Use of Granite and Basalt Rock Powders as Replacement Materials in Cement Production

A thesis

submitted in fulfilment

of the requirements for the degree

of

Masters of Engineering

School of Engineeringat

The University of Waikato

by

Kaiyue Ma

2019

Abstract

The use of pozzolanic materials, rock powder or fly ash, as an additive to replace some cement additives is considered an innovative and cost-effective way to reduce the negative impact of cement production on the environment. There is no report, however, on the addition of rock powder in cement, which is the key motivation for undertaking this research project. In this study, the physical, chemical and compression properties of cement mortart with different percentages of Granite Rock Powder and Basalt Rock Powder (10, 15, 20, and 25%) were investigated, and were compared to that of cement with fly ash. The compressive tests were conducted at 7 and 28 days. The effect of different percentages of rock powders and fly ash on the microstructure was also conducted in order to provide a better understanding on how these three materials affect cement mortar performance. The results showed that mortars with 10% of Granite Rock Powder and 10% Basalt Rock Powder first obtained higher strength, but were lower than control-1 (100% cement). Compared with ordinary concrete, the strength of the 25% fly ash group increases rapidly, and it is expected to obtain higher strengths in the later stages.

Acknowledgments

I am very grateful to the Australian company for their strong support for this research. This study is based on the available recommendations provided by colleagues.

Dr. Ginghis Maranan, my supervisor, for giving me the opportunity to do this project. I am deeply grateful for his guidance and technical advice.

In addition, I would like to thank Annette Rodgers, Helen Turnerand and Dr. Rajab Abousnina for their help. In the course of completing this research, they actively shared their wisdom and knowledge with me. At the same time, I am very grateful to the University of Waikato laboratory staff for their strong support. Through analysis and reference to their professional knowledge, I have further improved the research.

Table of Contents

List of Figures

List of Tables

Chapter 1: Introduction

1.1 Background of the study

Concrete has been regarded as the construction materals widely applied in different areas due to its high strength, strong water resistance, easy-to-use, low cost and other beneficial properties. The production and consumption of cement, the most imperative element for the concrete, have been rapidly increasing. Its environmental impact is of increasing concern. That is, the cement industry is one of the main producers of carbon dioxide, which is a potent greenhouse gas. According to data from the China Investment Consulting website (2019), the global cement production in 2015 was 4.1 billion tons, which doubled in the past decade compared with 2.13 billion tons in 2005. Cement production consumes a lot of non-renewable resources, including coal and limestone. Moreover, a lot of harmful gases and dust are emitted into the air. Calera Brent Constantz and Crystallographer pointed out that, "for every ton of cement we make, we are sequestering half a ton of CO_2". Globally, ordinary Portland cement (OPC) emits 1.35 billion tons of greenhouse gases per year worldwide, accounting for about 7% of global emissions (Rangan, et al., 2004). According to Portland Cement Association (PCA), about 60 percent of carbon dioxide comes from the by-products of roasting, and 40 percent comes from the fuel used to heat the kilns – often coal. Researchers, governments and industries are working to reduce greenhouse gas emissions. They are looking for various solutions to deal with environmental problems such as climate warming.

In addition, some environmental issues are closely related to emissions. Some developed countries and regions have already taken measures to convert waste into available materials. Furthermore, many additives have been found to replace some cement, while gaining considerable or higher strength. Some of these materials also require secondary processing, some of which are not from a wide range of sources but have been widely developed and used.

This research project is eager to find a new type of cement additive from volcanic rock powder. It is a waste material from a wide range of sources, eager to be recycled, and has the potential to become a cement additive due to their similar chemical properties as fly ash. The feasibility of rock powder as a cement additive is presented. The physical, chemical, and compression properties of cement mortars with granite and basalt rock powders as pozzolan materials were investigated, and were compared to that with fly ash. The cement mortars were made according ASTM (ASTM C311, 2000).

1.2 Statement of the problem

To solve this common human problem, we can start from two points, one is to reduce carbon dioxide emissions, and another one is to use or absorb carbon dioxide.

Finding alternatives to cemenit is a direct way of reducing cement production. Replacing some of the cement with fly ash is a common idea now. The uses of pozzolans materials, including fly ash, calcined clays and metakaolin are justified from a number of perspectives. Pozzolans is a common aluminum and siliceous material that does not have the value of cement. However, in the presence of water, the volcanic ash can react with the fine-grained calcium hydroxide to form a compound having a cementitous property. Concrete made with them are supposed to have similar strengths and appearances compared with ordinary Portland cement. The production of concrete partially replaced by new materials can minimize carbon dioxide emissions. High temperature calcined clay has become one important way of production of clay pozzolan, and this is a normally added gel material (Bediakoa et al., 2016), but finding waste as a supplementary material cement gel is more environmentally friendly.

Fly ash has been investigated extensively as a replacement cementing material. However, rock flour powder, one of the source materials for the binders, has lots of unknowns. This paper studies the replacement of cement with rock powder. The results were compared with the fly ash substitution effect. The results of the final experiment will enable people to have a broader understanding of the new material to replace cement, further reducing the overall amount of cement. Also, rock powder is a by-product of mechanical crushing of rocks to produce aggregates, the use of which can also create an economic value.

1.3 Objective of the study

The main aim of the research project is to explore the potential of using rock dust powder in concrete. This shall lead to the following specific objectives:

1) Conducting literature review related to the application of pozzolans in cement;
2) Investigating the physical property, chemical composition, and microstructure of Granite Rock Powder and Basalt Rock Powder, and compare to that with fly ash;
3) Inspecting the effect of various percentages of the two rock powder on the compressive strength and strength development of cement mortar, and compare to that with fly ash; and
4) Analysis and interpretation of the results to deside the most fitting dosages.

1.4 Expected outcomes

The major result of the work would be generating eco-cement on the basis of powder of rock dust. On the basis of the outcomes, there are promising results to use the Granite Rock Powder or Basalt Rock Powder in cement mortar at 90%. This experiment can help reduce the cement consumption and alleviate the carbon dioxide release from the source. Meanwhile, the results can help the factory to obtain the economic value of industrial by-products (rock powder).

1.5 Significance of the study

Previously published research did not study on the utilization of rock powder to replace cement. However, the technology and applications of other pozzolanic materials in cement has been observed over several years. The present study deals with the compressive strength and microstructure of cement with two different rock flour powder and compares them with fly ash. This is a new exploration in the research of new materials, which will explain more possibilities.

High-quality sources of supply of pozzolans have been fully developed. This research on alternatives to pozzolanic cement looks at expanding the use of industrial by-products or social waste and also increasing the use of naturally occurring rock powder. This would expand the range of resources available to humanity and improve its ability to recycle them. The development of modern cities cannot be separated from the production of cement. The research and development of green environment-friendly cement is a boost for the sustainable development of human society.

Because of the similarity between elements and compounds, it can be suggested that rock powder can also be used as cement additive like other volcanic ash. This entry point has reference significance for the research about replacement materials in the future.

1.6 Scope and limitations

The effect of rock powder on the properties of cement should be extensive. However, this report focused on the compressive strength with the replacement percentage of rock flour powder and fly ash. Meanwhile, the effect of rock flour powder on the performance of mortar of cement including polarisation and hydration, but the porosity is still unknown.

