Effectiveness of a Natural Pozzolanic Material from Southern Saskatchewan for Cement Replacement in Concrete

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ABSTRACT

Pozzolans are a category of supplementary cementitious materials that can be used as a partial replacement of portland cement in concrete. Aside from their environmental benefits, some pozzolans have been found to increase the strength, reduce the permeability, and thereby increase the durability of concrete. In this study, a natural pozzolanic material from deposits in Southern Saskatchewan was evaluated for its effectiveness as a partial replacement of portland cement in the production of concrete. Specimens with replacement amounts of 10%, 20%, and 30% by weight of cement were prepared and tested to measure compressive strength and permeability, along with a reference mix without pozzolan for comparison. The effect of sieving out particle sizes greater than 74 μm was investigated. The results showed that the 10% and 20% replacement amounts slowed down the strength development, but produced long-term compressive strengths at greater than six months that did not differ significantly from that of the reference mix, except when pozzolan particle sizes were not limited to less than 74 μm at the 20% replacement amount. The 30% replacement amount produced concrete that was weaker than the control mix by 16% and 8% at 56 days and one year, respectively, when the particle size was controlled. The permeability of samples prepared with 10% pozzolan was statistically lower than that of the reference mix and was also statistically lower when pozzolan particle sizes were limited to less than 74 μm. The natural pozzolan is therefore considered to be an effective cement replacement material.

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DEDICATION

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CHAPTER 1

INTRODUCTION

1.1. Background

Concrete is one of the essential materials for construction. No matter what type of structure it is used for, the concrete should be of high quality. During the Roman empire, lime mortars and natural pozzolans were used in combination for construction. The practice is still followed today by blending portland cement with mineral additives, although an advanced knowledge of the performance of these materials has still not been fully explored. The performance analysis of such materials started when historic buildings from ancient Greek and Egyptian kingdoms were discovered by archeologists in the early 16th century. Evidence of mortars made with volcanic ashes and tuffs in 500-400 BC by the Greeks were discovered in the ancient city of Kameiros in Rhodes. The practice of using such materials was later adopted by the Romans, the most famous examples being found in Pozzuoli (Naples), from which the name pozzolan was derived for such additives. The natural preservation and lifetime performance of the Pantheon, constructed using a blend of pozzolan, lime mortars, and concrete, show the durability of the binders and are also a testament to the high workmanship of their engineers (Idorn 1997; Valek et al. 2012).

These blended material practices were lost with the fall of the Roman empire but were rediscovered through “De architectura” (Ten Books on Architecture), a guide for building projects written by the famous Roman architect Marcus Vitruvius Pollio, which was dedicated to his sponsor, the emperor Caesar Augustus. It is the first book on the theory of architecture that describes the classical architecture, structural design, and innovative building materials in detail (Morgan 1914; Kruft 1994). During the 16th – 18th centuries, these materials became more common for construction projects due to their strength and durability, especially their hardening capability under water (Idorn 1997; Valek et al. 2012).

Over the period of the 20th century, the addition of pozzolanic materials into portland cement concrete has become more prevalent and standard practice. One of the motivations for their use has been the interest in sustainability. Industries have been inclined towards increasingly sustainable practices, and the cement industry is no exception. The emission of carbon dioxide into the air is a serious issue that needs to be addressed, as the release of greenhouse gases affects the whole atmospheric system and is believed to lead to global warming. Researchers assume that part of the reason for increased global warming is due to increased energy production, industrialization, agriculture, and transportation (Mehta 2002). A primary focus of many countries now is to control the emission of carbon dioxide into the atmosphere (Altwair and Kabir 2010). The use of natural pozzolan in concrete can help in reducing the production and consumption of cement, and can thereby lower the amount of carbon emissions into the environment (Tafheem et al. 2011). As a result, the use of blended cement has been gradually increasing. Also known as supplementary cementitious materials, they are increasingly being used to reduce the amount of portland cement needed and to improve the quality of concrete.

Natural pozzolans are natural materials that contain reactive silica and/or alumina which in themselves have little or no binding properties. These can be found in volcanic deposits, clays, shales, and diatomaceous earth. When mixed with portland cement, they react with the lime (calcium hydroxide) that is produced by the cement hydration reactions and thereby produce a denser hardened cement paste. The pozzolanic reaction enhances the strength and long-term durability of the concrete. (ACI 232.1R 1994). The process of extracting and processing the natural pozzolans is similar to that used for limestone, which is one of the prime constituents in cement manufacturing, but natural pozzolans are often ground into selected particle sizes and do not undergo the burning process like the traditional cement (Balog et al. 2014; Cobirzan et al. 2015).

Pozzolanic materials vary in their properties and composition depending on their origin. As described in the preceding paragraph, they can be naturally acquired (e.g., volcanic tuffs and pumice) or can be produced artificially as the by-product of various industrial processes (fly ash, silica fume, etc.). Natural pozzolans are found in abundance all around the world. There are three main benefits to using the pozzolans. Firstly, economic benefits are realized by replacing a portion of expensive portland cement with a lower cost natural or artificial pozzolan. Secondly, environmental benefits are realized because cement production emits greenhouse gases into the atmosphere, and the use of pozzolans reduces the amount of portland cements required. Thirdly, the use of pozzolans increases the durability of the blended concrete mixes, including increased resistance to thermal-attack, resistance to sulfate attack and chemical durability (Khan and Alhozaimy 2010).

The current prediction by researchers and engineers is that in the future, a concrete without pozzolanic material will be an exception. It is important for practicing civil engineers to develop a deep knowledge of the different kinds of pozzolanic materials available, their characteristics and influence on concrete properties (Malhotra and Mehta 1996; Malhotra 2002; Malhotra 2006).

The properties of concrete produced using pozzolanic materials vary with different types and amounts of the pozzolanic material, different concrete mixes and with curing time. The chemical composition of various natural pozzolans and the pozzolanic activity vary depending on their source. The key to determining the effectiveness of a particular pozzolan is to measure the properties of concrete produced with varying amounts of the pozzolan by trials. The choice of material to be used in concrete depends on the performance of the material and also on the information available for a certain material (Al-Chaar et al. 2011; Al-Chaar et al. 2013; Al-Chaar and Alkadi 2016).

In addition to contributing to the strength of concrete, natural pozzolans also contribute to the resistance to alkali-aggregate reactions (AAR). Expansion due to alkali-aggregate reactions may lead to damage of the concrete. Reactive aggregates are commonly found in eastern and central Canada. The introduction of pozzolans into the concrete can help in reducing the expansion caused by AAR and is a more economical option compared to introducing chemical admixtures or using low alkali cement (Malvar et al. 2002; Mielenz 1983). Natural pozzolans also contribute significantly to the resistance to sulfate attack, as the expansion of concrete can be reduced by the addition of these fine materials. Sulfate attack causes expansion in concrete leading to reduced strength. Permeability is the key to a more durable concrete; decreasing the permeability increases its resistance to aggressive environmental attacks, such as sulfate attack. The more impermeable concrete is, the more resistant it is to environmental attacks. Controlling the permeability of the mix is said to be even more important than the cement chemistry for the resistance to chloride attacks (Khatri and Sirivivatnanon 1997).

Volcanic deposits of natural pozzolans are widespread in western Canada. Numerous such deposits have been found in Saskatchewan. These volcanic deposits are widely distributed in several locations in southern Saskatchewan (Fig.1.1), including south-central areas near Waldeck, Duncairn, south-west of Neidpath at St. Victor, west of Rockglen and near Pickthall. Some traces of it are also found at the lower end of Big Muddy Lake (Crawford 1951).

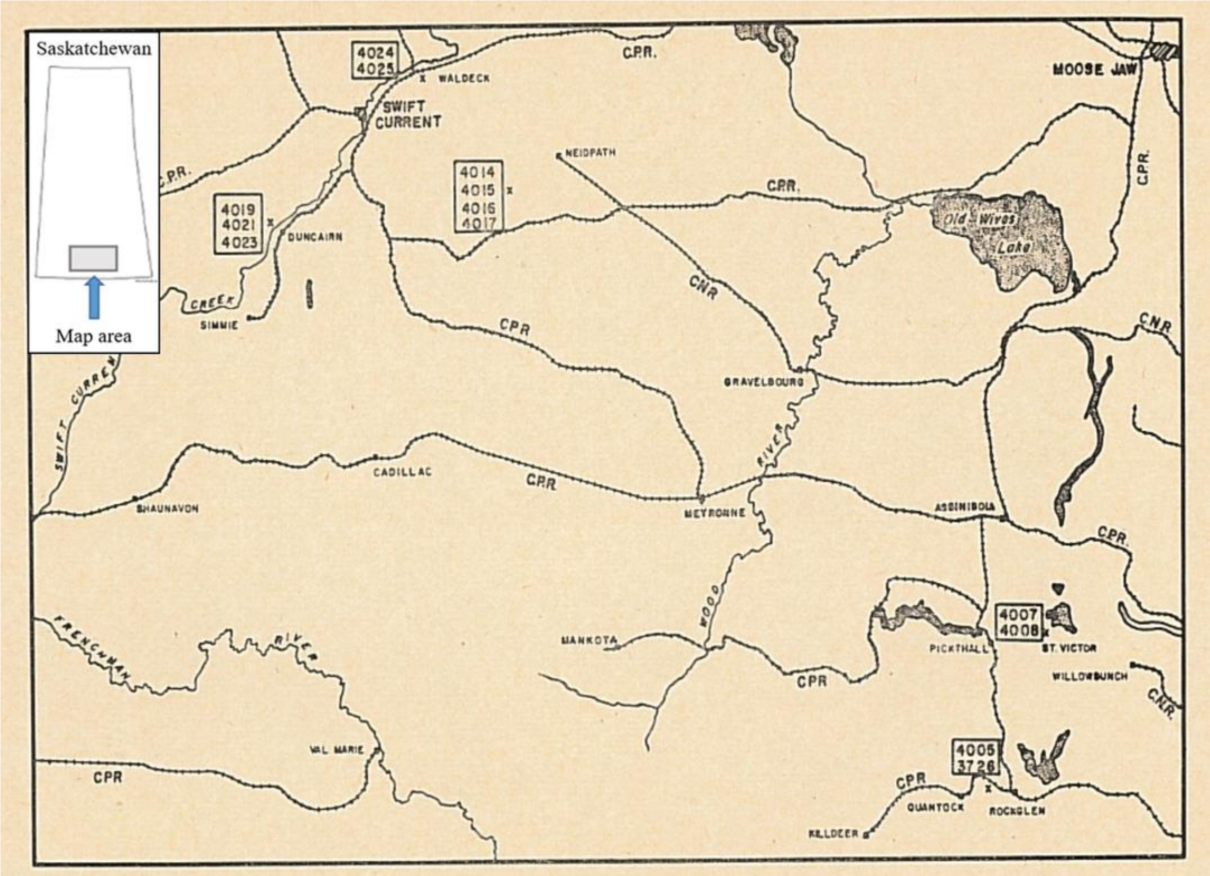

Figure 1.1. Pozzolan deposits in Southwestern Saskatchewan indicated by numbers within boxes (reproduced from Crawford 1955, Public Domain)

The effectiveness of these deposits as a replacement for portland cement is still not known; however, they could have economic value if they are found to be a suitable replacement. Therefore, it is essential that such deposits be evaluated for their effectiveness as a pozzolanic material in concrete.

1.2. Objectives

The primary objective of this research was to determine the effectiveness of the natural pozzolans from deposits in southern Saskatchewan as supplementary cementitious materials for partial replacement of portland cement in concrete.

The specific sub-objectives were:

- To determine the compressive strength of concrete mixes prepared with partial replacement of the cement by the natural pozzolans in two different forms (as-crushed and passing #200 sieve) over a replacement range of 0% – 30% at different curing ages up to one year; and
- To determine the permeability of concrete mixes prepared with partial replacement of the cement by the natural pozzolans in two different forms (as-crushed and passing #200 sieve) over a replacement range of 0% – 30%.

1.3. Scope and Methodology

1.3.1. Research Significance and Scope

The use of supplementary cementitious materials also known as SCM's, for making blended cement is becoming more common. Various studies on the use of supplementary cementitious materials have been done in many countries, along with some on the use of blended cements that include natural pozzolans. Their impact on the durability of a structure has received much attention. This research evaluated the effect of one particular natural pozzolan from southern Saskatchewan on the durability of concrete by measuring the compressive strength and permeability.

1.3.2. Research methodology

A laboratory testing program was undertaken to measure the compressive strength and permeability of concrete containing different amounts of the natural pozzolan.

Samples with four different cement replacement amounts (0%, 10%, 20%, and 30%) and two different forms of pozzolan (as-crushed and passing No. 200 sieve) were tested to measure compressive strength at six ages (7, 28, 56, 112, 182 and 364 days). Five specimens were tested at each age, except that 15 samples were tested at 56 and 364 days to provide more statistically reliable results. Compressive strength was measured on 100 x 200 mm cylinders according to ASTM standard C39.

Water permeability was measured using a centrifuge technique using 50 mm diameter x 15 mm thick disc samples. Similar pozzolan amounts and forms to those described above were used. Tests were conducted at the age of 442 days, except that 30% pozzolan samples were tested at two different ages (364 days and 442 days).

1.4. Structure of Thesis

This thesis comprises six chapters.

Chapter 1 gives an introduction to the use of natural pozzolans in concrete, along with the benefits, objectives and research significance.

Chapter 2 contains a review of the literature related to the use of natural pozzolans, including their properties and classifications, the pozzolanic reaction, and their effect on concrete properties, with a focus on the strength and durability of concrete prepared with natural pozzolans and its resistance to environmental attacks.

Chapter 3 discusses the experimental methods used for this investigation, including a sieve analysis of the natural pozzolan, and scanning electron microscopy to identify the shape of the pozzolan particles. In addition, the materials and mix design for this research is presented, along with a discussion of the workability of the material. This is follows an explanation of the procedures followed to measure the compressive strength of the pozzolanic concrete, as well as the concrete samples and centrifuge technique adopted for measuring the permeability.

Chapter 4 presents the results and a discussion of the results. Results of both the compressive strength tests and permeability tests are given in tabular and graphical forms.

Chapter 5 presents conclusions and recommendations for future work.

Experimental data and detailed calculations and analysis techniques are provided in five appendices.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

With global growth and development, the need for new buildings and infrastructure is increasing, and a considerable amount of construction material is therefore required. The increasing demand is leading to the introduction of new environment-friendly materials that can also be economical (Ababneh and Matalkah 2018; Malhotra 1996; Safiuddin and Zain, 2006).

According to Gartner (2004), the production of portland cement is responsible for emitting about 5% of globally produced carbon dioxide (CO_2) into the environment. The emission of CO_2 is approximately one ton per ton of clinker production if fossil fuel is used (Malhotra 2002; Hendriks et al. 2004; Malhotra 2006). CO_2 is released into the environment in two ways: first when calcium carbonate is decomposed thermally, and second by the burning of fossil fuels to produce the high temperature (1200°C) in the rotary furnace (Dhir 1999). In addition, the production of cement uses a great deal of energy; it is reported that about 2% of the global energy is consumed by the cement industry. Globally, approximately 1.89 billion tons of cement is produced each year. (Huntzinger and Eatmon 2009; Suhendro 2014).

Global warming has increased the need for green concrete that can help in reducing the GHG (greenhouse gases) released into the environment. Green concrete is described as an environment friendly concrete that incorporates waste material and that does not involve an extensive process that can harm the environment (Mehta 1987; Mehta 2002). There are three main factors that can define the green concrete, namely: amount of additives in portland cement (added or replaced), manufacturing processes, performance and life span of the concrete (Mehta 2002; Suhendro 2014). Natural pozzolans are considered to be economical and environmentally friendly as they do not involve extensive energy consumption processes, and the cost of quarrying, transportation, packaging and grinding of such materials is generally lower than the cost associated with the production of traditional cement (Suhendro 2014).

According to the National Ready Mix Concrete Association (NRMCA 2012), the Department of Energy states that 0.33% of energy is consumed in the production of cement in the U.S. A survey of Portland Cement Association (PCA) members found that for 1000 kg of portland cement production in the U.S., an average of 927 kg of CO_2 is emitted into the environment. On average, 1 m^3 of concrete weighs 2400 kg, which has an average cement quantity of 250 kg/m^3, depending on which approximately 100 – 300 kg of CO_2 is released for every cubic meter of concrete produced.

Apart from CO_2 production, each year the manufacturing of cement creates millions of tons of cement kiln dust, also commonly known as CKD, a waste product that leads to health hazards that most commonly include respiratory problems.

One alternative that can be adopted to reduce the production of CO_2 and mitigate the other negative impacts of cement production is to partially replace the cement with an alternative material (Ghrici et al. 2006; Antiohos et al. 2013; Abdollahi 2016; Malhotra 2006). The replacing of cement with supplementary cementitious materials can reduce the CO_2 emission into the environment. For example, the use of mineral additives such as fly ash and blast-furnace slag to replace 15 – 40% of cement can reduce CO_2 emission by 60 – 70%. Other replacement materials like volcanic ash, ground limestone, and broken glass can reduce CO_2 emission by 50% and also reduces energy use. The effectiveness of these materials as cement replacements depends on their physical and chemical attributes and also on their origin (NRMCA 2012; Miller et al. 2016).

As a result, the emphasis has now shifted to evaluating more and more natural or artificial pozzolans for use in concrete. The use of supplementary cementitious material in concrete is a practice that has been ongoing in North America since at least the 1970's. The use of these materials in modern concrete is motivated not only because they are economical and environmentally friendly materials, but also because they contribute to the strength and durability of the concrete (Mehta 1981; Mehta 1990). With an increasing focus on controlling the effects of emitted carbon dioxide on the environment, various alternative elements are now being introduced into portland cement concrete. Juenger and Siddique (2015) and Khan et al. (2017) explain that the addition of supplementary cementitious materials in concrete or mortar reduces the cost of the material and also minimizes the energy consumed by the production of portland cement. Substantial research has been done and is ongoing for alternative cementing materials. It is time-consuming to measure the strength development parameters produced by each of these supplementary cementitious materials separately, so a broad understanding of the mechanisms underlying the performance of the materials must be developed (Owaid et al. 2012l; AL-Jumaily et al. 2015).

The replacement of portland cement with various industrial, agricultural and thermoelectric plant residues, including mineral additives such as fly ash, silica fume, rice husk, granulated blast furnace slag, sugarcane bagasse and palm oil ash has been reported in previous studies, with amounts varying from 5% to 30% or even higher percentages (Uzal and Turanli 2003; Cheerarot et al. 2004; Owaid et al. 2012). Various supplementary cementitious materials are now commonly used as partial cement replacements, including fly ash, silica fume, metakaolin, rice husk, ground granulated blast furnace slag and volcanic tuff (natural pozzolans) (Zhang et al. 2002; Ghrici et al. 2007; Khan and Alhozaimy 2011). These materials improve some engineering properties of concrete, namely resistance to alkali-silica reaction, durability, enhanced long-term strength, resistance to freeze-thaw and reduced thermal cracking that occurs due to the heat of hydration (Kaid et al. 2009; Al-Swaidani and Aliyan 2015; Labbaci et al. 2017; Ababneh and Matalkah 2018).

2.2 History

As early as 5000 B.C., concrete was produced using a hydraulic binder in the form of diatomaceous earth, which was a combination of lime and natural pozzolan that was obtained from the Persian Gulf. Ash from volcanic eruptions (a natural pozzolan) was used in construction as early as 1500 and 1600 B.C. in the Mediterranean region (Ramezanianpour 2014; Thomas 2013). In medieval times, the Romans used natural pozzolans mixed with lime, and the reaction between the two created a high-performance binder (Baronio and Binda 1997; Ababneh and Matalkah 2018). The term pozzolan was derived from the volcanic region of Pozzuoli, Italy, where volcanic ash with pozzolanic properties was found. The word was later applied to materials with close composition.

Since pozzolans are found in numerous parts of the world, there is no benefit to keeping the definition to a specific region.

According to Crawford (1951), pozzolans are siliceous and do not have any cementitious properties, but they obtain cementitious properties when combined with lime and water under ambient conditions. As stated by Davis (1950), for these reasons, natural pozzolans were used in concrete as mineral admixtures for constructing massive structures such as dams in the nineteenth century. Los Angeles County Flood Control District got involved with the construction using such blended cement concretes; the Golden Gate Bridge, San Francisco-Oakland Bay Bridge, Bonneville Dam, and Friant Dam are some of the leading examples of projects that used portland cement-natural pozzolan blended concretes. The proven resistance of such concretes to sulfate attack from seawater, and their lower heat of hydration led the California Division of Highways to use such portland-pozzolan cement in the construction of several large bridge structures (Davis 1950).

The United States Bureau of Reclamation constructed Friant Dam with concrete containing naturally fine pumicite (rhyolite), which was procured from deposits near Friant; 20% of the mass of the cement was replaced by the natural pozzolan (Meissner 1950). It was called as one of the most expensive projects in American history that used natural pozzolans was the California State Water Project, which included the lining of the California Aqueduct; it has been noted that the pozzolan requirements surpassed the allowable limits given in ASTM C618 (Tuthill and Adams 1972). The use of supplementary cementitious materials (SCM's), has also been widespread in Canada, where three main types of SCMs are produced: fly ash, silica fume, and slag. Natural volcanic deposits are also avidly reported in different parts of Canada. The application of blended concretes is found in all kinds of construction, namely residential, commercial, and infrastructure (Bouzoubaa and Fournier 2005).

2.3 The Pozzolanic Reaction

Portland cement consists of five major constituents, namely tricalcium aluminate (C3A), gypsum (CSH2), tetra calcium aluminoferrite (C4AF), alite (C3S), and belite (C2S). During the hydration of belite and alite, calcium silicate hydrate (C-S-H) and calcium hydroxide

(CH) are formed. The C-S-H becomes the essential binding component of the hardened cement paste. Other less critical hydration products include certain aluminate phases. The aluminate and silicate components occupy between 60 - 65 % of the hardened cement paste, 20% is occupied by CH, while the remainder of the cement paste is composed of alumina and ferrite compounds and water (Dunstan 2011; Setina et al. 2013).

The properties of pozzolans vary widely, as they may have variable constituents depending on their origin (Weng et al. 1997). However, silica is one of the leading components of pozzolans that are found both in natural and artificial form. The silica in a pozzolan reacts with calcium hydroxide in the hardened cement paste to form new calcium silicate hydrates (C-S-H) (Taylor 2008). The pozzolanic reaction refines the pore structure and reduces the microcracks at the interfaces between the cement paste and aggregates. As a result, the permeability is reduced, and the durability and compressive strength of concrete is increased (Bustos et al. 2012).

The concrete's early strength is reduced by the addition of a natural or other pozzolan because the pozzolanic reaction occurs only after the initial hydraulic reactions have produced the calcium hydroxide required by the pozzolanic reaction.

2.4 Origin, Properties, and Classification of Natural Pozzolans

Pozzolans are finely divided siliceous or siliceous and aluminous materials that react with the calcium hydroxide of portland cement in the presence of water to form C-S-H (calcium-silicate hydrates) and other compounds with cementitious properties. Pozzolans may occur naturally or may be produced as a by-product of industrial processes. A distinguishing feature of pozzolans, as compared to other materials, is that they contain silica (Davis 1950).

Natural pozzolans may be divided into two forms:

1. Raw pozzolans, occurring as a calcined residue from the production of molten lava during volcanic eruptions. The resulting lightweight amorphous little stones and ashes are packed together on the surface of the earth in the form of volcanic tuffs, pumice, and pumicites.

2. Calcined pozzolans, including clays, shales, diatomites, and cherts, which attain pozzolanic properties after calcination in a furnace (Davis 1950; Crawford 1951; Mielenz et al. 1951).

The use of natural pozzolan and fly ash as an additive in cement concrete is covered in ASTM C618 and CSA A23.5. As stated in the standards, the raw and calcined natural pozzolans are classified as Class N pozzolans and include volcanic tuffs, volcanic ashes, pumicites, pumice, opaline cherts, and shales, which may or may not be processed by calcination. Some other additives that may require calcination, including clays and shales, are also covered under this category.

Volcanic tuffs (natural pozzolans) are found in abundance in various geographical locations, which make them an economical material for use in the production of concrete. However, they also have variable chemical, mineralogical and reactivity characteristics, so the use of volcanic tuffs as supplementary cementitious materials in concrete production should be selective (Lea 1960).

Pozzolan is found near Naples and Segni in Italy, various lower silica tuffs are located in Rome, while volcanic tuffs, pumice, diatomaceous earth, and opaline shales are found in multiple locations in North America (Meissner 1950). Pumicite is also one kind of volcanic ash that has proportions of crystal particles along with porous and angular particles of siliceous glass. Pumicites are commonly found in lake beds in large deposits and are rhyolite or dacites that are very acidic volcanic rocks widely known as igneous rocks (Mielenz et al. 1950). Deposits of such rocks are reported to be found in Saskatchewan (Crawford 1951). These deposits all have the same rhyolite nature in a finely divided powder containing small, angular grains of siliceous glass. According to Crawford (1951), the deposits are widely spread in the southern part of the province, mainly around St. Victor, Rockglen, Big Muddy Lake, Pickthall, Waldeck (also referred to as Swift Current deposits), Duncairn (also called Beverly or Webb deposits), and south-west of Neidpath. The colour of these deposits varies from white to gray or tan yellow (Crawford 1951; Crawford 1955). There information is limited on the use of volcanic tuff as supplementary cementitious materials in concrete. More investigation is therefore required to determine the effectiveness of this natural pozzolans as additional cementitious materials (Ababneh and Matalkah 2018).

The performance of pozzolans and the pozzolanic actions depend on both their physical and chemical properties. When blended with portland cement, supplementary cementitious materials contribute to the hardened concrete properties through either or both hydraulic and pozzolanic activities (Bouzoubaa and Fournier 2005).

The essential physical properties of pozzolans include particle fineness, particle size, specific gravity, and water absorption. The specific gravity of cement (3.1) is higher than most of the pozzolans, which have specific gravities that range from 2.3 to 2.8. As stated by Lea (1960) and later by Mielenz et al. (1951), the lower specific gravity of a pozzolan makes it occupy a higher volume in a pozzolanic paste than the equivalent weight of portland cement. Certain pozzolans consist of very fine materials that are porous and the particle shape of some fine elements may be irregular or angular. These attributes can increase the water demand in the mix and lead to increased drying shrinkage, low resistance to freeze-thaw effects, and reduced strength. On the other hand, the water requirement of fly ash concrete is reduced, as the fly ash mostly comprises spherical particles (Mielenz et al. 1951).

Natural pozzolans can be used as a replacement for, or an addition to, the cement in concrete, depending on the type of construction. The addition of a pozzolan to the portland cement is done to improve one or more properties of the mix. For example, 3% diatomite has been added in the concrete mix to improve the workability, and it was found to be useful at controlling segregation (Massazza 1998; Davis 1950). Pozzolans may be added in higher percentages when used as a replacement. Although the replacement can be done by volume or weight, most often they are replaced on the basis of the weight of cement. As the density of natural pozzolans is lower than that of portland cement, the replacement by mass results in higher total cementitious minerals, than when replaced on a volume basis (Bouzoubaa and Fournier 2005; ACI 232.1R-00 2000).

2.5 Effect of Natural Pozzolans on Concrete Properties

Certain pozzolans may increase the plasticity and decrease bleeding and segregation in the mix, fly ash being one the example. The replacement amount of the natural pozzolans depends on various factors, including the desired fresh and hardened concrete properties, fineness and nature of the pozzolanic material, portland cement composition, richness of the mix, and grading of the aggregates (Khatri and Sirivivatnanon 1995). These factors can be determined by experiments and trials on the material. Depending on the factors mentioned above, the percentage of pozzolan used may vary from as low as 5 – 6 % to as high as 40 - 50% by the weight of cement and depending on the application of the concrete (Davis 1950; Bouzoubaa and Fournier 2005). These replacement materials tend to increase the water demand of the mix. However, some fine fly ash with lower carbon content is an exception to this, probably due to the spherical shape of the glass-like particles present in it. Water reducing agents can be added to cut the additional water demand of the concrete mix.

2.5.1 Mixing and Proportioning Concrete containing Pozzolans

Evaluating the effectiveness of a particular pozzolan as a replacement for portland cement at different proportions involves the testing of trial batches, as the performance of different natural pozzolans varies widely (Nili et al. 2010; Celik et al. 2014). Proportioning techniques of concrete containing mineral admixtures, including natural pozzolans, are the same as those used for concrete that does not include the admixture. Finely fractioned natural pozzolans, as well as other fines, should be considered as part of the cement paste matrix when selecting the percentages of coarse and fine aggregates in the concrete mix. Water requirements should also be carefully determined in the natural pozzolanic concrete. Some mineral admixtures cause an increase in water demand while others have very low or no water demand effect, and certain others reduce the water demand of concrete (Nili et al. 2010; Kaid et al. 2014).

