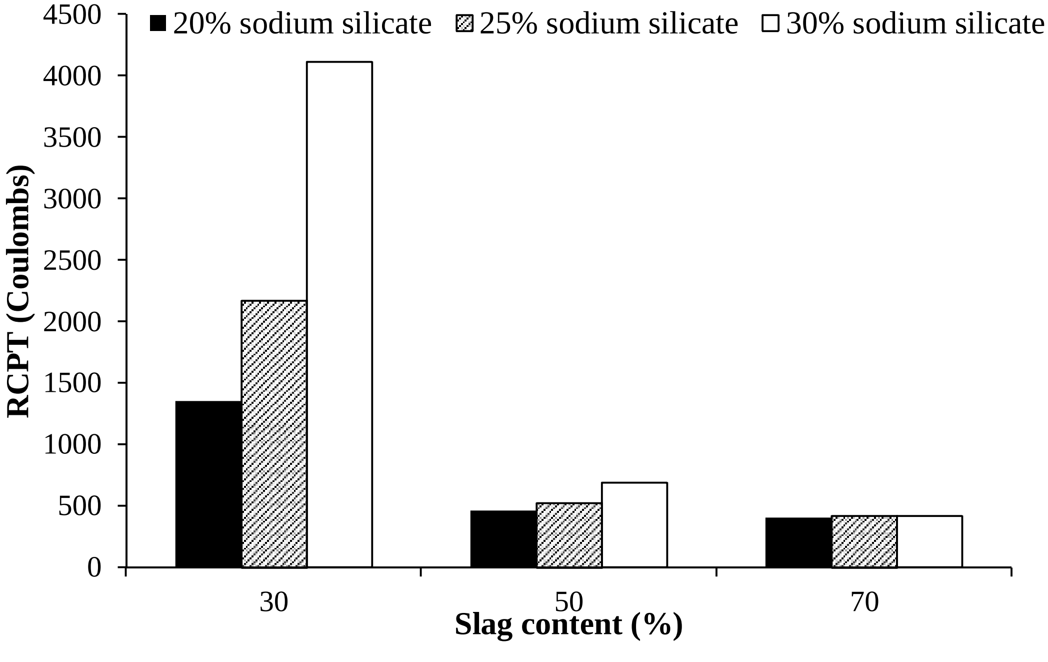


Figure 6.14 RCPT of 2.5M alkali-activated natural Pozzolan/slag concretes having different slag and sodium silicate contents

6.3.9. Rapid chloride migration test

Table 6.10 also reports results of rapid chloride migration test (RMT) for the studied alkali-activated natural Pozzolan/slag concretes. The effects of different variables on the results of RMT are discussed below.

6.3.9.1. Effects of binder combination

Figures 6.15 and 6.16 show the influence of binder combination on the chloride penetration depth of the studied alkali-activated natural Pozzolan/slag concretes. It can be seen that the chloride penetrated deeper as natural Pozzolan portion of the binder was increased.

On average, the chloride penetration depths into SLAG-30% concretes were 2.8 and 3.4 times of penetration depths into SLAG-50% and SLAG-70% concretes, respectively. The observed difference increased as sodium silicate content was increased. For concretes made with activators having 20, 25 and 30% sodium silicate, the chloride penetration depths into SLAG-50% concretes were 36.4, 58.8 and 73.3% lower than those into SLAG-30% concretes, respectively. For similar sodium silicate contents, the chloride penetration depths reduced by averagely 7.8, 16.3 and 19.9% when slag content was increased from 50 to 70%, respectively.

As mentioned in Chapter 5, the observed improvements can be related to the refinement of pore structure through increases in slag content which restricted the movement of chloride ions in the specimen. The improved pore size distribution of SLAG-50% and SLAG-70% concretes in comparison with that of SLAG-30% concretes can be seen in Figure 6.17 and Table 6.11. The total mesopores and macropores of SLAG-30% concretes were about 1.4 times of those of concretes made with binders having 50 and 70% slag. It can also be seen that the distribution of pores was more evenly when slag made up 50 and 70% of binder.

6.3.9.2. Influences of activator combination

Figure 6.16 shows the effect of sodium silicate and sodium hydroxide contents on the chloride penetration depth of alkali activated natural Pozzolan/slag concretes. Overall, for SLAG-30% concretes, the chloride penetration depth considerably increased as sodium silicate content was increased. The activator combination didn't have any considerable effect on the chloride penetration depth of concretes made with binders having 50 or 70% slag.

In case of concretes made with binders having 30% slag, increases in sodium silicate content from 20 to 25 and 25 to 30% increased the chloride penetration depths by averagely 58.3 and 59.5%, respectively. For similar increases in sodium silicate content, the penetrations depths increased by 4.2 and 8.6% for SLAG-50% concretes; and reduced by 5.2 and 5.1% for SLAG-70% concretes, respectively.

The significant increases in chloride penetration depth exhibited by SLAG-30% concretes can be explained through reviewing the results obtained for absorption and RCPT of the studied natural Pozzolan/slag concretes. The increases in the results of these two tests with increases in sodium silicate content suggested that the pore structure of SLAG-30% concretes were weakened with the higher dosage of sodium silicate content. This, in turn, allowed for higher penetration of chloride ions.

6.3.9.3. Effects of sodium hydroxide concentration

The influence of sodium hydroxide molarity on the chloride penetration depth is shown in Figure 6.15. Overall, the chloride penetration depths increased with increases in sodium hydroxide concentration; particularly for SLAG-30% concretes.

The chloride penetration depths of concretes made with 2.5M NaOH were averagely 43.2, 10.5 and 5.6% higher than those having 1M NaOH for slag contents of 30, 50 and 70%, respectively. The observed increases in the chloride penetration depth of SLAG-30% concretes through increasing NaOH concentration, which correlates well with the findings of second phase of the study (Chapter 5), may be related to their microstructure which also produced lower compressive strength.

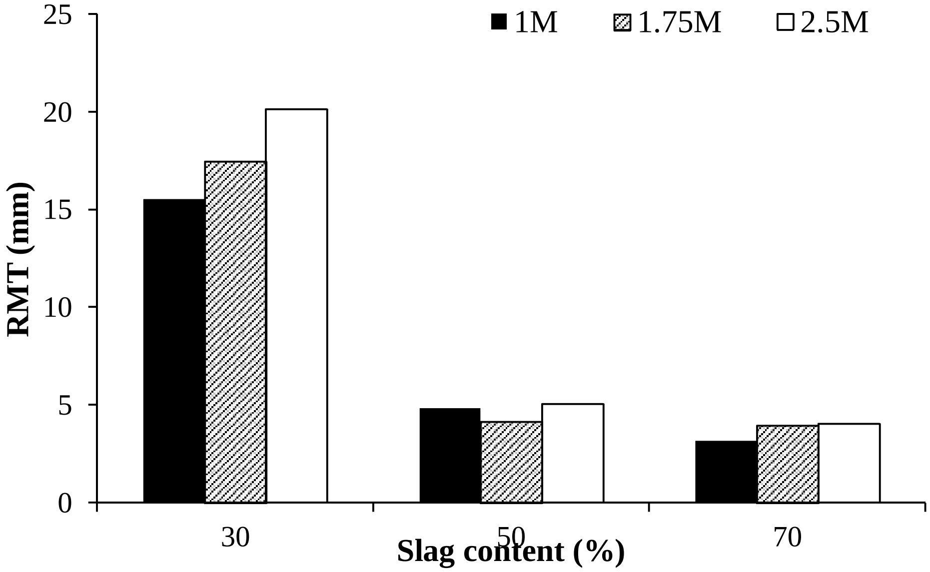


Figure 6.15 Chloride penetration depth of SILICATE-30% alkali-activated natural Pozzolan/slag concretes having different binder combination and NaOH concentration

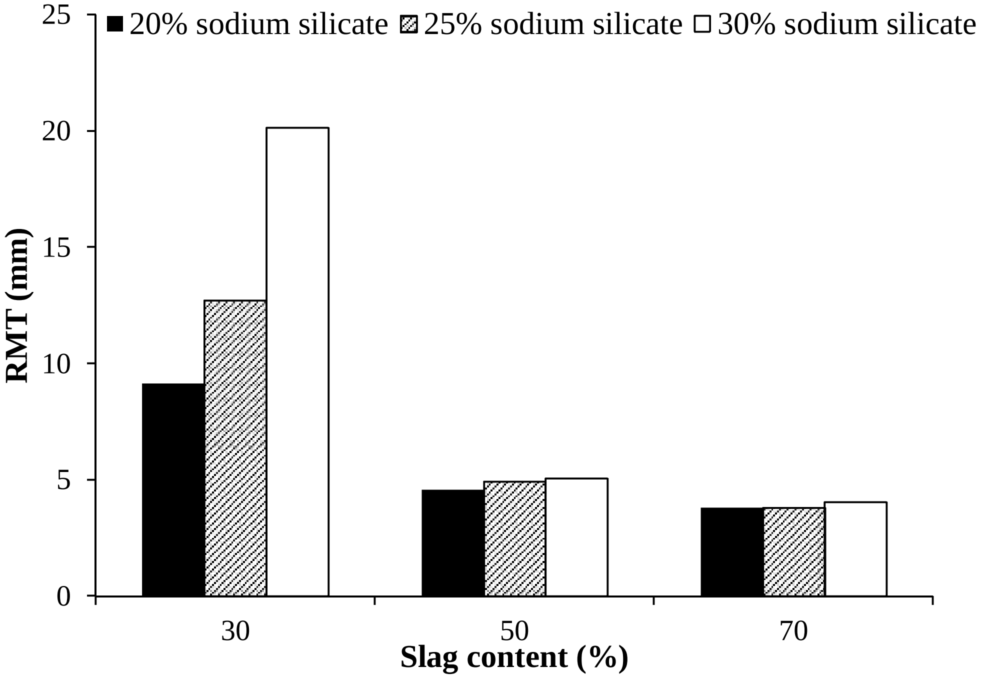
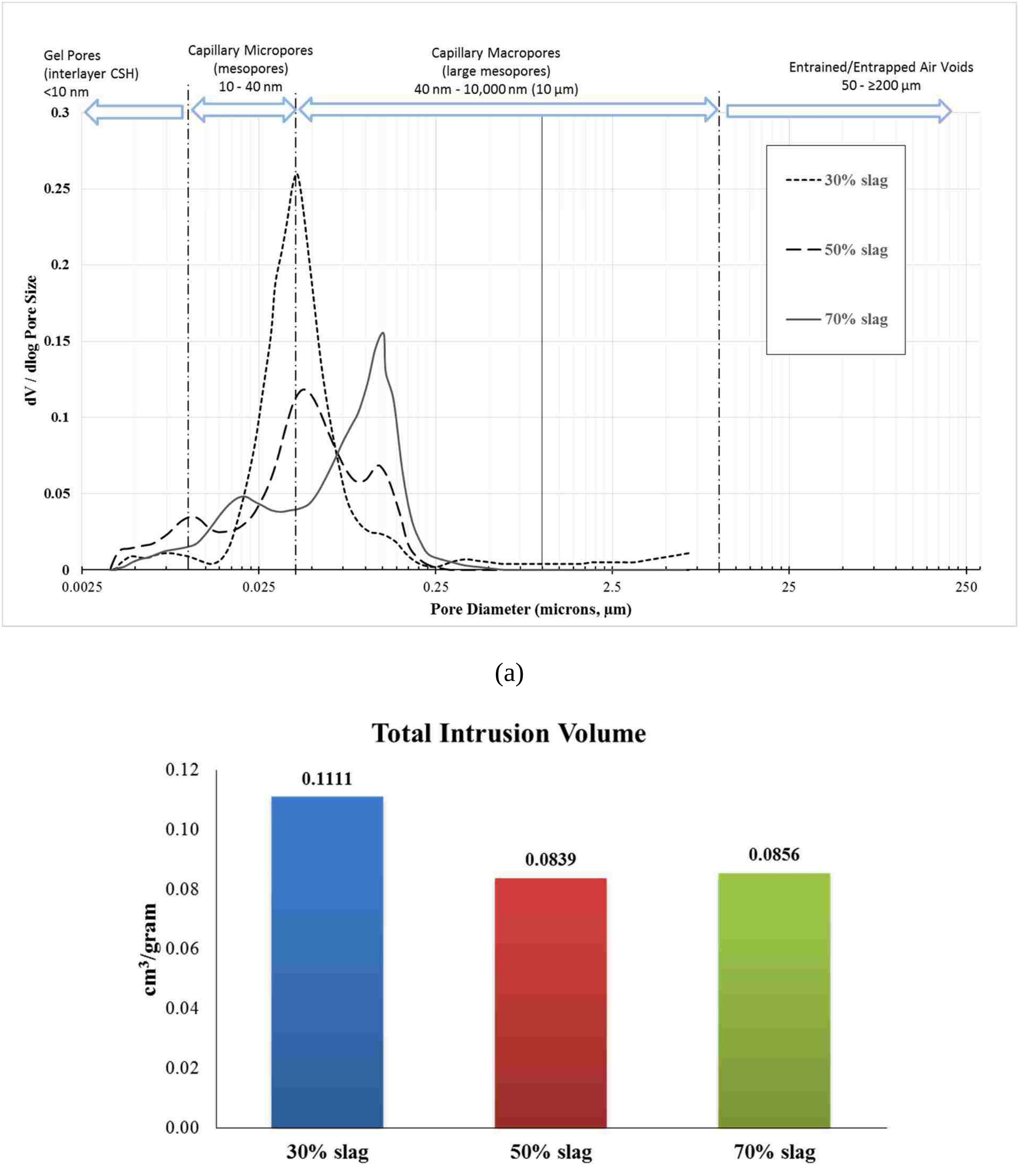


Figure 6.16 Chloride penetration depth of 2.5M alkali-activated natural Pozzolan/slag concretes having different binder and activator combinations

Table 6.11 Volume of micropores, macropores and gel pores for 1.75M alkali-activated natural Pozzolan/slag concretes made with activators having 30% sodium silicate

	Slag content (%)		
	30	50	70
Macropores (0.04-7 micron)	0.0583	0.0468	0.0581
Micropores (0.01-0.04 micron)	0.049	0.029	0.0228
Gel pores (below 0.01 micron)	0.0038	0.0081	0.0047
Total micropores and macropores	**0.1073**	**0.0758**	**0.0809**
Total pores	**0.1111**	**0.0839**	**0.0856**



(a)

(b)

Figure 6.17 Results of mercury intrusion porosimetry for 1.75M alkali-activated natural Pozzolan/slag concretes made with activators having 30% sodium silicate, (a) pore size distribution, (b) total volume of pores

6.3.10. Drying shrinkage

The drying shrinkage of alkali-activated natural Pozzolan/slag concretes was measured for a period of 6 months after 28 days of curing in a moist-curing room. Table 6.12 and Figure 6.18 report the ultimate drying shrinkage of alkali-activated natural Pozzolan/slag concretes. The effects of binder combination, activator combination and sodium hydroxide concentration on the drying shrinkage of alkali-activated natural Pozzolan/slag concretes are discussed in following subsections.