1.7 Thesis structure

Chapter 1 introduces the research background and significance of the subject, outlines the feasibility of rock powder to replace cement, the reference of using fly ash as admixture and the limitations in the current research process, and describes the objectives and expected results of this project.

Chapter 2 presents the literature review, which introduces the concept of pozzolanic ash and describes the history of human use of this material. Several major pozzolans were mentioned. The research status and working principle of rock powder as concrete admixture are emphatically introduced.

Chapter 3 describes the experimental procedures and equipment used. Two control groups and three experimental groups were set up. In three experimental compositions, the cement quantity was replaced by 10%, 15%, 20% and 25% of the three materials, namely fly ash, Granite Rock Powder and Basalt Rock Powder.

Chapter 4 discusses the experimental results, including workability, density, compressive strength, combined with SEM, XRF and other experimental equipment for analysis.

Chapter 5 presents the conclusions from this research.

Chapter 2: Literature Review

2.1 Introduction

Pozzolans are the material containing active silica and active alumina, which has no gel properties. At normal temperature, this kind of material can react with calcium hydroxide to form colloids. (ASTM C 618,2003). Pozzolans include fly ash, rock flour powder, glass power. Volcanic rocks are formed by cooling molten magma during a volcanic eruption. Both natural and artificial materials exhibit pozzolanic activity. The rock powder used in this experiment comes from factory by-products (Eaton & Murata, 1960).

2.2 Concrete

Cement and concrete are one of the most fundamental and vastly applied construction materials in the engineering of civil. Generally, concrete or Portland cement concrete refers to the use of cement as a cementing material, which can mixed with sand, fine aggregate, coarse aggregate, water (can contain admixture) in a certain proportion. After uniform mixing, compacting moulding, curing and hardening, it will be a composite materials (Soroka, 1979).

Table 1: Typical concrete mix design (Thomas & Jennings, 2019)

	Lb (yd^3)	**Kg (m^3)**	**Percent by weight**	**Percent by volume**
Water	325	195	8.1	19.5
Cement	591	355	14.7	11.3
Coarse aggregate	1863	1104	46.5	42
Fine aggregate	1231	721	30.7	27.2
Total	4010	2375	100	100

Concrete can be classified by cementing material:

(1) Inorganic cementing material concrete: cement concrete, gypsum concrete,

silicate concrete, sodium silicate concrete etc.

(2) Organic cement concrete: asphalt concrete, polymer concrete.

2.3 Cement

Cement is a powdery inorganic cementing material. The American Association of According to the Test Material (ASTM) standard, Portland cement can be divided into five types based on general purpose use, as required by Roman numeral I-V. This classification also appears in Canada. The cement slurry is made of IV Portland cement. The general properties, microstructure and chemical reaction are similar. Therefore, from this perspective, unless otherwise specified, the general term for "cement" can be recognized as this basic type. This type of cement can be referred to as Portland cement, referred to as "OPC". The main difference between these types of OPC is that the cement fineness and relative proportion are different. Because OPC can be turned into a water slurry, it can be hardened in water or air, and can be tightly bonded to stones, sand, and other materials. Because this cement produces a very high strength to concrete as a cementing material after hardening and is highly aggressive against salt water and fresh water, it is often used in water conservancy and construction projects.

2.4 Water

Since water is an indispensable part of the reaction, water plays a very important role in the reaction process. Under the action of water, the concrete and mud will become very strong. But cognac is the most dangerous factor in concrete. The importance of water to young cement mainly includes two aspects. First, the reaction of water and cement will last for many days or even weeks after mixing. However, if the moisture is removed by the drying method, the reaction of the material cannot be continued, and the concrete cannot be strengthened. Second, the concrete will shrink automatically during the drying process. However, since concrete has the characteristics of light weight and large volume, it cannot be uniformly shrunk. It is necessary to dry the surface first, then the inside is wet. During the dry surface pairing process, the concrete begins to shrink, but the interior does not shrink with the surface.This causes the surface layer of the concrete to become a tension state. When the stress of stretch has exceeded the concrete strength, it would crack. In this case, the concrete strength would be reduced by cracks and it would be not durable. As a result, usually using plastic or wet plates to protect the surface.Waterneeds to be added appropriately. The important parameters associated with this are the water/cement ratio, or "w/c".

If w/c is not high, the concrete would be clumsy and stiff and hard to be placed. Nevertheless, if the w/c is lower, it would be durable and strong. It is easy to understand that any pore in the fresh concrete come from the space of water. The pores reduce the intrinsic strength, making concrete more prone to corrosion, cracking and peeling. Therefore, w/c should be as low as possible. Many factors constrain this process, such as aggregate shape, size and quantity (see next section) and concrete to mold type, forming or cement to fineness and reinforcing pair type. In addition, a plasticizer or water-blocking agent can be added to the mixture to reduce the amount of water required and improve operability. (Thomas & Jennings, 2019)

2.5 Current admixtures in concrete/cement

In order to meet the requirements of modern structural complexity, people use admixtures to change the specific properties of concrete or cement. Common performance changes include hydration heat, setting time, workability and reduced water content.Potential CO_2 reductions and energy savings by using alternative materials (such as fly ash, calcium carbide slag) have been extensively studied. (Fairbairn et al., 2010; Hasanbeigi et al., 2012). Due to various environmental pressures, finding eco-cementing materials that can partially replace cement is a challenge for cement production in the world. They are mineral additives, both natural and industrial by-products. Some are even considered as waste. The application of some mineral additives in blending cement has been studied for more than 30 years (Davidovits, 1994). pozzolan materials.

Admixtures can be classified:

(1) Chemical admixtures: Air entraining agents, Super plasticizers, Water-reducing agents, Retarders and Accelerators, etc.

(2) Mineral admixtures: Rice husk Ash,Silica fume, Blast-furnace slag and Fly-ash, etc.

2.5.1.1 Chemical admixtures

(1)Water-reducing admixture / Plasticizers:

The active agent alters the physical and chemical force of the surface. They are blended into the particles of cement, making them to produce a negative charge leading to the rejection between the particles.

The development of static electricity leads to the dispersion of concrete flocculation particles, and free water becomes available and easy. At the same time, since these agents are organic in nature, they lubricate the mixture, reduce friction and improve operability. The formation of thin layers on cement particles increases the setup time. Because these films cover the cement particles and protect them from hydration, most ordinary plasticizers coagulate more than 30-90 minutes.

Figure 1: Plasticizers

(2)Air entrained admixtures

The air entrained admixtures allows air (usually a small amount) to enter concrete or mortar in the form of tiny bubbles during stirring, often to enhance the frost resistance and workability. Additive mixture of air is the surfactants altering the water surface tension. In tradition, they are on the basis of the vinsol resin or fatty acid salts, but surfactant mixtures or synthetic surfactants will replace these materials to enhance the void characteristics and air stability.