A natural pozzolan should be considered as a part of the cementitious materials. The amount of pozzolan that has to be added or used to substitute for cement usually depends on the reactivity of the particular pozzolan. Low reactive pozzolans can be used in percentages varying from 15 - 35%, whereas high reactive ones are used in smaller proportions ranging from 5 - 15%, depending on the amount of cement in the concrete mix (Davis 1950; Crawford 1955; Al-Chaar et al. 2011; ASTM C618-17a 2017).

2.5.2 Fresh Concrete Properties

The primary benefits of natural pozzolans relate to the properties of the hardened concrete. However, certain fresh concrete properties can also be influenced by the addition of a natural pozzolan, and fresh properties can also influence the hardened concrete properties. The fresh properties that can be affected by the addition of pozzolan include the water demand of the mix, bleeding, heat of hydration and setting time (Khatri and Sirivivatnanon 1995; Safiuddin, and Zain 2006). The addition of pozzolans can create a cohesive mix that has a plastic consistency with no signs of bleeding and segregation. The fine pozzolan particles increase the surface area of the minerals giving a denser and less permeable mix; this may result in surface and internal cracking, and also a reduction in workability and a slight increase in water demand that can be neutralized by the addition of superplasticizers. The use of superplasticizers improves the workability of the mix, in some cases giving self-consolidating properties to it (Davis 1950; Khan et al. 2014).

Bleeding does not always occur on the surface; the internal aggregates may become sites for pockets of water to form and internal bleeding can continue at these locations, which can reduce the homogeneity of the mix (ACI 232.1R-00 2000). Relatively large air pockets can develop that lead to a loss of bond between the concrete ingredients and can make the concrete more permeable and weaker. The addition of finely graded materials such as pozzolans is beneficial in filling the gaps between the aggregates, creating a denser mix and reducing both the external and internal bleeding in the mix. As stated in ACI 211.2-98 (1998), the aggregates used in concrete are generally missing the very fine materials, and the finely divided pozzolanic material, mainly passing a No. 200 sieve (75 µm), can fill the missing fines in the aggregate mix, making the concrete denser, which can minimize the bleeding and segregation and give increased strength to the concrete.

Heat produced from the hydration of cement is responsible for increased temperatures in concrete during curing. The production of heat creates a temperature difference between the exterior and interior of a structure and this difference can produce cracks in the structure due to differential thermal expansion. The occurrence of cracks is a big concern in structures because they can reduce the service life/durability of the structures (Woolley and Conlin 1989; Keck and Riggs 1997). Pozzolans lower the heat of hydration caused by the exothermic reaction during the hydration process of portland cement, thus reducing the propagation of thermal cracks (Newman and Owens 2003; Khan et al. 2014). As a result, pozzolans are beneficial for massive construction projects such as dams, for which the control of the heat production is essential.

According to Turanli et al. (2004), the addition of some natural pozzolans increases the water demand in the cement matrix; this is due to the shape and nature of the particles that are angular and have a microporous structure. Sioulas and Sanjayan (2000) confirmed that the pozzolanic reaction is slower than the hydration of C3S (tricalcium silicate), but the rate of reaction is similar to C2S; due to this, the pozzolanic reaction generates less heat than the one produced during the cement hydration.

Nili and Salehi (2010) studied the temperature profile, and rate of heat evolution in medium and high strength concretes as cementitious materials were added as supplements. They found that the heat of hydration is also affected by the water/cement ratio, and the heat of hydration can be reduced by the addition or replacement of pozzolans in the concrete. According to Nili and Salehi (2010), lower replacement levels on the order of 15% do not produce a significant effect on temperature, but increased levels of natural pozzolans lead to slightly lower peak temperatures. The mix with 15% natural pozzolan showed a decrease in peak temperature by 5 °C compared to a mix without the pozzolan while a reduction of 11 °C was observed at a 30% replacement amount. Thus, the addition of natural pozzolans was found to reduce the peak temperature, especially for high-strength concrete; this leads to minimizing the risk of potential cracking in massive structures. The use of natural pozzolans can produce slow hydration, delayed setting, and unusually low early strength (Wild et al. 1996; ACI 232.1R-00 2000).

2.5.3 Hardened concrete properties

Concrete exposed to the environment is affected by aggressive solvents and water, which can lead to its deterioration (Nili and Salehi 2010). The hardened properties that are affected by the presence of natural pozzolans, leading to an increase in durability, include reduced permeability, higher long-term strength, resistance to sulfate attack, and reduced expansion due to alkali-aggregate reaction (Kaid et al. 2015; Khan and Alhozaimy 2011).

2.5.3.1 Strength

The compressive strength of concrete produced using pozzolans develops more slowly but increases over time and can match or exceed the strength of a concrete mix prepared using only portland cement. For example, a concrete prepared from silica fume was shown to achieve a high compressive strength similar to that of concrete made from portland cement alone (Mehta 1990; Isaia et al. 2001; Ramezanianpour 2014; Joshaghani et al. 2017). The early age compressive strengths of concretes with pozzolans are significantly lower than those without pozzolans (Kaid et al. 2015). Nili and Salehi (2010) reported that the compressive strength decreases with increasing pozzolan percentages at early ages. It has also been reported that the addition of superplasticizer helps in meeting the additional water demand of the mixes in order to minimize the reduction in early-age strength (Celik et al. 2014). However, chemically reactive pozzolans are an exception. Higher early strength can be expected from concrete that incorporates metakaolin, as it is an active natural pozzolan (Ramezanianpour 2014).

The tensile strength of hardened concrete containing natural pozzolans can be higher than concrete with no pozzolans. The pozzolans that have a glass-like character, such as fly ash and pumicites, tend to gain tensile strength over a period of about a year, while the opaline pozzolans gain the ultimate tensile strength earlier (Zhang and Malhotra 1995). Lower tensile strength is observed for concrete containing opaline pozzolans than concrete without pozzolans, while an increased tensile strength is observed for glassy pozzolans in comparison to concrete without pozzolans. It is also found that the tensile strength of concrete with glassy pozzolans is higher at all ages as compared to the mixes that do not contain pozzolans (Davis 1950).

2.5.3.2 Creep and modulus of elasticity

It has been reported that the plastic flow of hardened concrete containing pozzolans such as fly ash is higher than concrete without added pozzolans. The creep of the concrete increases with the increase in pozzolan replacement amounts (Davis 1950). Lohita et al. (1976) observed that 15% replacement of cement with fly ash is an optimum amount to control the higher creep strains in the concrete. On the other hand, Ghosh and Timsuk (1981) reported that the behaviour and creep mechanism of OPC (ordinary portland cement) and fly ash concrete are the same, and a good quality fly ash in concrete reduces the creep. According to Sennour and Carrasquillo (1989), the creep of concrete is affected by the curing conditions and by the use of fly ash; heat curing was found to be helpful in reducing the creep of the fly ash concrete.

The modulus of elasticity is noted to be lower for mixes containing natural pozzolans, but there is no statistically significant difference that was observed from mixes without pozzolans (Choucha et al. 2017). Davis (1950) explains that factors such as cement to aggregate ratio, minerals present in aggregates, and moisture in concrete have a more significant effect on the modulus of elasticity than the percentage of pozzolan (added or replaced).

According to Uzal (2013), the modulus of elasticity of high volume natural pozzolan (HVNP) concrete is lower than the control concrete with same water/cement ratio for the zeolitic natural pozzolan. On the other hand, it was reported that the modulus of elasticity of concrete made with natural pozzolans with similar strengths is higher compared to portland cement concrete (Mehta 1990, Siddique 2004). The modulus of elasticity develops more slowly at early ages, just like compressive strength, but is higher at later ages in comparison to the concrete with no fly ash (Halstead 1986).

2.5.3.3 Drying shrinkage

Concrete mixes containing pozzolans tend to expand under moist curing conditions and shrink under drying conditions, similar to other types of concrete. The shrinkage is dependent on the water requirement of the fresh concrete mix containing pozzolans (Dunstan 1984). As reported by Mehta (1981), the drying shrinkage in blended natural pozzolan concrete mixes with replacement amounts varying from 10% to 30% was not significantly different from mixes without natural pozzolans. The reported values of all the samples were between 500 – 600 $\mu\varepsilon$ over a time period of 80 weeks. However, Zhang and Malhotra (1995) showed the opposite results for a 10% replacement of ordinary portland cement with metakaolin, with drying shrinkage being higher by 400 – 600 $\mu\varepsilon$, for mixes containing metakaolin. These results highlighted the fact that different pozzolans have different effects on the properties of concrete.

Some low carbon pozzolans such as fly ash has relatively low drying shrinkage compared to mixes without pozzolans, while the pozzolans having high opal constituents have higher drying shrinkage (Davis 1950). Davis (1950) also mentions that the mixes with and without pozzolans have been found to give the same magnitude of surface cracking caused by drying shrinkage. The addition of pozzolans has no additional effect to increase the propagation of surface cracks. Because the pozzolanic concrete has a lower modulus of elasticity than concrete without added pozzolans, the penetration of cracks from drying shrinkage is less in pozzolanic concrete than the concretes with no pozzolans (ACI 232.1R-00 2000).

As per Mehta (1981), the drying shrinkage of concrete with cement replaced by 10%, 20% and 30% Santorin earth was not significantly different as compared to concrete without added natural pozzolan. Concretes containing pozzolans have shown lower drying shrinkage than a low-heat cement without added pozzolans (Zhang and Malhotra 1995). The long-term drying shrinkage of concrete containing pozzolans or containing portland cement with a particular cement content and water/cement ratio can vary with the use of different grades of cement. Type I & II cements produce concrete with lower drying shrinkage than the low-heat Type IV cement (Davis 1950; Crawford 1955).

2.5.3.4 Resistance to freeze-thaw

The addition of pozzolans to concrete helps in resisting the freeze-thaw effect. The resistance to chemical attack by de-icing chemicals in freezing conditions depends on the proportioning of concrete, moisture in concrete, the presence of air voids, compressive strength and the exposure time (Lovewell and Hyland 1971).

The amount of air-entraining admixture required to provide adequate freeze-thaw resistance may vary depending on the type of pozzolan. Similar to ordinary concrete, pozzolan concrete without entrained air has lower resistance to freeze-thaw damage than that with entrained air (ACI 232.1R-00 2000). As per Elfert (1973), research by United States Bureau of Reclamation (USBR) has reported that curing conditions plays a vital role in the effect of pozzolan on resistance to freeze-thaw action. Rice husk ash was reported to have good resistance to freeze-thaw impact, while the resistance to attack by de-icing salt was the same as that of a control mix and slightly better than concrete containing silica fume (Zhang and Malhotra 1995). It has also been observed that the resistance of pozzolan concrete contain air-entraining agents to freeze-thaw damage is higher than concrete made with only portland cement and added air-entrainment agents (Halstead 1986). Mixes including a higher percentage of pozzolan as a cement replacement (30% and more) with entrained air can exhibit the equivalent resistance to freeze and thaw that is observed for air-entrained concretes containing only portland cement (Davis 1950; Crawford 1955).

2.5.3.5 Sulfate resistance

One of the leading causes of degradation of concrete is sulfate attack; this happens due to a series of chemical reactions that starts with the reaction of sulfate ions and calcium hydroxide in the hardened cement paste when exposed to a sulfate environment (Mather 1982). The resulting expansion can generate significant stresses that lead to cracking. The use of natural pozzolans in the concrete reduces the amount of calcium hydroxide available for the reaction, allowing the concrete to withstand the aggressive attacks by soils containing sulfates, as well as natural acidic water, and seawater (Binici et al. 2007). The presence of reactive silica is key to this effect (Binici and Aksogan 2006). The stresses can also be reduced if the penetration of aggressive solvents and water into the concrete can be minimized (Nastaranpoor 2013). ASTM C1012 elaborates on evaluation techniques for portland and blended cements to produce a mix that has high resistance to sulfate attack (Patzias 1987). The reduced permeability of the concrete when pozzolans are included in the mix reduces the chances of sulfate attack (ACI 226.3R-87 1987; Mehta 1990).

Pozzolans with high glass contents, such as in fly ash and pumice, have proven to provide exceptional resistance to sulfate attack, but the pozzolans that are opaline have proven to be most effective. Pozzolans having higher silica and lower alumina contents at higher replacement rates reduce the effect of sulfate water, although a little less than the pozzolans higher in opal contents (Dustan 1980).

Mehta (1981) found that sulfate attack in mixes containing higher percentages of pozzolans (i.e., 20% and 30%) was exceptionally low. The effect of fly ash in a sulfate environment is not understood thoroughly, but there is substantial evidence that the fly ash resulting from combustion of bituminous coal increases resistance to sulfate attack, to a similar extent as the pozzolans that have high silica, high opal, and low alumina contents (Dunstan 1987; Thomas 2007).

2.5.3.6 Permeability

When added as a cement replacement in concrete, pozzolans show tremendous results in reducing the permeability. The pozzolanic reaction reduces porosity by producing more C-S-H, but because the pozzolanic reaction takes place over an extended period of time, the decrease in permeability also occurs over a more extended period (Neville 2004; Bentz

2007). Pozzolans having opaline constituents show decreased early age permeability compared to pozzolans with glassy contents such as fly ash and pumice. According to Davis (1950), concretes containing fly ash or pumicite in replacement amounts up to fifty percent may result in permeabilities that are very large at early ages, as compared to concrete made with only portland cement. However, at later ages under moist curing conditions, the same fifty percent replacement amount can result in permeability that is lower than that of concrete with portland cement alone (Stanton 1935).

For concrete exposed to severe environments, the American Concrete Institute recommends a maximum water-cement ratio of 0.45 (Dhir et al. 2002; ACI 232.1R-00 2000). Since the initial water content during mixing determines the overall porosity of the system, the decrease in water content causes an equivalent reduction in permeability at any given strength and workability of concrete (Mehta and Monteiro 2006). The quantity of pozzolan added and the curing duration both also influence the porosity and the permeability of concrete (Ramezanianpour 2014). The finer pozzolans used as a replacement at moderate to higher percentages can make the concrete impermeable to a degree that cannot be achieved by plain portland cement concrete (Bentz 2005; Neville 2004; Mehta and Monteiro 2006).

2.5.3.7 Alkali-aggregate reactions

The alkali-silica reaction (ASR) in concrete happens due to the presence of reactive silica in some aggregates, which reacts with the alkalis in the cement to form an alkali-calcium-silica gel that expands when it absorbs water and causes cracking and spalling in mortars and concretes (Lerch 1950; Lerch 1956; Lauer 1990; Snellings et al. 2012). Since a pozzolan reacts with the same alkalis, but at a smaller and more dispersed scale, it can eliminate the alkali-aggregate reactions (Malhotra 1990; Al-chaar et al. 2011; Al-chaar and Alkadi 2016).

The process of cracking due to ASR is similar to that associated with sulfate attack, with one main difference: cracking due to sulfate attack occurs within the hardened cement paste while cracking due to ASR initiates at the aggregate-paste interface. The cracks penetrate deep into the member over time, potentially leading to the failure of the structural member (Colak 2003; Ezziane et al. 2007).

Adding finer pozzolans is useful for resisting ASR, as specified in ASTM C441. Volcanic tuffs (natural pozzolans) at a replacement rate of about 50% by weight of cement have been shown to be effective at imparting increased resistance to both ASR and sulfate attack (Ababneh and Matalkah 2018; Turanli et al. 2005; Binici and Aksogan 2005). Various other investigations using volcanic tuffs and pozzolans with high opal contents suggest that a 15 - 20% replacement rate is optimal for preventing expansion in concrete produced with cement containing high alkali content (Ababneh and Matalkah 2018).

2.6 Summary

Natural pozzolans have been shown to be effective as a partial replacement for portland cement. As natural pozzolans react with the calcium hydroxide in the hardened cement paste, the pozzolanic reaction produces additional C-S-H that reduces the permeability. The pozzolanic reaction takes place for a longer period of time, so the strength development can be slower, but it does not have much effect on the strength of concrete in the long term for certain pozzolans used in replacement amounts up to approximately 30%. The blended cements show a good resistance to the effects of sulphate attack and to ASR (alkali-silica reaction), that leads to a more durable concrete.

The literature also appears to report contradictory results concerning the effect of natural pozzolans on concrete properties, but this highlights the fact that each natural pozzolan is different and must be evaluated for its effectiveness as a partial cement replacement.

While the literature review has shown that natural pozzolans can affect a number of different concrete properties, two of the most important properties for evaluating the effectiveness of a pozzolan are the compressive strength and permeability of the concrete (Lane and Best 1982). Compressive strength is an important property controlling the behavior of concrete under load, but it is also a good indicator of the general quality of the concrete (Cook 1982; Mehta 1986; Mehta and Monteiro 2006). In addition, the permeability of concrete has a strong influence on its durability. Mehta (1986) explains that water is one agent that can lead to deterioration of concrete through reinforcement corrosion, alkali-aggregate reaction, sulfate attack, freeze-thaw damage, acid attack and leaching of CH (calcium hydroxide).

For these reasons, the focus of this investigation was on the effect of the natural pozzolan on compressive strength and permeability.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Overview

This research focused on the effectiveness of a natural pozzolan from Southern Saskatchewan as a partial replacement for portland cement. To evaluate the effectiveness of the material, two main tests were done, i.e., compressive strength tests and permeability tests. The material replaced the cement in a concrete mixture at four percentages (0%, 10%, 20% & 30% by weight) and in two different forms (as crushed and passing #200 sieve). Both tests followed standard procedures. The compressive strength was measured on samples at various curing ages, ranging from seven days to over a year, while the permeability tests were conducted at a single age of more than a year.

This chapter describes the experimental procedures followed to conduct all of the testing associated with this research.

3.2 Materials

The materials used for this study, along with their sources, are listed in Table 3.1.

Table 3.1. Material and their sources

Material	Source
Portland cement	Lafarge (Type GU)
Natural pozzolan	Roman Cement Corporation
Coarse aggregates	Lafarge (gravel)
Fine aggregates	Pit run (coarse sand)
Water	Tap water
Superplasticizer (Supercizer 5)	Fritz-Pak Corporation (Dallas, TX USA)
Air entrainment admixture (Air Plus)	Fritz-Pak Corporation (Mesquite, TX USA)

3.2.1 The Natural Pozzolan

The natural pozzolan used for this project was procured from Southern Saskatchewan and was supplied by Roman Cement Corporation. The first batch that was supplied was in the form of big chunks that were subsequently broken up and crushed by a large mortar and pestle. Because of the large amount of material that had to be crushed for use in the experimental program, it was not feasible to continue using the mortar and pestle method. Therefore, the material was taken for crushing in a ball mill by the client and was supplied after crushing. The purpose of the ball mill operation was to separate the particles into their natural sizes, rather than to break the natural particles into smaller sizes. The material was processed (i.e., crushed and sieved) by the Saskatchewan Research Council prior to use.

3.2.1.1 Chemical and physical properties of the natural pozzolan

The natural pozzolan used for this study was obtained from a source near St. Victor. The material is also known as volcanic ash (pumicite), which was light grey in color (Kelley and Swanson 1997). Chemical analysis of the material is reported in Table 3.2 (Worcester 1950; Crawford 1951; Crawford 1955; Kelley and Swanson 1997).

Table 3.2. Chemical analysis of natural pozzolan from a deposit near St. Victor in Southern Saskatchewan (Crawford 1955; Kelley and Swanson 1997)

Constituents	Values (percentage by weight)
SiO_2 (Silica or silicon dioxide)	69.35 – 70.43
Al_2O_3 (Alumina or aluminum oxide)	14.38 – 14.87
Fe_2O_3 (Iron oxide or ferric oxide)	2.50 – 3.10
TiO_2 (Titanium dioxide or titanium oxide)	0.25 – 0.28
CaO (Quick lime or burnt lime or calcium oxide)	0.98 – 1.06
MgO (Magnesia or magnesium oxide)	0.94 – 1.04
Na_2O (Sodium oxide)	2.45 – 2.75
K_2O (Potassium oxide)	2.52 – 2.54

According to ACI 232.1R-00 (2000) and Paiva et al. (2016), the main constituents of the natural or artificial pozzolans are silica and alumina, although the percentage of the constituents can differ according to the type of material and its source. They report typical amounts of different constituents in various pozzolans. The silica content in fly ash, metakaolin, Roman tuff, and diatomite is reported to be approximately 57.5%, 52.17%, 44.7%, and 81.71%, respectively. The alumina content is found to be less than silica, namely 32.9% in fly ash, 44.50% in metakaolin, 18.9% in Roman tuff and 0.56% in diatomite. Calcium oxide in fly ash is 26.3%, 0.01% in metakaolin, 10.3% in Roman tuff and 7.29% in diatomite. Other constituents comprise lower percentages in the material. The ferric oxide constituent varies from 1.2% - 5%, while manganese oxide varies from 0.42% to 6%. The constituents in the natural or artificial pozzolan depend on the type of pozzolan and its origin (ACI 232.1R-00 2000; Feng and Clark 2011; Paiva et al. 2016).

3.2.1.2 Sieve Analysis

Two different types of mixes were prepared, one by adding the natural pozzolan in as-crushed form, and the other with the natural pozzolan passing a No. 200 sieve (74 µm). Sieve analysis was conducted on the natural pozzolan to identify the range of particle sizes for both the as-crushed and sieved materials as it was important to know the particle size distribution of the material used for the study.

Each of the two materials was stored in three airtight containers. The material was taken from the three respective containers in equal portions to obtain uniform samples for the sieve analysis. While sieving, a few clumps of particles were found to be larger in size, and they were crushed before the sieve analysis using the mortar and pestle, to break the clumps into their natural particle sizes. These particles were then mixed with the batch from which the sample was taken for the sieve analysis of the as-crushed sample.

The sieve analysis was performed in the Geotechnical Lab because of the availability of the sieve shaker. As per the standards and the laboratory manual for the soil mechanics course, a minimum of 300 g should be sieved. For this analysis, 400 g of material was sieved for 15 minutes (ASTM C136 2001, CE 328 course notes: Fundamentals of Soil Mechanics 2016).

Table 3.3 presents the results of the sieve analysis for the two forms of pozzolans (as-crushed and passing No. 200 sieve). The results are presented in graphical form in Figure 3.1.

Table 3.3. Results of the sieve analysis for the pozzolan in as-crushed and sieved forms

		As crushed			**Passing # 200 sieve**		
Sieve No.	**Sieve Aperture (mm)**	**Mass retained (g)**	**Percentage retained (%)**		**Mass retained (g)**	**Percentage retained (%)**	
18	1.00	54.5	13.6%	**36.51%**	0.0	0.0%	**1.28%**
20	0.85	8.7	2.2%		0.0	0.0%	
30	0.60	11.1	2.8%		0.0	0.0%	
35	0.50	6.9	1.7%		0.0	0.0%	
40	0.43	3.8	0.9%		0.0	0.0%	
45	0.36	5.4	1.3%		0.0	0.0%	
50	0.30	4.6	1.1%		0.0	0.0%	
60	0.25	5.5	1.4%		0.0	0.0%	
70	0.21	2.6	0.6%		0.0	0.0%	
80	0.18	4.8	1.2%		0.2	0.1%	
100	0.15	4.6	1.1%		0.0	0.0%	
120	0.125	5.7	1.4%		0.5	0.1%	
140	0.104	5.5	1.4%		0.8	0.2%	
170	0.090	8.0	2.0%		1.9	0.5%	
200	0.075	14.4	3.6%		1.7	0.4%	
230	0.063	3.8	0.9%	**63.49%**	22.3	5.58%	**98.73%**
270	0.053	7.2	1.8%		27.8	6.95%	
325	0.044	227.9	56.9%		337.8	84.45%	
400	0.038	13.2	3.3%		2.1	0.52%	
PAN	PAN	2.0	0.5%		4.9	1.22%	
Total		**400.2**	**100.0%**		**400.0**	**100%**	

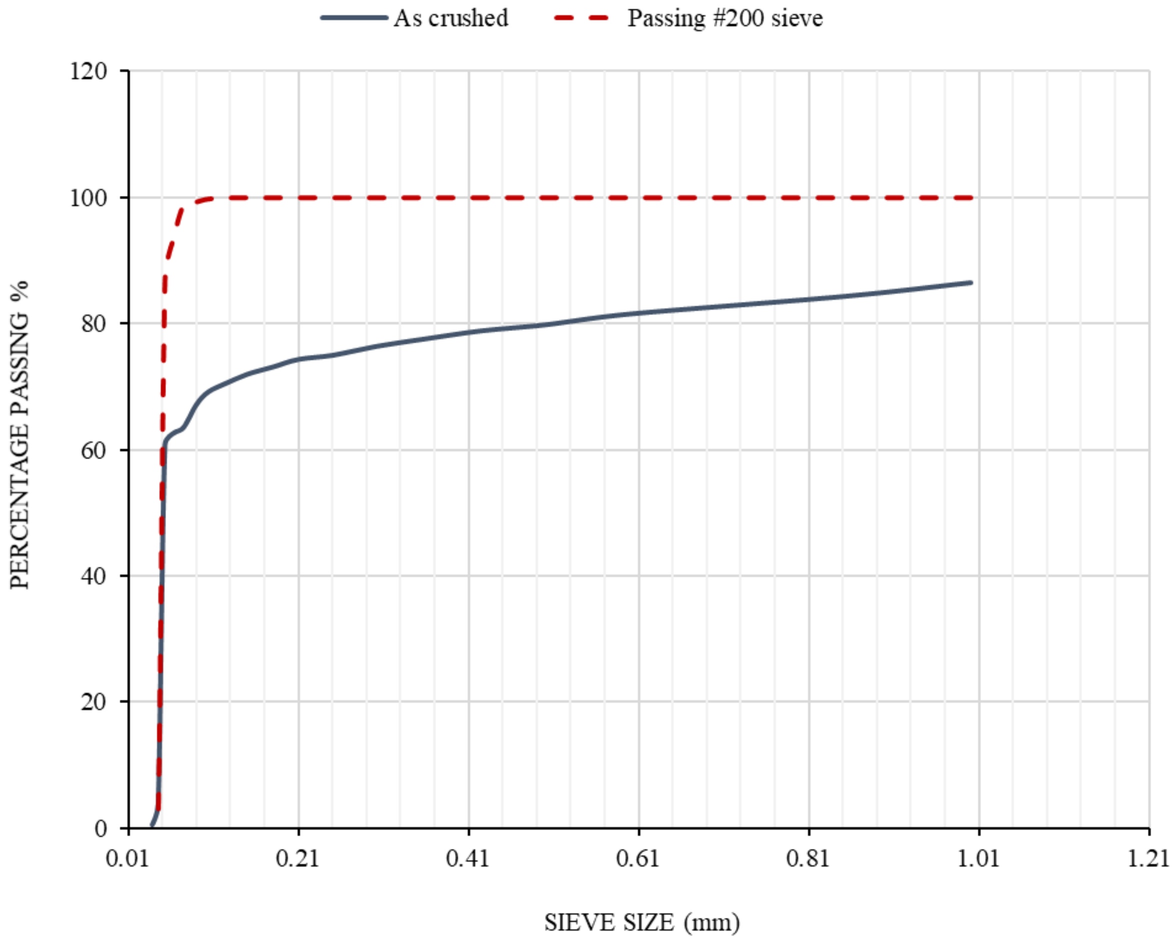

Figure 3.1. Sieve analysis of pozzolan in as-crushed and sieved form (passing No. 200 sieve)

For the pozzolan in as-crushed form, 36.51% of the material was retained on the sieves above No. 200 (74 microns) while 63.49% of the material was retained on the sieves less than 74 microns in size, out of which 89.6% was retained on No. 325 sieve (44 microns). On the other hand, for the pozzolan that was reported to have passed the No. 200 sieve, 98.73 % of the material passed the No. 200 sieve, of which 85.5% was retained on the No. 325 sieve. Thus, the pozzolans consisted of relatively uniform particle size, with approximately 57% of the as-crushed material and 85% of the sieved material having particle sizes between 44 and 53 µm.

The percentage of the material retained on No. 200 and smaller sieves for both as-crushed and sieved forms are presented in Figure 3.2.