6.3.10.1. Effects of binder combination

The influence of binder combination on the ultimate drying shrinkage of alkali-activated natural Pozzolan/slag concretes is presented in Figure 6.18. Overall, SLAG-50% and SLAG-70% concretes (made with binders having 50 and 70% slag) performed superior to SLAG-30% concretes. The ultimate drying shrinkage of SLAG-50% and SLAG-70% concretes were nearly similar. It was also seen that the positive influence of higher slag inclusion reduced with increases in NaOH concentration.

In case of 1M mixtures, the ultimate drying shrinkage of SLAG-50% and SLAG-70% concretes were averagely 39.3 and 41.9% lower than those of SLAG-30% concretes, respectively. These improvements were 35.2 and 31.8% for 1.75M; and 33.2 and 20.0% for 2.5M concretes, respectively.

For concretes made with activators having 20, 25 and 30% sodium silicate, the ultimate drying shrinkage improved by averagely 27.8, 38.6 and 31.3% when slag portion of binder was increased from 30 to 50%, respectively. For similar sodium silicate contents, SLAG-70% concretes shrank marginally by an average of 2% higher than SLAG-50% concretes.

A similar observation reported by Yusuf et al. (2014) attributed this behavior to reduction in internal micro-cracks and improvement in pore-filling and pore refinement with increases in slag content. The results of mercury intrusion porosimetry (porosity) presented in Figure 6.17 and Table 6.11 supported this argument for the studied alkali-activated natural Pozzolan/slag concretes. The total mesopores and macropores in SLAG-30% concretes were about 1.4 times of those of SLAG-50% and SLAG-70% concretes. It can also be seen that the distribution of pores was more evenly when slag made up 50 and 70% of binder.

6.3.10.2. Effects of activator combination

Figure 6.18 shows the effect of activator combination on the ultimate drying shrinkage of alkali-activated natural Pozzolan/slag concretes. It can be seen that the studied concretes shrank more when sodium silicate content was increased (sodium hydroxide dosage was reduced).

On average, the ultimate drying shrinkage of 1M concretes increased by 48.7 and 20.6% when sodium silicate content was increased from 20 to 25 and 25 to 30%, respectively. Similar increases in sodium silicate content increased the ultimate drying shrinkage by averagely 39.2 and 28.1% for 1.75M concretes; and 33.4 and 12.6% for 2.5M concretes, respectively.

As mentioned in Chapter 5, a similar trend was observed by other researchers (Cincotto et al. 2003, Atis et al. 2009, Aydin and Baradan 2014, Deb et al. 2015). Aydin and Baradan (2014) related the increases in the drying shrinkage of alkali-activated slag mortars to the increases in volume of mesopores when higher sodium silicate content was used. Similarly, it is deduced that an increase in sodium silicate content increased silica-to-Na_2O ratio, leading to increases in mesopores volume and subsequent increases in the drying shrinkage of the studied alkali-activated natural Pozzolan/slag concretes.

6.3.10.3. Influences of sodium hydroxide concentration

Figure 6.18 also presents the ultimate drying shrinkage of alkali-activated natural Pozzolan/slag concretes made with different sodium hydroxide concentrations. While sodium hydroxide concentration was less effective than binder and activator combinations, its influence on the ultimate drying shrinkage was highly dependent on these combinations.

For binders made of 30% slag, the drying shrinkage reduced as NaOH molarity was increased, whereas an almost opposite trend was seen for concretes made with binders having 50 and 70% slag. In case of SLAG-30% concretes, 2.5M mixtures shrank averagely 9.2% lower than 1M mixtures. On the other hand, the ultimate drying shrinkage of 2.5M concretes were averagely 15.1 and 25.7% more than those of 1M concretes for SLAG-50% and SLAG-70% concretes, respectively.

Increases in molarity of sodium hydroxide also increased the ultimate drying shrinkage of concretes having different sodium silicate dosages. Its effects, however, dwindled (diminished) as sodium silicate content was increased. As NaOH concentration was increased from 1 to 2.5M, the ultimate drying shrinkage of SILICATE-20% concretes increased by averagely 22.6%. Similar increases in sodium hydroxide molarity caused 8.0 and 1.0% increases in the ultimate drying shrinkage of SILICATE-25% and SILICATE-30% concretes, respectively.

Table 6.12 Ultimate drying shrinkage of alkali-activated natural Pozzolan/slag concretes (%)

Sodium silicate content (%)	Sodium hydroxide concentration (M)								
	1			1.75			2.5		
	Slag content (%)			Slag content (%)			Slag content (%)		
	30	50	70	30	50	70	30	50	70
20	-0.047	-0.031	-0.027	-0.046	-0.032	-0.035	-0.044	-0.036	-0.043
25	-0.072	-0.040	-0.045	-0.072	-0.040	-0.047	-0.066	-0.049	-0.049
30	-0.086	-0.054	-0.047	-0.085	-0.060	-0.054	-0.076	-0.056	-0.052

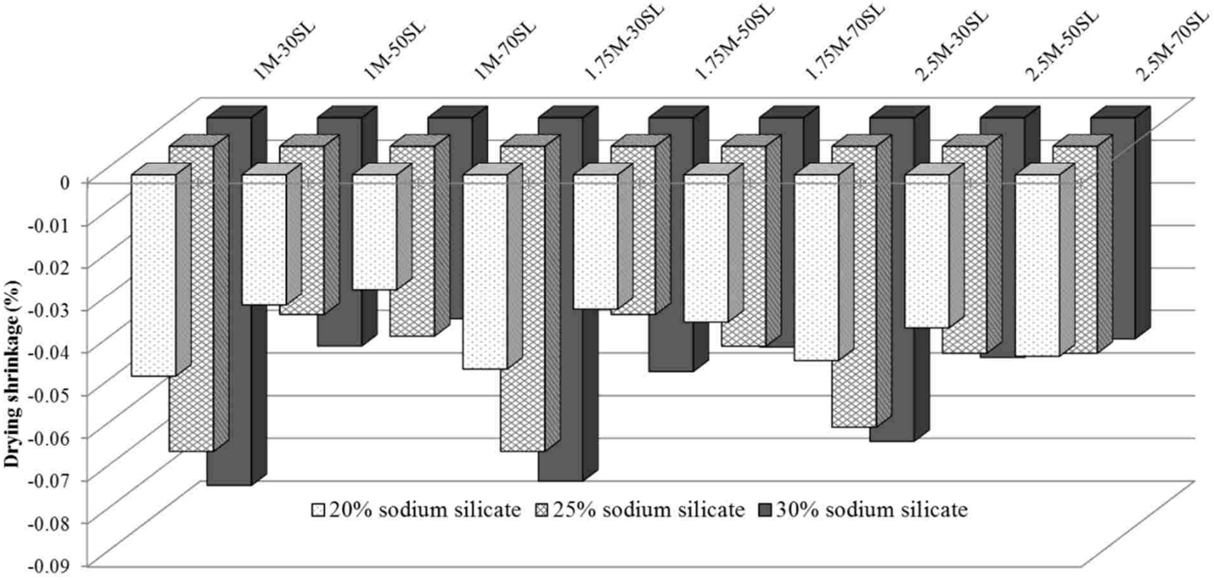


Figure 6.18 Ultimate drying shrinkage of alkali-activated natural Pozzolan/slag concretes (XM-YSL means NaOH molarity of X and slag content of Y%).

6.3.11. Acid resistance

Acid resistance of alkali-activated natural Pozzolan/slag concretes was assessed by immersing 28-day cured samples in sulfuric acid. Prior to immersion in acid, samples were weighted in their saturated state. After immersion in acid, their weights were measured every week for a period of 4 months. Each week, enough acid was added to keep solution pH below 1.

Figures 6.19 through 6.21 show the mass change of alkali-activated natural Pozzolan/slag concretes within the period of testing. Their ultimate mass changes (after 4 months) are reported in Table 6.13. It can be seen that within the first few weeks of immersion, the studied alkali-activated natural Pozzolan/slag concretes gained mass due to solution penetration, after which they started to lose mass due to destructive effect of sulfuric acid. The observed mass losses increased as slag dosage, sodium silicate content, and sodium hydroxide concentration were increased.

6.3.11.1. Effects of binder combination

It can be seen in Figures 6.19 through 6.21 and Table 6.13 that increases in slag content caused increases in mass loss of alkali-activated natural Pozzolan/slag concretes. This was particularly seen for SILICATE-30% concretes. For this sodium silicate dosage, SLAG-30% concretes made with sodium hydroxide concentration of 1, 1.75 and 2.5M gained 0.20, 0.46 and 0.22% weight within 4 months of exposure in acid, respectively. For similar sodium silicate content and sodium hydroxide concentrations, the mass losses were 1.11, 2.07 and 2.65% for SLAG-50% concretes; and 1.26, 1.83 and 3.35% for SLAG-70% concretes, respectively.

The time of mass loss initiation (time that the studied concretes had their maximum mass) are also reported in Table 6.13. This time reduced as binder’s slag content was increased. This time was in the range of 70 to 112, 35 to 98, and 35 to 91 days for concretes made with binders having slag contents of 30, 50 and 70% respectively.

The increased mass loss due to the increases in slag content can be related to the higher calcium content of slag in comparison with that of natural Pozzolan. Calcium compounds (such as calcium oxide, calcium hydroxide) react with sulfuric acid and form gypsum (calcium sulfate

($CaSO_4 \cdot 2H_2O$)). An increase in calcium content of binder through increases in its slag portion led to increased formation of gypsum and, thus, higher mass losses. Figure 6.22 shows that gypsum was formed in the surface of samples immersed in sulfuric acid. In this figure, it can also be seen that higher gypsum was formed on the surface of SLAG-70% concrete in comparison with that of SLAG-30% concrete (it's worth mentioning that the scale factor of gypsum in XRD examination was 0.867 for SLAG-70% concrete in comparison with 0.580 for SLAG-30% concrete).

6.3.11.2. Effects of activator combination

Figures 6.19 through 6.21 and Table 6.13 present the effect of activator combination on the mass loss of alkali-activated natural Pozzolan/slag concretes immersed in sulfuric acid. The mass loss of alkali-activated natural Pozzolan/slag concretes increased as sodium silicate portion of activator was increased; particularly for slag contents of 50 and 70%. In case of 50% slag dosage, while concretes made with activators having sodium silicate dosage of 20 and 25% gained weight within 4 month of immersion in acid, SILICATE-30% concretes lost 1.1 to 2.7% of their weights. Similar, and to a larger extent, was observed for concretes made with binders having 70% slag. For this slag dosage, the mass loss ranged between 1.2 and 3.4% for alkali-activated natural Pozzolan/slag concretes made with activators having 30% sodium silicate.

The time of mass loss initiation slightly reduced with increases in sodium silicate content. On average, the time that SILICATE-30% concretes started to lose weight were 30 and 28 days earlier than SILICATE-20% and SILICATE-25% concretes, respectively.

The increased mass loss due to the increases in sodium silicate content can be attributed to the increases in Na^+ cations with an increase in sodium silicate portion of activator. While assessing mechanisms of high concentration sulfuric acid attack (pH of about 1) on alkali-activated fly ash/slag paste, Allahverdi and Skavara (2005) showed that the first step of sulfuric acid attack was “the ion exchange reaction between the charge compensating cations of the framework (Na^+ and Ca^{2+}) and H^+ or H_3O^+ ions from the solution along with an electrophilic attack by acid protons on polymeric Si-O-Al bonds resulting in the ejection of tetrahedral aluminum from the aluminosilicate framework, continues until it results in the formation of shrinkage cracks” (Allahverdi and Skavara 2005, 2006). The second step is formation of gypsum through reactions of calcium ions with sulfate ions (SO_4^{2-}) when the shrinkage cracks become wide enough. The first step of reactions could have taken place more when calcium and sodium increased in the mixtures. While use of higher slag increased Ca^{2+} cations and also formation of gypsums, inclusion of higher sodium silicate content increased Na^+ cations of the framework (the used sodium silicate solution had higher sodium than the used sodium hydroxide solution). Accordingly, the process of ion exchange (first step) could have increased due to increases in sodium silicate dosage which, in turn, increased the formation of shrinkage cracks and, thus, the subsequent deterioration expressed in terms of mass loss.

6.3.11.3. Influences of sodium hydroxide concentration

Table 6.13 also documents the effect of sodium hydroxide concentration on the mass loss of alkali-activated natural Pozzolan/slag concretes immersed in sulfuric acid. It can be seen that the mass loss increased as molarity of sodium hydroxide solution was increased. For example, the mass losses of SLAG-70% concretes made with activators having 30% sodium silicate were 1.25, 1.833 and 3.35% for sodium hydroxide concentrations of 1, 1.75 and 2.5M, respectively. For similar molarities, the mass losses were 1.11, 2.07 and 2.65% for SLAG-50% concretes, respectively. Not any special trend was found for the time of mass loss initiation based on NaOH concentration.