2.5.1.2 Mineral admixtures

(1) Application history of of pozzolan materials

People have a long history of using this material. They were originally used as binders. The special service life and preservation conditions of some of the most famous Roman buildings, such as the Pantheon or the Dugar Bridge were built with pozzolanic mortar and concrete, testify to the excellent workmanship and durability of the adhesives used by Roman engineers. Over the course of the 20th century, the use of pozzolans as additions to Portland cement concrete mixtures has become common practice. Ordinary additions of materials are granulated limestone filler, fly ash, silica fume and blast furnace slag (Lagerblad, 2012).

(2) Action mechanism of pozzolan materials as a cement additive

Many previous studies have shown their chemical action as cement additives. That is pozzolanic activity. A large amount of calcium hydroxide is produced during cement hydration. The book "Natural Pozzolans in Eco-Efficient Concrete" has explained that they have constituents that at ambient temperature combine with lime in the presence of water to form permanently insoluble and stable compounds that behave like hydraulic binders (Gómez et. al., 2013). That is to say that after the pozzolanic filler is added to the cement, the hydrated product calcium hydroxide will cause lattice damage to the pozzolans by dissolving it. The dissolved pozzolanic material produces calcium insoluble hydrated calcium silicate and calcium hydrated calcium aluminate products with calcium ions. This is the secondary hydration of cement. As the curing period is extended, the more complete the reaction, the further the strength will be improved. The pore size refinement effect is related to the formation of additional C–S–H that fills up large capillary pores, thus improving the strength and the impermeable ability of the system; while the grain size refinement is caused by the reduction in the content and size of CH crystals improving the matrix and the transition zone densification.

The reaction equation is as follows:

$SiO_2 + xCa(OH)_2 + mH_2O = xCaO{\cdot}SiO_2\ nH_2O$ (calcium insoluble hydrated calcium silicate) (1)

$Al_2O_3 + yCa(OH)_2 + mH_2O = yCaO{\cdot}Al_2O_3\ nH_2O$ (calcium hydrated calcium aluminate) (2)

The product of the secondary hydration reaction is not only insoluble in water but also has a filling effect. This working principle has also been explained by Chindaprasirt and Rukzon (2008): the pozzolanic material reacts with calcium hydroxide liberated from the cement hydration. The obtained additional products fill the cavity of the matrix thus the average pore size is reduced. As a result, the concrete is denser and its resistance to corrosion is enhanced. (Chindaprasirt & Rukzon, 2008).

According to a report by Wang et al. (1995) on concrete and cement products published in China, physical action includes a micro-aggregate effect, morphologic effect, and dilution effect and in particular, its filling effect can significantly improve the properties of materials. The pozzolanic material can affect the state of accumulation of the system, thus reducing the amount of filling water, depending on the fineness of the material. When the finer particles are added, the amount of water in the surface layer will be increased, and the water requirement will be greatly reduced if the plasticizer is added together. Fine pozzolanic material can not only reduce porosity but also reduce pore size and improve cement strength.

Thus, the three effects of additives are summarized as follows:

1. Fillers: These additives/admixtures are thinner than cement, so when added to concrete, they occupy the small pores previously left vacant.

2. Denuclearization: These fine particles accelerate hydracy.

3. Volcanic ash reaction.

2.5.1.3 Current mineral (pozzolanic) admixtures

(1) Kaolin

Kaolin is also a kind of silica, alumina compound, which has long been used as an artificial pozzolanic additive. But it also has limitations. It can be seen in the book (Arikan et al., 2009) that kaolin is an important component of high-performance building concrete, but its production cost is high, so its use is limited. Furthermore, this book introduces another economical method: TAK produced by heating kaolin can be used as an additive, which can reduce the cost significantly.

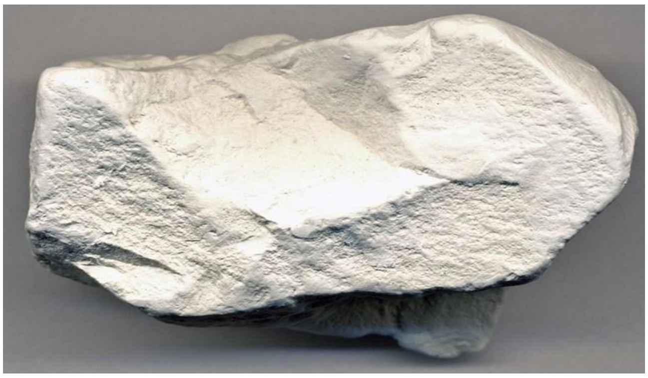


Figure 2: Kaolin

Nowadays, it has been the mainstream method to treat unprocessed kaolin as an additive after heat treatment. Guneyisi, Gesoglu, Ozturan, and Memerdas have studied Metakaolin, which is converted from kaolin by heat treatment. In their studies, different kaolin from four regions of Turkey also produced different pozzolanic activity at different temperatures (Guneyisi et al., 2012).

Kaolin is not anindustrial by-product, including fly ash, rock powder,silica fume, so many articles discuss the treatment of original kaolin in order to obtain the best cement additive. For example, the application of the super-fine particles of metakaolin results in a micro-filler effect and improves the packing of the cement matrix. Arıkan, M and other researchers explained the micro-bearings effect is provided by the flaky particles of metakaolin, resulting in the better sliding of more coarse cement particles. This was published in 2008. They also investigated the microstructure, the improvement of the strength of TAK-cement which is attributed to the pozzolanic reaction and the densification of the cement matrix. It is proposed that the TAK-based additive provided quite a significant improvement of cement properties, which is similar to the effect of “purified,” commercial grade metakaolin (Arikan et al., 2009).

(2) Fly ash

Fly ash is a by-product of the combustion process. Its value as a cement additive has been widely known. We know that fly ash has been extensively used as pozzolan to partially replace Portland cement and to enhance some of the properties of concrete such as resistance to chloride and resistance to surface attacks (Rukzon et al, 2009). According to American Coal Ash Association (ACAA), in the United

States, fly ash is generally stored at coal power plants or placed in landfills. About 43% is recycled.

Figure 3: Fly ash

Furthermore, its working principles have also been investigated many times. As early as 1997, Poon et al. (1997) reported that incorporation of fly ash in place of Portland cement produces mixes with increased workability due to the ball bearing effect of the spherical fly ash particles and it also reduces the average pore size of the cement paste (Poon et al., 1997). Rukzon and Chindaprasirt (2008) also explained that the spherical and solid particle of FA which exerted the ball bearing effect and reduced the friction between the cement particle and aggregate.

For fresh concrete, fly ash affects the plastic properties of concrete by improving workability, lowering water demand, lowering segregation and bleeding, and reducing heat of hydration. For fresh concrete, fly ash can affect the plastic properties of concrete, such as improving processability, lowering water demand and heat of hydration, reducing isolation, and bleeding. For hardened concrete, the addition of fly ash can increase compressive strength, reduce permeability, protect rebar, enhance resistance to sulfates, and reduces alkali aggregation (Mehta & Monteiro, 2006).