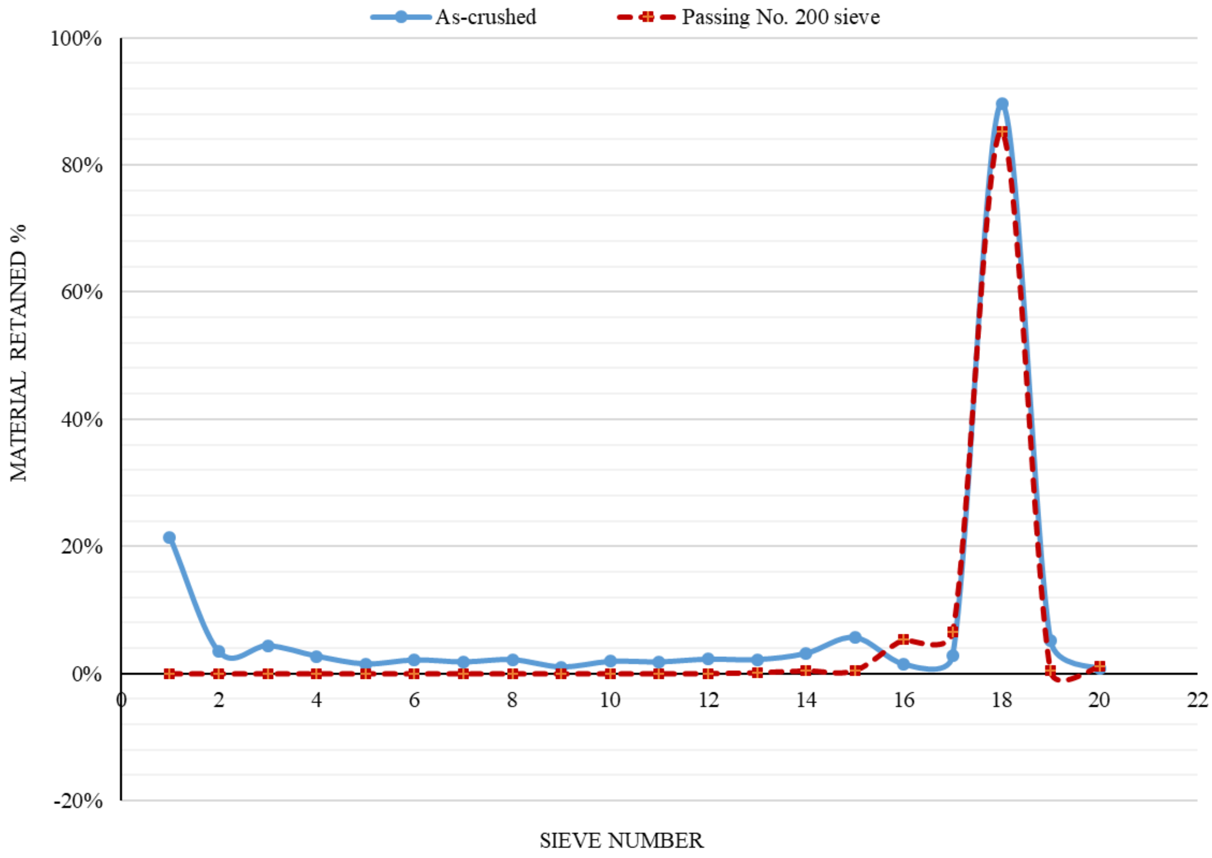

Figure 3.2. Comparison of as-crushed and sieved material on sieves finer than No. 200

3.2.1.3 Scanning Electron Micrographs

Scanning electron micrographs of two forms of the pozzolan were obtained using a JSM-6010LA scanning electron microscope (SEM) manufactured by JEOL USA Inc. The SEM was located in the Microphotography Lab in the Department of Mechanical Engineering and has a resolution of 4 nanometers at 20 kV and a magnification of 5X to 300,000X. It can hold a specimen up to 15 mm in diameter. The microscope generates an image by scanning the surface of the sample with a focused beam of electrons. The beam of the microscope interacts with the atoms in the sample to create signals that contain information on the features of the sample, such as composition and topography. The material features are detected by backscattered electrons and the composition of the sample may be analyzed by an energy dispersive X-ray analyzer (EDS), although an EDS analysis was not performed on the pozzolan. The images for this particular study were used to identify the surface features and texture of the pozzolanic particles. The pozzolan sample was mounted on a specimen holder by putting some of the material on carbon tape and gently shaking off the excess material to leave a thin layer of the pozzolan powder.

Figure 3.3 shows the SEM micrographs of the two forms of the pozzolan. The micrographs show some angular shaped particles and some plate-like particles with sharp corners. These features are characteristic of volcanic tuffs, which generally have glass-like and angular particles (Davis 1950, Cobirzan et al. 2015, Nastaranpoor 2013).

The shape of the particles can influence the workability of concrete; due to the larger surface area of the particles and their irregular shape (angular particles), some inconsistency in the packing of the minerals in concrete may occur when mixed, leading to a reduction in workability (Srinivasreddy et al. 2013). According to Davis (1950) and Tafheem et al. (2011), the low water demand of fly ash is due to its spherical and smooth particles that can pack well in fresh concrete and reduce the frictional resistance of the aggregate and lead to an improved fluidity of the mix. The water demand of concrete with plate-like particles can be compensated by the addition of superplasticizers into the concrete, without adding more water. Furthermore, the water demand of the material depends on its physical and chemical properties and also its origin (Tafheem et al. 2011; Srinivasreddy et al. 2013; Ramezanianpour 2014).

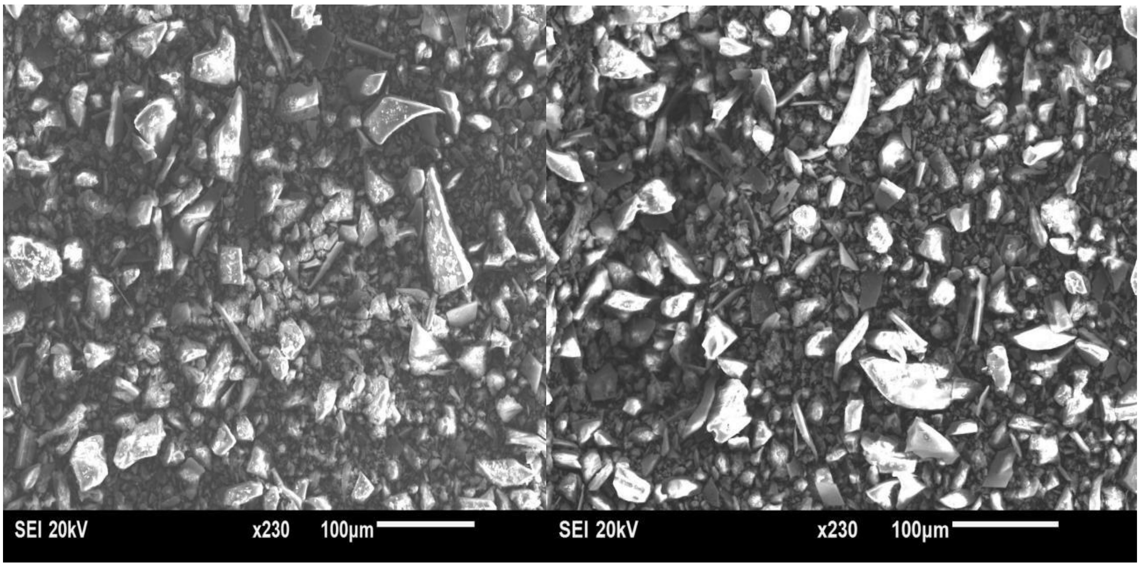

Figure 3.3. Scanning electron micrographs of natural pozzolan in two forms: a) passing a No. 200 sieve, and b) as-crushed

Although not visible in these micrographs, the as-crushed pozzolan had some larger size particles that were also visible to the naked eye, as would be expected based on the sieve analysis.

3.2.2 Aggregates

The fine aggregate (Lafarge, Floral location) consisted of natural sand with most particles smaller than 5 mm (0.2 in.), while coarse aggregates (Lafarge, Floral location) had particles predominantly larger than 5 mm and generally in the 9.5 mm to 20 mm range. All aggregates were prepared to a saturated surface dry condition (SSD) by soaking them in a tub for a day and drying them the next day in accordance with ASTM Standard C128 (2007). Drying was accomplished by spreading a thin layer of each type of aggregate separately on towels and allowing them to dry for a day with a floor fan blowing on them at room temperature. The samples were stirred periodically so that they could dry evenly and a saturated surface-dry condition was confirmed by visual inspection to ensure that no signs of moisture were noticeable to the naked eye (You et al. 2009). The dried material was then used the next day for preparing the mixes.

A sieve analysis was performed on the coarse and fine aggregates at the time that the trial batches were prepared. A sieve analysis is also known as a gradation test and is used for determining the particle sizes of the fine and coarse aggregates. The procedure used for the sieve analysis followed the requirements of ASTM Standard C136 (2014).

Table 3.4 and Figure 3.4 show the sieve analysis for the coarse aggregates.

Table 3.4. Results of sieve analysis for coarse aggregates

Sieve aperture (mm)	Retained wt. (g)	Retained percent %	Cumulative wt. (g)	Cumulative percent %	Pass percentage %
25	0.00	0.00	0.00	0.00	100.00
22.6	0.00	0.00	0.00	0.00	100.00
19	24.40	4.86	24.40	4.86	95.14
16	16.90	3.36	41.30	8.22	91.78
13.35	104.00	20.70	145.30	28.92	71.08
9.51	163.50	32.54	308.80	61.46	38.54
8	75.40	15.01	384.20	76.47	23.53
6.35	81.50	16.22	465.70	92.70	7.30
4.75	35.30	7.03	501.00	99.72	0.28
Pan	1.40	0.28	502.40	100.00	0.00

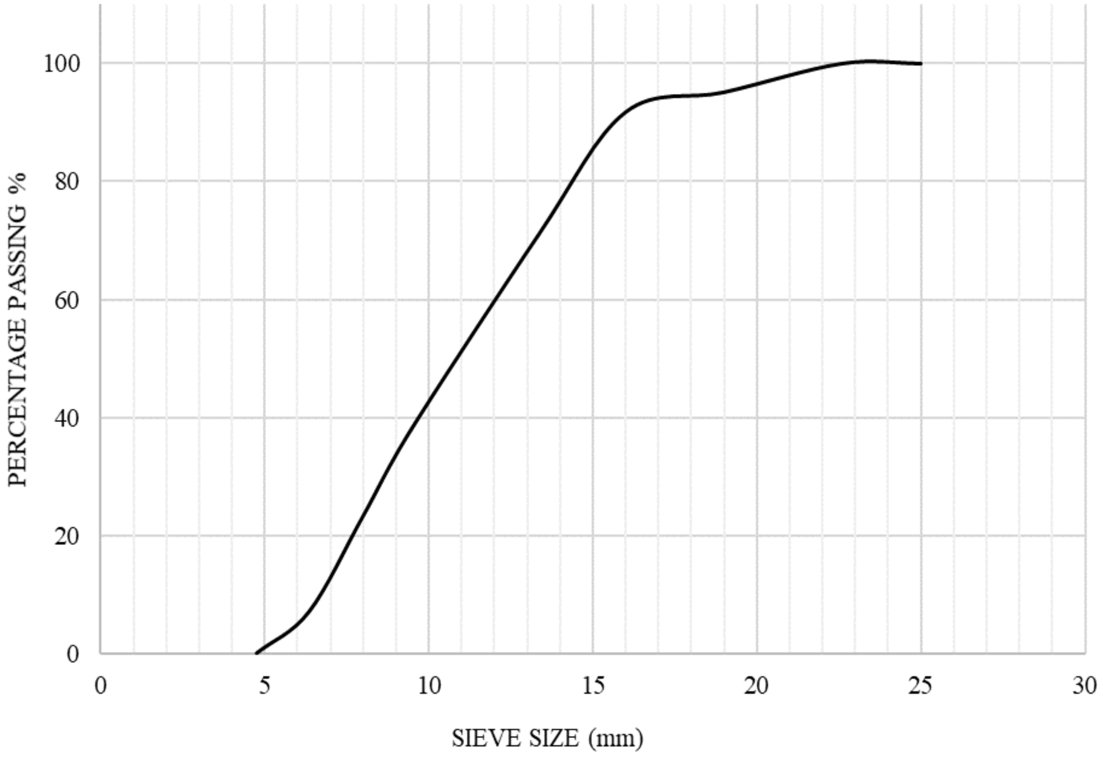

Figure 3.4. Sieve analysis of coarse aggregates

Figure 3.4 Shows that the coarse aggregate was relatively well graded. No material was retained on 25 and 22.6 mm sieves, while 4.86% of the aggregate was retained on the 19 mm sieve. The No. 4 (4.75 mm) sieve and pan retained 7.03% and 0.28% of the material, respectively. Table 3.5 and Figure 3.5 shows the sieve analysis of fine aggregates.

Table 3.5. Results of sieve analysis for fine aggregates

Sieve aperture (mm)	**Retained wt. (g)**	**Retained percent %**	**Cumulative wt. (g)**	**Cumulative percent %**	**Pass percentage %**
9.51	0	0.00	0	0.00	100.00
4.75	2.1	0.42	2.1	0.42	99.58
3.35	2.7	0.54	4.8	0.96	99.04
2.8	2.2	0.44	7	1.40	98.60
2.36	2.6	0.52	9.6	1.92	98.08
2	2.7	0.54	12.3	2.46	97.54
1.7	4.4	0.88	16.7	3.34	96.66
1.41	6.6	1.32	23.3	4.66	95.34
1.18	4.2	0.84	27.5	5.49	94.51
1	8.5	1.70	36	7.19	92.81
0.85	18.9	3.78	54.9	10.97	89.03
0.6	78.6	15.70	133.5	26.67	73.33
0.5	70.9	14.17	204.4	40.84	59.16
0.425	44.9	8.97	249.3	49.81	50.19
0.355	67.6	13.51	316.9	63.32	36.68
0.3	53	10.59	369.9	73.91	26.09
0.25	54.9	10.97	424.8	84.88	15.12
0.21	21.1	4.22	445.9	89.09	10.91
0.18	15.3	3.06	461.2	92.15	7.85
0.15	32.3	6.45	493.5	98.60	1.40
0.075	6.1	1.22	499.6	99.82	0.18
Pan	0.9	0.18	500.5	100.00	0.00

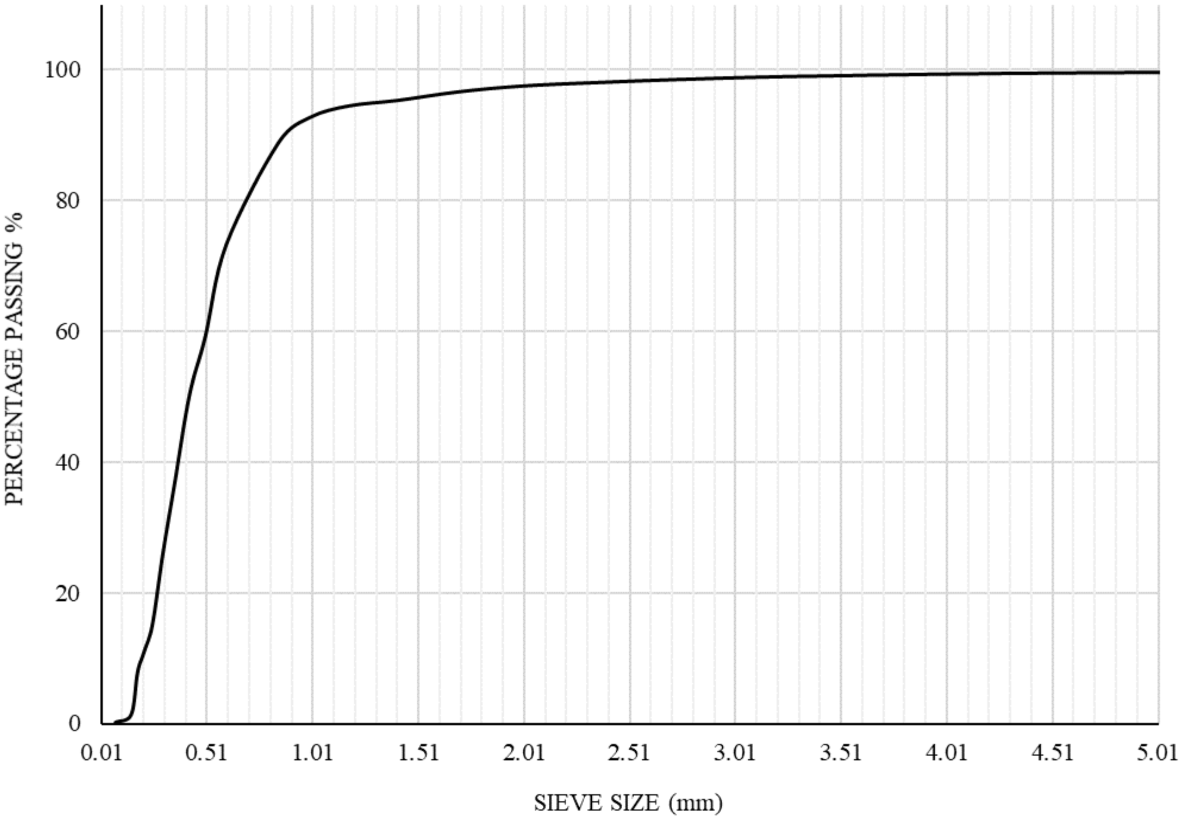

Figure 3.5. Sieve analysis of fine aggregates

For the fine aggregates, no material was retained on the 9.51 mm sieve, while 0.42% material was retained on the No. 4 (4.75 mm) sieve, and 0.84% on the No. 16 (1.18 mm) sieve. The finest sieve used in this analysis was No. 200 (0.075 mm), and only 0.18% of the aggregate passed this sieve.

3.2.3 Admixtures

3.2.3.1 Superplasticizer

Superplasticizers are water reducing agents that improve the workability of the concrete mix. The superplasticizer used for this study was Supercizer 5, High Performance Superplasticizer, manufactured by Fritz-Pak Corporation (Dallas, TX USA). This product was said to be good for a mix that has a low water content and yields durable concrete with reduced permeability. Two different amounts of superplasticizer were used for different mixes in order to obtain the desired workability: the 0%, 10%, and 20% pozzolan mixes contained 0.70% by weight of cement, while the 30% pozzolan mix used 0.85% by weight of cement. The 30% pozzolan mix was a stiff mix, and the required slump was not reached using 0.70% superplasticizer, so the amount of superplasticizer was increased. Trial batches were prepared to determine the required superplasticizer amount.

3.2.3.2 Air-entraining admixture

Air entrainment agents are widely used in concrete mixes in colder regions to improve the resistance to freeze and thaw damage. The air-entraining agent used for this study was Air Plus, Air Entraining Admixture, manufactured by Fritz-Pak Corporation (Mesquite, TX USA). The amount used for this study was 0.04% relative to the mass of cement. This product was a compatible admixture that did not contain nitrates or calcium chloride. As was done for the superplasticizer, trial mixes were prepared to select the required amount of the admixture.

3.2.4 Water and W/C ratio (water requirement)

Regular tap water from the Structures Lab was used to prepare the mixes. Water/cement ratio is the major factor that determines the strength of concrete. The water/cement ratio used for this study was 0.34. This relatively low water/cement ratio was adopted because it results in a higher long term strength, which is particularly useful for structures like bridge decks.

3.3 Mix Design

The concrete mix proportions that were adopted for the study are shown in Table 3.6. In addition to a control mix that did not contain any pozzolan, pozzolan in three different cement replacement amounts (10%, 20% and 30% by mass) and two different forms (as-crushed and passing # 200 sieve) was used. A water cementitious materials ratio of 0.34 was adopted for all the mixes.

The mix design was intended to correspond to a high-quality concrete for a bridge deck application.

Table 3.6. Mix proportions

Material	Quantity (kg/m^3)
Gravel (saturated surface dry condition)	1074
Sand (saturated surface dry condition)	706
Cement + Pozzolan	439
▪ 0% replacement	439.0 + 0.0
▪ 10% replacement	395.1 + 43.9
▪ 20% replacement	351.2 + 87.8
▪ 30% replacement	307.3 + 131.7
Water (water/cement ratio (w/c = 0.34))	151
Superplasticizer	3.12 – 3.73
Air entrainment admixture	0.17

3.4 Mixing and Curing Procedures

3.4.1 Mixing

Firstly, the aggregates were prepared to a saturated surface dry (SSD) condition, as the materials available in the Structures Lab were quite dry. This was necessary to avoid the increased water demand of the materials for the consistent workability of the mix. All the materials were weighed prior to mixing. Before commencing the mixing process, the molds in which samples were to be cast were oiled with Rich-Cote form release oil, a product of Acrow-Richmond (Toronto, ON). A traditional drum mixer available in the Structures Lab (Model C9-CE, with 9 cu. ft. drum capacity, Monarch Industries, Winnipeg, Manitoba) was used for mixing the ingredients.

A portion of the aggregates was added first, followed by a portion of water, then a portion of cement. The mix was allowed to mix for less than a minute before adding the pozzolan, a little at a time to avoid the formation of lumps of the material that can be created when adding fine material. The admixtures (superplasticizer and air entrainment agent, both in powder form) were then added. The material was allowed to mix for another minute before adding the remaining materials in the same order. Mixing was done for approximately 5 - 10 minutes, depending on the consistency of the paste, and the mixing was continued until a homogeneous mix was obtained. The mix was then checked for workability by performing a slump test, also the air content was measured.

3.4.2 Slump

The workability of the mix was measured using a standard slump test, described in ASTM C143 (2015). The amount of superplasticizer used for each batch of the mix and their measured slumps are shown in Table 3.7.

Table 3.7. Slump and amount of superplasticizer for all batches

Pozzolan amount	**Superplasticizer (kg/m^3)**	**Slump (mm)**	
		As crushed	**Passing #200 sieve**
0%	3.12	80	80
10%	3.12	90	95
20%	3.12	85	90
30%	3.73	92	98

It is evident that the slump was relatively consistent for all mixes, ranging from 80 to 98 mm. Unlike fly ash, which has more spherical particles and can make a mix more workable (less stiff), the angular and plate-like shape of the pozzolan did not appear to have a significant effect on the workability.

3.4.3 Air content

The air content of several of the mixes was measured while the mix was in the plastic state using the pressure method (ASTM C 231, 2017). Table 3.8 shows the measured air content of fresh concrete, along with the air content measured on hardened samples, as described below.

Table 3.8. Air content measured on fresh and hardened concrete samples (%)

Pozzolan Replacement Amount	Fresh air content of pozzolan		Hardened air content of pozzolan	
	As crushed	Passing No. 200 sieve	As crushed	Passing No. 200 sieve
0 %	5.5 ± 0.05	5.5 ± 0.05	5.32	5.32
10 %	5.5 ± 0.05	5.5 ± 0.05	5.19	5.70
20 %	--	--	5.74	5.54
30 %	5.8 ± 0.05	5.8 ± 0.05	--	--

Air content of 0%, 10%, and 30% samples was checked at the time of mixing the batches. However, this was not done for the 20% batches, and therefore the air content was measured on the hardened samples using microscopic analysis. This analysis was performed by a summer undergraduate research assistant following the linear traverse method according to ASTM C457-16 (2016). Results, as reported by Ji (2017), are also presented in Table 3.8. As can be seen, air contents measured by the two methods were similar for measurements made on the same batches. It can be seen that the air contents for all batches were very consistent, the values ranging from 5.2 % to 5.8 %.

3.4.4 Specimen Preparation

After the slump and air content testing, the samples were cast into cylindrical molds in three consecutive layers. Each layer was rodded 25 times, and the surfaces of the specimen were finished. After casting, a plastic sheet was used to cover the samples to avoid excessive evaporation of water. The samples were allowed to cure for 24 hours before demolding. They were then immersed in lime saturated water for curing (Figure 3.6.) until they reached the desired age of testing. The permeability and compressive strength specimens were cast together in different sizes of molds, 50 mm diameter x 100 mm long cylindrical specimens for the permeability tests, and 200 mm long x 100 mm in diameter cylindrical specimen for compressive strength tests. Permeability specimens were also used to test the hardened concrete air content.

Figure 3.6. Curing of samples in lime-saturated water

3.5 Compressive Strength Testing

The cylindrical specimens for the compressive strength tests were 200 mm long x 100 mm in diameter. They were cast in plastic molds, as it is a non-absorbent material. As mentioned above, they were removed from molds one day after casting and placed in a lime-saturated water bath. The samples were left in the curing room to cure in the water bath until they were ready for testing, i.e., at 7 days, 28 days, 56 days, 112 days, 182 days and 364 days.

At the age of maturity, the cured samples were taken out of the water bath, and the samples were allowed to dry for 5 to 6 hours. The specimens were then capped with sulfur before compression testing. After capping, the samples were placed between the top and bottom bearing plates in the compression testing machine and were loaded in axial compression until failure. A UTM –HYD compression testing machine (Model 600DX-B1-C3-G1A INSTRON, Grove City, PA USA) with a frame capacity of 600 kN was used. As per ASTM C39/C39M, the load was applied at a rate of 0.25 ± 0.05 MPa/s.

The compressive strength of the sample was calculated as the ratio of maximum load reached during the test to the cross-sectional area of the sample. Five samples were tested at each age, except for 56 days and 364 days, at which 15 samples were tested for more reliable results. Procedures for the compression tests followed ASTM Standard C39/C39M- 17b (2017).

3.6 Permeability Testing

3.6.1 Overview

A centrifuge technique was used to measure the hydraulic conductivity or permeability of saturated concrete samples following the method described by Ramadani (2013). The method is based on applying a rotational speed to a concrete specimen to force water to flow through the specimen. The centrifuge techniques were initially used to measure the permeability of soils, and the method was lately introduced as a standard (ASTM D6527, 2008) to measure the permeability of porous materials (Phung et al. 2013).

The permeability of the concrete mix was determined by measuring the amount of water that passed through the specimens over a 24 hour period and was collected in the permeability bucket. The coefficient of saturated hydraulic conductivity was then calculated using Darcy’s equation, presented later which is a function of the specimen dimensions, properties of water, applied pressure and rate of flow. The centrifuge technique was adopted because it was less time consuming than other alternatives.

3.6.2 Centrifuge machine

The centrifuge (J6-Hc, Beckman Coulter) consisted of a rotor attached to six swing buckets with their corresponding soil sample holders, as shown in Figure 3.7.

Figure 3.7. Centrifuge machine

When the centrifuge begins to spin, the buckets swing out horizontally, forcing the water to pass through the samples. Table 3.9 shows the specifications of the centrifuge machine.

Table 3.9. Specifications of centrifuge machine

Specifications	Comments
Model	J6-HC Centrifuge-Beckman Coulter
Rotor	JS - 4.2 Swinging Bucket
Operative arm radius range (cm)	19 - 25.4
Angular velocity range (RPM)	50 - 6000

The centrifuge can run at angular velocities ranging from 50 to 6000 RPM, but an angular velocity of 2900 RPM was used for the set of tests described here. The centrifuge machine stops if it reaches a temperature higher than 40°C, and overheating of the machine was observed at a speed of 3000 RPM. Therefore, the samples were tested with the lower velocity, which proved effective over the full test length of 24 hours.

3.6.3 Specimen preparation

The centrifuge machine had sample holders, which are generally used for soil samples (see Figure 3.8.), so special holders were designed and manufactured for concrete samples by Engineering Shops. The sample holders used for the study were identical to those used by Ramadani (2013), but additional holders had to be manufactured so that a total of six were available. The concrete sample holders were designed to fit into the soil sample holders, as seen in Figure 3.8 and Figure 3.9.

As shown in Figure 3.10, the concrete sample holders were made from aluminum and included an acrylic lid that could be threaded into the aluminum tube and sealed with a rubber O-ring. The lid contained graduations that could be used to monitor the decrease in water level. Figure 3.11 shows a schematic section through the concrete sample holder, identifying the dimensions used for calculations.