The observed increases in mass loss, due to increases in NaOH molarity, can be related to the tendency of bases to react with acids. Increases in molarity of sodium hydroxide increased the alkalinity of concretes' pore solution which, in turn, increased their tendency to react with sulfuric acid. Particularly, the designed test method helped these reactions as pH of acid solution kept below 1 during the testing period by adding fresh acid. While the reactions between sulfuric acid and alkali-activated natural Pozzolan/slag concrete and formation of gypsum increased pH of acid solution, addition of fresh acid refreshed the chemical reactions.

Table 6.13 Ultimate mass change of alkali-activated natural Pozzolan/slag concretes immersed in sulfuric acid (%)

Property	Sodium silicate content (%)	Sodium hydroxide concentration (M)								
		1			1.75			2.5		
		Slag content (%)			Slag content (%)			Slag content (%)		
		30	50	70	30	50	70	30	50	70
Weight loss (%)	20	1.06	1.49	1.08	1.03	0.91	1.10	0.63	0.11	0.62
	25	1.06	0.78	0.29	1.34	0.40	0.89	1.09	0.40	-0.27
	30	0.20	-1.11	-1.26	0.46	-2.07	-1.83	0.22	-2.65	-3.35
Weight loss starting time (days)	20	98	98	70	91	98	70	98	42	63
	25	84	84	49	98	63	91	112	70	63
	30	70	42	42	98	35	35	70	35	35

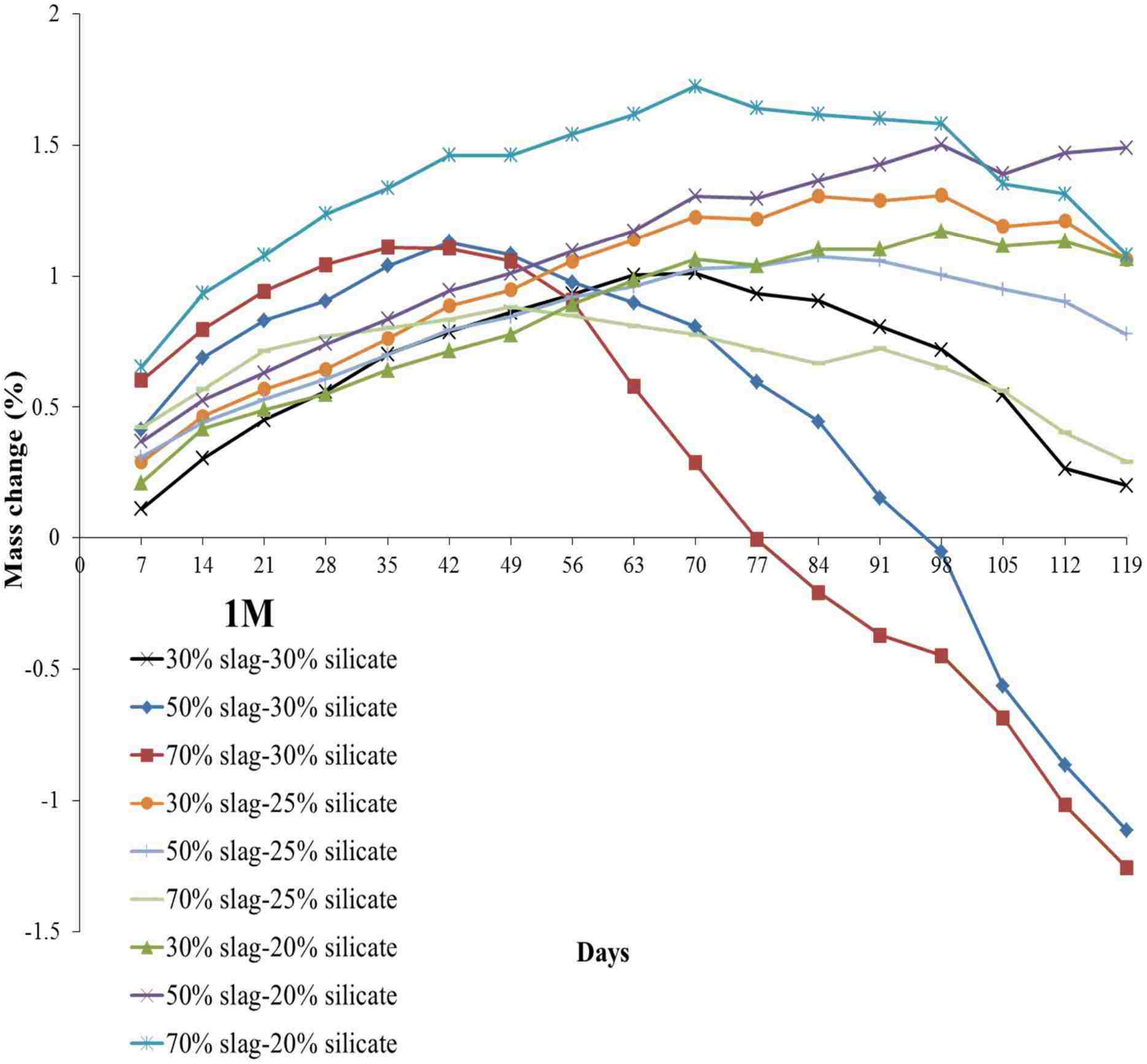


Figure 6.19 Acid-induced mass change of 1M alkali-activated natural Pozzolan/slag concretes

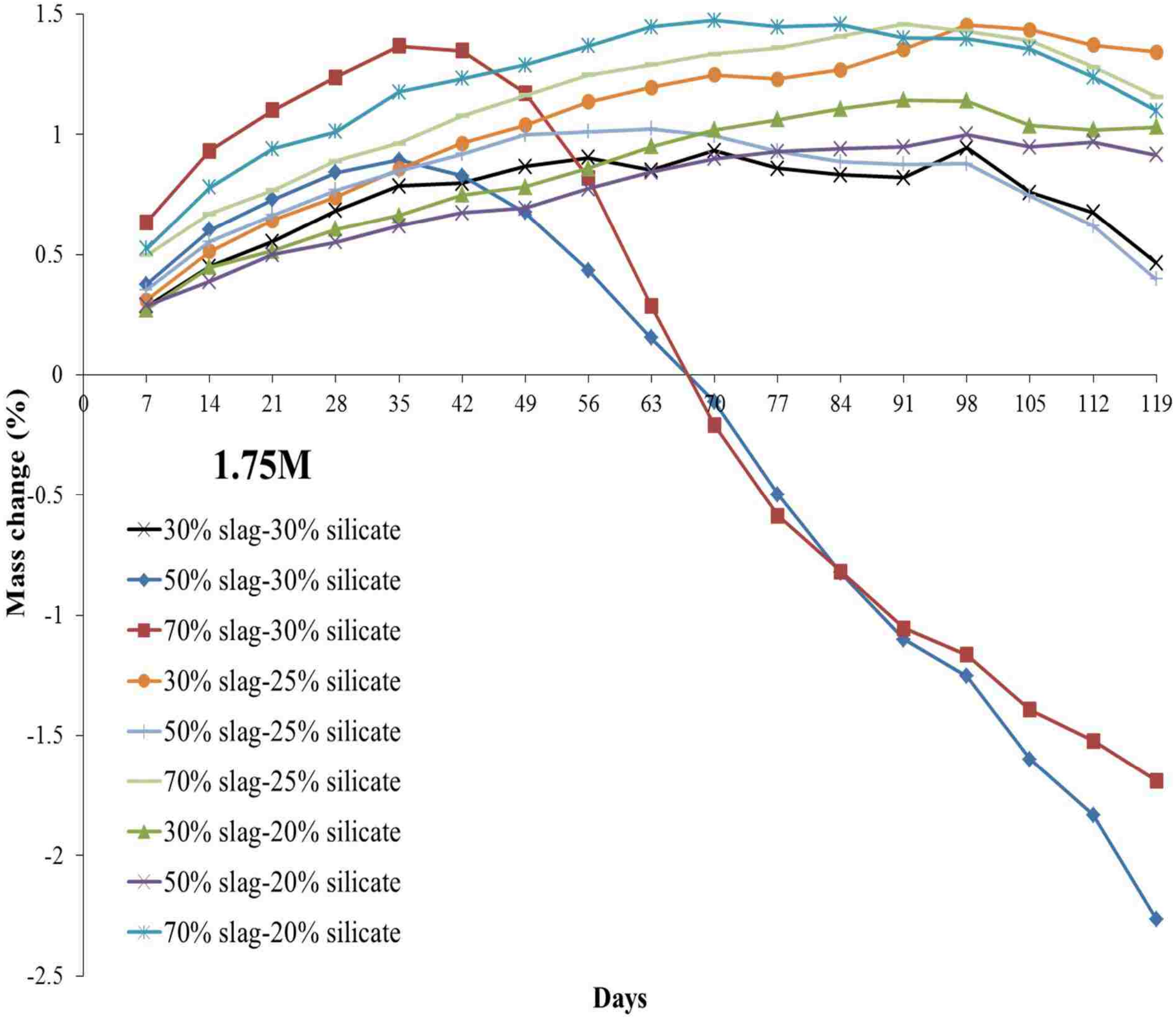


Figure 6.20 Acid-induced mass change of 1.75M alkali-activated natural Pozzolan/slag concretes

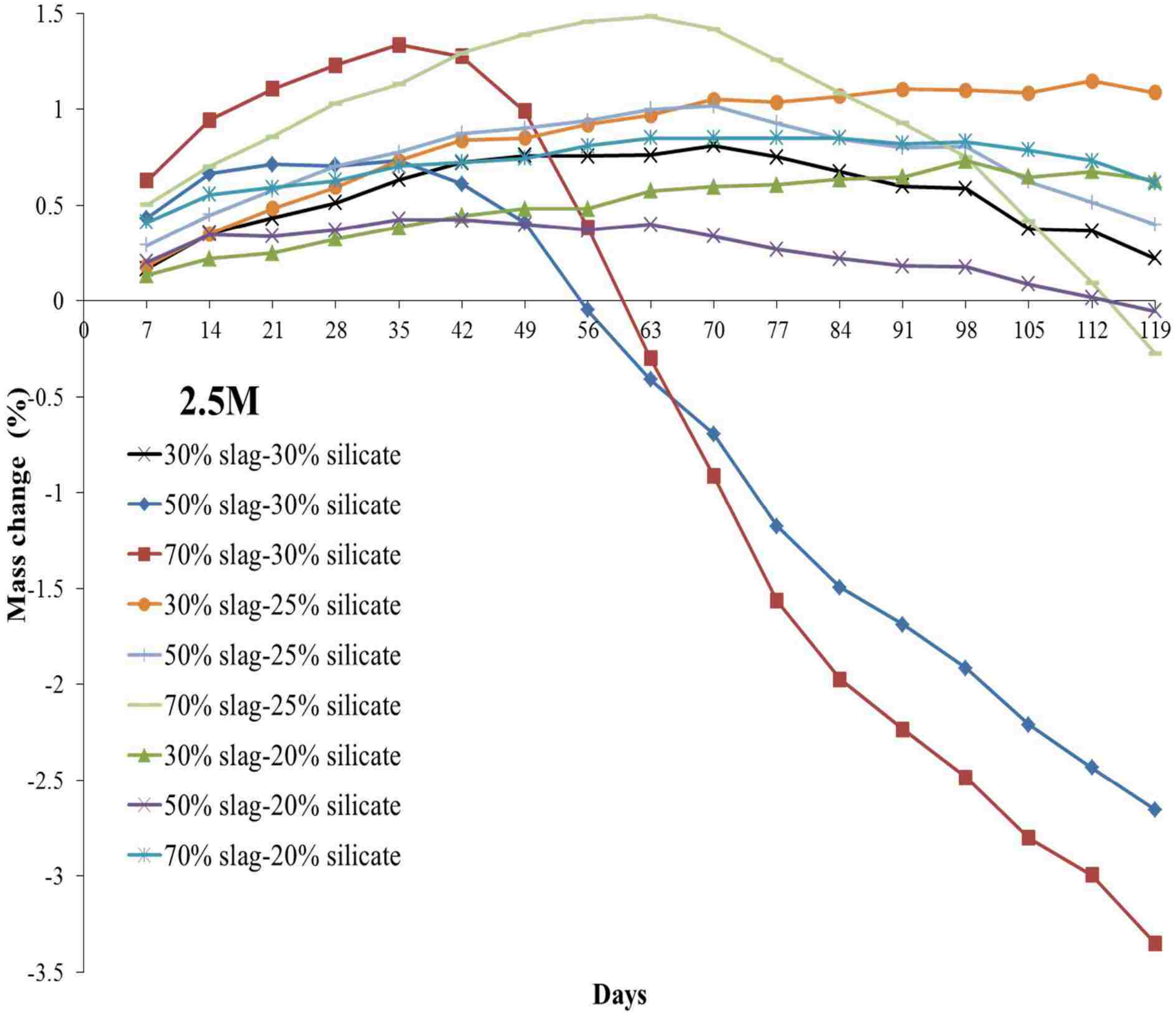


Figure 6.21 Acid-induced mass change of 2.5M alkali-activated natural Pozzolan/slag concretes