Several studies (e.g. Saeki & Monteiro, 2005; Schindler & Folliard, 2005; Wang & Lee, 2010) indicated that fly ash can be mixed with concrete (such as calcium hydroxide evolution, chemical lybinding water evolution, thermal evolution and microstructure evolution) can be predicted by using cement hydration degree and fly ash reaction levels. But there is some controversy about the degree of fly ash reactiton. The amount of calcium hydroxide consumed by 1 gram of fly ash was not clarified. In some reports (e.g. Maekawa, et al., 2008; Papadakis, 1999) the chemical measurement ratio of fly ash and calcium hydroxide is constant and is not affected by the displacement ratio. But some reporters (e.g. Wang et al., 2004; Wang, 2014) found that the higher the replacement ratio, the less calcium hydroxide per gram of fly ash can react. Therefore, it is necessary to discuss the reaction degree of fly ash under different displacement ratios.

(3) Glass powder

The use of recycled waste glass in Portland cement and concrete has attracted worldwide attention due to the increasing cost and environment care. Glass is a combination of a variety of inorganic mineral raw materials, by controlling the cooling process, become hard, uniform, stable, inert, amorphous and anisotropy material (Ortiz, 1996). As learned in Kumarappan`sarticle (Kumarappan, 2013): the glass used in containers, cans, and bottles is sodium carbonate, lime, and silica, accounting for 80% of the recycled glass. His experiments show that replacing glass with 10% of cement can give concrete with higher strength than the control group. Glass can be considered a gel material without taking into account alkalis.

To avoid alkali reactions, the glass powder particle size used should be less than 300 lm. These articles mention that finely ground glass does not have an "ASR" reaction. And aslo, the pozzolanic properties of glass are significant when the particle size is less than 300 lm (Shi et al., 2004, Schwarz, et al., 2008; Saccani & Bignozzi, 2010). The combination of coal fly ash, ground blast furnace slag, and other cementing materials can also reduce the expansion rate of ASR. In any case, when waste glass is used as a cement substitute. The compressive strength will be lower, especially in the early stages. (Shi et al., 2004; Schwarz & Neithalath, 2008; Schwarz, et al., 2008).

Figure 4: Glass powder

(4) Rice husk ash

Rice husk ash is a agricultural residue obtained from the outer layer during the grinding of rice grains. It accounts for 20 per cent of the world's 500 million tons of rice production (Bhanumathidas & Mehta, 2001).

Figure 5: Rice husk ash

In Ganesan's experiment (Ganesan, et al., 2008), the cement replacement ratio was 5% to 35%, and the compressive strength increased and then decreased. The peak is a replacement rate of 10 percent. After 30 percent, the strength of the resistance is lower than that of the control group. The reason of increasing is the pozzolanic reationt and the high speicific surface area.

(5) Metakaolin

Calcined clays adhesive can be used as a partial substitute for cement,which can enhance resistance, increase sulfate attack, control alkali-silicon reaction, and reduce permeability. Previous studies have shown that Metakaolin has a very positive effect on cement strength after 2 days, especially 28 days and 180 days, The demand for water from mixed cement is significantly higher than that of relatively pure cement, and the higher the content, the higher the demand for water (Badogiannis et al., 2005).

Figure 6: Metakaolin

(6) The synergy between more than one pozzolanic powder

In addition to a single material replacement, some researchers will mix the pozzolanic substances together. We can see that some combinations have synergistic effects and better properties. The same weight of fly ash and bagasse ash or grated pair of fly ash and rice husk ash was taken by Chindaprasirt and Rukzon. Their experimental results show that concrete has high corrosion resistance to FARB and FABA and chloride ions in concrete are higher than concrete containing a volcanic ash. (Rukzon & Chindaprasirt, 2008). In addition, the mixture of volcanic ash also includes many construction waste, and demolition waste and construction waste (C&D waste) are often made up of materials in the building. When the organic materials and metals are removed, the C&D waste is ground to form a recycled aggregate and then reused depending on its chemical and mechanical properties. The economic and environmental benefits will be significantly reduced in civil engineering.

2.6 Pollution by production of cement and concrete

Cement is the main cementing material of concrete. Construction projects are very demanding for both cement and concrete. The cement production flow chart is as follows: The first (S1) is the extraction and preparation of quarry raw materials. The second process (S2) is the clinker production of cement plants. It includes a fine blend of raw materials and cement kiln processes, during which the decomposition of carbonates and the combustion of fuel emit large amounts of carbon dioxide and other harmful gases and dust. The third process (S3) is the production of cement, including the grinding of clinker and the mixing of gypsum.

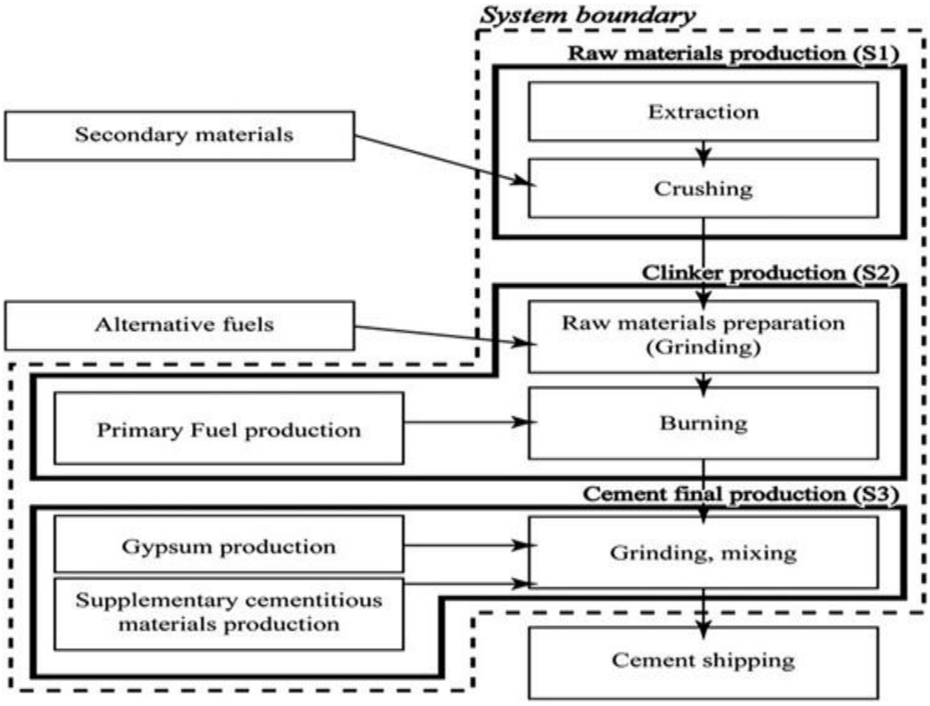


Figure 7: Precess of cement production (Chen et al., 2010)

Cement's manufacturing industry is under intense scrutiny in recent years because of the amount of carbon dioxide it emits. Actually, the data accounts for 5% - 7% of total human emissions. (Hendricks et al., 1998; Humphreys & Mahasenan, 2002). The cement industry is also an important source of other harmful compounds such as carbon monoxide (CO) and heavy metals. (Lei et al., 2011; Wang, 2013). In Chen's report (Chen et al., 2010), it has shown that direct kiln emissions are major contributors to the five main impact categories: global warming, terrestrial ecotoxicity, photochemical oxidation, acidification and eutrophication.