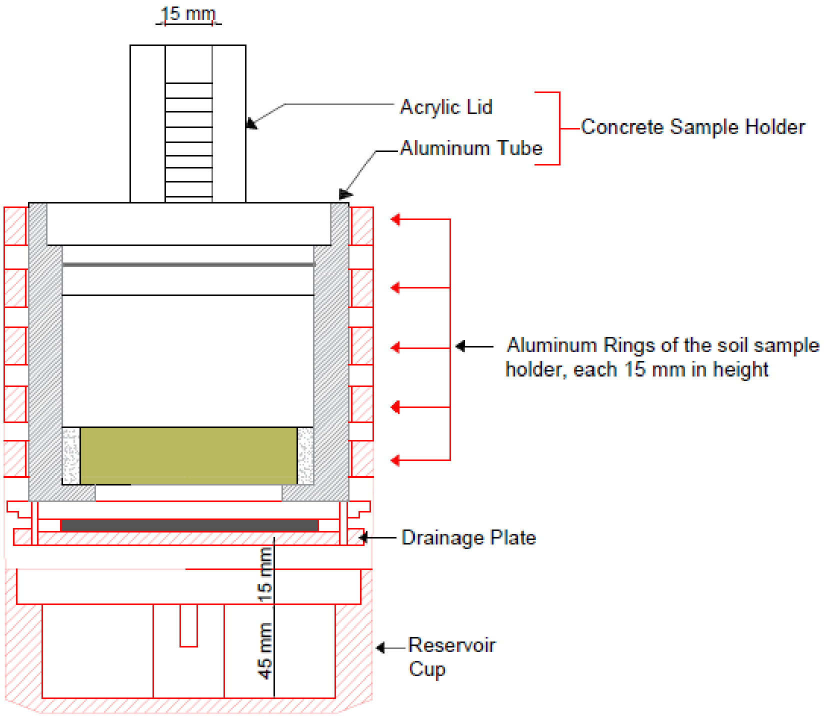

Figure 3.8. Schematic section of sample holder for soil, with additional concrete sample holder shown inside

Figure 3.9. Soil sample holder with concrete sample holder inside

Figure 3.10. Sample holder for concrete

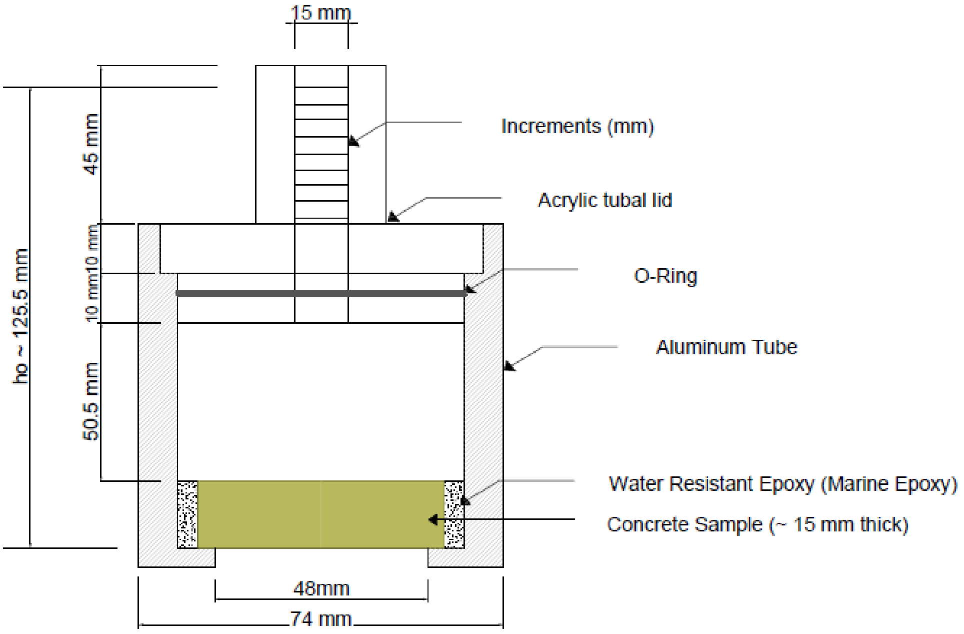

Figure 3.11. Schematic section through a concrete sample holder

The cylindrical specimens 50 mm in diameter and 100 mm long were cast for the permeability tests. Near the time of the testing, the samples were removed from the water bath and cut into disks 50 mm in diameter x 15 mm in thickness with a concrete cutter. Six samples of each type were tested at the age of 442 days. The selection of six samples was based on the capacity of the centrifuge. Also, for comparison, the 30% pozzolan samples were also tested at one year of age, in order to determine whether ongoing pozzolanic reaction affected the permeability over one year of age.

3.6.4 Testing Procedure

After cutting the disks, each sample was saturated by immersing it in lime saturated water for 24 hours. The sample was then sealed in the sample holder using Lepage marine epoxy around the circumference of the sample to prevent leakage of water. Lepage marine epoxy is a two-part system that consists of a hardener and an epoxy resin. The syringe dispenses equal amounts of each component. Before sealing the sample, the holder was cleaned by air pressure so that there were no dust particles in it to hinder adhesion of the epoxy. The holder was then kept on a flat surface, and the concrete disk was placed in the centre of the holder. Various trials were done to coat the disk effectively by epoxy, and finally, a syringe and a needle were used to coat the epoxy around the sample. The epoxy was slowly applied to avoid the formation of air bubbles.

After applying the epoxy, the samples were left to dry at room temperature for 8-12 hours, as directed by the manufacturer’s instructions for the marine epoxy. Once the epoxy had dried, the samples were immersed entirely, along with the sample holders, in water for 72 hours to ensure complete saturation. After that, the samples were taken out of the water, and the sample holder was filled with water to the highest point of graduation. It was confirmed that there were no air bubbles in the holders so that there would be no disturbance in the water flow while testing. The initial height of water was recorded, and the top was covered with plastic wrap to avoid any water loss from the top surface. The concrete sample holders were then placed into the soil sample holders, and each bucket assembly was individually weighed. To maintain the balance of the swinging buckets, sample holders with similar weights were placed opposite to each other in the centrifuge for testing.

After starting the centrifuge, an initial check was made after four hours, at which time the centrifuge was stopped, and the height of the water was recorded. The samples were checked again after twelve hours, while the third and fourth checks were made at four hour intervals. The total test period was 24 hours. The checking process took approximately 1-2 minutes each time, and the additional time was taken into account when calculating permeability. The water loss was used to calculate permeability. If the holder was emptied in the first four hours of testing, it meant that the concrete disk contained cracks or other flaws or that the epoxy seal was imperfect. Such samples were thrown away, and new samples were tested. The complete period for conducting the test was 24 hours, based on the test procedures described by Ramadani (2013, p. 63).

3.6.5 Calculation of Saturated Permeability

The saturated permeability of samples was measured at the age of 442 days, except that an additional permeability measurement was made for 30% pozzolan specimens at one year of age.

The coefficient of saturated hydraulic conductivity was calculated using Darcy’s equation (Ramadani 2013; Liu et al. 2016):

$$q = -K_s A\left(\frac{dh}{dl}\right) \tag{3.1}$$

where:

q = Volumetric discharge rate (m^2/s),

K_s = coefficient of permeability or saturated hydraulic conductivity (m/s),

A = cross-sectional area (m^2),

dh/dl = hydraulic gradient,

h = hydraulic head created by centrifugal force (m),

l = length of flow path (m),

The equation was used in a modified form that accounted for the test setup as follows (Ramadani 2013):

$$k_s = \frac{1}{N}\frac{aL}{At}\ln\frac{h_0}{h_t} \tag{3.2}$$

where a is cross-sectional area of the graduated water tube in the acrylic lid [m^2];

L is the thickness of the specimen parallel to the direction of flow [m];

A is the cross-sectional area of the specimen [m^2];

t is the time of the flow [s];

h_0 is the initial height of the water relative to the bottom surface of the specimen [m]; and

h_t is the final height of the water at time t [m].

The centrifuge scale factor, N, is calculated by:

$$N = \frac{a_r}{g} \tag{3.3}$$

where a_r is the acceleration experienced by the sample, and g is gravitational acceleration (m/s^2).

The acceleration experienced by the specimen is calculated by:

$$a_r = \omega_r^2 R_{cen} \tag{3.4}$$

where ω_r is the applied rotational speed [rad/s^2] and R_{cen} is the centrifuge operating radius, measured to mid-thickness of the sample.

The values for the variables that were used in Eqs. 3.2 to 3.4 for the calculation of the saturated permeability are listed in Table 3.10, along with their estimated precisions. The precision calculations are provided in Appendix B.

Table 3.10. Values for variables used for calculation of saturated permeability

Variable	Value and precision
Rotational speed (RPM)	2900 ± 100 rpm
Rotational speed (rad/s)	304 ± 10.5 rad/s
R_{cen} (m)	0.19 ± 0.005 m
a (m^2)	0.000177 ± 0.01 mm^2
A (m^2)	0.001963 ± 3 mm^2
t (sec)	86400 ± 60 sec
h_0 (m)	0.1255 ± 0.5 mm
h_t (m)	Varied, 0.1215 to 0.1245 ± 0.5 mm
L (m)	Varied, approx. 0.015 ± 0.02 mm

The precision of the measured coefficient of saturated hydraulic conductivity was calculated using the standard propagation of error techniques, assuming that all variables were independent.

This method is based on the calculation of the variance (σ_f^2) of a derived value $f(x_i)$, using the variance of the n variables (x_i) from which the derived value is obtained:

$$\sigma_f^2 = \sqrt{\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}\right)^2 \sigma_i^2} \tag{3.5}$$

For these calculations, it was assumed that the precision of measured variables corresponded to the 90% confidence limits for the particular variable so that the variances of measured variables could be estimated. Detailed calculations are provided in Appendix A, and the precision measurements are shown in Appendix B.

3.7 Data analysis

The detection of the outliers was done with compressive strength and permeability results. An outlier is a value or data point that differs from the other data points present in the whole population of specimens, suggesting that it is not a member of the same population. In statistical analysis, the outliers can be taken as experimental errors in the measurements. These outliers were omitted from the data set, as they can result in significant unwanted changes in the results. Both physical and statistical outliers were noted in some of the data sets. Physical outliers were detected by the shape or condition of the sample (e.g., honeycombing was noted for some samples) or by anomalies observed during testing. All data sets were also analyzed for statistical outliers. The outliers for this study were investigated using Grubb’s test, also known as the extreme studentized deviate (ESD). More details are provided in Appendix C of this thesis.

The statistical comparison of mean compressive strengths and coefficients of permeability at the 90% confidence limit was analyzed using a 2-sided Student’s t-test. For each comparison, two different distributions of compressive strength values and their standard deviations were taken into consideration. A pooled variance was used for these comparisons, as it has been found to be more consistent than using separate variances. The statistical comparison of the mean coefficients of permeability followed the same procedure. The detailed statistical comparisons for mean compressive strength results are provided in Appendix D, and the statistical comparison of the mean coefficients of permeability can be seen in Appendix E.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter focuses on the results of the experiments performed for evaluating the natural pozzolan. The results of the compression strength tests are presented first, followed by comparisons of the various materials and a discussion of the effect of the pozzolan in as-crushed and sieved forms. The results of permeability tests are then presented, along with a comparison of the permeabilities of the two different materials (as-crushed and passing No. 200 sieve) with different pozzolan replacement rates. Lastly, a discussion of the effect of the pozzolans on permeability is presented.

4.2 Compressive strength

The compressive strengths of all the different batches are listed in Table 4.1. Also listed in the table are the coefficients of variation, which indicate the variability of measured compressive strength. A graphical presentation of the results is provided in Figure 4.1.

The measured compressive strengths for individual samples are found in Appendix C. A statistical comparison of mean compressive strengths at the 90% confidence limit was performed using a 2-sided Student’s t-test; the detailed analysis is shown in Appendix D of this thesis.

Table 4.1. Mean compressive strength of each group of specimens at all test ages (MPa)

Pozzolan amount[1] & type[2]	7 days (5)[6]	28 days (5)	56 days (15)	112 days (5)	182 days (5)	364 days (15)
0%	38.6 *(2.0)*[3]	50.3 *(2.6)*[4,5]	46.9 *(6.1)*	47.0 *(15.5)*[4]	51.1 *(9.6)*[4]	54.6 *(8.2)*
10% (ac)	35.9 *(5.4)*	40.0 *(9.3)*	44.1 *(4.4)*	45.9 *(4.9)*	49.4 *(4.4)*	54.2 *(5.6)*
10% (-200)	38.2 *(6.9)*	39.7 *(5.9)*	47.4 *(6.4)*	48.9 *(8.3)*	48.5 *(6.5)*	55.2 *(5.1)*[4,5]
20% (ac)	30.1 *(8.0)*	34.1 *(2.5)*[4]	35.1 *(6.6)*	38.8 *(10.7)*	39.3 *(4.8)*	44.8 *(9.4)*
20% (-200)	33.7 *(7.6)*	37.4 *(4.4)*	42.9 *(6.3)*	46.0 *(8.9)*[4]	46.4 *(14.4)*[4]	52.1 *(9.7)*
30% (ac)	32.0 *(19.4)*	39.2 *(1.0)*[4,5]	36.4 *(8.9)*[4]	39.8 *(16.2)*	34.7 *(20.7)*	48.1 *(3.8)*[4]
30% (-200)	35.0 *(4.7)*	38.9 *(6.2)*	39.3 *(7.7)*	46.2 *(6.8)*	43.8 *(12.7)*	50.3 *(5.1)*

1. Percentage of total cementitious materials by weight
2. ac = as crushed; -200 = passing #200 sieve
3. The italicized values shown in parentheses are the coefficients of variation in percent
4. Indicates that a physical outlier was removed, the tests failed. See the details in Appendix C.
5. Indicates that a statistical outlier was removed, the test failed. See the details in Appendix C.
6. The bracketed values indicates the number of samples tested at the given age.

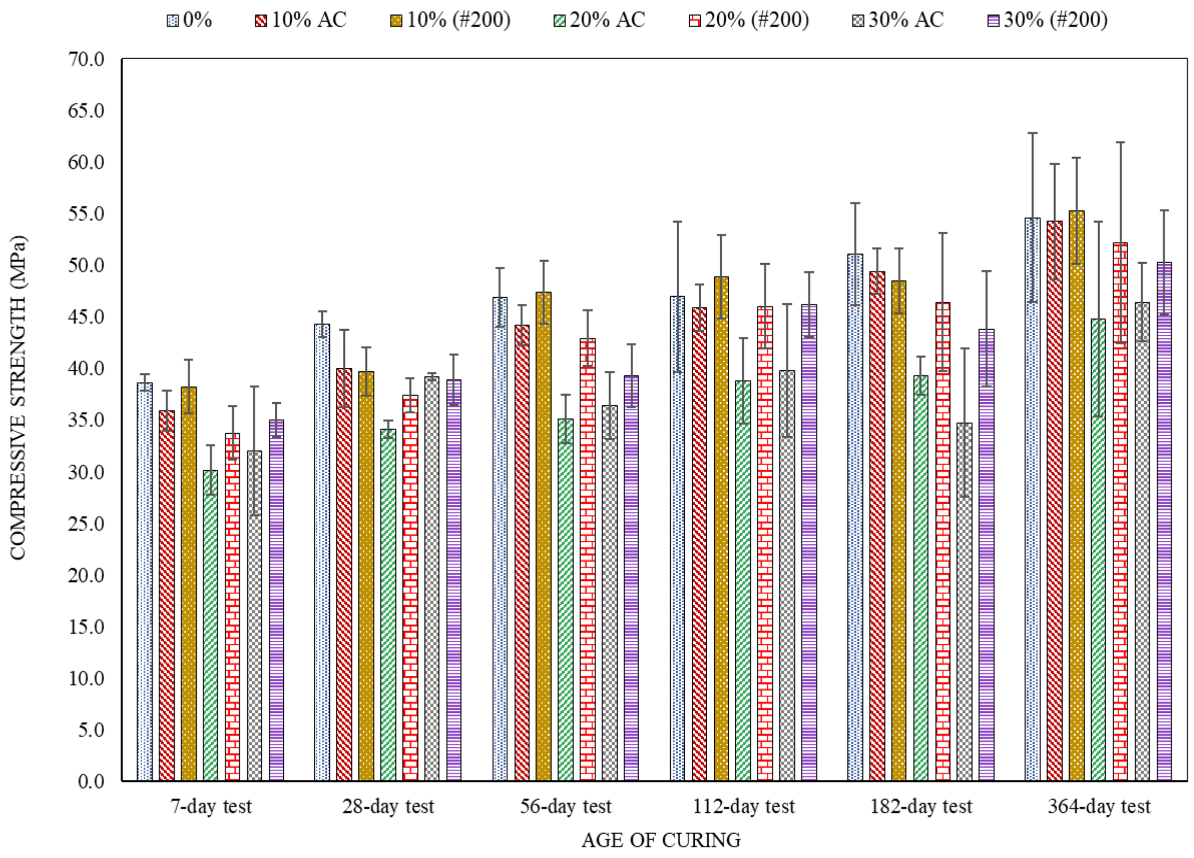

Figure 4.1. Variation in compressive strength with age (ac= as crushed, #200 = passing #200 sieve). The error bars here indicate the standard deviation of measurements.

Despite some apparent inconsistencies in the measured data (e.g., the high strength of the control mix at 28 days and some lower values at 182 days), some trends are observed. First, at earlier ages (up to 56 days), with two exceptions, the compressive strengths of all mixes differed significantly from that of the control mix. The two exceptions were the 10% pozzolan -200 samples at 7 and 56 days, which did not differ from the control group at a 90% level of confidence. At later ages (112 days and later), the 20% as-crushed batch and the two 30% batches at 182 days and 364 days differed significantly from the control group, but the other batches did not. Thus, replacing 10 or 20% of the cement with the natural pozzolan appears to slow the strength development, but does not have a significant effect on the compressive strengths developed in the long term (i.e., higher than six months), except if the maximum particle size is not controlled at the 20% replacement rate.

The 30% as-crushed and passing No. 200 sieve batches differed significantly from the control group at all ages except at 112 days. However, the mixes with the pozzolan continued to gain strength over the entire testing period, with the strength gains for the pozzolan mixes between 182 days and 364 days all being statistically significant. This differs from the control mix, which did not show statistically significant strength development at later ages. This confirms that the pozzolanic reaction occurs over a more extended period, allowing the hardened cement paste to densify and generate increased strength.

A comparison of the compressive strengths of the samples prepared with the pozzolan in as-crushed form and with particle sizes below 74 µm (see Appendix D) shows that at the 10% replacement rate, there was generally no significant difference between the two, while at the 20% replacement rate, the samples prepared with the pozzolan in as-crushed form were significantly weaker than those prepared with particle sizes below 74 µm. A similar trend was observed for the 30% samples, for which the as-crushed mix had a lower compressive strength than the blend that incorporated pozzolan passing the No. 200 sieve. Thus, limiting the maximum particle size to 74 µm appears to be essential to ensure that compressive strength is not compromised at the 20% and 30% replacement rate.

It should be recalled that the data for 56 and 364 day compressive strengths are considered more reliable since a larger number of samples were tested at these ages. The statistical comparisons of the mixes show that at early ages, up to and including 56 days, the compressive strengths of all mixes except the 10% -200 blends were significantly lower than the control mix. At later ages (1 year), both 10% mixes and the 20% -200 mix had strengths that were not significantly different from that of the control group. At the 10% replacement rate, the particle size made a statistically significant difference at 56 days but not at one year. On the other hand, at the 20% and 30% replacement rates the particle size made a significant difference at both 56 days and one year.

In general, both the as-crushed and -200 batches showed a decrease in strength with an increase in the pozzolanic content. Comparing the batches with pozzolan passing the No. 200 sieve at one year of age, the mean compressive strengths of the 10% and 20% batches were 1% higher and 5% lower than that of the control mix, respectively (although the differences were not statistically significant) while the mean strength of the 30% batch was 9% lower than that of the control batch.

The decrease in compressive strength with increasing pozzolan amount can be explained, in part, by recalling that the pozzolanic reaction occurs between the silica present in pozzolan and the calcium hydroxide in the hardened cement paste to produce additional C-S-H (Taylor 2008; Bustos et al. 2012). As increasing amounts of pozzolan are added, the amount of portland cement decreases, resulting in lower amounts of the hydration products (hardened cement paste) and therefore lower strength. The amount of additional CSH produced from the pozzolanic reaction is limited by the calcium hydroxide available in the hardened cement paste, and calcium hydroxide is also present in smaller amounts as the amount of pozzolan increases. At the 10% replacement rate, the additional CSH produced from the pozzolanic reaction is sufficient to make up for the reduction in the amount of CSH produced by the hydration reactions. At higher replacement amounts, however, the reduction in hydration products combined with smaller amounts of pozzolanic reaction products (CSH) leads to an overall reduction in strength (Dustan 2011; Osei and Jackson 2012; Setina et al. 2013).

4.3 Permeability

The mean values for the coefficient of permeability of all samples tested are listed in Table 4.2 and presented graphically in Figure 4.2. Coefficients of variability are also listed in the table, and error bars in the graph correspond to one standard deviation from the mean. Also, the table contains the precision of the measured values, which corresponds to the 90% confidence limits. The measured permeability for individual samples is found in Appendix A, while the precision of the measured permeability is calculated in Appendix B. The statistical comparison calculations of the measured permeability are in Appendix E.

Table 4.2. Mean coefficients of permeability at curing age of 442 days

Pozzolan amount1 & type	Coefficient of permeability (m/s x 10^{-13})	Precision (±m/s) (m/s x 10^{-13})
0%	1.51 *(31)*[2]	0.54
10% (as crushed)	0.99 *(35.3)*	0.51
10% (passing #200 sieve)	0.75 *(17.9)*	0.50
20% (as crushed)	1.76 *(13.3)*	0.56
20% (passing #200 sieve)	1.35 *(38.3)*	0.54
30% (as crushed)	2.34 *(16.1)*	0.60
30% (passing #200 sieve)	2.10 *(0.78)*	0.58

1. Percentage of total cementitious materials by weight.
2. The values shown in parentheses are the coefficients of variation in percent.

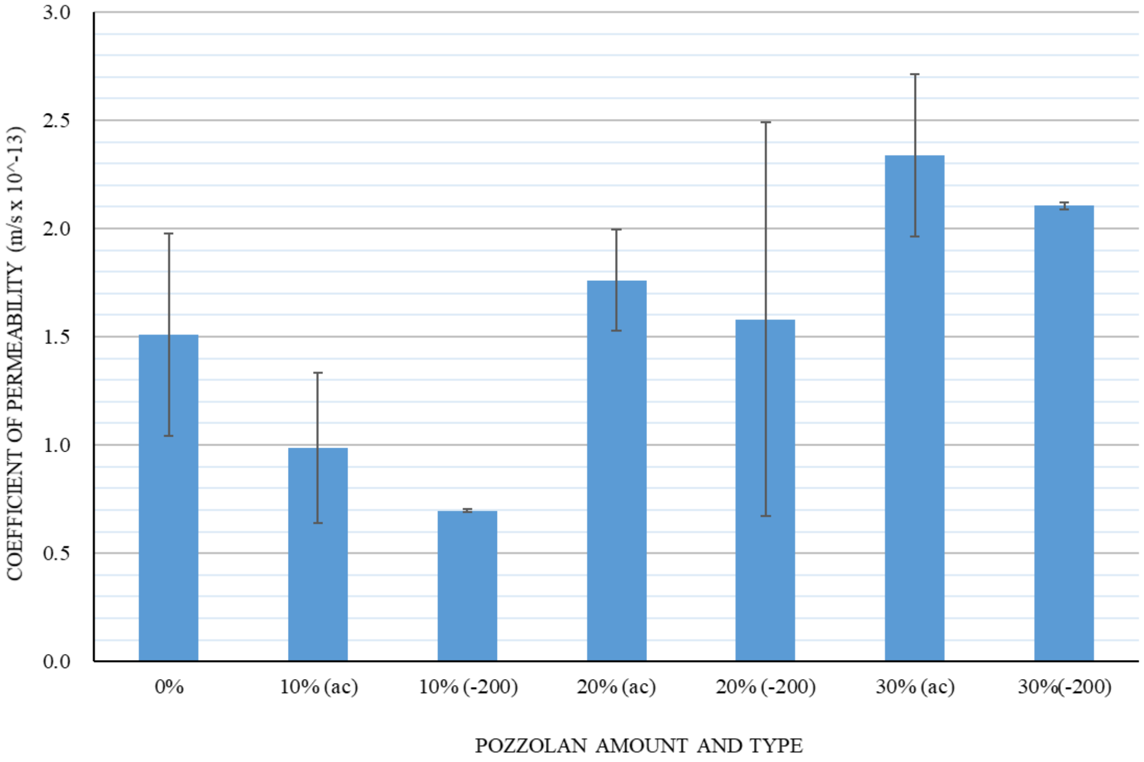

Figure 4.2. Coefficient of permeability as measured at 442 days. The error bars here indicate the standard deviation of measurements.

The concrete used for this study was a relatively high-quality mix, with low permeability. As a result, very little water passed through any of the samples over a 24-hour period, producing measured values for permeability lying close to the margin of error for the tests, as shown in Table 4.2. Despite this, some differences are apparent among the samples. Both of the mixes prepared at the 10% pozzolan replacement rate had permeabilities that were significantly lower than that of the control mix at the 90% level of confidence. At this replacement rate, the reductions in permeability were 35% and 54% for the as-crushed and -200 mixes, respectively. The two 10% mixes did not differ significantly from each other at the 90% level of confidence, although the 10% -200 mix did produce the lowest mean coefficient of permeability of all the mixes studied, 29% lower than that of the 10% as-crushed mix. The permeability of samples prepared at the 20% replacement rate did not differ significantly from that of the control mix or from each other, although the mean value for the 20% -200 mix was 5% higher than that of the control mix and 10% lower than the 20% as-crushed mix, while that of the 20% as-crushed mix was 17% higher than the control mix.

The permeability of samples prepared at the 30% replacement rate did not differ significantly from each other, but they did differ significantly from that of the control mix. The permeability of the as-crushed mix was 55% higher than that of the control mix, while that with material passing the No. 200 sieve was 39% higher. The natural pozzolan, therefore, appears to be effective at reducing the permeability of the concrete at the 10% replacement rate and is most effective when the maximum particle size is limited. It is noted that there are quite large differences among the standard deviations of the different groups of samples. This is likely because very little loss of water was observed and the increments with which water loss was measured were not much smaller than the total water lost. Therefore, in some cases, the small differences in water loss were sufficient to exceed a measurement increment, producing a large standard deviation, while for other groups, the small differences were not large enough to exceed an increment, producing a small standard deviation.

Table 4.3, shows the coefficient of permeability for the 30% pozzolan samples at two different ages (364 days and 442 days). Graphical representation of the results is shown in Figure 4.3. The results show that the measured permeabilities at the two ages were virtually identical. If any pozzolanic reaction occurred over that 2.5-month period, it did not affect the permeability.

Table 4.3. Mean coefficient of permeability of 30% pozzolan batch at ages of 364 and 442 days

Pozzolan amount[1] & type	Coefficient of permeability (m/s x 10^{-13})	
	364 days	442 days
30% (as crushed)	2.35 *(15.2)*[2]	2.34 *(16.1)*
30% (passing #200 sieve)	2.12 *(0.56)*	2.10 *(0.78)*

1. Percentage of total cementitious materials by weight

2. The values in parentheses are the coefficients of variation in percent

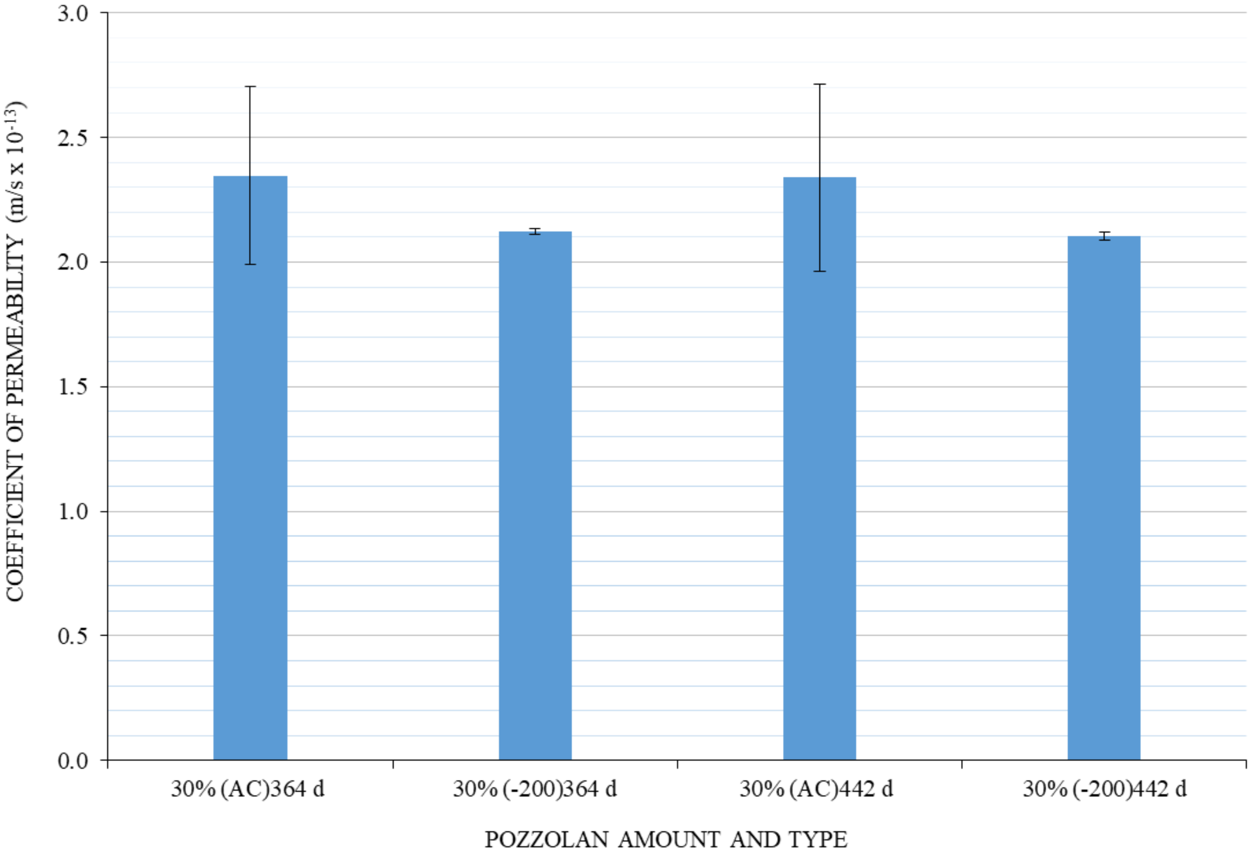

Figure 4.3. Variation in coefficient of permeability for 30% pozzolan batch at ages of 364 and 442 days. The error bars here indicate the standard deviation of measurements.