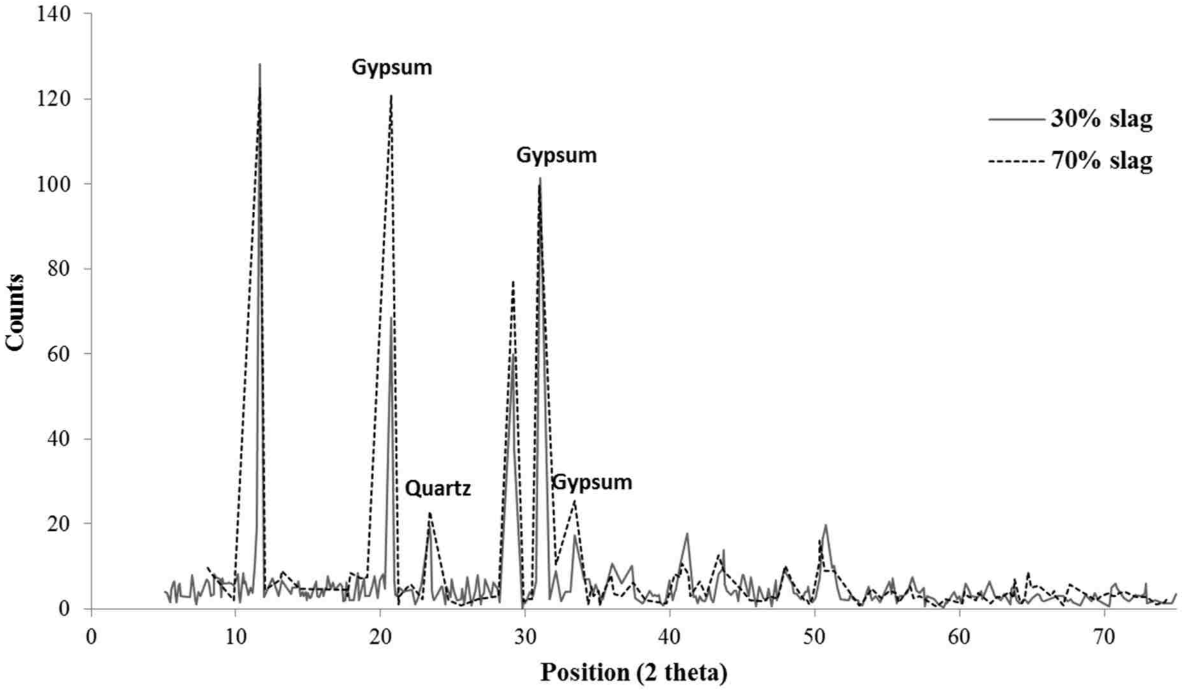


Figure 6.22 Formation of gypsum on surface of acid-induced samples (XRD of Mixture 1M-SL30-SS30 and 1M-SL70-SS30)

6.3.12. Corrosion resistance

The corrosion resistance of alkali-activated natural Pozzolan/slag concretes was measured according to an accelerated experiment described in Chapter 3. Failure time of concrete due to reinforcement corrosion is reported in Table 6.14 for the studied alkali-activated natural Pozzolan/slag concretes. It can be seen that the failure time increased with increases in natural Pozzolan content, sodium silicate dosage and sodium hydroxide concentration.

As slag portion of binder was increased, the studied alkali-activated natural Pozzolan/slag concretes failed faster. When slag content was increased from 30 to 70%, the time to failure reduced by averagely 93.6, 86.8 and 62.3% for sodium silicate contents of 20, 25 and 30%, respectively. For similar sodium silicate contents, the corrosion resistances of SLAG-30% concretes were averagely 54.4, 46.3 and 40.3% superior to those of SLAG-50% concretes, respectively. These observations were opposite to the trend found in rapid chloride migration and penetration tests which showed reduction in chloride permeability by increasing slag content. As discussed earlier, it can be inferred from the results of compressive strength and rapid chloride penetration tests that more hydroxyl ions (OH^-) remained free in concretes made with binders having lower slag content (higher natural Pozzolan dosage; i.e. binders which contained 70% natural Pozzolan and 30% slag). These ions could have passivated reinforcement effectively, thus reducing the corrosion rate and increasing the failure time. Indeed, the test method using voltage might have migrated a great deal of hydroxyl ions towards reinforcement and made it corrosion-resistant. For the same reason, although concretes made with binders having high slag content (such as 70%) showed considerably low chloride penetration depth, they didn’t sufficiently passivate reinforcement to avoid corrosion. The observed behavior can also be due to the increased chloride binding capacity of concretes through increases in natural Pozzolan content. Ismail et al. (2013a) concluded that for alkali-activated fly ash/slag concrete, the chloride binding capacity increased as fly ash portion of the binder was increased which, in turn, reduced the free chloride ions that are responsible for reinforcement corrosion. Due to similarity between the chemical composition of fly ash and natural Pozzolan, the above explanation is also valid for the studied alkali-activated natural Pozzolan/slag concretes.

The corrosion resistance improved as sodium silicate content was increased. On average, the time to failure of concretes made with binders having 30, 50 and 70% slag increased by 45.5, 61.6 and 196.4%, when sodium silicate portion of activator was increased from 20 to 25%, respectively. For similar slag dosages, further increases of sodium silicate content from 25 to

30% led to 8.1, 81.8 and 241.5% further improvements in corrosion resistance of alkali-activated natural Pozzolan/slag concretes, respectively. This can also be related to the higher alkaline content of sodium silicate solution than sodium hydroxide solution which was seen in rapid chloride penetration test as well. It can also be related to the enhanced paste microstructure and improved binding ability of C-S-H gel by reduction of Ca/Si ratio through inclusion of higher amounts of sodium silicate.

Use of higher sodium hydroxide concentration also improved the corrosion resistance. On average, the time to failure of 2.5M concretes were 1.9, 5.1 and 2.8 times of 1M concretes for binders made with slag contents of 30, 50 and 70%, respectively. Similarly, this observation can be related to the improved passivation of reinforcement in the presence of higher alkaline concentration.

Table 6.14 Time to failure of alkali-activated natural Pozzolan/slag concretes in corrosion test

Sodium silicate content (%)	Sodium hydroxide concentration (M)								
	1			1.75			2.5		
	Slag content (%)			Slag content (%)			Slag content (%)		
	30	50	70	30	50	70	30	50	70
20	120	27	7	--	--	--	201	138	14
25	167	36	16	--	--	--	305	262	51
30	169	93	55	284	129	89	351	276	173

-- Not available

6.3.13. Frost resistance

The frost resistance of a group of alkali-activated natural Pozzolan/slag concretes (1.75M mixtures) was assessed using an accelerated test method described in Chapter 3. The mass loss of alkali-activated natural Pozzolan/slag concretes, measured for a period of 56 freezing and thawing cycles, is reported in Figure 6.23. It can be seen that while SLAG-30% concretes lost significant mass during freezing and thawing cycles, the deterioration (mass loss) considerably reduced with increases in slag content of the binder to 50 and 70%. The ultimate mass loss of SLAG-50% and SLAG-70% concretes were lower than SLAG-30% concretes by 51.4 and 55.8% for sodium silicate content of 20%; 80.8 and 78.8% for sodium silicate dosage of 25%; and 92.6 and 95.3% for sodium silicate content of 30%, respectively. This observation can be related to the effect of binder combination on pore size distribution presented in Figure 6.17 and Table 6.13. The total mesopores and macropores of SLAG-30% concretes (having 30% sodium silicate) were about 1.4 times of those of SLAG-50% and SLAG-70% concretes (with similar sodium silicate content). It can also be seen that with increases in slag content of concrete binder, the pores were distributed more evenly. The gel pores, which are not involved in freezing and thawing deteriorations, also increased by inclusion of higher slag in the mixture.

For SLAG-50% and SLAG-70% mixtures, the mass loss of the studied alkali-activated natural Pozzolan/slag concretes reduced as sodium silicate content was increased. An opposite trend was observed for SLAG-30% concretes. In case of concretes made with binders having 30% slag, the mass loss increased by 34.7 and 50.3% when sodium silicate content was increased from 20 to 25 and 25 to 30%, respectively. Similar increases in sodium silicate dosage reduced mass loss by 46.9 and 41.7% for SLAG-50% concretes; and 35.5 and 66.9% in case of SLAG-

70% concretes, respectively. These observations correlate well with the results of absorption test (volume of permeable voids) which is shown in Figure 6.24. It can be deduced that for these mixtures, there was a relationship between mass loss and voids volume. The mass loss of samples exposed to freezing and thawing cycles reduced as volume of permeable voids decreased. Therefore, the increases in mass loss of SLAG-30% concretes by increasing sodium silicate content can be related to the increases in their voids volume. The opposite trends which were observed for SLAG-50% and SLAG-70% concretes can be attributed to the reduction of their voids volumes.

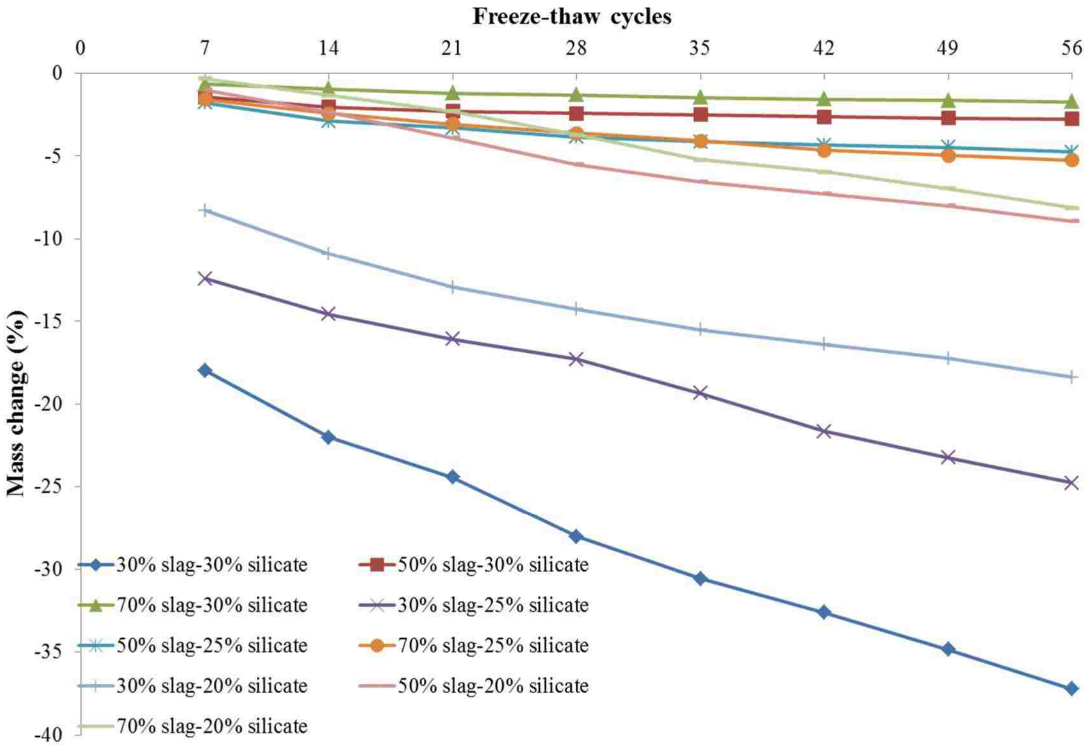


Figure 6.23 Mass change of alkali-activated natural Pozzolan/slag concretes subjected to freezing and thawing cycles

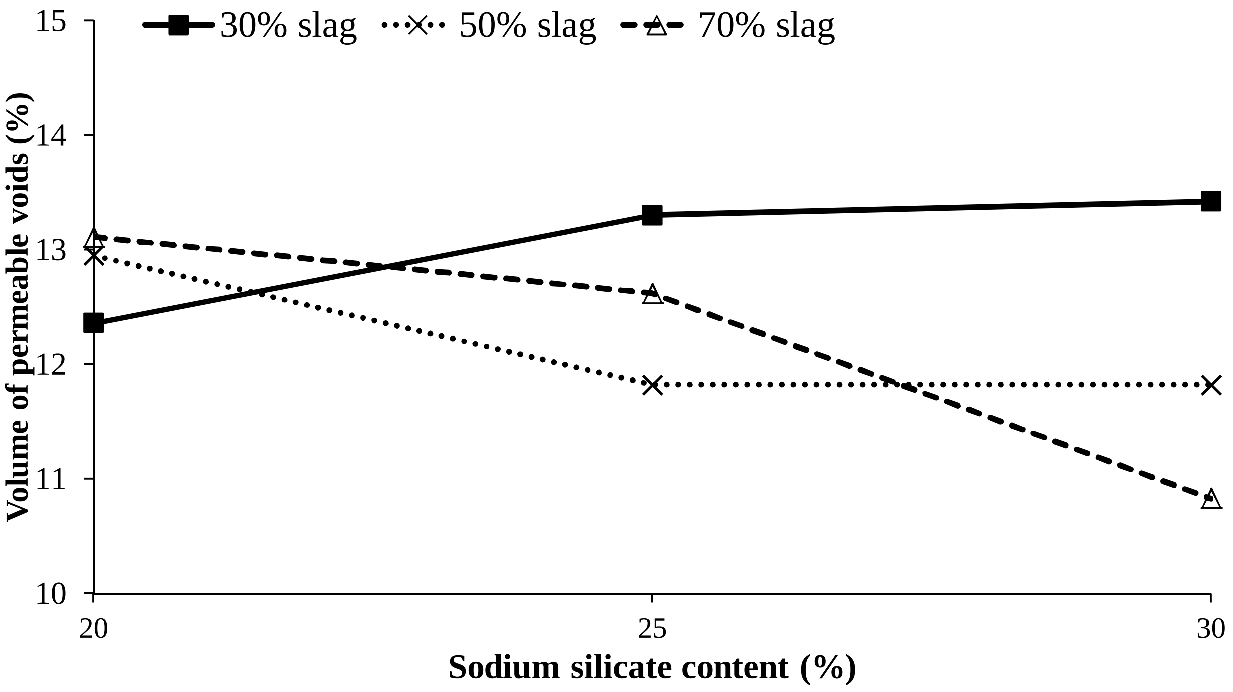


Figure 6.24 Effect of sodium silicate content on volume of permeable voids of 1.75M natural Pozzolan/slag concretes

6.4. Comparison with Portland cement concrete

A reference Portland cement (PC) concrete with a water-to-cement ratio of 0.54 was made to compare its results with those of studied alkali-activated natural Pozzolan/slag concretes. Its mixture proportion is reported in Table 6.15 as per cubic meter and per batch size. Table 6.16 documents the fresh properties of reference Portland cement concrete. The flow of reference PC concrete was 26.25 cm, thus it was compacted and casted easily. No sign of bleeding was observed. Its initial and final setting times were 240 and 360 minutes (4 and 6 hr), respectively. It can be seen that compared to the reference Portland cement concrete, alkali-activated natural Pozzolan/slag concretes had a wider range of setting times which were dependent on combinations of binders and activators used. The initial and final setting times of alkali-activated natural Pozzolan/slag concretes were in the ranges of 95 to 705 min, and 130 to 1050 min, respectively. The average setting times of alkali-activated natural Pozzolan/slag concretes, however, was nearly similar to those of the reference Portland cement concrete.