Furthermore, cement production is a process of highly energy consumption. It is estimated that the cement industry consumes about 2 percent of the world's primary energy and nearly 5 percent of global energy (Martin et al., 1995). Clinker production is the most energy-intensive part of cement manufacturing, resulting in significant CO_2 emissions. In blended cements, some clinkers are replaced by industrial by-products such as fly ash, blast furnace slag and other pozzolanic materials (e.g. volcanic materials). These products are mixed with grated clinker to produce new type of cement.

2.7 Waste materials as admixtures

Modern lifestyles have led to an increase in the amount and type of waste generated, leading to a waste disposal crisis. Such as glass, plastic, rock powder and so on. In order to treat or at least reduce the accumulation of some waste, some of the waste has to be reused to replace a certain percentage of the main material used in ordinary Portland cement concrete (OPC). Waste research can help protect natural resources and address the growing waste management crisis. In the study (Batayneh et al., 2007) ground plastic and glass were used to replace up to 20% of the fine aggregates in the concrete mixture, while broken concrete was used to replace up to 20% of the coarse aggregates.

2.7.1 Rock dust

Rock powder, also known as rock dust, rock minerals, and mineral powder, consists of fine rock, processed by natural or mechanical methods, and contains minerals and trace elements widely used in organic agriculture practice, so rock dust can be applied to the soil.There are many applications of rock powder in production, such as acting as a heat sink to help prevent coal dust explosions in coal mines. The dust is usually made of pulverized limestone. Rock dust has been used since the early 1900s, but there have not been technological investigations on cement with rock powder (Harteis et al., 2016).

The classification of rock powder is mainly divided according to the type of rock. A rock is a solid polymer of minerals and natural glass, stable in shape. A rock made up of a mineral is called a single mineral rock, such as marble rock and quartz rock. Rocks with a variety of mineral prosands are called complex rocks, such as granite and long rocks.

At present, the widespread use of rock powder is to replace the natural river sand in concrete. Some reports (Babu et al., 1997; Nagaraj & Banu, 1996; Ilangovana, et al., 2008) have studied the consumption, workingability, compressive strength and cost of concrete made of rock dust. Sahu (2003) reported a significant increase in compression strength, modulus of rupture, and split tensile strength when 40% of the sand was replaced by rock dust in concrete. Indian Journal of Science and Technology (Bai, 2011) has described the performance of concrete with crushedrock powder. The purpose is to study the properties of mortar and concrete with crushed rock powder (CRP) as a partial substitute for natural sand. For mortar, CRP is replaced by 20%, 40%, 60%, 80% and 100%. For concrete,at the substitution levels of 20%, 30%, and 40%. The results show that the compressive strength, splitting tensile strength and flexural strength of concrete is not affected by the use of CRP instead of sand as fine aggregate by up to 40%. Therefore, CRP can effectively replace natural sand without reducing the strength of concrete. The replacement level of CRP is as high as 40%. At present, the role of rock powder in foam concrete is studied and analyzed. The results show that by controlling the volcanic rock powder content to 20%, it is possible to prepare foam concrete with excellent performance and compressive strength of 1.36 MPa.(Su et al., 2014)

Hameed and Sekar (2009) introduced the feasibility of using quarries rock dust and marble sludge powder to replace natural sand in concrete. Compared with natural sand concrete, the compression, cracking and tensile strength and durability of quarry rock dust concrete are nearly 14% higher than that of conventional concrete. Resistance to sulphate attack was enhanced greatly The application of green concrete is an effective way to reduce environmental pollution and improve the durability of concrete under harsh conditions. The study of the usage of rock powder to replacer cement in mortar is still rare.

Based on limestone, the product is sprinkled on the rock wall of the coal mine to maintain the level of coal dust and avoid black lung disease and explosion.

Figure 8: Rock dust

2.7.2 Ceramic roof tile

Pozzolanic material is divided into artificial pozzolans and natural pozzolans, fired clay is a major man-made volcanic ash.Before the invention of cement, it was often used with limestone (Vitruve, 1960). Before heating, the material does not have pozzolanic properties, and when it is heated, high temperature destroys its crystal structure, resulting in a quasi-crystal structure and a disordered aluminum silicate structure (Erdoğan, 1997). The raw materials for tiles are clay, quartz and feldspar, often used on roofs, and when old buildings are abandoned, a large number of discarded tiles need to be recycled.

Previous reports have explored the feasibility of replacing Portland cement concrete with waste generated from the building site (Batayneh et al., 2007). This study (Lavat et al., 2009) confirms that the calcined ceramic waste bricks at about 950 degrees can be a very effective cement additive with a proper degree of grinding. Feldspars, quartz, and metal impurities found in tiles do not affect the volcanic properties of the tiles.In this paper (Ay & Ünal, 2000), waste tiles can be replaced with up to 35% of cement.

Figure 9: Ceramic roof tile

2.8 Summary

As previous mentioned in the overview points, there are many studies of pozzolans used in cement or concrete mixes. Although other pozzolans have been used as cement fillers, there is a little research on the replacement of stone powder in this field. In the future, it is hoped that more experimental projects will do research on rock powder in cement to solve more engineering problems.

Chapter 3: Methodology

3.1 Introduction

This chapter describes the methods implemented for the experiment and analysis of the project. It covers a brief description of all resources, provides detailed information on the hybrid design, which including cement replacement ratio, module size,casting, curing and testing of the samples.

It well known that rock powder is a kind of waste with a high economic value. Mainstream processes are to replace the natural river sands in concrete, which has not been studied as a cement additive. This alternative additive can also significantly reduce CO_2 emissions from cement production. This chapter mainly introduces the cement, basar rock powder, granite powder, fly ash, sand and water in the experimental process. Includes physical and chemical properties, specifications used and sample production processes. The instruments and methods used in the whole experimental process are also introduced.

3.2 Experiment

The research scheme adopted is as follows:

(1) Two different samples of pozzolan materials were used, namely Granite Rock Powder and Basalt Rock Powder. At the same time, the more well-known fly ash was also used in the experiment.SEM, EDS, XRF and other instruments were used to determine their physical and chemical properties.

(2) Mix the collected rock powder or fly ash with cement and sand in different proportions to make cement mortar samples. The experiment is divided into four groups and two controls, namely group1, group2, and group3. Different groupspecimens will be prepared to determine which will bethe best ratio for cement paste and which material is best for compressive strength. Five replicates will be prepared for each specimen type to test the data under two hardening times at -7 days and 28 days.However, in the calculation, the quantity of every type will be calculated as six replicates to ensure sufficient materials.

(3) Samples of cement mortar with different admixtures were placed in water at room temperature for 24 hours after incubation, and then samples of curing ages of 7 days and 28 days were obtained respectively, and their compressive strength was tested to find out the influence of admixtures on sample strength. SEM, XRF and other instruments were used to analyze the change rule.

(4) Finally, based on the evaluation of the cement mortar, determination of their internal reaction, chemical formula, and microstructure, the law of the cement mortar with different percentages of replacement is obtained and thus lays a good theoretical foundation for the actual application of volcanic rocks.

To clarify, my experimental section only focuses on the results of day 7 and day 28 observation will be completed by my colleagues.