4.4 Discussion

At the 10% replacement rate, the pozzolan is quite effective. The compressive strength was found to be similar to that of the control mix, and a significant reduction in permeability was observed as compared to the control mix.

On the other hand, the performance at the 30% replacement rate was significantly worse. The compressive strength at the 30% replacement rate in both pozzolan forms was lower than that of the control mix and the other two replacements rate (10% and 20%). The strength of the 30% as-crushed mix was also lower than that prepared with pozzolan passing No. 200 sieve. The permeability of the two mixes prepared at the 30% replacement rate was higher than that of the control mix, as well as the other two mixes (10% and 20%).

Although not all of the differences were statistically significant, the pozzolan was generally found to be more effective when the maximum particle size was limited. Smaller particles have more surface area for the pozzolan to react with calcium hydroxide in the cement paste, leading to a more complete reaction and denser material. This is reflected in both the higher compressive strengths and lower permeabilities of the concrete containing natural pozzolans at the smaller particle size.

These results suggest that the addition of pozzolan in finer form (i.e., with particle sizes smaller than 74 µm) could be more effective, as the pozzolanic reaction would be quicker and more complete. This could produce a denser paste to improve the strength of concrete and further reduce the permeability, leading to a durable concrete mix (ACI 211.2-98 1998; ACI 232.1R-00 2000).

For the permeability tests, very little water passed through the samples, producing measured values for permeability lying close to the margin of error for the tests. It was observed, however, that the natural pozzolan was effective at reducing the permeability of the concrete at the 10% replacement rate, and was particularly useful when the maximum particle size of the pozzolan was limited to 74 µm. This suggests that the benefits of the natural pozzolan, in terms of its ability to reduce permeability, may become more pronounced if a lower quality concrete is used.

According to Mehta (1981), the replacement of portland cement with santorin earth at 10, 20 and 30% rates resulted in gradual strength development and reduced permeability over a year period. The 10% and 20% replacement amounts showed similar strength development to the control mix, while the 30% amount showed lower compressive strength. These results are similar to the results presented in this thesis, where the 10% replacement amounts in both forms and the 20% in sieved form showed similar strength development to the control batch, while all the other batches, i.e., 20% as-crushed and 30% replacement (both forms) showed lower compressive strengths in comparison to the control batch. Mehta (1981) also states that the water permeability of the concrete decreased with an increase in the amount of pozzolan for all the batches. In his work, the permeability of the concrete with 10% and 20% replacement in both forms showed significant decrease in permeability from control batch and did not differ from each other, while 30% batch (both forms) showed lower permeability from all the other batches (0%, 10%, and 20%), but did not significantly differ from each other. Similar patterns have been reported in the literature for the natural pozzolans (Mehta 1981; Mehta and Gjorv 1982; Nili and Salehi 2010; Kaid et al. 2015). This differs from the results of the current work, in which permeability decreased with the addition of 10% pozzolan, but increased as the amount of pozzolan increased.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary and Conclusions

The effectiveness of a natural pozzolan from volcanic deposits in southern Saskatchewan was investigated for use as a partial replacement for portland cement in concrete. Two different forms of the pozzolan were investigated, namely as-crushed in a ball mill to separate it into its natural particle sizes and passing a No. 200 sieve. Concrete with four different cement replacement amounts (0%, 10%, 20% and 30% by weight) were tested to measure compressive strength at ages ranging from seven days to one year and saturated permeability at an age of approximately 15 months using a centrifuge technique. A relatively low water/cementitious materials ratio of 0.34 was used, and superplasticizer was required to achieve adequate workability, with slump varying from 80 mm – 98 mm for all batches. The same superplasticizer amount was adequate to achieve the desired workability for all the mixes except the 30% pozzolan batch, for which a higher amount (0.85% by weight of cement) of superplasticizer was required to achieve a workable mix.

Replacing 10% or 20% of the cement with the natural pozzolan slowed the strength development, but did not have a significant effect on the compressive strengths developed in the long term (i.e., greater than six months), except when the maximum particle size was not controlled. Replacing 30% of the cement with the natural pozzolan produced long-term strengths that were 15% and 8% lower than the control batch for as-crushed and sieved pozzolan, respectively. At earlier ages (up to 56 days), only the samples prepared with 10% pozzolan in sieved form kept pace with the compressive strength of the control batch.

The permeability of all samples tested was relatively low, with measured values lying close to the margin of error for the tests, such that differences among the various groups of specimens were not as apparent as might have been the case if a concrete mix with a higher permeability had been used. Nonetheless, the tests showed that replacing 10% of the cement with the natural pozzolan significantly reduced the permeability, by 34% and 50% for the pozzolan in as-crushed and sieved forms, respectively. The 20% replacement rate did not result in a statistically significant difference in permeability from each other or from the control mix, while the 30% replacement rate showed a significantly higher permeability than the control mix, by 55% and 39% for the pozzolan in as-crushed and sieved forms, respectively.

Considering the effect of the particle size of the natural pozzolan, very little difference was observed between the compressive strengths of samples prepared with as-crushed and sieved pozzolan at the 10% replacement rate. At the 20% and 30% replacement rates, the samples prepared with the as-crushed pozzolan had compressive strengths that were statistically lower than those prepared with the pozzolan that had been sieved to a maximum particle size of 74 µm. Thus, not limiting the maximum particle size negatively impacted the compressive strength at the 20% and 30% pozzolan replacement rates. Samples prepared with particle sizes smaller than 74 µm had mean coefficients of permeability that were 24%, 23%, and 10% lower for the 10%, 20% and 30% replacement rates, respectively, compared to their companion specimens prepared with the as-crushed pozzolan.

Based on the compression and permeability tests conducted using concrete samples prepared with 10%, 20% and 30% pozzolan replacement of cement by mass, in both as-crushed form and with a maximum size of 74 mm, the natural pozzolan from sources in southern Saskatchewan was found to be effective as a cement replacement.

5.2 Future Recommendations

1. More experiments should be done to evaluate the natural pozzolan procured from Southern Saskatchewan for analyzing the heat of hydration in the mix and its effects on various water/cement ratios.

2. The mix design for this study was intended to correspond to a high-quality concrete for a bridge deck application, but different mix designs could be adopted for a lower-quality concrete for applications such as sidewalks or residential basements.

3. The use of some natural pozzolans has been shown to prevent excessive expansion due to alkali-silica reaction. The pozzolans from southern Saskatchewan should be tested for this application.

4. Apart from a sieve analysis, individual particle size distributions could also be measured using laser diffraction based particle size analyzer.

5. Tests to identify the physical and chemical composition of the natural pozzolan could be performed and compared to similar replacement materials such as fly ash, metakaolin, etc.

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APPENDIX A

CALCULATION OF SATURATED PERMEABILITY

The permeability measurements and calculations for all the mix variations (i.e., control mix (0%), 10%, 20%, and 30% replacement amounts) are presented in this appendix.

The coefficient of saturated hydraulic conductivity (also referred to as permeability) was calculated using the following equation (Ramadani 2013):

$$k_s = \frac{1}{N}\frac{aL}{At}\ln\frac{h_0}{h_t} \tag{A.1}$$

where a is cross-sectional area of the graduated water tube in the acrylic lid [m^2];

L is the thickness of the specimen parallel to the direction of flow [m];

A is the cross-sectional area of the specimen [m^2];

t is the time of the flow [s];

h_0 is the initial height of the water relative to the bottom surface of the specimen [m]; and

h_t is the final height of the water at time t [m].

The centrifuge scale factor, N, is calculated by:

$$N = \frac{a_r}{g} \tag{A.2}$$

where a_r is the acceleration experienced by the sample, and

g is gravitational acceleration (9.8 m/s ^{2}).

The acceleration experienced by the specimen is calculated by:

$$a_r = \omega_r^2 R_{cen} \tag{A.3}$$

where ω_r is the applied rotational speed [rad/s^2]; and

R_{cen} is the centrifuge operating radius, measured to mid-thickness of the sample [m].

The values for the variables that were used in Equation (A.1) for the calculation of the saturated permeability are listed in Table A.1 along with their estimated precision.

Table A.1. Values for variables used for calculation of saturated permeability

Variable	Value and precision
Rotational speed (RPM)	2900 ± 100 rpm
Rotational speed (rad/s)	304 ± 10.5 rad/s
R_{cen} (m)	0.19 ± 0.005 m
a (m^2)	0.000177 ± 0.01 mm^2
A (m^2)	0.001963 ± 3 mm^2
t (sec)	86400 ± 60 sec
h_0 (m)	0.1255 ± 0.5 mm
h_t (m)	Varied, 0.1215 to 0.1245 ± 0.5 mm
L (m)	Varied, approx. 0.015 ± 0.02 mm

The results of permeability calculations for all of the samples from each material are presented in Tables A.1 through A.10. Six samples per batch were tested for more reliable results. All the materials were tested at a curing age of 442 days, and 30% replacement was tested at 364 days and 442 days for comparison. Results are presented in graphical form in Figure A.1 through A.9.

Table A.2. Results of permeability calculations for the control mix (0% pozzolan) at 442 days

Pozzolan variations	**Rot. Speed Rad/sec**	a_r **(m/s^2)**	N	L **(m)**	Δh **(m)**	h_t **(m)**	k_s **(m/s) x 10^{-13}**
0% (1)	303.7	17523	1786	0.0148	0.002	0.1235	1.387
0% (2)	303.7	17523	1786	0.0149	0.002	0.1235	1.396
0% (3)	303.7	17523	1786	0.01452	0.003	0.1225	2.049
0% (4)	303.7	17523	1786	0.0150	0.003	0.1225	2.116
0% (5)	303.7	17523	1786	0.0152	0.0015	0.124	1.066
0% (6)	303.7	17523	1786	0.0150	0.0015	0.124	1.052
			Mean				1.511
			Standard Deviation				0.468
			Coefficient of Variation				31.0%

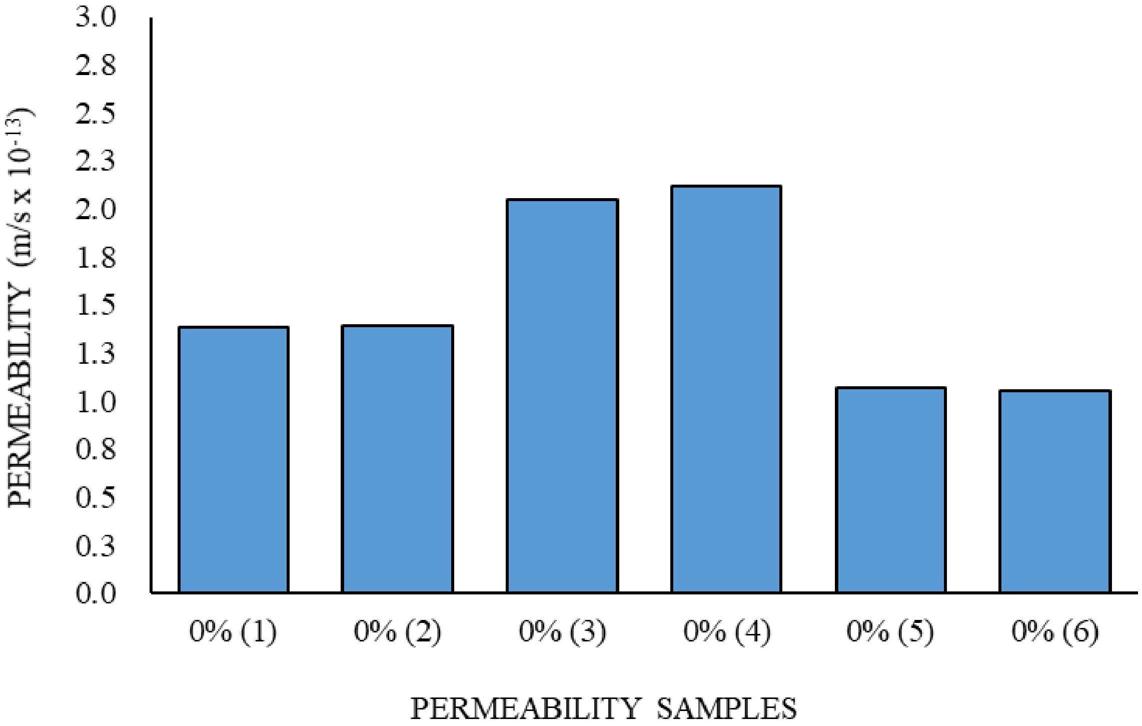

Figure A.1. Graphical representation of permeability of control mix (0% pozzolan) at 442 days

Table A.3. Results of permeability of 10% as-crushed pozzolan at 442 days

Pozzolan variations	**Rot. Speed Rad/sec**	a_r **(m/s^2)**	N	L **(m)**	Δh **(m)**	h_t **(m)**	k_s **(m/s) x 10^{-13}**
10% AC (1)	303.7	17523	1786	0.0150	0.002	0.1235	1.405
10% AC (2)	303.7	17523	1786	0.0149	0.002	0.1235	1.396
10% AC (3)	303.7	17523	1786	0.0148	0.001	0.1245	0.690
10% AC (4)	303.7	17523	1786	0.0148	0.001	0.1245	0.690
10% AC (5)	303.7	17523	1786	0.0149	0.001	0.1245	0.695
10% AC (6)	303.7	17523	1786	0.01481	0.0015	0.124	1.038
			Mean				0.986
			Standard Deviation				0.348
			Coefficient of Variation				35.30%

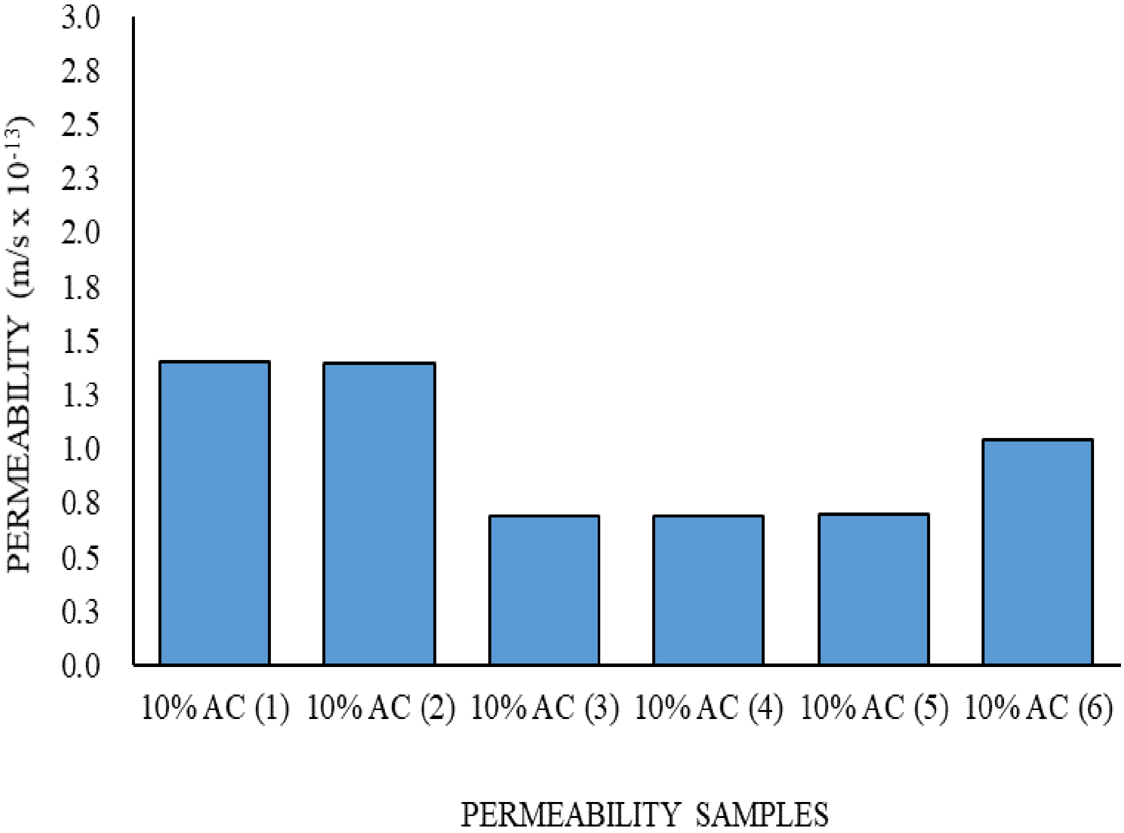

Figure A.2. Graphical representation of permeability of 10% as-crushed pozzolan at 442 days

Table A.4. Results of permeability of 10% passing no. 200 sieve pozzolan at 442 days

Pozzolan variations	**Rot. Speed Rad/sec**	a_r **(m/s²)**	N	L **(m)**	Δh **(m)**	h_t **(m)**	k_s **(m/s) x 10⁻¹³**
10% #200 (1)	303.7	17523	1786	0.0148	0.001	0.1245	0.690
10% #200 (2)	303.7	17523	1786	0.01474	0.001	0.1245	0.688
10% #200 (3)	303.7	17523	1786	0.0150	0.001	0.1245	0.700
10% #200 (4)	303.7	17523	1786	0.01462	0.0015	0.124	**1.025 (Stat. outlier*)**
10% #200 (5)	303.7	17523	1786	0.0152	0.001	0.1245	0.709
10% #200 (6)	303.7	17523	1786	0.01492	0.001	0.1245	0.696
			Mean				0.697
			Standard Deviation				0.008
			Coefficient of Variation				1.2%

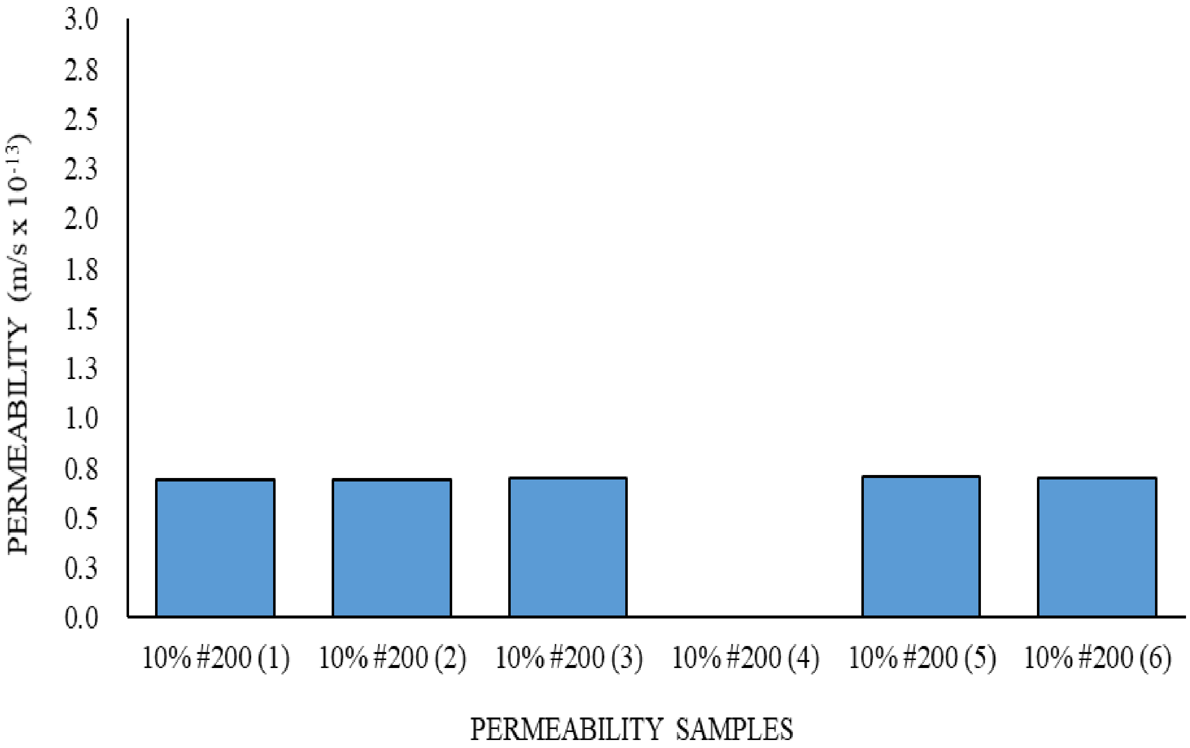

Figure A.3. Graphical representation of permeability of 10% passing No. 200 sieve pozzolan at 442 days

Table A.5. Results of permeability of 20% as-crushed pozzolan at 442 days

Pozzolan variations	**Rot. Speed Rad/sec**	a_r **(m/s^2)**	N	L **(m)**	Δh **(m)**	h_t **(m)**	k_s **(m/s) x 10^{-13}**
20% AC (1)	303.7	17523	1786	0.0150	0.0025	0.123	1.760
20% AC (2)	303.7	17523	1786	0.0151	0.0025	0.123	1.772
20% AC (3)	303.7	17523	1786	0.0150	0.003	0.1225	2.116
20% AC (4)	303.7	17523	1786	0.0150	0.0025	0.123	1.760
20% AC (5)	303.7	17523	1786	0.0152	0.0025	0.123	1.784
20% AC (6)	303.7	17523	1786	0.0147	0.002	0.1235	1.377
			Mean				1.762
			Standard Deviation				0.234
			Coefficient of Variation				13.30%

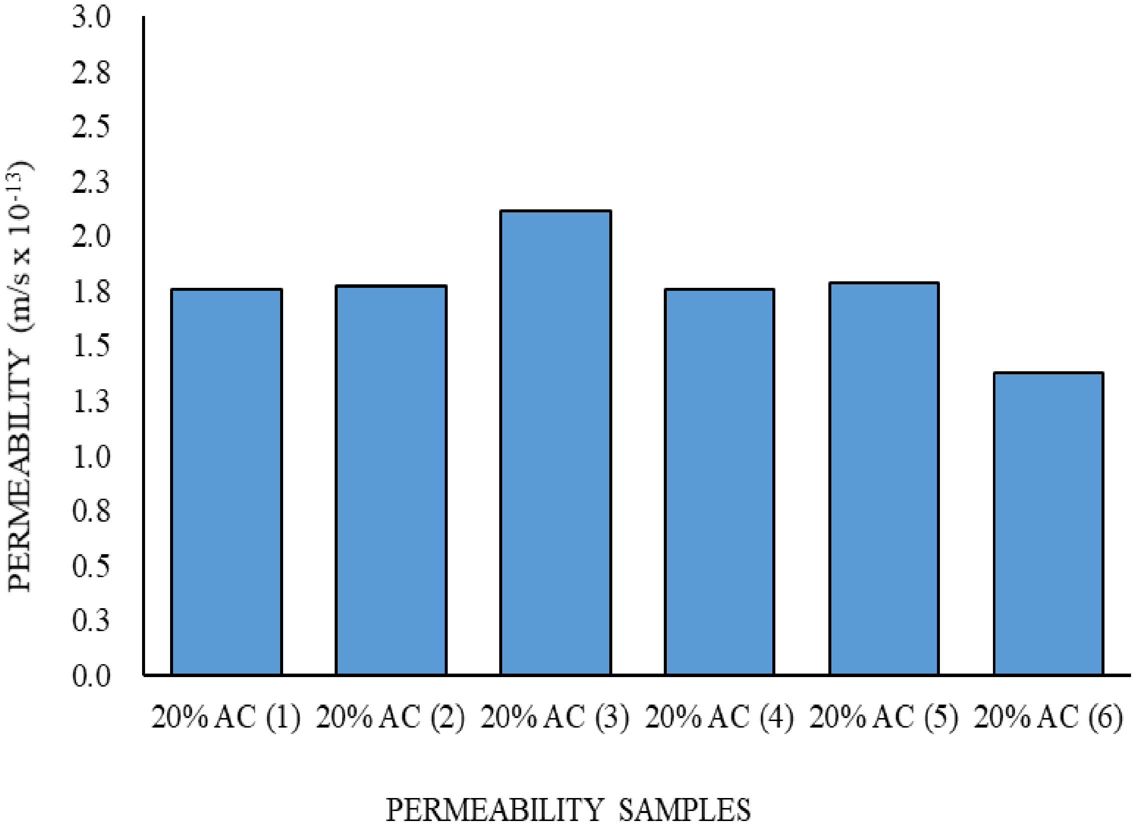

Figure A.4. Graphical representation of permeability of 20% as-crushed pozzolan at 442 days

Table A.6. Results of permeability of 20% passing no. 200 sieve pozzolan at 442 days

Pozzolan variations	**Rot. Speed Rad/sec**	a_r **(m/s^2)**	N	L **(m)**	Δh **(m)**	h_t **(m)**	k_s **(m/s) x 10^{-13}**
20% #200 (1)	303.7	17523	1786	0.0153	0.0025	0.123	1.795
20% #200 (2)	303.7	17523	1786	0.0148	0.0025	0.123	1.737
20% #200 (3)	303.7	17523	1786	0.01482	0.0025	0.123	1.739
20% #200 (4)	303.7	17523	1786	0.01494	0.002	0.1235	1.400
20% #200 (5)	303.7	17523	1786	0.0150	0.001	0.1245	0.700
20% #200 (6)	303.7	17523	1786	0.0153	0.001	0.1245	0.714
			Mean				1.347
			Standard Deviation				0.516
			Coefficient of Variation				38.26%

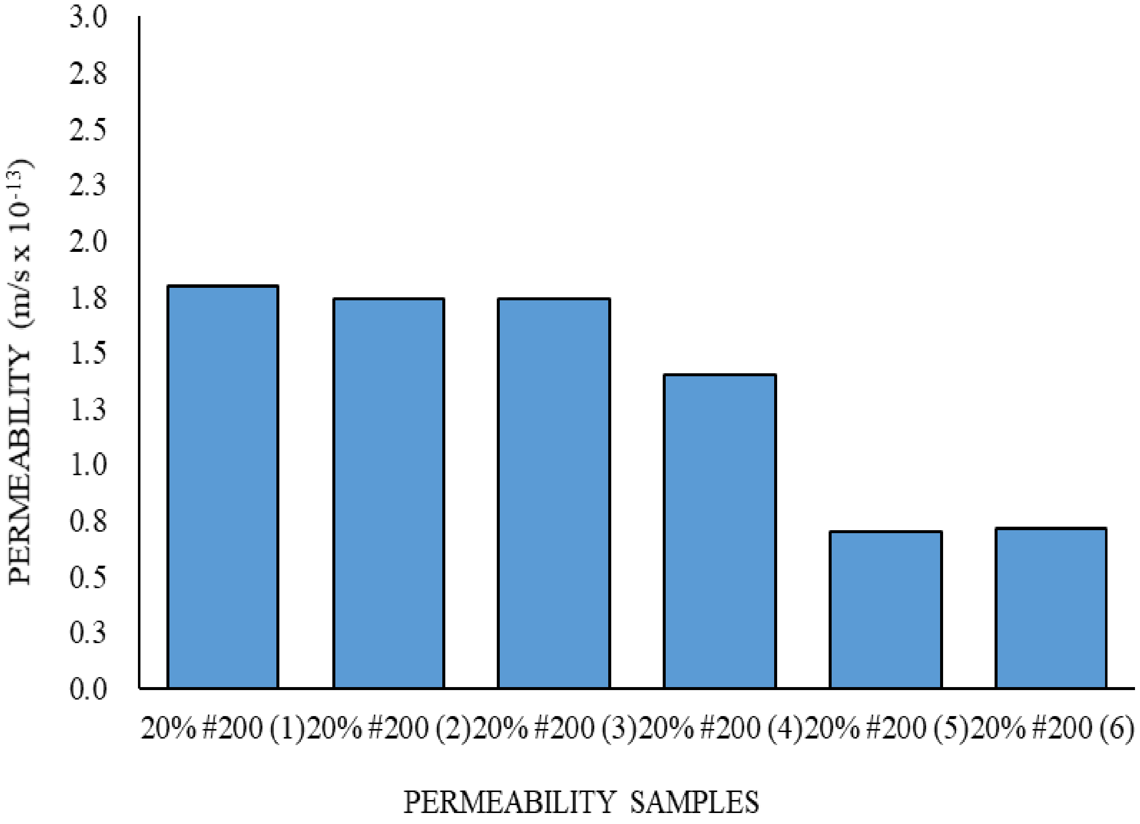

Figure A.5. Graphical representation of permeability of 20% passing No. 200 sieve pozzolan at 442 days

Table A.7. Results of permeability of 30% as-crushed pozzolan at 364 days

Pozzolan variations	**Rot. Speed Rad/sec**	a_r **(m/s^2)**	***N***	***L*** **(m)**	**Δ*h*** **(m)**	h_t **(m)**	k_s **(m/s) x 10^{-13}**
30% AC (1)	303.7	17523	1786	0.0149	0.004	0.1215	2.815
30% AC (2)	303.7	17523	1786	0.0148	0.004	0.1215	2.796
30% AC (3)	303.7	17523	1786	0.0145	0.003	0.1225	2.046
30% AC (4)	303.7	17523	1786	0.0151	0.003	0.1225	2.131
30% AC (5)	303.7	17523	1786	0.0153	0.003	0.1225	2.159
30% AC (6)	303.7	17523	1786	0.0151	0.003	0.1225	2.131
			Mean				2.346
			Standard Deviation				0.358
			Coefficient of Variation				15.25%