Table 6.15 Mixture proportions of reference Portland cement concrete

	Mixture Id.	Portland cement, Kg	Water, Kg	Coarse aggregate, Kg	Fine aggregate, Kg
Per cubic meter	Reference	422.2	228.0	877.7	810.9
Per batch size		7.8937	4.2626	16.4084	15.1607

Table 6.16 Fresh properties of reference Portland cement concrete

Mix id.		Slump flow, cm	Initial set, min	Final set, min
Reference Portland cement concrete		**26.25**	**240**	**360**
Alkali-activated concretes	Minimum	3.8	95	130
	Average	**18.9**	**238**	**345**
	Maximum	26.0	705	1050

Table 6.17 reports unit weights of reference Portland cement concrete along with the unit weight ranges for the studied alkali-activated natural Pozzolan/slag concretes. Overall, the unit weight of PC and alkali-activated natural Pozzolan/slag concretes (average value) were nearly similar.

Table 6.17 Unit weight of reference Portland cement concrete (Kg/m^3)

Mix id.		Fresh	Demolded	Oven-dry
Reference Portland cement concrete		**2411.6**	**2397.7**	**2292.8**
Alkali-activated concretes	Minimum	2377.6	2370.1	2246.9
	Average	**2405.9**	**2402.5**	**2293.2**
	Maximum	2436.6	2433.6	2336.3

The strength properties of reference Portland cement concrete is shown in Table 6.18. The reference PC concrete developed 28-day compressive strength of 41.8 MPa which was almost the same as its designed 28-day compressive strength (41.4 MPa or 6000 psi). Figure 6.25 shows a comparison between 28-day compressive strength of reference Portland cement and alkali-activated natural Pozzolan/slag concretes. The 28-day compressive strengths of alkali-activated natural Pozzolan/slag concretes were in the range of 18 and 48 MPa. While the compressive strengths of SILICATE-20% and SILICATE-25% alkali-activated natural Pozzolan/slag concretes were lower than those of reference PC concrete, SILICATE-30% alkali-activated natural Pozzolan/slag concretes (made with activators having 30% sodium silicate) developed nearly similar compressive strength to those of the reference PC concrete.

Similar trends were seen for the tensile strength and modulus of elasticity as shown in Figures 6.26 and 6.27, respectively. The average tensile strength and elastic modulus of SILICATE-30% alkali-activated natural Pozzolan/slag concretes were 4.5 MPa and 37.7 GPa, which were almost similar to 4.7 MPa and 36.2 GPa found for the reference PC concrete, respectively.

Table 6.18 The strength properties of reference Portland cement concrete

Mix id.	Compressive strength (MPa)					Tensile strength (MPa)	Modulus of elasticity (GPa)
	1 day	3 days	7 days	28 days	90 days		
Reference	15.9	23.4	31.1	41.8	53.6	4.7	36.2

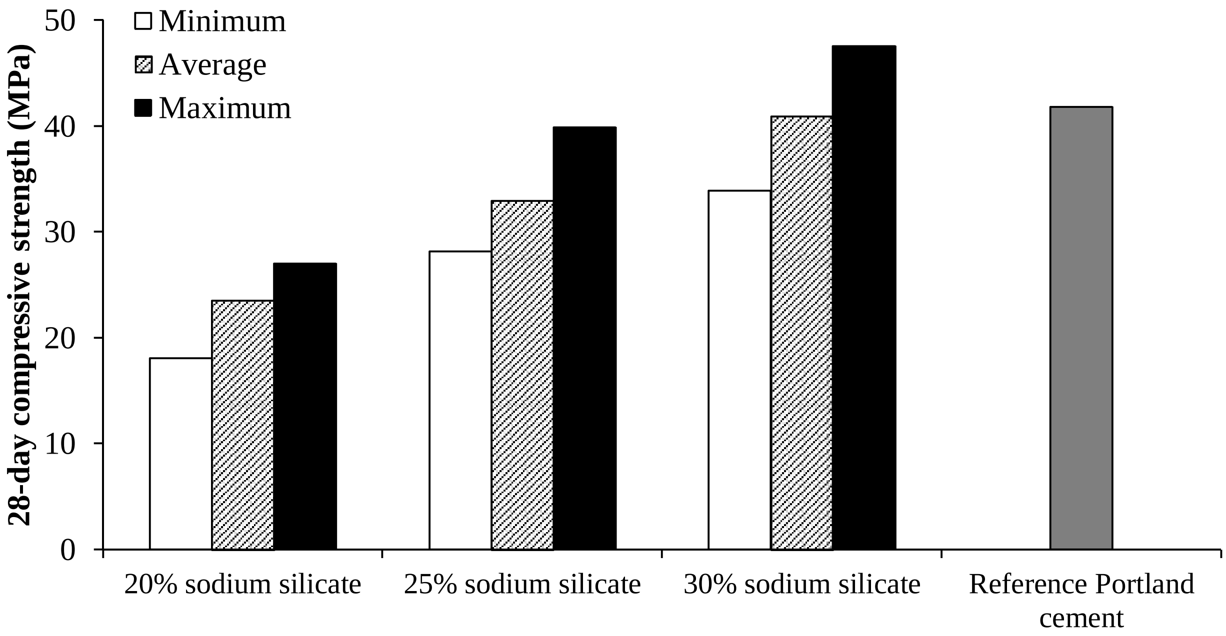


Figure 6.25 The 28-day compressive strength of reference Portland cement and alkali-activated natural Pozzolan/slag concretes

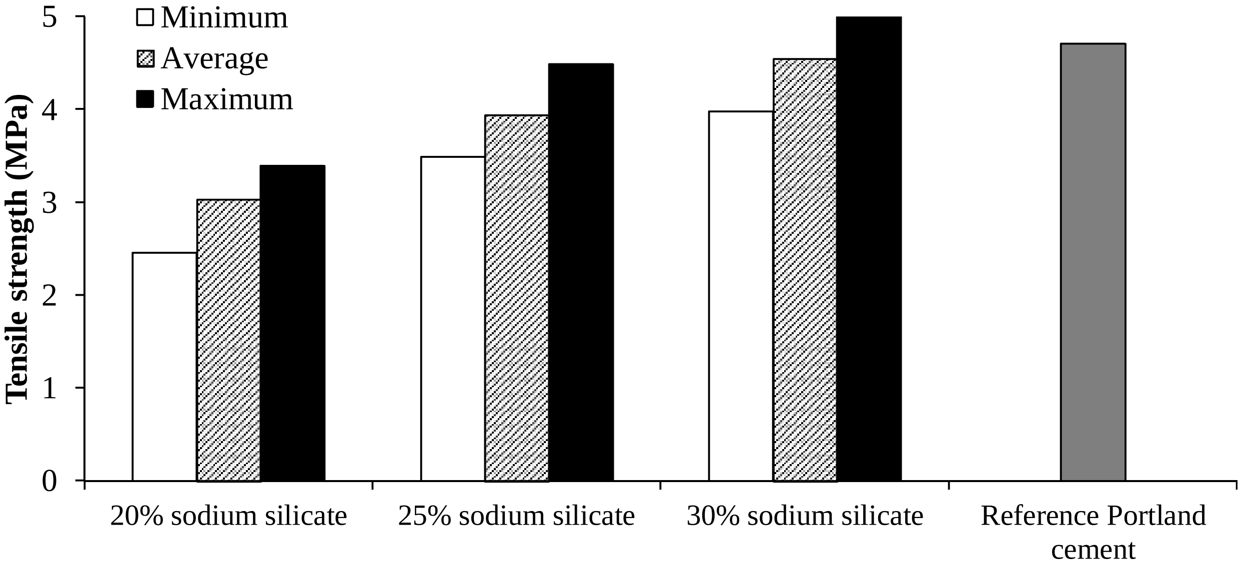


Figure 6.26 The tensile strength of reference Portland cement and alkali-activated natural Pozzolan/slag concretes

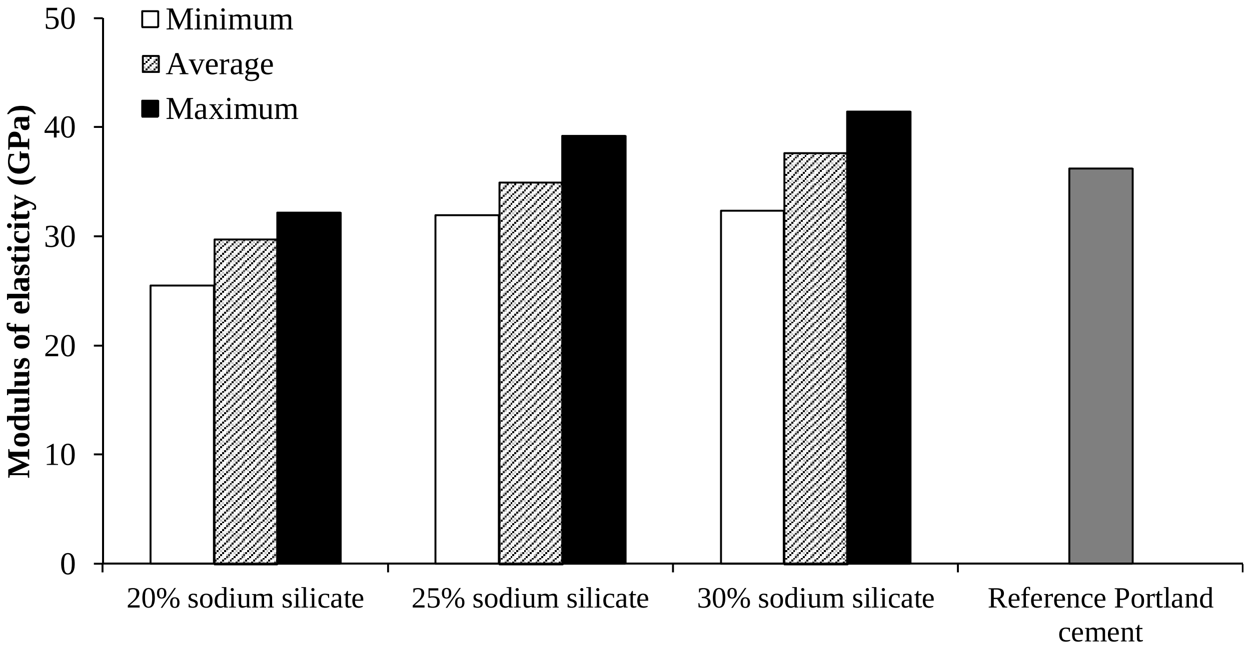


Figure 6.27 The elastic modulus of reference Portland cement and alkali-activated natural Pozzolan/slag concretes

Transport properties of reference PC concrete, i.e. absorption, volume of permeable voids, RCPT passing charges and chloride penetration depth, are reported in Table 6.19. Figure 6.28 compares results of absorption test for reference Portland cement and alkali-activated natural Pozzolan/slag concretes. It can be seen that the total pore volume of reference PC concrete was nearly similar to that of the worst performed alkali-activated natural Pozzolan/slag concrete (Mixture 1M-SL70-SS20). The average volume of permeable voids of alkali-activated natural Pozzolan/slag concretes was 13.2% lower than that of the reference PC concrete.

Figures 6.29 and 6.30 compare passing charges and chloride penetration depths of alkali-activated natural Pozzolan/slag concretes with those of the reference PC concrete, respectively. It can be seen that chloride penetrations of alkali-activated natural Pozzolan/slag concretes were significantly lower than those of the reference PC concrete. The average passing charges and chloride penetration depth of alkali-activated natural Pozzolan/slag concretes were 80.6 and 81.7% lower than those of the reference PC concrete, respectively. Even the worst performed alkali-activated natural Pozzolan/slag concrete (Mixture 2.5M-SL30-SS30 with the highest chloride permeability) was still considerably less chloride permeable than the reference PC concrete. This concrete had 24.5 and 47.9% lower passing charges and chloride penetration depth than the reference PC concrete, respectively.