3.3 Materials and method

3.3.1 Fly ash

Class F (lower calcium) flying ash of about 15 μm was utilized in the research, which sources from Millmerran of Pozzolanic in Queensland, Australia. The fly ash's chemical composition is offered in Table 2. The fly ash density is 1100 kg/m^3 (Abousnina, 2015).

Table 2: Chemical composition of fly ash (%)

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
Percentage (%)	51.8	24.4	9.62	4.37	1.5	0.34	1.41	0.26

As can be seen from the picture, there are two kinds of structures, one is honeycomb, another isa ball. Spherical particles vary in size from 5 to 2000 μm. The surface of most spherical particles is smooth, while the surface of a few large spherical particles is rough. In honeycomb tissue, we can also see small spherical particles interspersed among them. Compared with rockdust, the contact surface of fly ash particles is smoother.

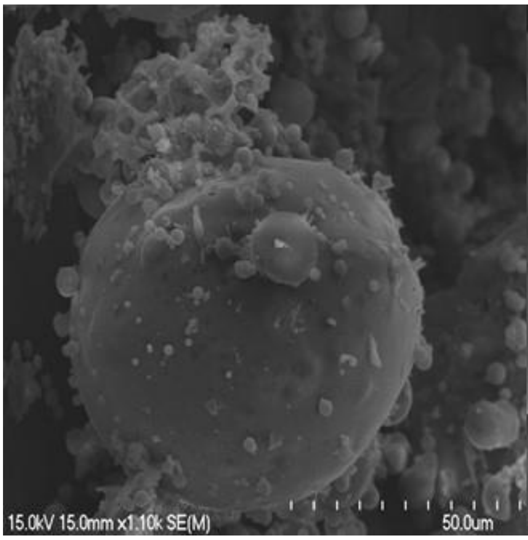


Figure 10: Fly ash (1.1k)

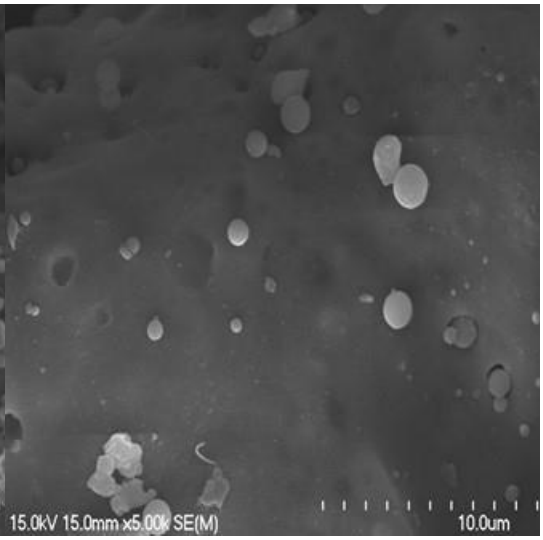


Figure 11: Fly ash (5k)

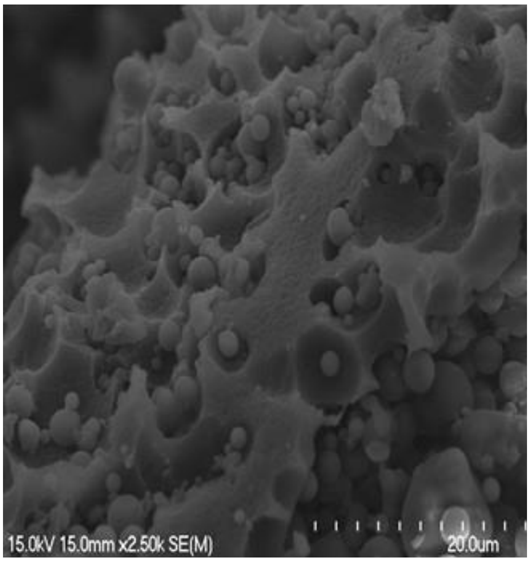


Figure 12: Fly ash (2.5k)

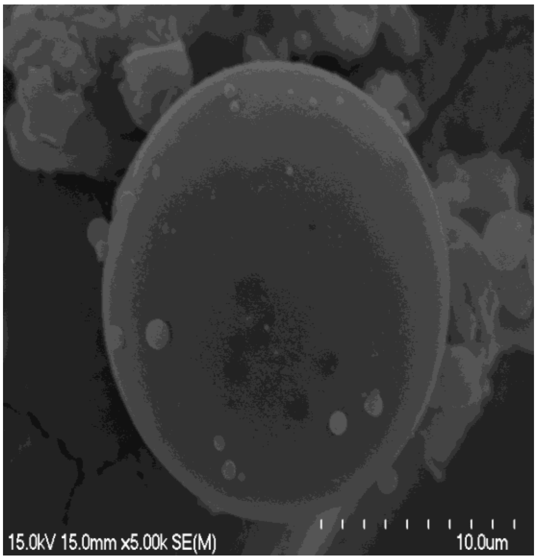


Figure 13: Fly ash (5k)

Combining the elemental analysis of the two areas, the corrected elemental analysis is as follows:

Table 3: Elements of fly ash (1)

Element	Wt. %		Atom %	
C K	7.13	+/-1.12	11.7	+/- 1.86
O K	42.59	+/-0.64	52.45	+/- 0.79
Al K	20.07	+/-0.39	14.66	+/- 0.29
Si K	30.2	+/-0.53	21.18	+/- 0.37
Total	100		100	

Table 4: Elements of fly ash (2)

Element	**Wt. %**		**Atom %**	
O K	38.71	+/-0.91	52.27	+/- 1.22
Al K	24.83	+/-0.55	19.88	+/- 0.44
Si K	35.6	+/-0.79	27.38	+/- 0.61
K K	0.86	+/-0.23	0.48	+/- 0.13
Total	100		100	

The comprehensive analysis of the two electricity charge elements is as follows, because this EDS analysis is limited to a small area, it cannot represent the entire material element situation.

Table 5: Elements of fly ash

Element	Wt. %	Atom %
C K	3.565	5.85
O K	40.65	52.36
Al K	22.45	17.27
Si K	32.9	24.28
K K	0.43	0.24
Total	100	100

Generally, the elements of the specimen contain Carbon, oxygen,aluminum, silicon,and potassium. There may be other trace elements that have not been detected. The highest concentrations are oxygen, aluminum, and silicon, which are widely distributed. Moreover, the distribution of carbon and potassium is local, because not every region has these two elements.

Table 6: Compound composition of fly ash

SiO_2 (%)	Al_2O3 (%)	TiO_2 (%)	Fe_2O_3 (%)	Na_2O (%)	MgO (%)
58.69	29.23	1.182	2.67402	0.586	0.572
CaO (%)	P_2O_5 (%)	CO_2 (%)	Sum (%)	Compton(%)	K_2O (%)
2.484	0.304	3.59	100.35	104.896	0.611

In chemical composition analysis (XRF), the chemical compositions of fly ash are shown in Table 6. The sum of SiO_2 and Al_2O_3 of fly ash is 87.92%.

3.3.2 Granite Rock Powder

Granite Rock Powder like the previous Basalt Rock Powder has irregular angular shapes. But the difference between them is that most of its particles tend to be stable in size. As can be seen from Figure 14, most of the particles are at the size of 200 μm. Although the largest particle reaches 2000 μm, it is more uniform thanBasalt Rock Powder. At the same time, the other two materials have rounder particles.