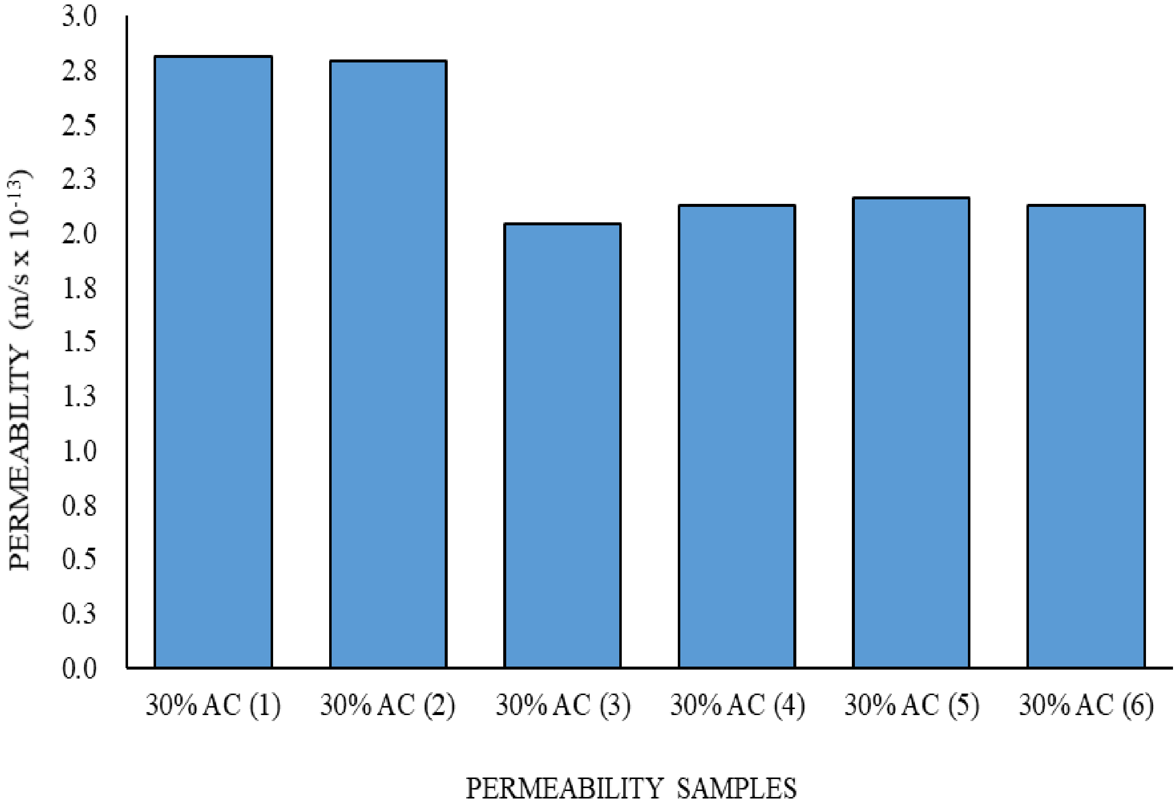

Figure A.6. Graphical representation of permeability of 30% as-crushed pozzolan at 364 days

Table A.8. Results of permeability of 30% passing No. 200 sieve pozzolan at 364 days

Pozzolan variations	**Rot. Speed Rad/sec**	a_r **(m/s^2)**	N	L **(m)**	Δh **(m)**	h_t **(m)**	k_s **(m/s) x 10^{-13}**
30% #200 (1)	303.7	17523	1786	0.0151	0.003	0.1225	2.131
30% #200 (2)	303.7	17523	1786	0.0150	0.003	0.1225	2.116
30% #200 (3)	303.7	17523	1786	0.0152	0.003	0.1225	2.145
30% #200 (4)	303.7	17523	1786	0.0150	0.003	0.1225	2.116
30% #200 (5)	303.7	17523	1786	0.0150	0.003	0.1225	2.116
30% #200 (6)	303.7	17523	1786	0.0150	0.003	0.1225	2.116
			Mean				2.123
			Standard Deviation				0.012
			Coefficient of Variation				0.56%

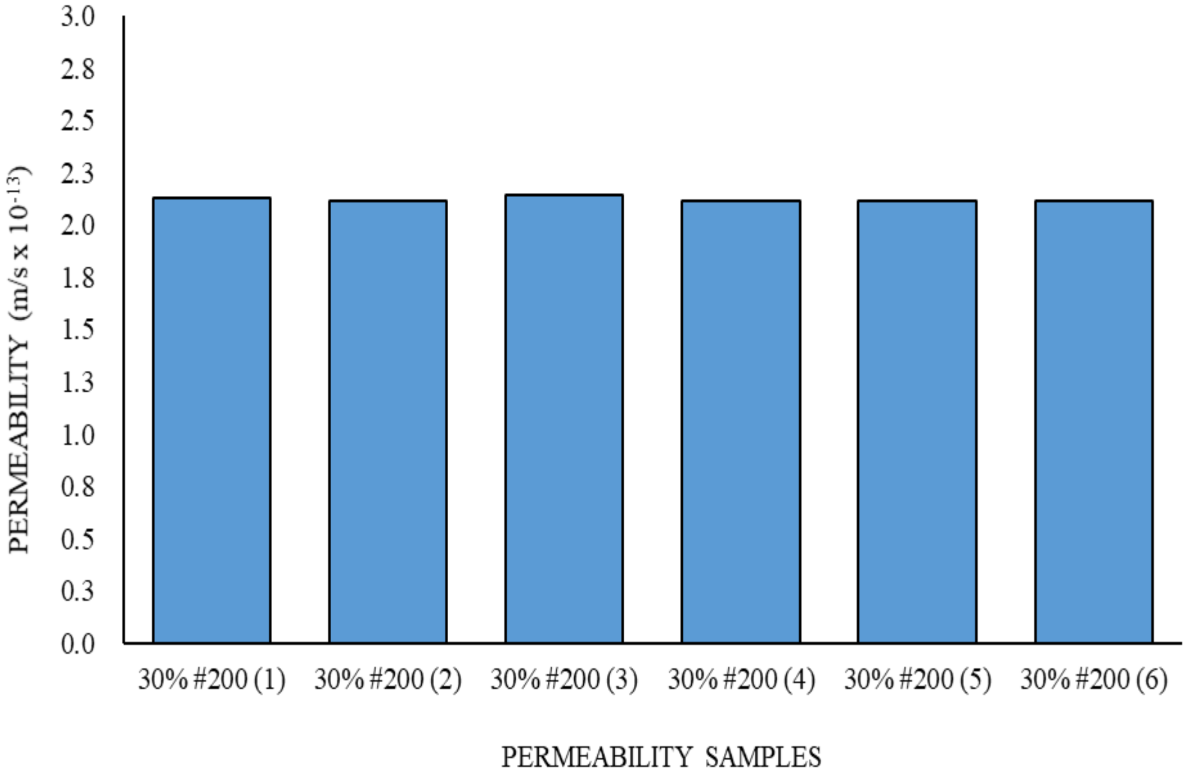

Figure A.7. Graphical representation of permeability of 30% passing No. 200 sieve pozzolan at 364 days

Table A.9. Results of permeability of 30% as-crushed pozzolan at 442 days

Pozzolan variations	**Rot. Speed Rad/sec**	a_r **(m/s^2)**	N	L **(m)**	Δh **(m)**	h_t **(m)**	k_s **(m/s) x 10^{-13}**
30% AC (1)	303.7	17523	1786	0.0150	0.003	0.1225	2.116
30% AC (2)	303.7	17523	1786	0.0147	0.003	0.1225	2.074
30% AC (3)	303.7	17523	1786	0.0149	0.004	0.1215	2.815
30% AC (4)	303.7	17523	1786	0.0150	0.004	0.1215	2.833
30% AC (5)	303.7	17523	1786	0.0149	0.003	0.1225	2.102
30% AC (6)	303.7	17523	1786	0.0148	0.003	0.1225	2.088
			Mean				2.338
			Standard Deviation				0.377
			Coefficient of Variation				16.11%

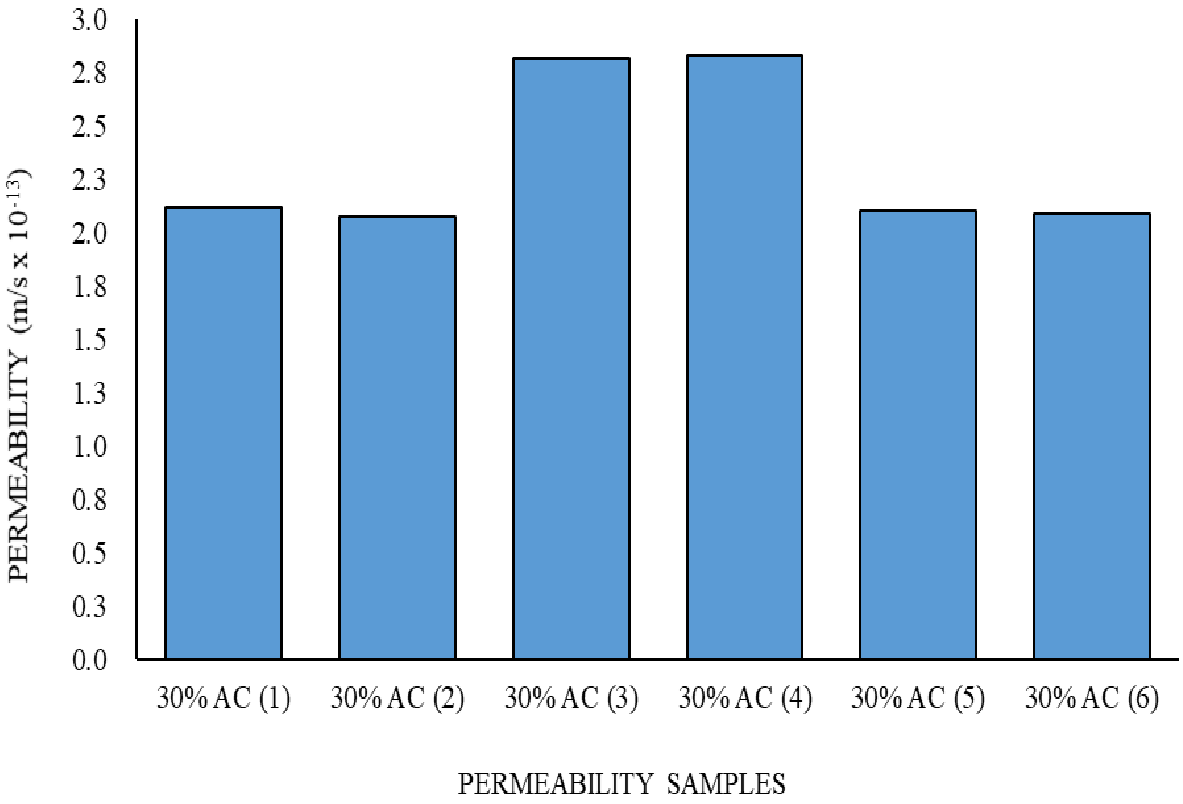

Figure A.8. Graphical representation of permeability of 30% as-crushed pozzolan at 442 days

Table A.10. Results of permeability of 30% passing No. 200 sieve pozzolan at 442 days

Pozzolan variations	**Rot. Speed Rad/sec**	**a_r (m/s^2)**	**N**	**L (m)**	**Δh (m)**	**h_t (m)**	**k_s (m/s) x 10^{-13}**
30% #200 (1)	303.7	17523	1786	0.0148	0.003	0.1225	2.088
30% #200 (2)	303.7	17523	1786	0.0148	0.003	0.1225	2.088
30% #200 (3)	303.7	17523	1786	0.0149	0.003	0.1225	2.102
30% #200 (4)	303.7	17523	1786	0.0151	0.003	0.1225	2.131
30% #200 (5)	303.7	17523	1786	0.0149	0.003	0.1225	2.102
30% #200 (6)	303.7	17523	1786	0.0150	0.003	0.1225	2.116
			Mean				2.105
			Standard Deviation				0.016
			Coefficient of Variation				0.78%

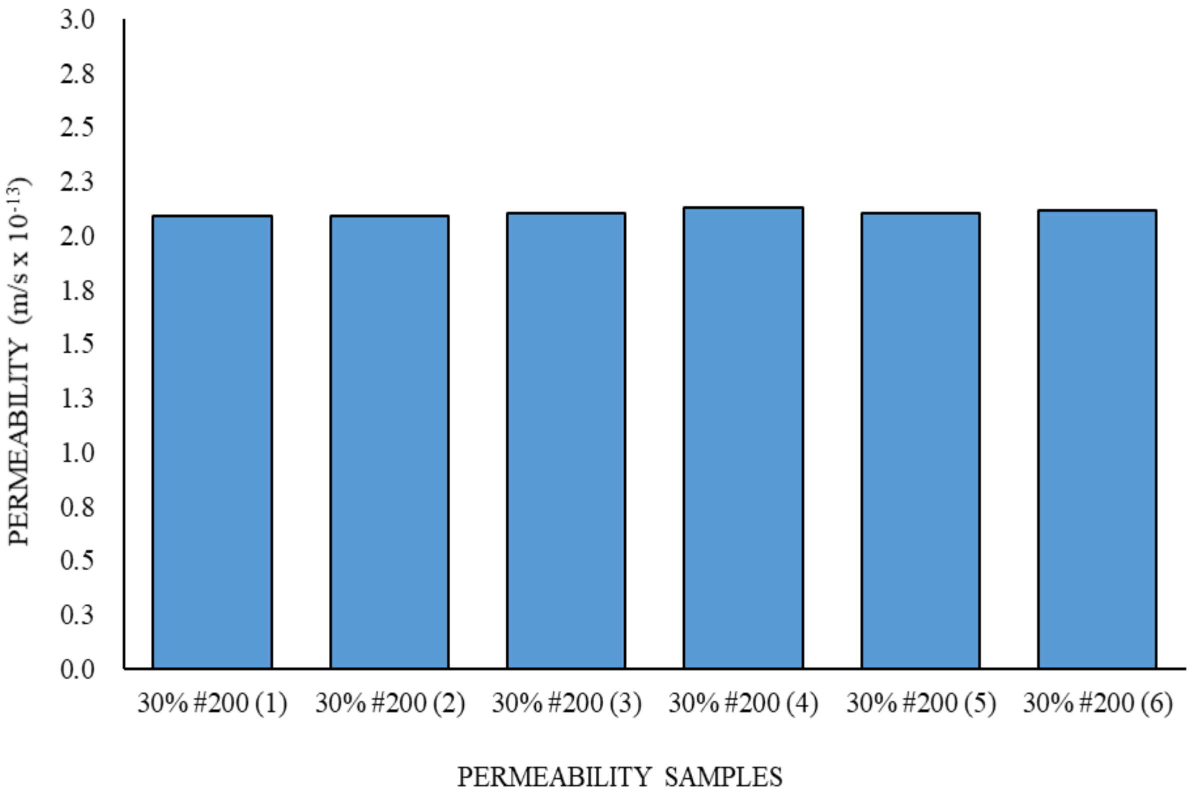

Figure A.9. Graphical representation of permeability of 30% passing No. 200 sieve pozzolan at 442 days

APPENDIX B

PRECISION OF PERMEABILITY MEASUREMENTS

The method to estimate the precision of permeability measurements is presented in this appendix. Also shown are a sample calculation and tables of the precision calculations for each material.

Error in a reading is the difference between a calculated or observed value and the true value. The true value is not known with certainty, which necessitates the calculation of precision. When data are acquired through experiments and measurements of certain quantities, the possibility of error in experimental readings and the calculations is very high. These erroneous values are difficult to measure directly so the variance of quantities can be estimated using a relationships between the independent variables of a function (Bevington and Robinson 1992; Peters 2001).

The precision of the measured coefficient of saturated hydraulic conductivity was calculated using standard propagation of error techniques, assuming that all variables were independent. This method is based on the calculation of the variance σ_f^2, of a derived value, $f(x_i)$, using the variance of the variables $n(x_i)$ from which the derived value is obtained:

$$\sigma_f^2 = \sqrt{\sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}\right)^2 \sigma_i^2} \qquad \text{(B.1)}$$

For calculations, it was assumed that the precision of measured variables corresponded to the 90% confidence limits for the particular variable so that the variances of measured variables could be estimated (Bevington and Robinson 1992; Peters 2001).

As described in Appendix A, saturated permeability is calculated as:

$$k_s = \frac{1}{N}\frac{a_L}{A_t}\ln\frac{h_0}{h_t} \qquad \text{(B.2)}$$

where $a_r = \omega_r^2.R_{cen}$

ω_r = rotational speed [rad/sec]

R_{cen} = centrifuge operative radius (0.190 m)

$N = \frac{a_r}{g}$

a = x-sectional area of water tube, $\pi\left[\frac{15mm}{2}\right]^2$ = 176.715 mm^2 ≈ 0.000177 m^2

L = length of specimen (thickness of disc) => Nominally 15 mm (varied)

A = cross-sectional area of sample = $\pi\left(\frac{50mm}{2}\right)^2$ = 1963.495 mm^2 ≈ 0.001963 m^2

t = time of the flow = 24 hrs.3600 s/hr = 86,400 s

h_0 = initial height of water tube = 125.5 mm

h_t = height at time (t) = varies

Sample calculation of coefficient of permeability for the first sample of the 10% as-crushed batch is as follows:

Here, you need to convert ω_r from RPM to rad/s, so the equation must be reversed

$$\omega_r = 2900RPM \times \frac{2\pi \frac{rad}{rev}}{60 \frac{s}{\min}} = 303.7 \frac{rad}{s}$$

R_{cen} = 0.190 m

$$a_r = \omega_r^2 .R_{cen} = \left(303.7 \frac{rad}{s}\right)^2 0.190m = 17523 \frac{m}{s^2}$$

$$N = \frac{a_r}{g} = \frac{17523\frac{m}{s^2}}{9.81\frac{m}{s^2}} = 1786$$

$$a = \pi\left(\frac{15mm}{2}\right)^2 = 176.715mm^2 \approx 0.000177 \text{ m}^2$$

L = 0.015 m

A = 1963.495 mm^2 ≈ 0.001963 m^2

t = 86,400 s (24 hours ± 60 seconds)

h_0 = 125.5 mm ≈ 0.1255 m

h_t = 125.5 mm - 2 mm = 123.5 mm ≈ 0.1235 m

$$k_s = \frac{1}{N}\frac{aL}{At}\ln\frac{h_0}{h_t}$$

$$k_s = \frac{1}{1786}\frac{(0.000177m^2)(0.015m)}{(0.001963m^2)(86{,}400s)}\ln\frac{0.1255m}{0.1235m}$$

$$k_s = 1.408\times10^{-13}\frac{m}{s}$$

Sample calculation of the precision of the coefficient of permeability for the same sample is as follows:

Variance for a_r [$a_r = \omega_r^2 R_{cen}$]

$$\sigma_{a_r} = \left(\frac{\partial_{a_r}}{\partial_{\omega_r}} \right)^2 \sigma_{\omega_r}^2 + \left(\frac{\partial_{a_r}}{\partial_{R_{cen}}} \right)^2 \sigma_{R_{cen}}^2$$

$$= (2\omega_r R_{cen})^2 \sigma_{\omega_r}^2 + (\omega_r^2)^2 \sigma_{R_{cen}}^2$$

Estimated precision of rotational speed = ± 100 rpm. This must be converted to units of rad/s.

$$\delta_{\omega_r} = \pm \frac{100}{60} 2\pi = \pm 10.5 \frac{rad}{s}$$

The precision is assumed to correspond to the 90% confidence limits, which, in turn, corresponds to ± 1.645 σ, assuming a normally distributed variable:

$$\delta_{\omega_r} = \frac{10.5}{1.645} = 6.4 \frac{rad}{s}$$

R_{cen} = 0.190 ± 0.005 m

$$\sigma_{R_{cen}} = \frac{0.005}{1.645} = 0.00304m$$

$$\sigma_{a_r}^2 = \left(2X303.7 \frac{rad}{s^2} X0.190m \right)^2 \left(6.4 \frac{rad}{s} \right)^2 + \left(\left(303.7 \frac{rad}{s} \right)^2 \right)^2 (0.00304m)^2$$

$$\sigma_{a_r}^2 = 6.18 \times 10^5 \frac{m}{s^2}$$

$$N = \frac{a_r}{g} \Rightarrow \sigma_N^2 = \left(\frac{\partial N}{\partial a_r} \right)^2 \sigma_{a_r}^2 = \left(\frac{1}{g} \right)^2 \left(6.18 \times 10^5 \frac{m}{s^2} \right) = (0.1019368)^2 \left(6182723 \frac{m}{s^2} \right) = 6424.536$$

$$k_s = \frac{1}{N}\frac{aL}{At}\ln\frac{h_0}{h_t}$$

$$\sigma_{k_s}^2 = \sum_{i=1}^{n}\left(\frac{\partial f}{\partial xi}\right)^2 \sigma_{xi}^2$$

$$\sigma_{k_s}^2 = \left(\frac{\partial k_s}{\partial N}\right)^2 \sigma_N^2 + \left(\frac{\partial k_s}{\partial a}\right)^2 \sigma_a^2 + \left(\frac{\partial k_s}{\partial L}\right)^2 \sigma_L^2 + \left(\frac{\partial k_s}{\partial A}\right)^2 \sigma_A^2 + \left(\frac{\partial k_s}{\partial t}\right)^2 \sigma_t^2 + \left(\frac{\partial k_s}{\partial h_0}\right)^2 \sigma_{h_0}^2 + \left(\frac{\partial k_s}{\partial h_t}\right)^2 \sigma_{h_t}^2$$

$$\frac{\partial k_s}{\partial N} = \frac{-1}{N^2}\frac{aL}{At}\ln\left(\frac{h_0}{h_t}\right)$$

$$\sigma_N^2 = 6424.536$$

Therefore, $\frac{\partial k_s}{\partial N} = \frac{-1}{(1786)^2}\frac{(0.000177m^2)(0.015m)}{(0.001963m^2)(86400s)}\ln\left(\frac{0.1255m}{0.1235m}\right) = -7.867\times10^{-17}\frac{m}{s}$

$$\frac{\partial k_s}{\partial a} = \frac{1}{N}\frac{L}{A_t}\ln\left(\frac{h_0}{h_t}\right) = \frac{1}{1786}\frac{0.015m}{(0.001963m^2)(86400s)}\ln\left(\frac{0.1255m}{0.1235m}\right)$$

$$= 7.952\times10^{-10}\frac{1}{m.s}$$

Precision of diameter measurement for top graduated cylinder ≈ ± 0.01 mm for a (cross sectional area of water tube (m^2)).

$$\sigma_d = \frac{0.01}{1.645} = 0.00608mm \approx \frac{0.00001m}{1.645} = 6.079\times10^{-06}m$$

$$a = \frac{\pi}{4}(d)^2$$

$$\sigma_a^2 = \left(\frac{\partial a}{\partial d}\right)^2 \sigma_d^2 = \left(\frac{\pi}{2}(0.015m)\right)^2 (6.079\times10^{-06}m)^2 = 2.052\times10^{-14}m^4$$

$$\frac{\partial k_s}{\partial L} = \frac{1}{N}\frac{a}{At}\ln\left(\frac{h_0}{h_t}\right) = \frac{1}{1786}\frac{(0.000177m^2)}{(0.001963m^2)(86400s)}\ln\left(\frac{0.1255m}{0.1235m}\right) = 9.368\times10^{-12}\frac{1}{s}$$

Precision of sample thickness measurement ≈ ± 0.00002 m

$$\sigma_L = \frac{0.00002m}{1.645} = 1.22\times10^{-05}m$$

$$\sigma_L^2 = 1.478\times10^{-10}m^2$$

$$\frac{\partial k_s}{\partial A} = \frac{-1}{N}\frac{aL}{A^2t}\ln\left(\frac{h_0}{h_t}\right) = \frac{-1}{1786}\frac{\left(0.000177m^2\right)\left(0.015m\right)}{\left(0.001963m^2\right)^2\left(86400s\right)}\ln\left(\frac{0.1255m}{0.1235m}\right) = -7.157\times10^{-11}\frac{m}{s}$$

$$\sigma_A^2 : A = \frac{\pi}{4}.\left(dia\right)^2$$

$$\frac{\partial A}{\partial dia} = \frac{\pi}{2}\left(dia\right)$$

Precision of diameter measurement ≈ ± 2 mm

Therefore, $\sigma_{dia}^2 = 1.478mm^2$ ≈ 0.001478 m^2

$$\sigma_A^2 = \left(\frac{\pi}{2}\left(0.05m\right)\right)^2 \times 0.001478m^2 = 2.051\times10^{-08}m^4$$

$$\frac{\partial k_s}{\partial t} = \frac{-1}{N}\frac{aL}{At^2}\ln\left(\frac{h_0}{h_t}\right) = \frac{-1}{1786}\frac{\left(0.000177m^2\right)\left(0.015m\right)}{\left(0.001963m^2\right)\left(86400s\right)^2}\ln\left(\frac{0.1255m}{0.1235m}\right)$$

$$= -1.626\times10^{-18}\frac{m}{s^2}$$

Precision of time (t) is taken as 1 minute (60 seconds).

$$\sigma_t = \frac{60}{1.645} = 36.47s$$

$$\sigma_t^2 = 1330.4 \text{ s}^2$$

$$\frac{\partial k_s}{\partial h_0} = \frac{1}{N}\frac{aL}{At}\frac{1}{h_0} = \frac{1}{1786}\frac{\left(0.000177m^2\right)\left(0.015m\right)}{\left(0.001963m^2\right)\left(86400s\right)}\frac{1}{0.1255m} = 6.970\times10^{-11}\frac{1}{s}$$

Precision of *h_o* measurement = 0.5 mm ≈ 0.0005 m

$$\sigma_{h_0} = \frac{0.0005m}{1.645} = 0.000304m$$

$$\sigma_{h_0}^2 = 9.239\times10^{-08} m^2$$

$$\frac{\partial k_s}{\partial h_t} = \frac{-1}{N}\frac{aL}{At}\frac{1}{h_t} = \frac{-1}{1786}\frac{\left(0.000177m^2\right)\left(0.015m\right)}{\left(0.001963m^2\right)\left(86400s\right)}\frac{1}{0.1235m} = -7.083\times10^{-11}\frac{1}{s}$$

$$\sigma_{h_t} = \frac{0.0005m}{1.645} = 0.000304m$$

$$\sigma_{h_t}^2 = 9.239\times10^{-08} m^2$$

$$\sigma_{k_s}^2 = \left(-7.867\times10^{-17}\frac{m}{s}\right)^2\left(6424.536\right) + \left(7.952\times10^{-10}\frac{1}{m.s}\right)^2\left(2.052\times10^{-14}m^4\right) +$$

$$\left(9.368\times10^{-12}\frac{1}{s}\right)^2\left(1.478\times10^{-10}m^2\right) + \left(7.157\times10^{-11}\frac{m}{s}\right)^2\left(2.051\times10^{-08}m^4\right) +$$

$$\left(1.626\times10^{-18}\frac{m}{s^2}\right)^2\left(1330.4s^2\right)+\left(6.970\times10^{-11}\frac{1}{s}\right)^2\left(9.239\times10^{-08}m^2\right)+$$

$$\left(7.083\times10^{-11}\frac{1}{s}\right)^2\left(9.239\times10^{-08}m^2\right)$$

$$\sigma_{k_s}^2=1.057\times10^{-27}\frac{m^2}{s^2}\Rightarrow\sigma_{k_s}=3.251\times10^{-14}\frac{m}{s}$$

Precision of k_s at the 90% level of confidence = $\sigma_{k_s}.1.645=3.1651E^{-13}\frac{m}{s}$

Table B.1 through Table B.9 list the values used to calculate the precision of all of the permeability measurements. Also shown are the measured permeability coefficients for reference. It is noted that the measured coefficients are not that much greater than the precision.