Table 6.19 Transport properties of reference Portland cement concrete

Mix id.	Absorption (%)			RCPT (coulombs)	RMT (mm)
	Absorption after immersion	Absorption after immersion and boiling	Volume of permeable voids		
Reference	5.92	6.23	14.28	5448	38.7

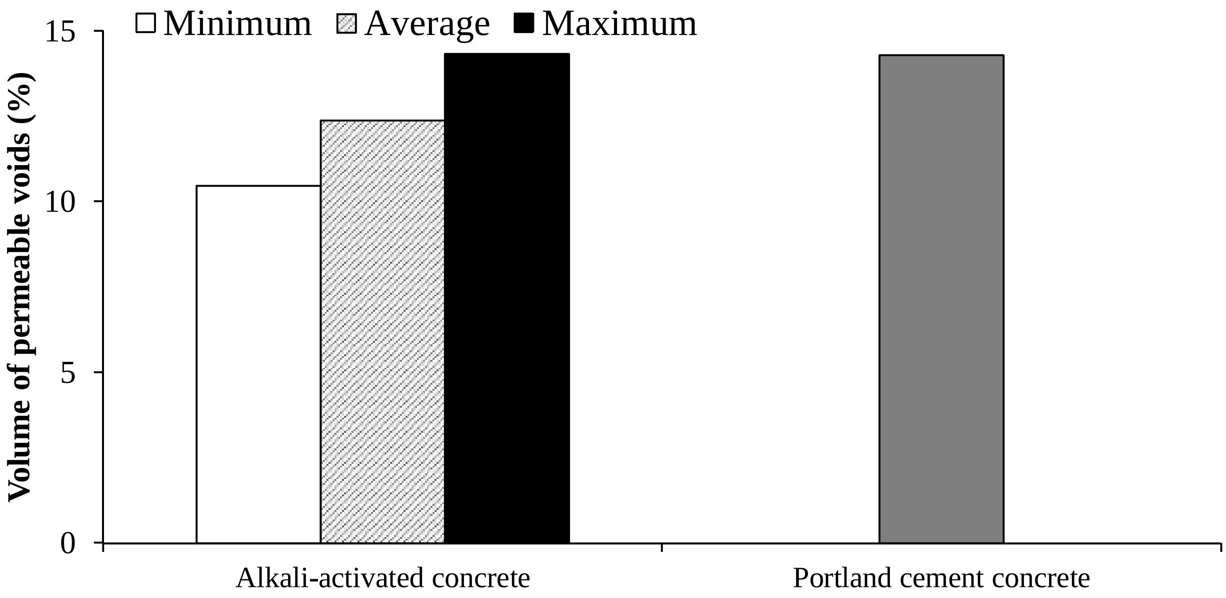


Figure 6.28 The volume of permeable voids of reference Portland cement and alkali-activated natural Pozzolan/slag concretes

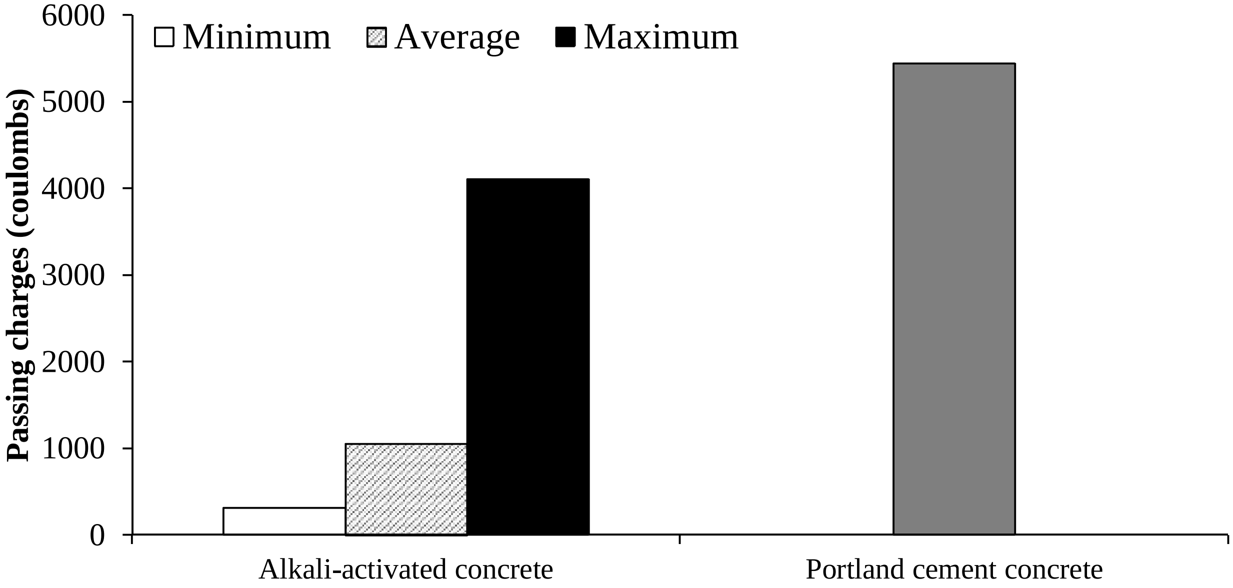


Figure 6.29 The passing charges of reference Portland cement and alkali-activated natural Pozzolan/slag concretes

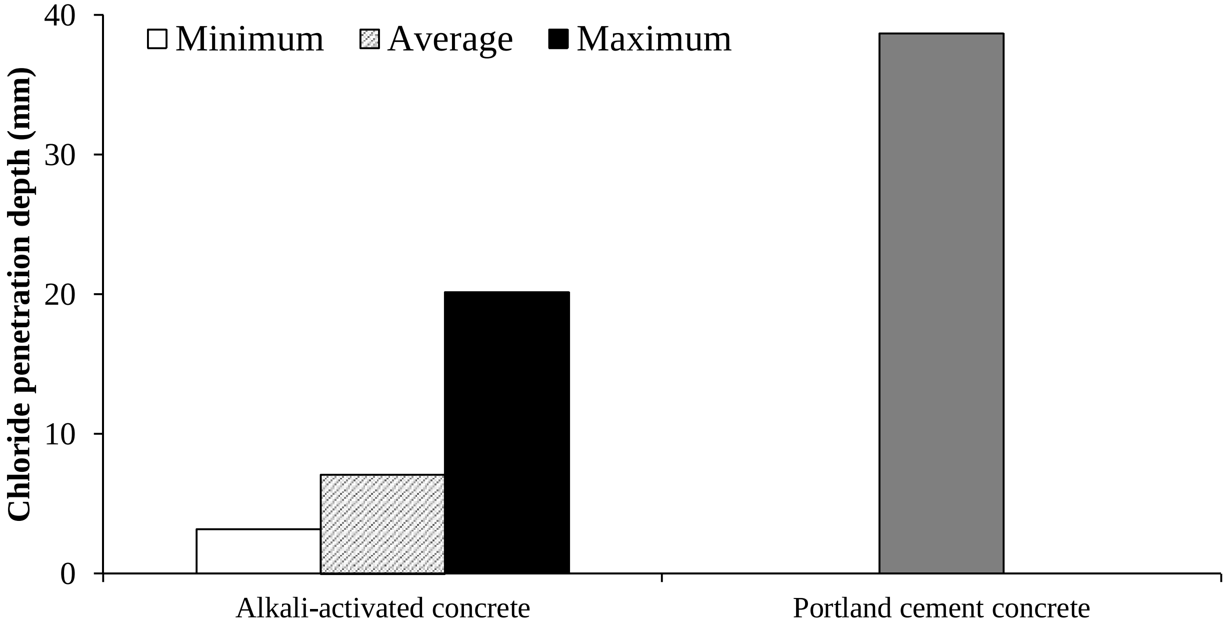


Figure 6.30 The chloride penetration depth of reference Portland cement and alkali-activated natural Pozzolan/slag concretes

The drying shrinkage of reference Portland cement concrete is presented in Figure 6.31. Figure 6.32 compares the ultimate drying shrinkage of reference PC and alkali-activated natural Pozzolan/slag concretes. It can be seen that the average ultimate drying shrinkage of alkali-activated natural Pozzolan/slag concretes was lower than that of the reference PC concrete by almost 26%. Indeed, while the ultimate drying shrinkage of the worst performed alkali-activated natural Pozzolan/slag concrete (Mixture 1M-SL30-SS30 with the highest drying shrinkage) was only 25% more than that of the reference PC concrete, there were several mixtures that shrank considerably less than the reference PC concrete.

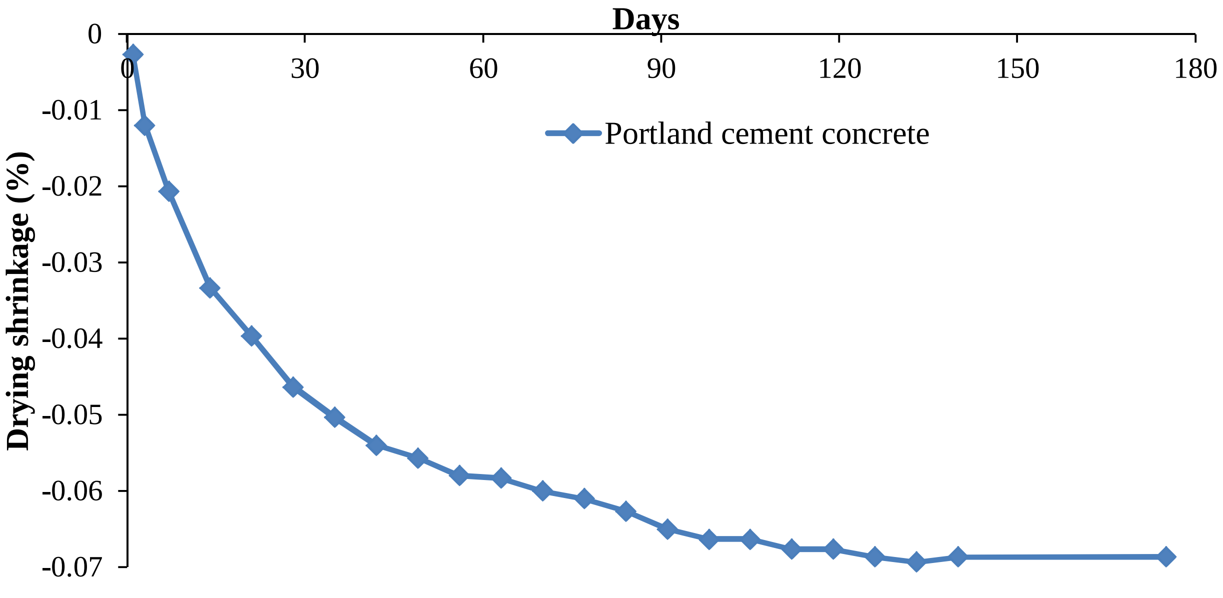


Figure 6.31 The drying shrinkage of reference Portland cement concretes

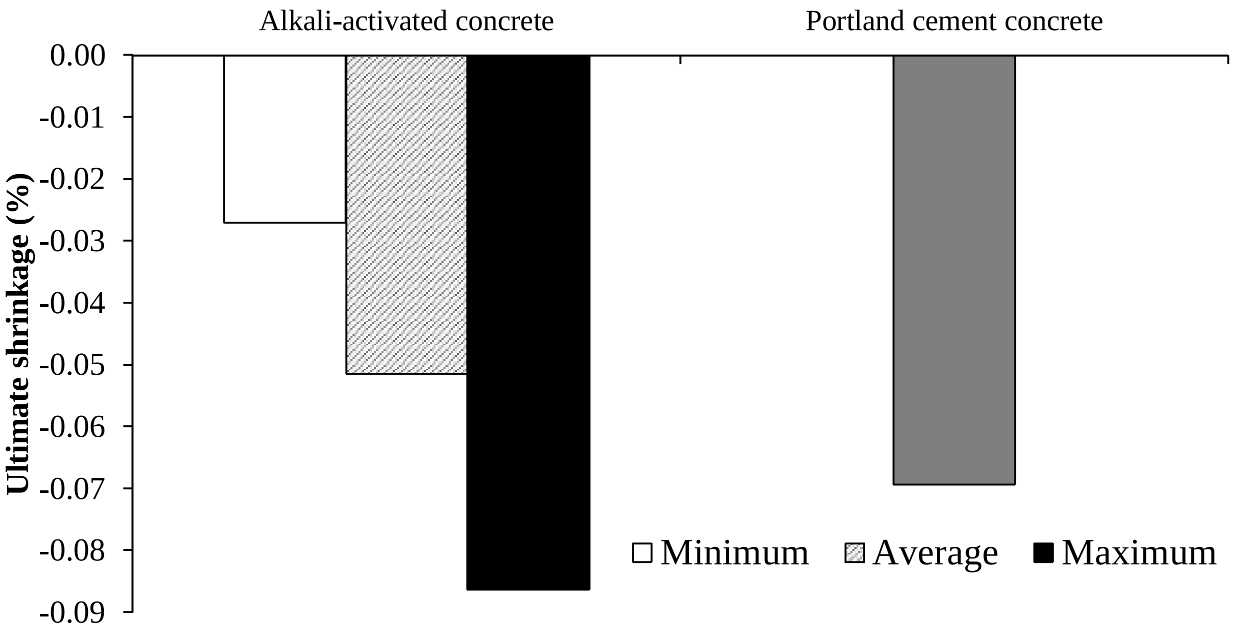


Figure 6.32 The ultimate drying shrinkage of reference Portland cement and alkali-activated natural Pozzolan/slag concretes

Table 6.20 and Figure 6.33 show the mass loss of reference PC concrete when immersed in sulfuric acid. Unlike the studied alkali-activated natural Pozzolan/slag concretes, the reference PC concrete lost its mass since the first days of immersion in acid. Figure 6.34 compares the ultimate mass loss of reference PC concrete with the worst performed alkali-activated natural Pozzolan/slag concrete (Mixture 2.5M-SL70-SS30). It can be seen that the mass loss of reference PC concrete was almost 3 times of that of the worst performed alkali-activated natural Pozzolan/slag concrete. This observation can be related to high calcium oxide content of Portland cement. Calcium hydroxide (Portlandite), as a major reaction product of Portland cement, reacts easily with sulfuric acid and produce calcium sulfate (gypsum), which easily detached from the sample surface.