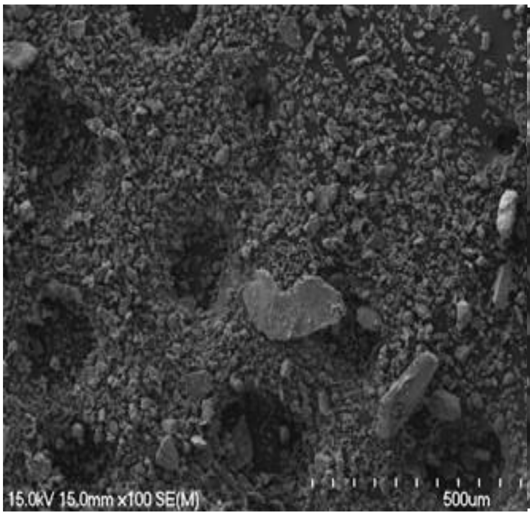


Figure 14: Granite Rock Powder (0.1k)

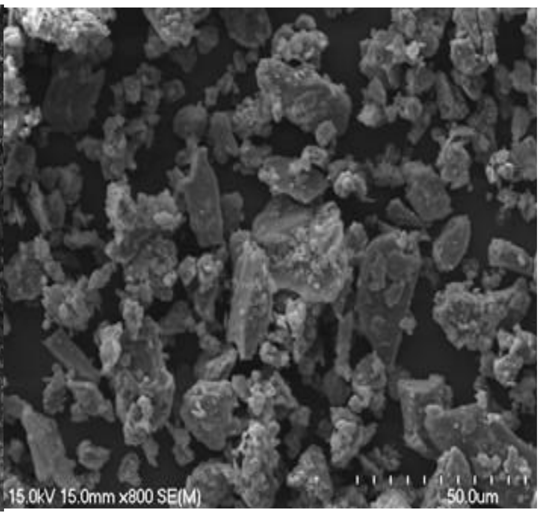


Figure 15: Granite Rock Powder (0.8k)

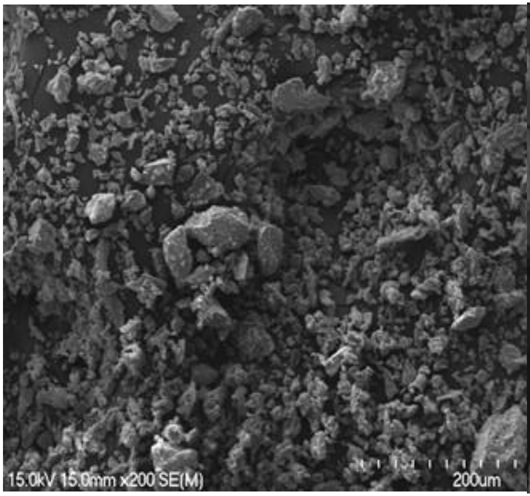


Figure 16: Granite Rock Powder (0.2k)

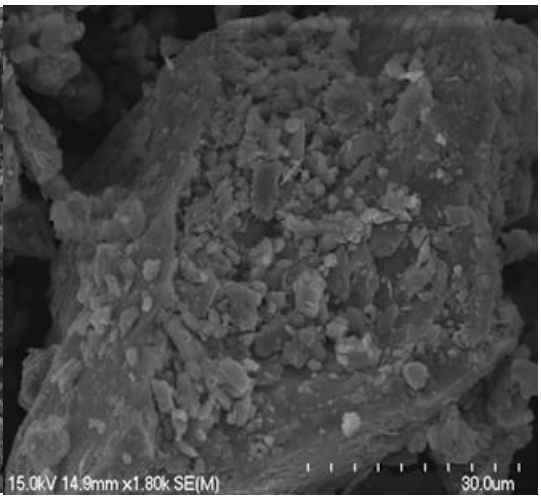


Figure 17: Granite Rock Powder (1.8k)

Table 7: Elements of Granite Rock Powder (1)

Element	**Wt. %**		**Atom %**	
O K	36.74	+/-0.94	52.23	+/- 1.34
Mg K	0.97	+/-0.19	0.91	+/- 0.18
Al K	6.52	+/-0.53	5.5	+/- 0.44
Si K	44.27	+/-0.84	35.85	+/- 0.68
K K	2.73	+/-0.36	1.59	+/- 0.21
Ca K	2.19	+/-0.42	1.24	+/- 0.23
Fe K	6.58	+/-1.61	2.68	+/- 0.66
Total	100		100	

The selected-area (three areas) EDS of Granite Rock Powder are as follows:

Table 8: Elements of Granite Rock Powder (2)

Element	**Wt. %**		**Atom %**	
O K	36.57	+/-0.92	50.77	+/- 1.28
Na K	4.2	+/-0.45	4.06	+/- 0.44
Al K	15.21	+/-0.64	12.52	+/- 0.53
Si K	34.91	+/-0.91	27.6	+/- 0.72
Ca K	9.11	+/-1.00	5.05	+/- 0.55
Total	100		100	

Table 9: Elements of Granite Rock Powder (3)

Element	**Wt. %**		**Atom %**	
O K	29.27	+/-1.13	45.08	+/- 1.74
Mg K	0.92	+/-0.23	0.93	+/- 0.23
Al K	12.86	+/-0.66	11.74	+/- 0.60
Si K	29.06	+/-0.90	25.5	+/- 0.79
P K	2.3	+/-0.43	1.83	+/- 0.34
K K	9.17	+/-1.03	5.78	+/- 0.65
Ca K	6.89	+/-0.60	4.24	+/- 0.37
Ti K	9.52	+/-1.58	4.9	+/- 0.82
Total	100		100	

According to the analysis of the three areas, the comprehensive situation is as follows:

Table 10: Elements of Granite Rock Powder

Element	**Wt. %**	**Atom %**
O K	34.1	49.4
Mg K	0.6	0.7
Al K	11.5	9.9
Si K	36.1	29.7
P K	0.8	0.6
K K	4.0	2.5
Ca K	6.1	1.8
Ti K	3.2	1.6
Fe K	2.2	0.9
Na K	1.4	1.4
Total	100.0	98.3

XRF examination results are as follows:

Table 11: Compound composition of Granite Rock Powder

SiO_2 (%)	Al_2O_3 (%)	TiO_2 (%)	Fe_2O_3 (%)	Na_2O (%)	MgO (%)
63.14	14.16	0.674	5.92443	2.547	2.704
K_2O (%)	CaO (%)	P_2O_5 (%)	CO_2 (%)	Sum (%)	Comp (%)
3.501	3.63	0.216	3.55	100.53	99.589

By compound analysis, most of them are SiO_2, Al_2O_3 and Fe_2O_3.

3.3.3 Basalt Rock Powder

Micrographs of the sample surfaces are shown in Figures 18-21. The surface contains greater numbers of visible particles, and they are the irregular shapes of variying sizes, which distribute from 100 to 1500 um, with a median particle size of nearly 400 um. These particles are usually solid. It shows the selected area. The surfaces look angular and dense.