Constant values used for all the calculations are listed as follows:

Rotational Speed = 2900 RPM ≈ 303.7 Rad/sec

R_{cen} = 0.19 m

a = 0.000177 m^2

A = 0.001963 m^2

t = 86400 s

h_0 = 0.1255 m

a_r = 17523 m/s^2

N = 1786

Table B.1. Permeability precision results for six samples of 0% pozzolan mix at the testing age of 442 days

Samples	L (m)	Δh (m)	h_t (m)	k_s (m/s x 10^{-13})	Precision (± m/s) (m/s x 10^{-13})
1	0.0148	0.002	0.1235	1.387	0.528
2	0.0149	0.002	0.1235	1.396	0.531
3	0.01452	0.003	0.1225	2.049	0.563
4	0.0150	0.003	0.1225	2.116	0.581
5	0.0152	0.0015	0.1240	1.066	0.524
6	0.0150	0.0015	0.1240	1.052	0.518
Mean				1.511	0.541
Standard Deviation				0.468	
Coefficient of Variation				31%	

Table B.2. Permeability precision results for six samples of 10% as-crushed pozzolan mix at testing age of 442 days

Samples	L (m)	Δh (m)	h_t (m)	k_s (m/s x 10^{-13})	Precision (± m/s) (m/s x 10^{-13})
1	0.0150	0.002	0.1235	1.405	0.535
2	0.0149	0.002	0.1235	1.396	0.531
3	0.0148	0.001	0.1245	0.690	0.498
4	0.0148	0.001	0.1245	0.690	0.498
5	0.0149	0.001	0.1245	0.695	0.501
6	0.01481	0.0015	0.1240	1.038	0.511
Mean				0.986	0.512
Standard Deviation				0.348	
Coefficient of Variation				35.3%	

Table B.3. Permeability precision results for six samples of 10% passing No. 200 sieve pozzolan mix at testing age of 442 days

Samples	L (m)	Δh (m)	h_t (m)	k_s (m/s x 10^{-13})	Precision (± m/s) (m/s x 10^{-13})
1	0.0148	0.001	0.1245	0.690	0.498
2	0.01474	0.001	0.1245	0.688	0.496
3	0.0150	0.001	0.1245	0.700	0.505
4	0.01462	0.0015	0.124	1.025	0.504
5	0.0152	0.001	0.1245	0.709	0.511
6	0.01492	0.001	0.1245	0.696	0.502
Mean				0.697	0.503
Standard Deviation				0.008	
Coefficient of Variation				1.2%	

Table B.4. Permeability precision results for six samples of 20% as-crushed pozzolan mix at testing age of 442 days

Samples	L (m)	Δh (m)	h_t (m)	k_s (m/s x 10^{-13})	Precision (± m/s) (m/s x 10^{-13})
1	0.0150	0.0025	0.123	1.760	0.556
2	0.0151	0.0025	0.123	1.772	0.560
3	0.0150	0.003	0.1225	2.116	0.581
4	0.0150	0.0025	0.123	1.760	0.556
5	0.0152	0.0025	0.123	1.784	0.564
6	0.0147	0.002	0.1235	1.377	0.524
Mean				1.762	0.557
Standard Deviation				0.234	
Coefficient of Variation				13.3%	

Table B.5. Permeability precision results for six samples of 20% passing No. 200 sieve pozzolan mix at the testing age of 442 days

Samples	L (m)	Δh (m)	h_t (m)	k_s (m/s x 10^{-13})	Precision (± m/s) (m/s x 10^{-13})
1	0.0153	0.0025	0.123	1.795	0.567
2	0.0148	0.0025	0.123	1.737	0.549
3	0.01482	0.0025	0.123	1.739	0.550
4	0.01494	0.002	0.1235	1.400	0.533
5	0.0150	0.001	0.1245	0.700	0.505
6	0.0153	0.001	0.1245	0.714	0.515
Mean				1.347	0.536
Standard Deviation				0.516	
Coefficient of Variation				38.3%	

Table B.6. Permeability precision results for six samples of 30% as -crushed pozzolan mix at testing age of 364 days

Samples	L (m)	Δh (m)	h_t (m)	k_s (m/s x 10^{-13})	Precision (± m/s) (m/s x 10^{-13})
1	0.0149	0.004	0.1215	2.815	0.636
2	0.0148	0.004	0.1215	2.796	0.632
3	0.0145	0.003	0.1225	2.046	0.562
4	0.0151	0.003	0.1225	2.131	0.585
5	0.0153	0.003	0.1225	2.159	0.593
6	0.0151	0.003	0.1225	2.131	0.585
Mean				2.346	0.599
Standard Deviation				0.358	
Coefficient of Variation				15.2%	

Table B.7. Permeability precision results for six samples of 30% passing No. 200 sieve pozzolan mix at testing age of 364 days

Samples	L (m)	Δh (m)	h_t (m)	k_s (m/s x 10^{-13})	Precision (± m/s) (m/s x 10^{-13})
1	0.0151	0.003	0.1225	2.131	0.585
2	0.0150	0.003	0.1225	2.116	0.581
3	0.0152	0.003	0.1225	2.145	0.589
4	0.0150	0.003	0.1225	2.116	0.581
5	0.0150	0.003	0.1225	2.116	0.581
6	0.0150	0.003	0.1225	2.116	0.581
Mean				2.123	0.583
Standard Deviation				0.012	
Coefficient of Variation				0.56%	

Table B.8. Permeability precision results for six samples of 30% as-crushed pozzolan mix at testing age of 442 days

Samples	L (m)	Δh (m)	h_t (m)	k_s (m/s x 10^{-13})	Precision (± m/s) (m/s x 10^{-13})
1	0.0150	0.003	0.1225	2.116	0.581
2	0.0147	0.003	0.1225	2.074	0.570
3	0.0149	0.004	0.1215	2.815	0.636
4	0.0150	0.004	0.1215	2.833	0.641
5	0.0149	0.003	0.1225	2.102	0.577
6	0.0148	0.003	0.1225	2.088	0.574
Mean				2.338	0.596
Standard Deviation				0.377	
Coefficient of Variation				16.11%	

Table B.9. Permeability precision results for six samples of 30% passing No. 200 sieve pozzolan mix at testing age of 442 days

Samples	L (m)	Δh (m)	h_t (m)	k_s (m/s x 10^{-13})	Precision (± m/s) (m/s x 10^{-13})
1	0.0148	0.003	0.1225	2.088	0.574
2	0.0148	0.003	0.1225	2.088	0.574
3	0.0149	0.003	0.1225	2.102	0.577
4	0.0151	0.003	0.1225	2.131	0.585
5	0.0149	0.003	0.1225	2.102	0.577
6	0.0150	0.003	0.1225	2.116	0.581
Mean				2.105	0.578
Standard Deviation				0.016	
Coefficient of Variation				0.78%	

APPENDIX C

DETAILED COMPRESSIVE STRENGTH RESULTS

This appendix presents the results of compressive strength tests for all samples tested. A description of the methods used for the detection of outliers is also provided.

Detection of outliers

An outlier is a value/data point that differs from the other data points present in the whole population of specimens, suggesting that it is not a member of the same population. In statistical analysis, the outliers can be taken as experimental errors in the measurements. These are often omitted from the data set, as they can result in significant unwanted changes in the results.

Both physical and statistical outliers were noted in some of the data sets. Physical outliers were detected by the shape or condition of the sample (e.g., honey combing was noted for some samples) or by anomalies observed during testing. All data sets were also analyzed for statistical outliers. The outliers for this study were analyzed using Grubb's test, also known as the extreme studentized deviate (ESD) method (Grubbs 1969).

Grubbs method identifies an outlier as a quantity of that is too far from the range considered for approval, i.e. it is too out of the range the minimum and maximum values in the data set. Statistically, it is a value that deviates markedly from other observations in the same data set. This could happen due to incorrect recording of the data or due to some discrepancies in running the experiment; the value is then marked as an erroneous value.

The way to deal with an outlier is to either improve it or remove it from the data set to achieve a more reliable result. In the case of experimental data, improving a value becomes impossible so the anomlalous observation is removed from the set of observations (Grubbs 1969; Stanimirova et al, 2007; Hueste et al, 2003). It is common to have an outlier in a data set obtained experimentally which is why more than one sample is normally tested to obtain a reliable result.

Grubb's Test

The first step to consider in detecting a statistical outlier is to quantify how far the value of the sample is from other values in the data set. This can be calculated as the number of standard deviations the sample value is from the mean value of the data set, Z:

$$Z = |\text{mean} - \text{value}| / \text{SD} \qquad \text{(C.1)}$$

If the value of Z is large then the value is far from other sample values. Assuming that the data set follows a normal distribution, the probability that the value can lie that far from the mean can be calculated. The value is determined to be an outlier if that probability is small enough (typically 5%).

The Grubb's test uses this rule for detecting outliers.

The hypothesis that the Grubb's test is defined for, is:

H_0: No outliers in the data set

H_a: Presence of one outlier in the data set

The statistical equation is: $G = \max\left|Y_t - \overline{Y}\right| / s$ (C.2)

where $\overline{Y}$ is the mean of sample, Y_t is the value furthest from the mean, and s is the standard deviation.

The two-sided test was considered for this research, with a significance level of $\alpha = 0.05$. An outlier is one for which

$$G > (N-1)/(N)^{1/2} \, [(t^2 (\alpha/(2N), N - 2)) / N - 2 + t^2 (\alpha/(2N), N - 2)\,]^{1/2} \qquad \text{(C.3)}$$

where $t (\alpha/(2N), N - 2)$ is the critical value of the t-distribution with $(N - 2)$ degrees of freedom and a significance level of $\alpha/(2N)$.

An example of detecting of a statistical outlier for the compressive strength of the 0% sample at 28 days is presented as follows, for which the QuickCalcs of Graph Pad Software

(https://www.graphpad.com/quickcalcs/ttest1.cfm) was used for quickly detecting the outliers.

The measured compressive strengths for the five samples tested are listed in Table C.1. In this case, the mean value was 44.28 MPa, with a standard deviation of 13.40 MPa. Thus, the maximum value for Z is associated with sample 3, for which

$$Z = \frac{|20.4 - 44.28|}{13.40} = 1.783$$

For a two-sided test with a level of significance of 0.05, the calculation of 0% compressive strength samples at 28 days had a the critical value for Z is 1.715, found by using the QuickCalcs of Graph Pad Software. The set of values are entered in the software and it gives a critical value for Z. Since the actual value of Z is greater than this, it means that there is less than a 5% probability that the value of sample 3 is from the same population, and it is identified as an outlier and removed from the data set.

Table C.1. Compressive strength data for 0% pozzolan samples at 28 days

Sample No.	**Strength (MPa)**	**Z**	**Significant Outlier?**
1	52.0	0.576	-
2	49.0	0.352	-
3	20.4	1.783	Significant outlier. P < 0.05
4	49.7	0.405	-
5	50.3	0.449	-
Mean Value	44.28		
Standard Dev.	13.40		

The compressive strengths of all specimens tested are listed in Tables C.2 through C.7, and mean values are presented in graphical form in Figure C.1 through C.7.

Table C.2. Compressive strength of specimen at 7 days curing age (MPa)

Specimen	Compressive Strength (MPa)						
	0%	10% As crushed	10% Passing # 200 sieve	20% As crushed	20% Passing # 200 sieve	30% As crushed	30% Passing # 200 sieve
1	39.0	35.6	38.6	29.2	38.1	23.3	34.5
2	39.8	37.0	39.6	31.0	31.5	27.6	35.4
3	38.3	33.4	41.0	31.5	33.7	35.1	36.0
4	37.9	35.1	34.0	26.4	32.7	37.0	36.8
5	38.2	38.5	38.0	32.5	32.7	37.0	32.5
Mean C. Strength	38.6	35.9	38.2	30.1	33.7	32.0	35.0
Standard Deviation	0.76	1.93	2.63	2.40	2.56	6.22	1.65
Coefficient of variation (%)	1.98	5.38	6.87	7.97	7.58	19.43	4.71
Outliers	None						

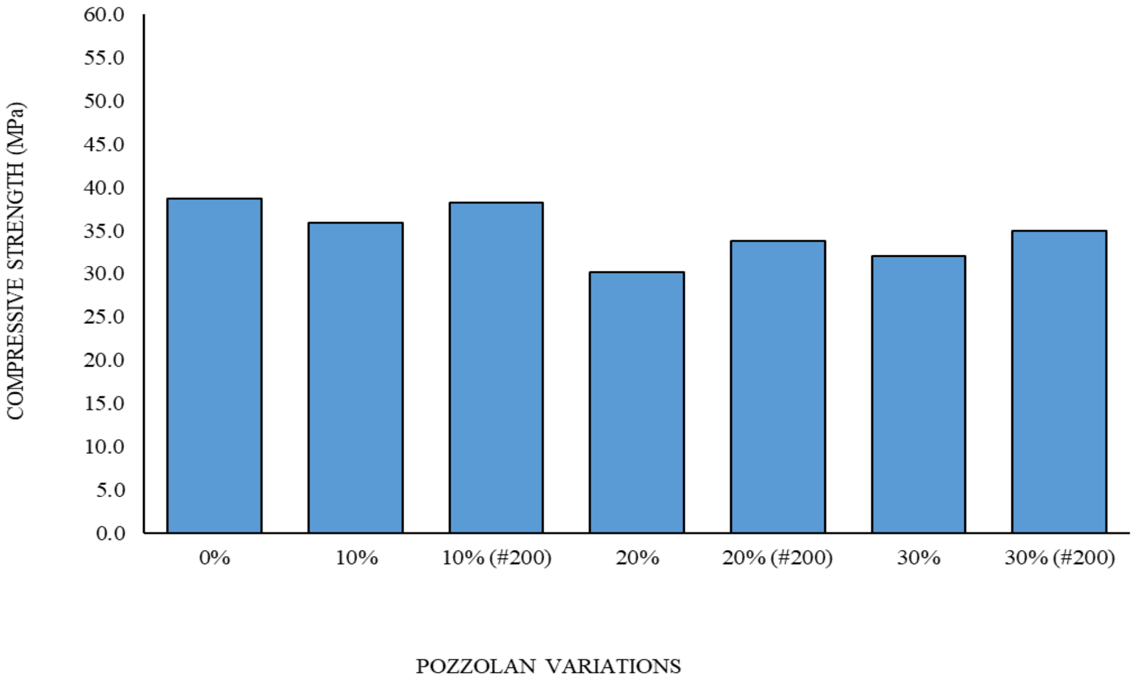

Figure C.1. Graphical representation of compressive strength of specimens at 7 days curing age (MPa)

Table C.3. Compressive strength of specimens at 28 days curing age (MPa)

Specimen	Compressive Strength (MPa)						
	0%	10% As crushed	10% Passing # 200 sieve	20% As crushed	20% Passing # 200 sieve	30% As crushed	30% Passing # 200 sieve
1	52.0	38.9	37.6	35.1	36.2	39.1	35.4
2	49.0	42.9	38.4	Test failed	38.6	35.9*	38.7
3	20.4*	36.2	39.0	33.0	35.2	38.8	41.4
4	49.7	37.1	43.6	34.0	38.3	39.7	38.2
5	50.3	44.8	40.0	34.3	38.9	39.3	41.0
Mean C. Strength	50.3	40.0	39.7	34.1	37.4	39.2	38.9
Standard Deviation	1.28	3.73	2.34	0.87	1.64	0.38	2.42
Coefficient of variation (%)	2.55	9.32	5.89	2.55	4.38	0.96	6.22
Outliers	# 3, $P < 0.05$	None	None	None	None	# 2, $P < 0.05$	None

Note: The 0% and 30% as-crushed pozzolan had one sample (highlighted) that had physical outliers, i.e. honey combing was seen in these samples. As a result, these samples happened to fail earlier than other samples and were detected as statistical outliers. The highlighted entities are not included in the mean strength as well as standard deviation and coefficient of variation.

The 20% as-crushed sample was noticed as a physical outlier and the sample failed sooner than other samples.

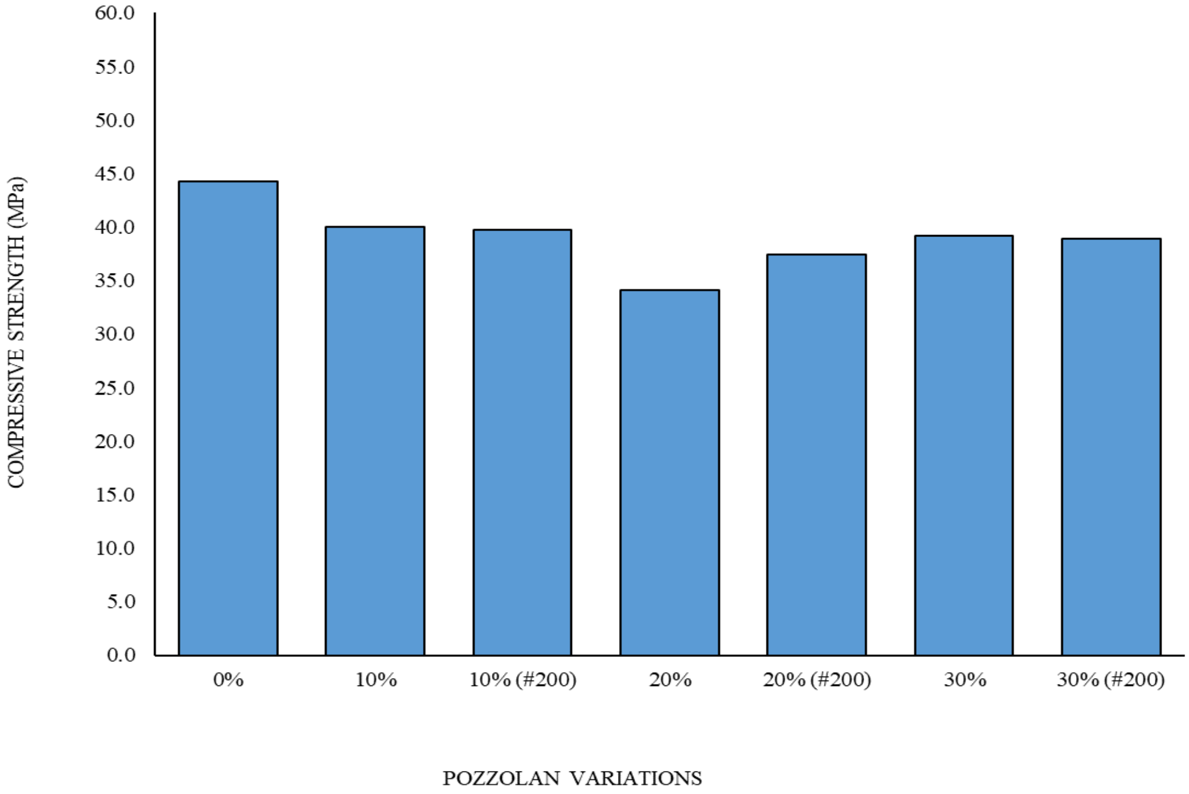

Figure C.2. Graphical representation of compressive strength of specimens at 28 days curing age (MPa)

Table C.4. Compressive strength of specimens at 56 days curing age (MPa)

	Compressive Strength (MPa)						
Specimen	0%	10% As crushed	10% Passing # 200 sieve	20% As crushed	20% Passing # 200 sieve	30% As crushed	30% Passing # 200 sieve
1	51.0	44.2	45.9	35.8	37.6	36.9	39.0
2	47.0	42.5	51.2	37.6	41.3	26.9*	34.5
3	45.6	44.2	45.1	40.1	46.5	28.9*	36.5
4	53.0	45.6	44.4	34.5	42.5	27.3*	35.0
5	47.0	42.3	51.1	36.1	45.9	29.1	36.1
6	48.8	46.1	44.2	33.4	43.1	38.5	38.6
7	49.5	43.5	43.5	32.8	42.0	33.3	42.7
8	45.6	42.6	47.0	31.3	42.0	38.2	40.8
9	43.3	42.1	43.0	32.7	48.7	39.6	41.0
10	46.0	43.8	48.6	34.4	44.8	37.0	42.4
11	48.4	45.4	50.9	37.7	42.3	35.8	39.6
12	44.6	40.7	48.6	33.9	41.1	32.8	37.8
13	42.2	44.7	49.3	36.9	42.1	40.0	43.5
14	45.1	47.4	46.6	35.0	40.5	39.4	37.8
15	46.4	47.2	52.0	34.4	43.5	36.4	43.8
Mean C. Strength	46.9	44.2	47.41	35.10	42.92	36.4	39.3
Standard Deviation	2.86	1.94	3.05	2.30	2.70	3.26	3.04
Coefficient of variation (%)	6.10	4.40	6.43	6.56	6.30	8.94	7.73
Outliers	None						

Note: The 30% as-crushed samples had three samples that were physical outliers, i.e. honey combing was seen in the highlighted samples, and they happened to fail earlier than other samples. The highlighted entities are not included in the mean strength as well as standard deviation and coefficient of variation.

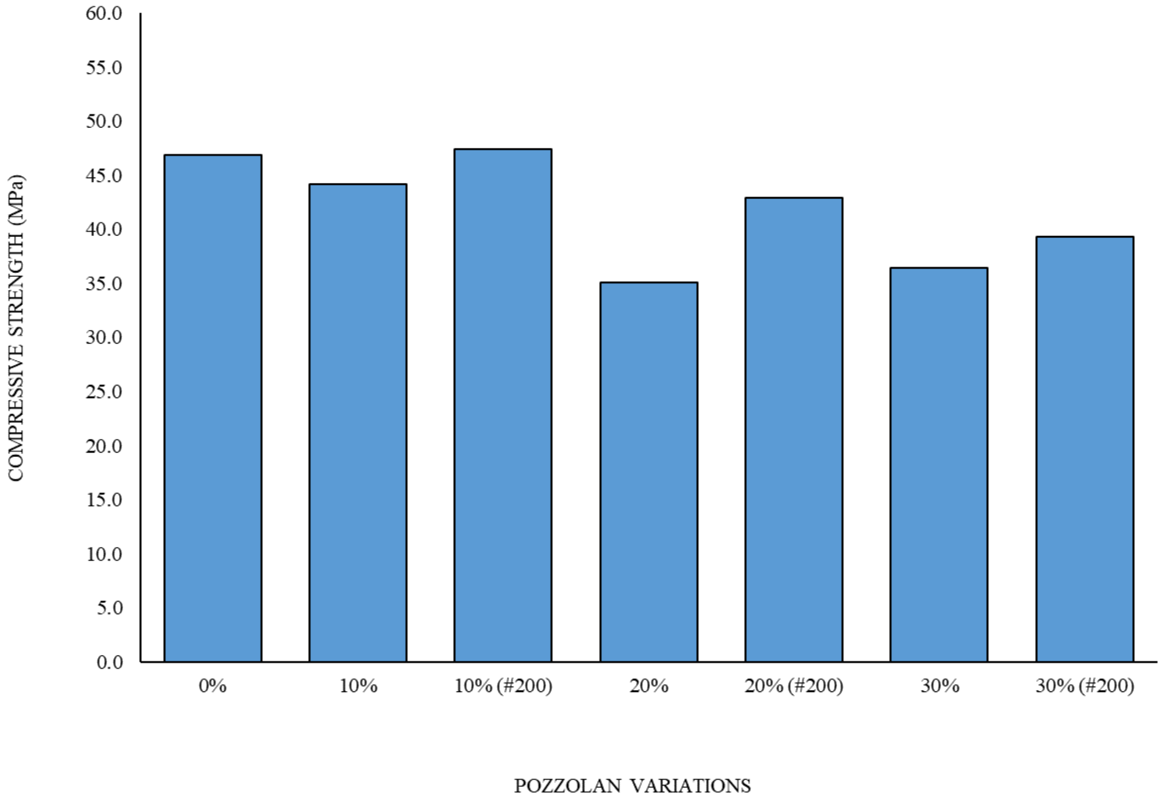

Figure C.3. Graphical representation of compressive strength of specimen at 56 days curing age (MPa)

Table C.5. Compressive strength of specimen at 112 days curing age (MPa)

Specimen	Compressive Strength (MPa)						
	0%	10% As crushed	10% Passing # 200 sieve	20% As crushed	20% Passing # 200 sieve	30% As crushed	30% Passing # 200 sieve
1	51.7	43.3	51.3	36.1	45.0	43.9	46.9
2	51.1	46.6	46.0	42.9	Test failed	32.4	49.4
3	Test failed	47.6	43.6	38.4	40.8	43.1	44.2
4	36.2	48.1	53.6	43.1	47.9	46.3	41.8
5	48.8	43.7	49.9	33.7	50.3	33.4	48.5
Mean C. Strength	47.0	45.9	48.9	38.8	46.0	39.8	46.2
Standard Deviation	7.27	2.23	4.04	4.15	4.09	6.44	3.14
Coefficient of variation (%)	15.49	4.85	8.27	10.67	8.89	16.16	6.80
Outliers	None						

The 0% and 20% passing No. 200 sieve pozzolan samples noted as ‘Test failed’ were physical outliers, i.e. honey combing, which resulted in their failure in compression sooner than other specimens, although no special failing pattern was noticed in this sample.

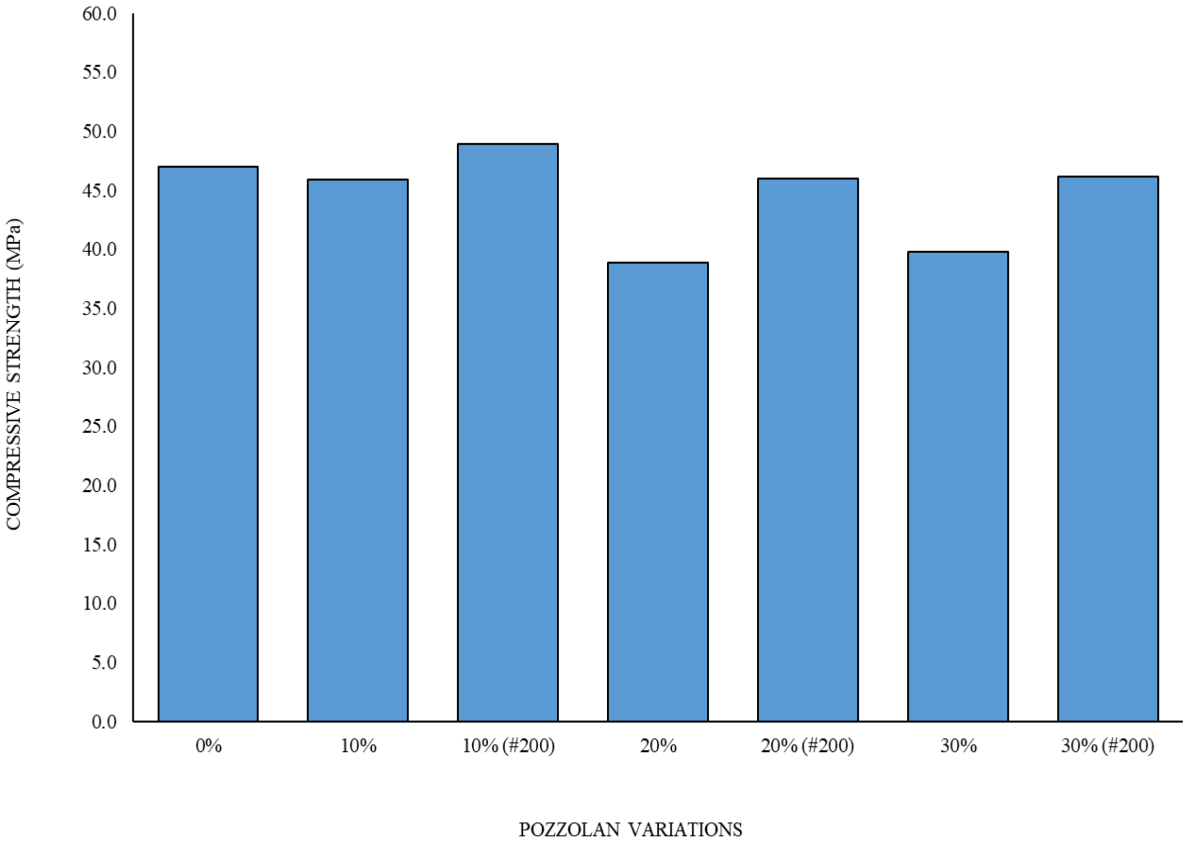

Figure C.4. Graphical representation of compressive strength of specimen at 112 days curing age (MPa)

Table C.6. Compressive strength of specimen at 182 days curing age (MPa)

Specimen	Compressive Strength (MPa)						
	0%	10% As crushed	10% Passing # 200 sieve	20% As crushed	20% Passing # 200 sieve	30% As crushed	30% Passing # 200 sieve
1	Test failed*	47.3	53.6	40.4	46.3	29.3	36.0
2	45.9	47.7	45.4	36.9	50.4	29.1	44.3
3	47.9	48.7	46.5	39.2	Test failed*	30.1	44.1
4	55.6	51.4	48.6	38.2	37.0	41.6	51.7
5	54.9	52.0	48.3	41.7	51.9	43.5	43.0
Mean C. Strength	51.1	49.4	48.5	39.3	46.4	34.7	43.8
Standard Deviation	4.90	2.15	3.15	1.87	6.70	7.19	5.57
Coefficient of variation (%)	9.59	4.36	6.50	4.75	14.44	20.71	12.72
Outliers	None						

The 20% passing No. 200 sieve pozzolan highlighted sample was a physical outliers and the sample failed sooner than others, although no special failing pattern was noticed in this sample. The highlighted sample of 0% pozzolan reached the load limit for the testing machine and the machine tripped and stopped itself.