Table 6.20 Mass loss (in acid) and failure time (in corrosion test) of the reference PC concrete

Mix id.	Ultimate mass loss in acid attack test (%)	Time to failure in corrosion test (days)
Reference	9.254	4

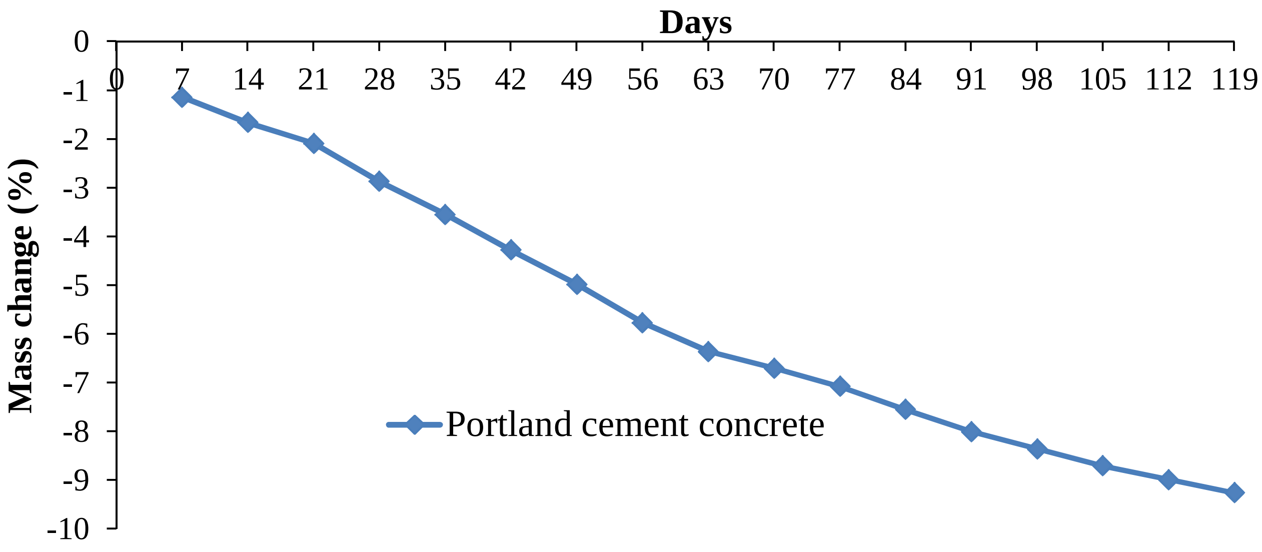


Figure 6.33 The mass loss of reference Portland cement concrete immersed in sulfuric acid

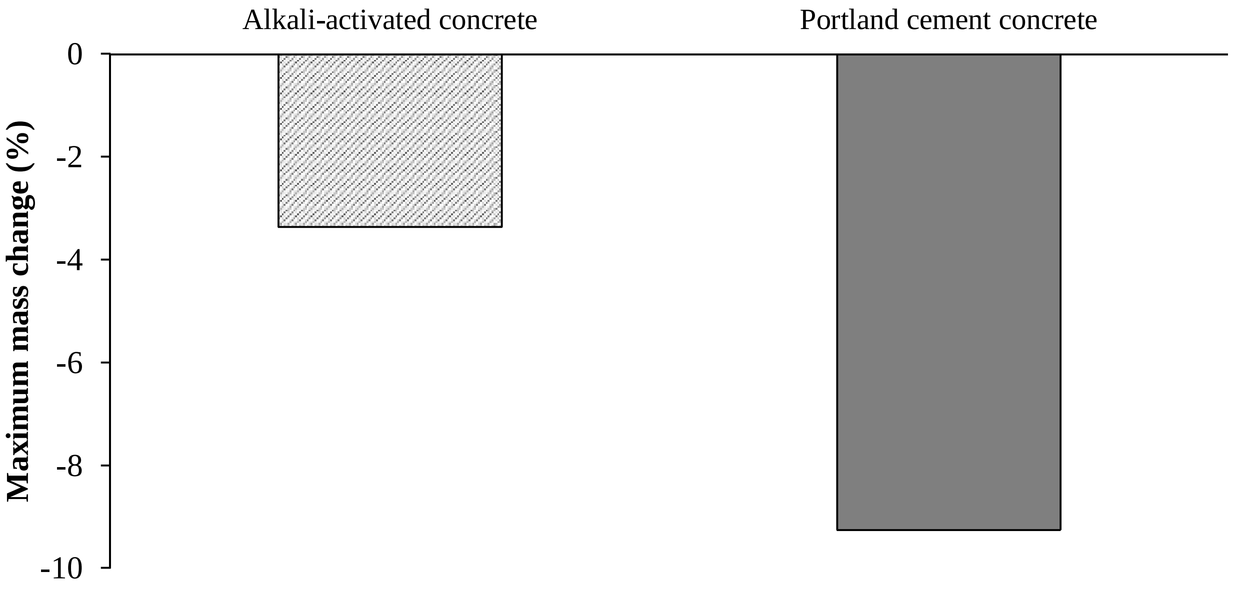


Figure 6.34 The ultimate mass loss of reference Portland cement and the worst performed alkali-activated natural Pozzolan/slag concretes subjected to acid attack

Table 6.20 also reports the failure time of reference PC concrete in corrosion test. It can be seen that it took only 4 days for the reinforcement protected by reference PC concrete to corrode. Figure 6.35 compares failure time of reference PC and alkali-activated natural Pozzolan/slag concretes. The corrosion resistance of alkali-activated natural Pozzolan/slag concretes was significantly higher than that of reference PC concrete. Their resistances against corrosion were about 2 to 90 times of that of the reference PC concrete. The high passivation of reinforcement due to availability of hydroxyl ions in the studied alkali-activated natural Pozzolan/slag concretes could be the reason for this observation.

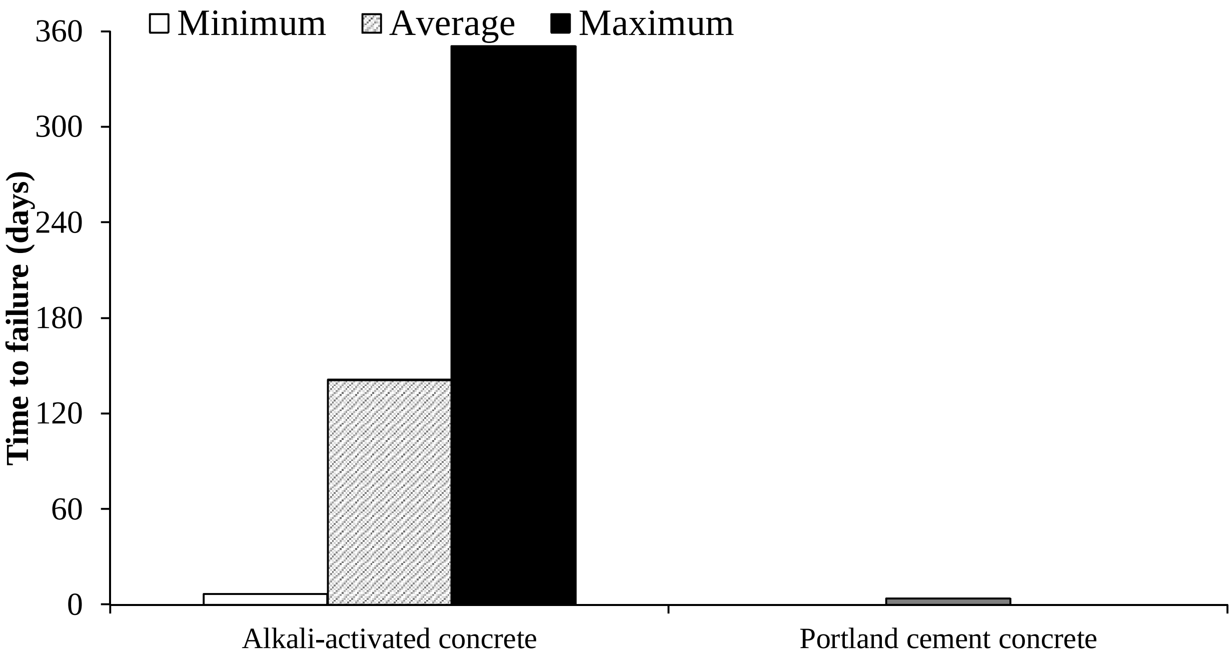


Figure 6.35 Time to failure of reference Portland cement and alkali-activated natural Pozzolan/slag concretes in corrosion test

Figure 6.36 compares the ultimate mass loss of reference PC and alkali-activated natural Pozzolan/slag concretes subjected to 56 freezing and thawing cycles. It can be seen that the average mass loss of alkali-activated natural Pozzolan/slag concretes was lower than the mass loss of reference Portland cement concrete by about 25%. Indeed, the mass losses of 50 and 70% slag contained concretes subjected to freezing and thawing cycles were significantly lower than that of the reference PC concrete. On the other hand, the frost resistance of 30% slag contained concretes was similar to or less than that of the reference PC concrete.

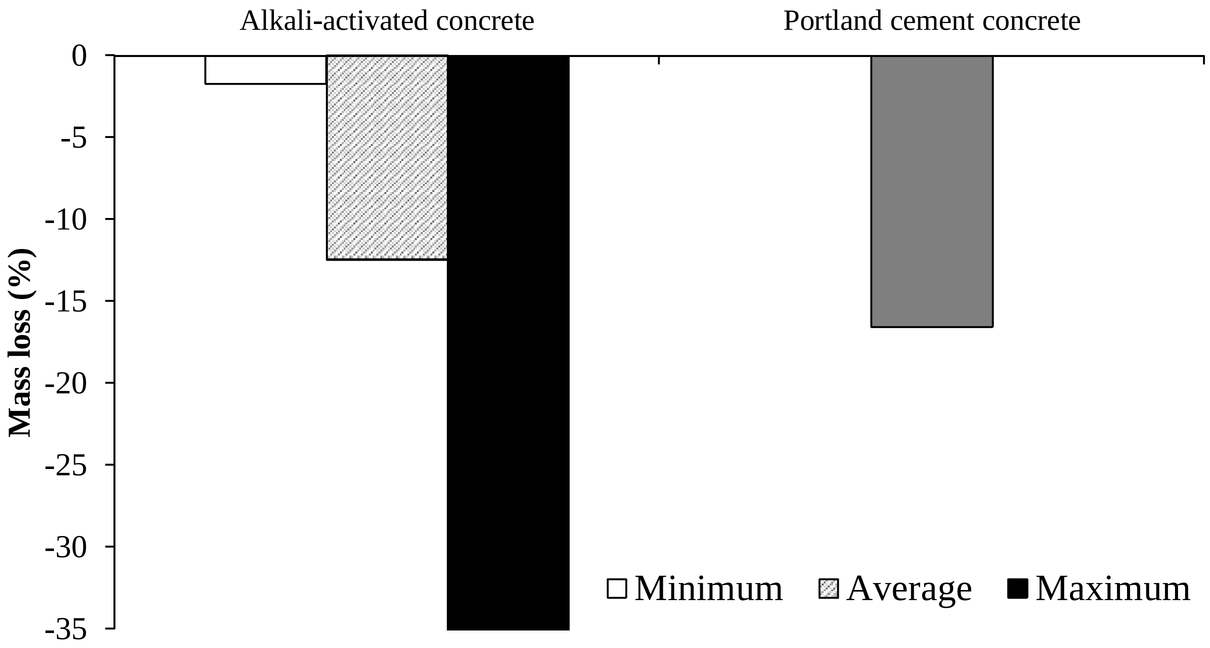


Figure 6.36 The ultimate mass loss of reference Portland cement and alkali-activated natural Pozzolan/slag concretes subjected to 56 freezing and thawing cycles

CHAPTER 7- CONCLUSTIONS AND RECOMMENDATIONS

7.1. Introduction

With an intent to improve longevity of concrete, this study focused on the full replacement of Portland cement (PC) with environmentally friendly binders. It was hypothesized that this goal can be achieved through proper combinations of natural Pozzolan and slag as binders, and sodium silicate and sodium hydroxide as alkaline activators. As it was well-understood that replacement of Portland cement is only possible through a step-by-step process beginning with the development of proper pastes having adequate fresh and strength properties, production of strong and durable mortars, and finally development of high-performance concretes; the following steps were designed to achieve the objectives of this study:

- *Development of alkali-activated natural Pozzolan/slag pastes with adequate flow, proper setting time, and adequate compressive strength.*
- *Production and assessment of alkali-activated natural Pozzolan/slag mortars.*
- *Development of alkali-activated natural Pozzolan/slag concretes and evaluation of their fresh, mechanical and durability properties.*

The conclusions drawn from the results of these steps, which were conducted chronologically towards development of Portland cement free concretes, are presented below.

7.2. Chapter 4: Alkali-activated natural Pozzolan/slag pastes

First phase of this study was devoted to the development of alkali-activated natural Pozzolan/slag pastes with satisfactory fresh and hardened properties. The goal was to produce pastes that can provide similar fresh properties, particularly setting time, to those of Portland cement pastes, as well as adequate strength. Different strategies; including reduction of NaOH concentration and use of different set-retarding admixtures; were considered to achieve this objective. The most suitable alkali-activated natural Pozzolan/slag pastes were also tested for compressive strength, drying shrinkage, hydration heat, and absorption. From the results of this chapter, the following conclusions can be drawn:

1. Commercial admixtures, developed for Portland cement, were found ineffective to delay (retard) the setting times of alkali-activated natural Pozzolan/slag binders.
2. The setting times of alkali-activated natural Pozzolan/slag pastes were delayed by use of malic acid. Its inclusion, however, resulted in a drastic reduction in compressive strength.
3. It was found impossible to use sodium phosphate and phosphoric acid to retard the setting times of pastes activated using sodium hydroxide and sodium silicate.
4. Although lignosulfonate-based admixture delayed the setting time of alkali-activated pastes, it couldn’t delay the setting process to a reasonable time. In addition, its inclusion drastically reduced flowability and strength.
5. Sodium gluconate wasn’t useful for retarding setting times of alkali-activated pastes. Its inclusion, however, improved their flowability and compressive strength.
6. Use of gypsum not only didn’t improve setting time, but also reduced flow, setting time and strength.
7. Reduction of sodium hydroxide concentration was found the best strategy for delaying the setting times of natural Pozzolan/slag pastes activated with sodium hydroxide and sodium silicate. Not only this strategy effectively delayed setting times, it also improved flowability and maintained the expected compressive strength of studied pastes.

8. sodium hydroxide concentrations of 0.5, 1 and 2M were selected for the next phase of investigation (alkali-activated natural Pozzolan/slag mortars) as these molarities satisfied the target requirements
9. The workability of the studied alkali-activated pastes improved with reductions in natural Pozzolan content, sodium hydroxide molarity and sodium silicate content.
10. The setting times reduced with increases in slag content and sodium hydroxide concentration. Increasing sodium silicate content from 20 to 30% increased the setting times of alkali-activated natural Pozzolan/slag pastes. Further increases (from 30 to 40%), however, reduced the setting times.
11. The hydration heat of alkali-activated pastes increased by inclusion of higher slag and use of more concentrated sodium hydroxide. However, they reduced the time to reach the peak temperature.
12. Regarding the results of compressive strength, there was an optimum combination of natural Pozzolan and slag which depended on sodium hydroxide concentration. The optimum slag content of binder increased with increases in sodium hydroxide molarity.
13. The compressive strength of alkali-activated natural Pozzolan/slag pastes slightly improved with increases in sodium hydroxide concentration and considerably increased with an increase in sodium silicate content.
14. The drying shrinkage of alkali-activated natural Pozzolan/slag pastes reduced and time to reach ultimate shrinkage increased with increases in slag content of the binder. There was insignificant difference in the drying shrinkage of pastes having different sodium hydroxide molarities.