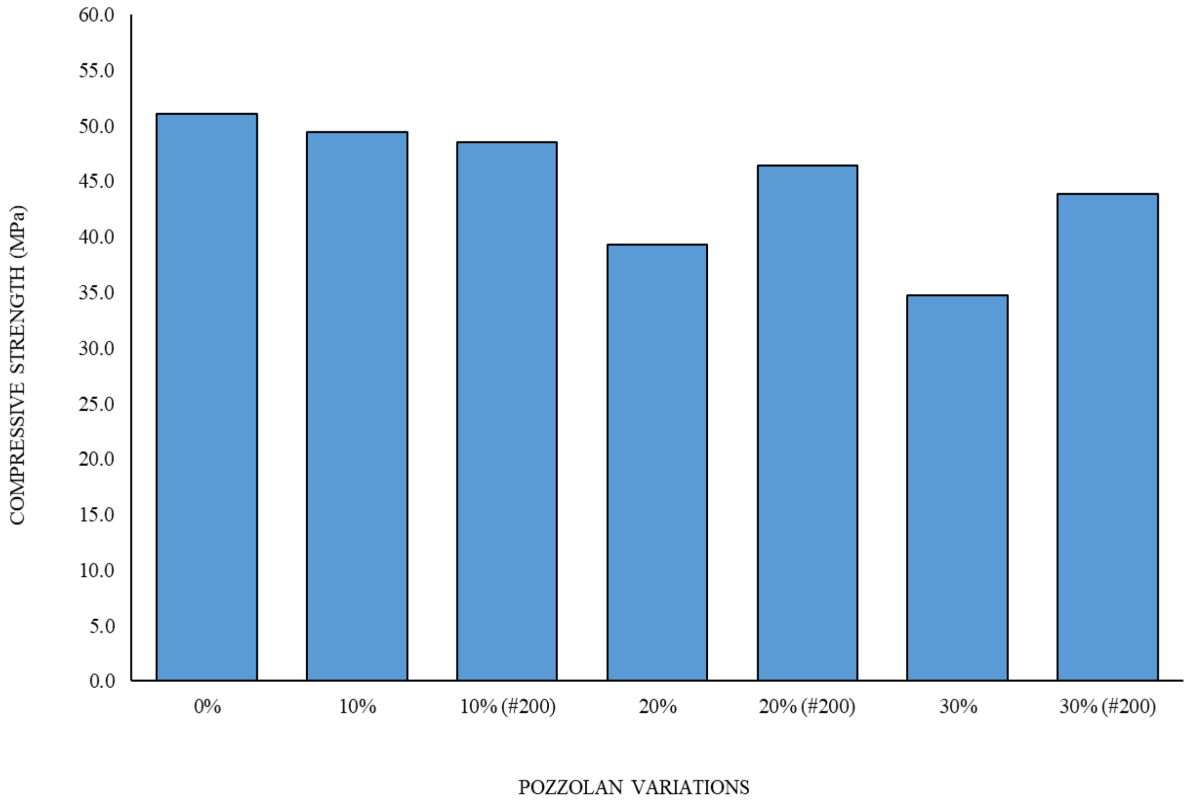

Figure C.5. Graphical representation of compressive strength of specimen at 182 days curing age (MPa)

Table C.7. Compressive strength of specimens at 364 days curing age (MPa)

Specimen	Compressive Strength (MPa)						
	0%	10% As crushed	10% Passing # 200 sieve	20% As crushed	20% Passing # 200 sieve	30% As crushed	30% Passing # 200 sieve
1	60.4	54.8	43.3*	45.0	59.5	47.3	48.6
2	47.5	54.6	58.7	43.1	53.6	42.5*	51.3
3	53.1	56.0	56.9	45.3	58.3	39.2*	46.1
4	60.9	48.4	56.6	40.2	47.6	43.0*	54.2
5	56.6	51.2	54.2	44.5	49.0	42.6*	48.6
6	53.1	53.1	53.4	46.6	43.9	44.4	51.0
7	56.4	53.6	53.8	40.8	53.5	49.5	51.4
8	50.5	56.4	55.5	48.0	52.5	49.9	50.9
9	57.1	53.9	53.4	38.9	47.8	49.0	46.1
10	56.6	53.5	56.1	51.6	58.0	48.9	52.5
11	59.5	58.9	56.7	51.7	57.4	48.1	52.0
12	52.0	49.1	47.8	46.1	53.8	49.7	49.8
13	58.1	57.0	58.4	40.4	50.1	45.1	54.2
14	48.4	58.8	Test failed*	49.4	43.5	49.2	50.3
15	48.8	54.1	56.6	40.0	53.7	47.9	47.4
Mean C. Strength	54.6	54.2	55.24	44.77	52.15	48.09	50.29
Standard Deviation	4.45	3.05	2.84	4.21	5.07	1.84	2.55
Coefficient of variation (%)	8.16	5.63	5.14	9.40	9.72	3.82	5.07
Outliers	None	None	# 1, $P < 0.05$	None	None	None	None

Note: The 30% as-crushed highlighted samples were physical outliers, i.e. honey combing was seen in the highlighted samples. These samples happened to fail earlier than other samples but no special failing pattern was noticed for these samples. The highlighted entities are not included in the mean strength as well as standard deviation and coefficient of variation.

The 10% passing No. 200 sieve sample No. 1 failed sooner than others and is noticed as a statistical outlier, no special failing pattern was noticed in this sample.

The highlighted sample No. 14 of 10% passing No. 200 sieve reached the load limit for the testing machine and the machine tripped and stopped itself.

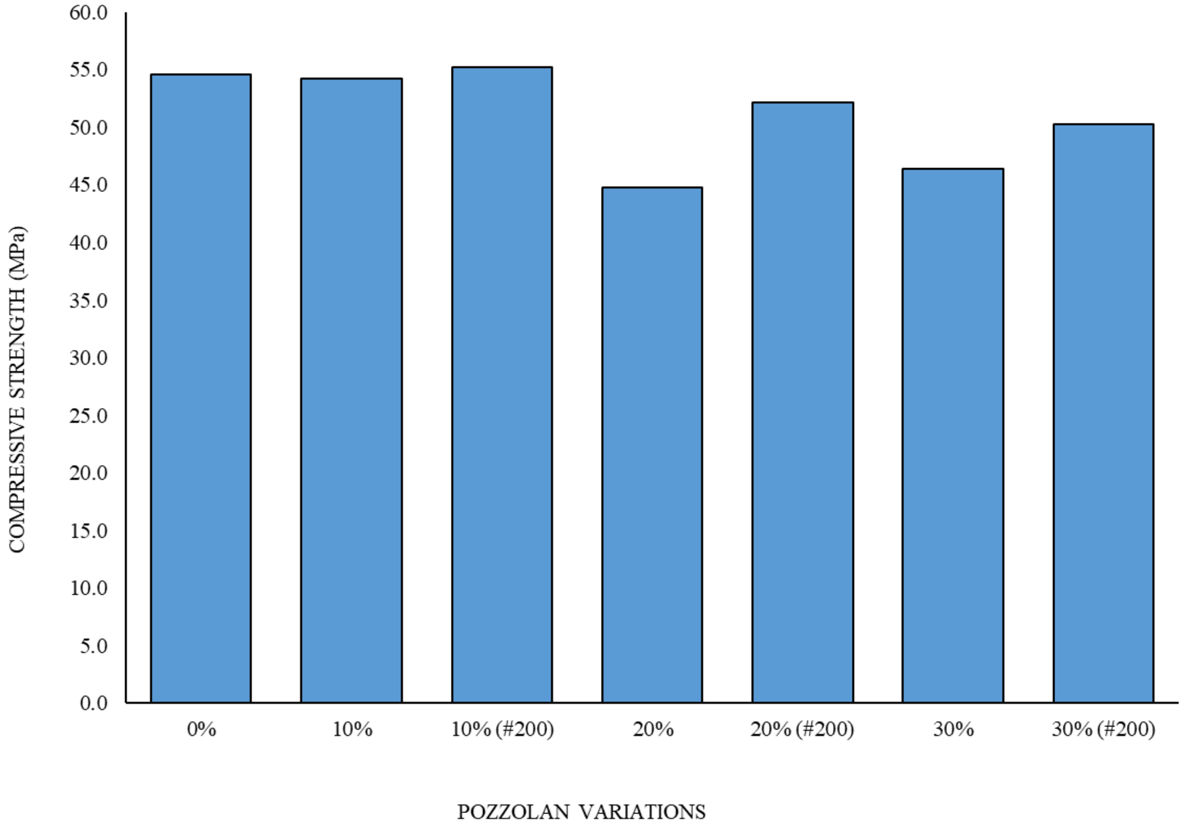

Figure C.6. Graphical representation of compressive strength of specimen at 364 days curing age (MPa)

Table C.8. Compressive strength of specimens at all curing ages (MPa)

Constants	**7 days**	**28 days**	**56 days**	**112 days**	**182 days**	**364 days**
0%	38.6	44.3	46.9	47.0	53.2	46.9
10%	35.9	40.0	44.1	45.9	49.4	44.1
10% (#200)	38.2	39.7	47.4	48.9	48.5	47.4
20%	30.1	34.1	35.1	38.8	39.3	35.1
20% (#200)	33.7	37.4	42.9	46.0	46.4	42.9
30%	32.0	38.6	36.4	39.8	34.7	46.4
30% (#200)	35.0	38.9	39.3	46.2	43.8	50.3

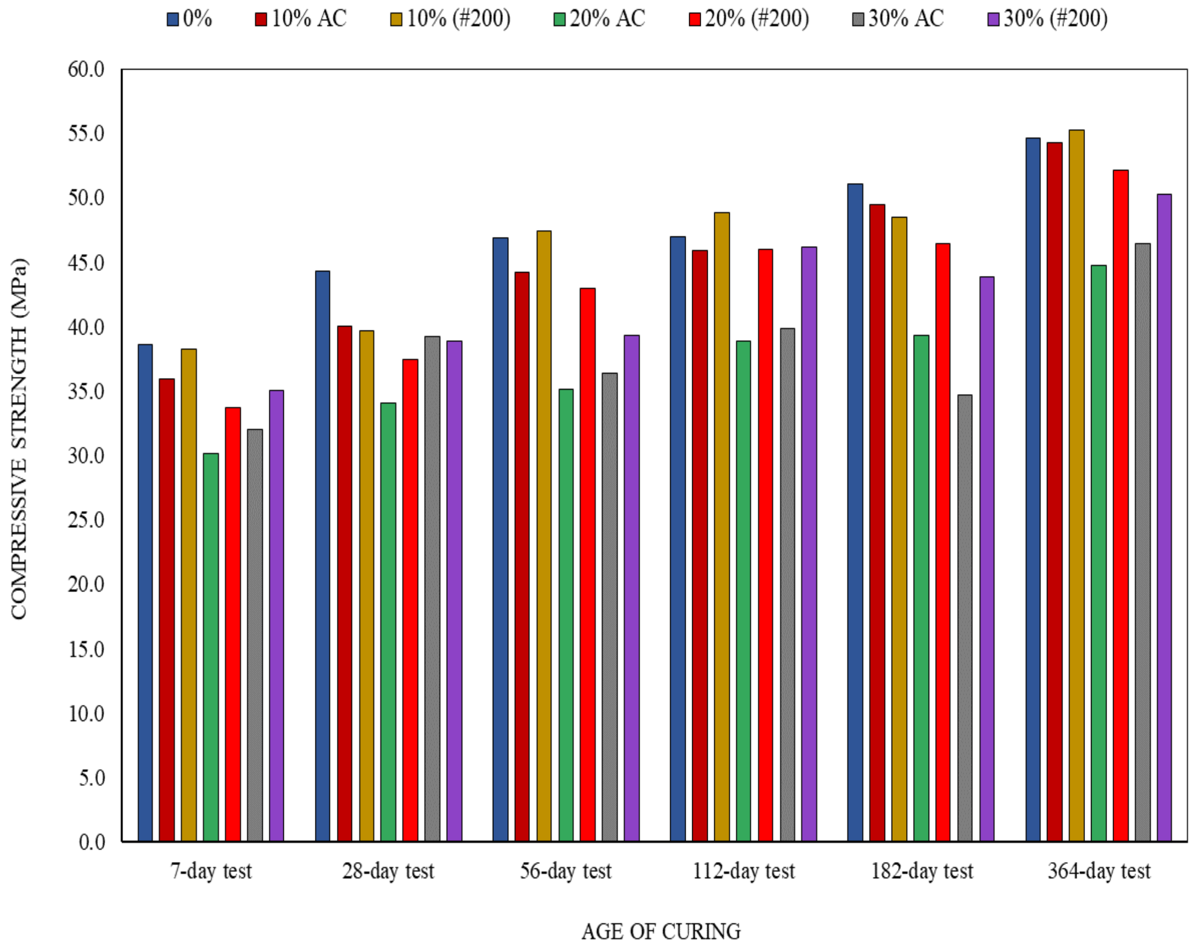

Figure C.7. Graphical representation of compressive strength of specimens at all curing age (MPa)

APPENDIX D

STATISTICAL COMPARISON OF MEAN COMPRESSIVE STRENGTHS

The statistical comparison of mean compressive strengths at the 90% confidence limit was analyzed using a 2-sided Student's t-test. For each comparison two different distributions of compressive strength values and their standard deviations were taken into consideration. A pooled variance was used for these comparisons, as it has been found to be more consistent than using separate variances (Debella 2004; Debella and Ries 2006; Jin 2013; Helgeson 2014).

The formula for pooled variance is:

$$s_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2} \tag{D.1}$$

where s_1 and s_2 are the standard deviations of the two samples and

n_1 and n_2 are the two sample sizes.

For comparing the means of two different samples using pooled variance, a t value is calculated as follows:

$$t = \frac{\bar{x}_1 - \bar{x}_2 - \Delta}{\sqrt{s_p^2\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}} \tag{D.2}$$

where $\bar{x}_1$ and $\bar{x}_2$ are the means of the two samples,

Δ is the hypothesized difference between the two means (zero if testing for equal means),

s_p^2 is the pooled variance, and

n_1 and n_2 are the sizes of the two samples. The t value is then compared to the critical value for t that corresponds to the desired level of significance.

The degrees of freedom are as follows:

$$df = n_1 + n_2 - 2 \tag{D.3}$$

The null hypothesis for the two tailed test is stated as follows:

H$_0$: $\bar{x}_1 - \bar{x}_2 = 0$ (D.4)

Alternatively: H$_a$: $\bar{x}_1 \neq \bar{x}_2$, or H$_a$: $\bar{x}_1 - \bar{x}_2 \neq 0$

The statistical comparisons of the mean compressive strengths for all tested materials at all testing ages are presented in Table D.1. – Table D.9. Also presented in Table D.10 is the comparison of the mean strengths ages of 182 days and a year.

The explanation of table column headings is as follows:

Age (days): Age of curing at the time of testing.

$\bar{x}_1$ = mean value of compressive strengths of the samples of data set 1 [MPa].

s_1 = standard deviation of data set 1 [MPa].

$\bar{x}_2$ = mean value of compressive strengths of the samples of data set 2 [MPa].

s_2 = standard deviation of data set 2.

n_1 = number of samples in data set 1.

n_2 = number of samples in data set 2.

df = degrees of freedom ($n_1 + n_2 - 2$).

s_p^2 = Pooled variance

sd = standard error of difference, corresponding to the denominator in Eq. D.2.

Actual t = the actual t-value, calculated by Eq. D.2.

Tin V (v) = in Excel, the function TinV calculates the inverse of two-tailed student's T distribution, which is used in hypothesis testing on smaller data set samples. It corresponding to the critical value of t associated with a particular level of significance (or probability that the two mean values are equal) and sample sizes (degrees of freedom).

Abs (Actual t / TinV) = the absolute value of the ratio of the actual t value to the critical t value.

Statistically Significant = if the difference is statistically significant, the value of Abs (absolute) (Actual t/TinV) > 1, and "YES" is listed in the table. If the difference is not statistically significant, "NO" appears.

Probability = If less than 10%, then the difference is statistically significant at the 90% confidence limit.

Table D.1. Comparison between 10% as-crushed and passing no. 200 sieve, at all curing ages

Age (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
7	35.92	1.93	38.24	2.63	5	5	8	5.32	1.46	-1.59	1.86	0.86	NO	15%
28	39.98	3.73	39.72	2.34	5	5	8	9.69	1.97	0.13	1.86	0.07	NO	90%
56	44.15	1.96	47.41	3.05	15	15	28	6.57	0.94	-3.48	1.70	2.05	YES	0%
112	45.86	2.23	48.88	4.04	5	5	8	10.65	2.06	-1.46	1.86	0.79	NO	18%
182	49.42	2.15	48.48	3.15	5	5	8	7.27	1.71	0.55	1.86	0.30	NO	60%
1 year	54.23	3.05	55.24	2.84	15	13	26	8.73	1.12	-0.90	1.71	0.53	NO	38%

Table D.2. Comparison between 20% as-crushed and passing no. 200 sieve, at all curing ages

Age (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
7	30.12	2.40	33.74	2.56	5	5	8	6.16	1.57	-2.31	1.86	1.24	YES	5%
28	34.10	0.87	37.44	1.64	4	5	7	1.86	0.92	-3.65	1.89	1.93	YES	1%
56	35.10	2.30	42.92	2.70	15	15	28	6.29	0.92	-8.54	1.70	5.02	YES	0%
112	38.84	4.15	46.00	4.09	5	4	7	17.01	2.77	-2.59	1.89	1.37	YES	4%
182	39.28	1.87	46.40	6.70	5	5	8	47.16	4.34	-0.86	1.86	0.46	NO	41%
1 year	44.77	4.21	52.15	5.07	15	15	28	21.71	1.70	-4.34	1.70	2.55	YES	0%

Table D.3. Comparison between 30% as-crushed and passing no. 200 sieve, at all curing ages

Age (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
7	32.00	6.22	35.04	1.65	5	5	8	20.71	2.88	-1.06	1.86	0.57	NO	32%
28	39.23	0.38	38.94	2.42	4	5	7	3.41	1.24	0.23	1.89	0.12	NO	82%
56	36.42	3.26	39.27	3.04	12	15	25	9.85	1.22	-2.34	1.71	1.37	YES	3%
112	39.82	6.44	46.16	3.14	5	5	8	25.67	3.20	-1.98	1.86	1.06	YES	8%
182	34.70	7.20	43.80	5.60	5	5	8	41.60	4.08	-2.23	1.86	1.20	YES	6%
1 year	48.09	1.84	50.29	2.55	11	15	24	5.20	0.90	-2.43	1.71	1.42	YES	2%

Table D.4. Comparison between 10% and 20% as-crushed samples, at all curing ages

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
7	35.92	1.93	30.12	2.40	5	5	8	4.74	1.38	4.21	1.86	2.26	YES	0%
28	39.98	3.73	34.1	0.87	5	4	7	8.27	1.93	3.05	1.89	1.61	YES	2%
56	44.15	1.96	35.1	2.30	15	15	28	4.57	0.78	11.60	1.70	6.82	YES	0%
112	45.86	2.23	38.84	4.15	5	5	8	11.10	2.11	3.33	1.86	1.79	YES	1%
182	49.42	2.15	39.28	1.87	5	5	8	4.06	1.27	7.96	1.86	4.28	YES	0%
1 year	54.23	3.05	44.77	4.21	15	15	28	13.51	1.34	7.05	1.70	4.14	YES	0%

Table D.5. Comparison between 10% and 20% passing no. 200 sieve samples, at all curing ages

Age (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
7	38.24	2.63	33.74	2.56	5	5	8	6.74	1.64	2.74	1.86	1.47	YES	3%
28	39.72	2.34	37.44	1.64	5	5	8	4.08	1.28	1.78	1.86	0.96	NO	11%
56	47.41	3.05	42.92	2.70	15	15	28	8.30	1.05	4.27	1.70	2.51	YES	0%
112	48.88	4.04	46.00	4.09	5	4	7	16.50	2.72	1.06	1.89	0.56	NO	33%
182	48.48	3.15	46.40	6.70	5	5	8	50.37	4.49	1.22	1.86	0.65	NO	26%
1 year	55.24	2.84	52.15	5.07	13	15	26	17.56	1.59	1.95	1.71	1.14	YES	6%

Table D.6. Comparison of 10% and 30 % as-crushed samples, at all curing ages

Age (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
7	35.92	1.93	32.00	6.22	5	5	8	21.21	2.91	1.35	1.86	0.72	NO	22%
28	39.98	3.73	39.23	0.38	5	4	7	8.01	1.90	0.39	1.89	0.21	NO	70%
56	44.15	1.96	36.42	3.26	15	12	25	6.83	1.01	7.64	1.71	4.47	YES	0%
112	45.86	2.23	39.82	6.44	5	5	8	23.22	3.05	1.98	1.86	1.07	YES	8%
182	49.42	2.15	34.70	7.20	5	5	8	28.23	3.36	4.38	1.86	2.36	YES	0%
1 year	54.23	3.05	48.09	1.84	15	11	24	6.83	1.04	5.92	1.71	3.46	YES	0%

Table D.7. Comparison between 10% and 30% passing no. 200 sieve samples, at all curing ages

Age (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
7	38.24	2.63	35.04	1.65	5	5	8	4.82	1.39	2.30	1.86	1.24	YES	5%
28	39.72	2.34	38.94	2.42	5	5	8	5.67	1.51	0.52	1.86	0.28	NO	62%
56	47.41	3.05	39.27	3.04	15	15	28	9.27	1.11	7.32	1.70	4.30	YES	0%
112	48.88	4.04	46.16	3.14	5	5	8	13.09	2.29	1.19	1.86	0.64	NO	27%
182	48.48	3.15	43.80	5.60	5	5	8	20.64	2.87	1.63	1.86	0.88	NO	14%
1 year	55.24	2.84	50.29	2.55	13	15	26	7.22	1.02	4.86	1.71	2.85	YES	0%

Table D.8. Comparison of 20% and 30% as-crushed samples, at all curing ages

Age (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
7	30.12	2.40	32.00	6.22	5	5	8	22.22	2.98	-0.63	1.86	0.34	NO	55%
28	34.10	0.87	39.23	0.38	4	4	6	0.45	0.47	-10.81	1.94	5.56	YES	0%
56	35.10	2.30	36.42	3.26	15	12	25	7.64	1.07	-1.23	1.71	0.72	NO	23%
112	38.84	4.15	39.82	6.44	5	5	8	29.35	3.43	-0.29	1.86	0.15	NO	78%
182	39.28	1.87	34.70	7.20	5	5	8	27.67	3.33	1.38	1.86	0.74	NO	21%
1 year	44.77	4.21	48.09	1.84	15	11	24	11.75	1.36	-2.44	1.71	1.43	YES	2%

Table D.9. Comparison between 20% and 30% passing no. 200 sieve samples, at all curing ages

Age (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
7	33.74	2.56	35.04	1.65	5	5	8	4.64	1.36	-0.95	1.86	0.51	NO	37%
28	37.44	1.64	38.94	2.42	5	5	8	4.27	1.31	-1.15	1.86	0.62	NO	28%
56	42.92	2.70	39.27	3.04	15	15	28	8.27	1.05	3.48	1.70	2.04	YES	0%
112	46.00	4.09	46.16	3.14	5	5	8	13.29	2.31	-0.07	1.86	0.04	NO	95%
182	46.40	6.70	43.80	5.60	5	5	8	61.09	4.94	-0.16	1.86	0.08	NO	88%
1 year	52.15	5.07	50.29	2.55	13	15	26	15.36	1.49	1.25	1.71	0.73	NO	22%

Table D.10. Comparison of all variations with both type of materials at later curing ages

(182 days to 1 year)

Samples	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig?	Prob.
0%	51.1	4.9	54.6	4.5	4	15	17	20.6	2.6	-1.4	1.7	0.8	NO	19%
10% ac	49.4	2.2	54.2	3.1	5	15	18	8.3	1.5	-3.2	1.7	1.9	YES	0%
10% -200	48.5	3.2	55.2	2.8	5	13	16	8.5	1.5	-4.4	1.8	2.5	YES	0%
20% ac	39.3	1.9	44.7	4.2	5	15	18	14.6	2.0	-2.8	1.7	1.6	YES	1%
20% -200	43.0	9.5	52.1	5.1	5	15	18	40.2	3.3	-2.8	1.7	1.6	YES	1%
30% ac	34.7	7.2	48.0	1.8	5	11	14	17.2	2.2	-6.0	1.8	3.4	YES	0%
30% -200	43.8	5.6	50.2	2.6	5	15	18	12.0	1.8	-3.6	1.7	2.1	YES	0%

APPENDIX E

STATISTICAL COMPARISON OF MEAN COEFFICIENTS OF PERMEABILITY

The statistical comparison of mean coefficients of permeability at the 90% confidence limit was analyzed using a 2-sided Student's t-test following the same procedures as were described in Appendix D for compression test results. Statistical comparisons are made in Tables E.1 through E.18, for which table headings have been defined in Appendix D.

Table E.1. Comparison of coefficients of permeability for 0% and 10% as-crushed samples at curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig?	Prob.
442	1.51	0.47	0.99	0.35	6	6	10	0.17	0.24	2.17	1.81	1.20	YES	5.5%

Table E.2. Comparison of 0% and 10% passing no. 200 sieve samples at selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig?	Prob.
442	1.51	0.47	0.75	0.13	6	5	9	0.13	0.22	3.48	1.83	1.90	YES	0.7%

Table E.3. Comparison of 0% and 20% as-crushed at the selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig?	Prob.
442	1.51	0.47	1.76	0.23	6	6	10	0.14	0.21	-1.17	1.81	0.65	NO	26.9%

Table E.4. Comparison of 0% and 20% passing no.200 sieve sample at selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	1.51	0.47	1.35	0.52	6	6	10	0.25	0.29	0.56	1.81	0.31	NO	58.8%

Table E.5. Comparison of 0% and 30% as-crushed at selected curing age of 364 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
364	1.51	0.47	2.35	0.36	6	6	10	0.18	0.24	-3.48	1.81	1.92	YES	0.6%

Table E.6. Comparison of 0% and 30% passing no. 200 sieve samples at selected curing age of 364 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
364	1.51	0.47	2.12	0.01	6	6	10	0.11	0.19	-3.18	1.81	1.75	YES	1.0%

Table E.7. Comparison of 0% and 30% as-crushed at the selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	1.51	0.47	2.34	0.38	6	6	10	0.18	0.25	-3.36	1.81	1.86	YES	0.7%

Table E.8. Comparison of 0% and 30% passing no. 200 sieve samples at the selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	1.51	0.47	2.10	0.02	6	6	10	0.11	0.19	-3.07	1.81	1.69	YES	1.2%

Table E.9. Comparison of 10% as-crushed and 10% passing no. 200 sieve sample at selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	0.99	0.35	0.75	0.13	6	5	9	0.08	0.17	1.44	1.83	0.79	NO	18.3%

Table E.10. Comparison of 20% as-crushed and 20% passing no. 200 sieve samples at selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	1.76	0.23	1.35	0.52	6	6	10	0.16	0.23	1.77	1.81	0.97	NO	10.8%

Table E.11. Comparison of 30% as crushed and 30% passing no. 200 sieve sample at selected curing age of 364 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
364	2.35	0.36	2.12	0.01	6	6	10	0.06	0.15	1.56	1.81	0.86	NO	14.9%

Table E.12. Comparison of 30% as-crushed and 30% passing no. 200 sieve samples at selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	2.34	0.38	2.10	0.02	6	6	10	0.07	0.16	1.54	1.81	0.85	NO	15.3%

Table E.13. Comparison of 10% as-crushed and 20% as-crushed samples at selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	0.99	0.35	1.76	0.23	6	6	10	0.09	0.17	-4.53	1.81	2.50	YES	0.11%

Table E.14. Comparison of 10% passing No. 200 sieve and 20% passing No. 200 sieve samples at selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	0.75	0.01	1.35	0.52	5	6	9	0.15	0.23	-2.56	1.83	1.40	YES	3.1%

Table E.15. Comparison of 10% as-crushed and 30% as-crushed samples at selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	0.99	0.35	2.34	0.38	6	6	10	0.13	0.21	-6.45	1.81	3.56	YES	0.01%

Table E.16. Comparison of 10% passing No. 200 sieve and 30% passing No. 200 sieve samples at selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	0.75	0.01	2.11	0.02	5	6	9	0.00	0.01	-171.16	1.83	93.37	YES	0.0%

Table E.17. Comparison of 20% as-crushed and 30% as-crushed samples at selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	1.76	0.23	2.34	0.38	6	6	10	0.10	0.18	-3.18	1.81	1.75	YES	1.0%

Table E.18. Comparison of 20% passing No. 200 sieve and 30% passing No. 200 sieve samples at selected curing age of 442 days

Test (days)	$\bar{x}_1$	s_1	$\bar{x}_2$	s_2	n_1	n_2	df	s_p^2	sd	Actual t	TinV	Abs (t/TinV)	Stat. Sig.?	Prob.
442	1.35	0.52	2.11	0.02	6	6	10	0.13	0.21	-3.60	1.81	1.98	YES	0.5%