15. In comparison with the reference mixture, the flow and setting times of the selected alkali-activated natural Pozzolan/slag pastes were similar to those of the reference Portland cement paste. On the other hand, the hydration heat and maximum temperatures of alkali-activate natural Pozzolan/slag pastes were significantly lower than those of reference Portland cement paste.
16. The compressive strength of reference Portland cement paste was higher than that of alkali-activated natural Pozzolan/slag paste due to its low water-to-cement ratio. The absorptions of alkali-activated pastes were slightly higher than that of the reference Portland cement paste.
17. Alkali-activated natural Pozzolan/slag pastes shrank considerably more than reference Portland cement paste.

7.3. Chapter 5: Alkali-activated natural Pozzolan/slag mortars

In this chapter, the influence of sodium hydroxide molarity (0.5, 1 and 2M), binder combination (natural Pozzolan/slag combinations of 70/30, 50/50 and 30/70), activator combination (sodium silicate/sodium hydroxide combinations of 20/80, 25/75 and 30/70), and alkaline activator solution-to-binder ratio (0.52, 0.56 and 0.60) on properties of alkali-activated natural Pozzolan/slag mortars were studied. The results of alkali-activated mortars were also compared with the results of control Portland cement mortars. From the findings of this chapter, the following conclusions can be drawn:

18. Nearly for all studied alkali-activated mortars, the workability and setting times were in the acceptable ranges. The flow and setting times of alkali-activated natural Pozzolan/slag mortars reduced by reducing natural Pozzolan content of binder and

solution-to-binder ratio. The setting time of alkali-activated mortars also reduced with increases in sodium hydroxide dosage and concentration. The flow improved by increasing sodium hydroxide portion of activator and NaOH molarity for up to 1M.

19. The results of hydration heat showed that the initial reactivity accelerated as slag portion of binder increased, sodium hydroxide portion of activator increased, solution-to-binder ratio reduced, and sodium hydroxide concentration increased.
20. Overall, alkali-activated mortars having 50/50 combination of natural Pozzolan and slag developed the highest compressive strengths. At the early ages of curing (1 and 3 days), however, the strength increased with increases in slag content resulting in the highest early strengths for the mortars made with binders having 70% slag. Overall, strength development accelerated with increases in slag portion of the binder for all studied alkali-activated natural Pozzolan/slag mortars.
21. The compressive strength of alkali-activated natural Pozzolan/slag mortars improved with increases in sodium silicate portion of activator and decreases in solution-to-binder ratio.
22. Regarding the effects of NaOH molarity on compressive strength of studied alkali-activated mortars, there were optimum NaOH concentrations which increased with an increase in slag portion of the binder.
23. The absorption of alkali-activated natural Pozzolan/slag mortars reduced as solution-to-binder ratio reduced and sodium hydroxide molarity increased. A 50/50 combination of natural Pozzolan and slag was the optimum combination for the absorption results. For majority of the studied alkali-activated mortars, the absorption results didn’t change considerably when sodium silicate content in the range of 20 to 30% was used.

24. The chloride penetration depth reduced with decreases in natural Pozzolan portion of binder, sodium silicate dosage, NaOH concentration, and solution-to-binder ratio. A similar trend was seen for the drying shrinkage, as reduction of these variables also decreased the drying shrinkage.
25. In comparison with the control Portland cement mortars, alkali-activated mortars generated significantly lower heat of hydration, offering a great benefit for mass concreting. The compressive strengths of studied alkali-activated natural Pozzolan/slag mortars were lower than those of the studied control Portland cement mortars. However, it is not out of reach to produce comparable mortar strengths when lower solution-to-binder ratio or higher sodium silicate content is used.
26. While absorption of alkali-activated natural Pozzolan/slag mortars were slightly higher than that of Portland cement mortars, their chloride penetration depths were significantly lower than those of control Portland cement mortars.
27. The drying shrinkage of alkali-activated natural Pozzolan/slag mortars was significantly higher than those of control Portland cement mortars.

7.4. Chapter 6: Alkali-activated natural Pozzolan/slag concretes

In this chapter, the influence of sodium hydroxide molarity (1, 1.75 and 2.5M), binder combination (natural Pozzolan/slag combinations of 70/30, 50/50 and 30/70), and activator combination (sodium silicate/sodium hydroxide combinations of 20/80, 25/75 and 30/70) on properties of alkali-activated natural Pozzolan/slag concretes was studied. The results of alkali-activated concretes were also compared with the results of reference Portland cement concrete. From the findings of this chapter, the following conclusions can be drawn:

28. Nearly for all studied alkali-activated natural Pozzolan/slag concretes, the workability and setting times were in the acceptable ranges. The flow and setting times of these concretes reduced by reducing natural Pozzolan potion of binder. The setting time of alkali-activated natural Pozzolan/slag concretes also reduced by increasing sodium hydroxide dosage and concentration. The slump flow improved (increased) by increasing sodium hydroxide portion of activator and its molarity for up to 1.75M.
29. Overall, alkali-activated concretes having 50/50 combination of natural Pozzolan and slag developed the highest compressive strengths. Increasing slag portion of binder to 70%, however, resulted in the highest compressive strengths for the concretes made with NaOH concentrations of 2.5M. The increase in slag portion of binder to 70% also accelerated the initial reactions, leading to the highest early-age (1 and 3 days) compressive strengths in all studied alkali-activated natural Pozzolan/slag concretes.
30. The compressive strength of alkali-activated natural Pozzolan/slag concretes improved with increases in sodium silicate portion of activator.
31. Regarding effects of NaOH molarity on the compressive strength of alkali-activated natural Pozzolan/slag concretes, there were optimum NaOH concentrations which increased with an increase in slag portion of the binder.
32. The influences of the studied dominant variables (binder combination, activator combination and NaOH molarity) on the tensile strength and modulus of elasticity were nearly similar to their effects on the compressive strength.
33. The absorption and volume of permeable voids of alkali-activated concretes slightly reduced as sodium hydroxide concentration was increased. An increase in sodium silicate content marginally increased the absorption of concretes made with binders having 30%

slag, whereas an opposite trend was seen for concretes made with binders having 50 and 70% slag. Overall, 50/50 combination of natural Pozzolan and slag proved to be the optimum binder combination in producing the least absorption results.

34. The chloride penetration depth increased with increases in natural Pozzolan portion of binder, sodium silicate dosage and NaOH concentration. A nearly similar trend was seen for the drying shrinkage, as increases of these variables also increased the drying shrinkage.
35. The mass loss of alkali-activated natural Pozzolan/slag concretes subjected to acid attack increased with increases in slag content, sodium silicate dosage, and sodium hydroxide concentration.
36. The failure time in corrosion test improved (increased) with increases in natural Pozzolan content, sodium silicate dosage, and sodium hydroxide concentration.
37. The frost resistance of alkali-activated concretes improved when slag portion of binder was increased. An increase in sodium silicate dosage was beneficial in improving frost resistance of alkali-activated concretes made with binders having 50 and 70% slag. An opposite trend was found when slag portion of the binder was reduced to 30%.
38. The compressive strengths of alkali-activated natural Pozzolan/slag concretes made with activators having 20 and 25% sodium silicate were lower than those of the reference Portland cement concrete. As sodium silicate dosage of activator was increased to 30%, the compressive strengths of alkali-activated natural Pozzolan/slag concretes reached to similar values produced by the reference Portland cement concrete. A similar trend was found for tensile strength and modulus of elasticity.

39. Absorption and volume of permeable voids of the studied alkali-activated natural Pozzolan/slag concretes were averagely 13% lower than that of the reference Portland cement concrete. Their chloride penetration depths were significantly lower, nearly 80%, than that of the reference Portland cement concrete.
40. Unlike alkali-activated pastes and mortars, drying shrinkage wasn’t a major concern for alkali-activated concretes. The average of ultimate drying shrinkage of alkali-activated natural Pozzolan/slag concretes was lower than that of reference Portland cement concrete by nearly 26%. There were several alkali-activated natural Pozzolan/slag concretes that shrank considerably less than the reference Portland cement concrete. The ultimate drying shrinkage of the worst performed alkali-activated concrete was only 25% higher than that of the reference Portland cement concrete.
41. The mass loss of reference Portland cement concrete subjected to acid attack was several times of that of the studied alkali-activated natural Pozzolan/slag concretes.
42. The corrosion resistance of alkali-activated natural Pozzolan/slag concretes was significantly higher than that of the reference Portland cement concrete.
43. The frost resistances of alkali-activated concretes having binders made with 50 and 70% slag were significantly higher than that of the reference Portland cement concrete. On the other hand, the frost resistance of concretes made with binders having 30% slag were similar to or less than (depending on sodium silicate content) that of the reference Portland cement concrete.
44. In view of the results obtained for mechanical, dimensional, transport and durability properties of the studied alkali-activated concretes, an equal proportion of natural Pozzolan and slag (50/50) proved to be the optimum binder combination. Overall, the

30/70 combination of sodium silicate and sodium hydroxide provided the most satisfactory performance for the studied alkali-activated natural Pozzolan/ slag concretes.

7.5. Future studies

The followings are recommended for further studies:

1. *Development of admixtures for alkali-activated binders:* It was found that the majority of admixtures developed for Portland cement are ineffective (unstable) for alkali-activated concretes. In order to produce an economically viable binder to fully replace Portland cement, it’s essential to develop stable admixtures that can work for alkali-activated concretes. Further research should be devoted to production of suitable admixtures for alkali-activated concretes. In this study, sodium gluconate was found to be an effective superplasticizer for alkali-activated binders with positive influence on compressive strength. Additional studies on influence of sodium gluconate on properties of alkali-activated concretes will be meritorious.
2. *Alkali-activated natural Pozzolan/slag concretes as corrosion inhibitors:* The studied alkali-activated natural Pozzolan/slag concretes showed a great potential to protect reinforcement against chloride-induced corrosion. Therefore, further studies in corrosion resistance of reinforced alkali-activated natural Pozzolan/slag concretes are recommended.
3. *Development of new testing techniques and standard specifications:* Test methods developed for Portland cement concrete may not fully reflect the inherent properties of alkali-activated natural Pozzolan/slag concretes. Some of the existing specifications have not kept pace with the advancement in concrete technology to properly evaluate

properties of newly developed concretes. These standards have evolved from relatively simple requirements in the early 20th century, typically based on measurements of setting time, strength development, volume stability, as well as prescriptive limits on chemical components. Accordingly, it will be valuable to visit and revise the existing testing techniques and standard specifications more applicable to alkali-activated natural Pozzolan/slag concretes.

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Master of Science, Civil and Environmental Engineering, 2006
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Awards as Teaching Assistant/ Researcher

Outstanding Graduate Student Teaching Award, Second place, UNLV, 2015-2016

Award Winning Papers, 4th International Conference on Sustainable Construction Materials and Technologies (SCMT4), Las Vegas, US, 2016

Award Winning Papers, 3rd International Conference on Sustainable Construction Materials and Technologies (SCMT3), Kyoto, Japan, 2013

Distinguished Researcher, Building and Housing Research Center, The Ministry of Housing & Urban Development, Iran, 2010

Member of Scientific/ Organizing Committee

4th International Conference in Sustainable Construction Materials and Technologies (SCMT4), Las Vegas, USA, 2016

Recent Developments on High Performance Concretes Workshop, Building and Housing Research Center, Iran, 2008

First Disaster Management Conference, University of Tehran, Iran, 2006

Accomplished Research Activities

High Early-Strength High-Performance Concrete for Rapid Pavement Repair 2015-2016

Mechanical, Transport and Durability Properties of Self-Consolidating Concretes Containing Natural Pozzolan and Fly Ash 2014-2015

Assessment of Nano-Silica Contained Mortars and Concretes under Sulfate Attack 2013-2015

Alkali-Activation of Fly Ash and Natural Pozzolan for Precast Concrete 2013-2015

Alkali-Activated Natural Pozzolan/Slag Concrete for Cast in Place Members 2012-2016

Modeling Durability and Transport Properties of Concrete 2012-2014

Transport Properties of Self-Consolidating Concretes Containing Limestone Powder 2011-2013

Transport Properties of Self-Consolidating Concretes Containing Nano-Silica 2011-2013

Application of Natural Zeolite in Concrete as Supplementary Cementitious Materials 2010-2011

Use of Copper Slag Waste as Supplementary Cementing Materials 2009-2011

Electrochemical Impedance Behavior of Silica Fume Contained Concretes 2009-2011

Improving Quality of Ready-Mixed Concrete Batching Plants 2009-2011

Application of Natural Pozzolans as Supplementary Cementitious Materials 2007-2011

Implementation of Nano-Silica in Concrete 2008-2009

Improving Durability of Sewage Concrete Pipes 2006-2008

Development of Lightweight Concretes for different applications 2004-2005

Working Experience

Concrete Technology Department, Building and Housing Research Center, Iran
Head of concrete Laboratory, 2010-2011

Duties: Management of concrete laboratory for ISO (International Organization for Standardization) certifications, Design of experimental programs and supervision

Concrete Technology Department, Building and Housing Research Center, Iran
Researcher, 2005-2010

Duties: Research on properties of different types of concrete, Quality assurance/ control of precast concrete plants, Preparation of national standards and manuals

Rah-Azma Consultant Company, Iran

Civil Engineer Fall and Winter 2004

Duties: Feasibility study to widen Behbahan- Aghajari Road

Markazi Province Waste and Wastewater, Iran
Intern Summer 2004

Duties: Inspection of construction of wastewater treatment plant

Publications

- **Book Chapter**

1. M. Shekarchi, B. Ahmadi and **M. Najimi**, Use of natural zeolite as Pozzolanic material in cement and concrete composites, In: V.J. Inglezakis and A.A. Zorpas ed. Handbook of natural zeolite, Bentham Science 2012, Page: 665-694 (30), DOI: 10.2174/97816080526151120101, Chapter DOI: 10.2174/978160805261511201010665.

- **Journal Papers**

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