Figure 18: Basalt Rock Powder (0.1k)

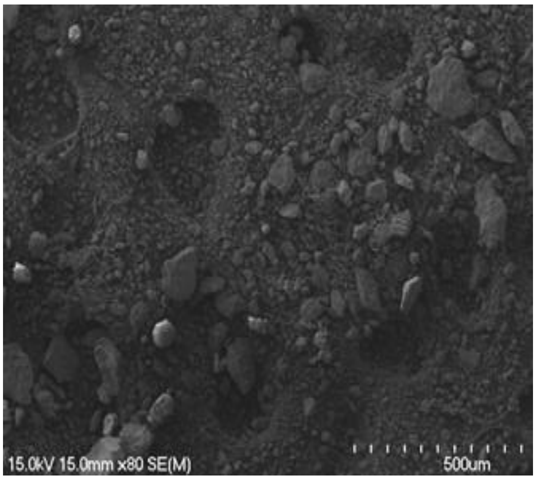


Figure 19: Basalt Rock Powder (0.08k)

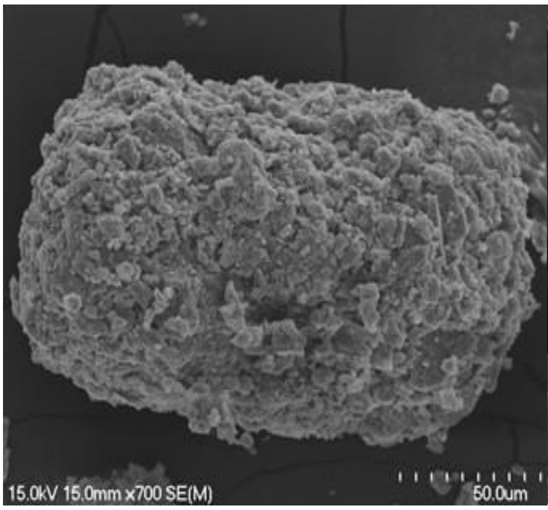


Figure 20: Basalt Rock Powder (0.7k)

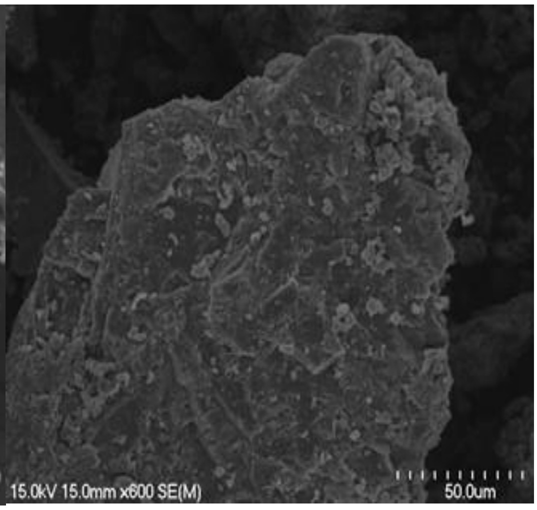


Figure 21: Basalt Rock Powder (0.6k)

The selected-area EDSs (seven areas) of Basalt Rock Powder are shown as follows.

Table 12: Elements of Basalt Rock Powder

Wt. % elements	**A**	**b**	**c**	**d**	**e**	**f**	**g**
C	6.00 +/-1.13	0	0	4.78+/-0.76	8.25+/-0.87	0	7.86+/-0.70
O	33.49+/-0.75	26.48+/-0.85	27.05+/-0.74	31.08+/-0.74	33.38+/-0.90	28.69+/-0.96	29.67+/-0.85
Na	1.93 +/-0.20	1.52+/-0.19	3.29 +/-0.46	4.24 +/-0.40	1.43 +/-0.21	1.73+/-0.23	1.35 +/-0.18
Mg	2.57 +/-0.18	8.97 +/-0.58	2.49+/-0.24	0.83+/-0.21	1.16 +/-0.17	1.87 +/-0.21	1.17+/-0.17
Si	27.56+/-0.58	33.23+/-0.81	32.92+/-0.77	33.69+/-0.71	28.31+/-0.68	30.33+/-0.81	32.20+/-0.70

K	4.38 +/- 0.52	8.75+/- 0.76	2.64 +/-0.29	2.90 +/-0.27	4.57 +/-0.31	3.73+/- 0.35	8.61+/- 0.65
Ca	5.42 +/- 0.63	6.78+/- 0.45	4.26 +/-0.38	3.74 +/-0.65	6.33 +/-0.75	14.28+ /-1.02	2.39 +/-0.35
Fe	10.30+/- 1.10	14.27+ /-2.57	16.97+ /-1.36	9.72 +/-1.21	8.81 +/-0.51	11.29+ /-1.53	7.80 +/-1.21
Al	0	0	10.37+ /-0.63	9.02 +/-0.52	8.81 +/-0.51	8.10+/- 0.59	8.95 +/-0.50
Ti	0	0	0	0	1.53+/- 0.47	0	0

Further analysis shows that:

Table 13: Revised elements of Basalt Rock Powder

Elements	Average Wt. %
C	3.841429
O	29.97714
Na	2.212857
Mg	2.722857
Si	31.17714
K	5.082857
Ca	6.171429
Fe	11.30857
Al	6.464286
Ti	0.218571

Generally, the elements of the specimens contains carbon, oxygen, sodium, magnesium, silicon, kalium, calcium, iron, aluminum, titanium (see Table 13). The samples had higher silicon and oxygen levels than the others, nearly 30%, while carbon, aluminium, and titanium was localized.

In a chemical composition analysis, the chemical compositions of rock flour are shown in Table 13. The sum of SiO_2 and Al_2O_3 of Basalt Rock Powder is about 65%.

Table 14: Compound composition of Basalt Rock Powder

Chemical composition (%)	Basalt Rock Powder
SiO_2	50.48
Al_2O_3	14.64
MgO	4.12
CaO	8.809

Na_2O	3.56
K_2O	3.73
P_2O_5	0.86
Fe_2O_3	8.05

3.3.4 Horizontal comparison

As cement admixtures, the silica and aluminaplay a role in the process, and their contents are as follows:

Table 15: Composition comparison

	FA	**GFP**	**AFP**
SiO_2 (%)	58.69	63.14	50.48
$Al2O_3$ (%)	29.24	14.16	14.64
Fe_2O_3 (%)	2.6	5.9	8.5
Sum	90.53	83.2	73.62

In fly ash, the silica content (59%) is almost double the alumina content (30%), while for both types of rock powder, the alumina content is significantly reduced to about 14%. The silica content is increased to 63% and decreased to 50% respectively. This experiment can determine which of the two influences strength of cement hardening more.

The other maincompound in the mix is an iron oxide, FA for 2.7%, AFP for 6.0%, GFP for 8.0%. In the present theory, iron oxide is not directly related to the experimental results. Physical properties are summarized as follows:

Table 16: Physical properties

	Granite Rock Powder	**Basalt Rock Powder**	**FA**
Average diameter	200 μm	400 μm	-
Diameter range	＜2000 μm	100-1500 μm	5-2000 μm
Shape	most irregular	irregular	ball
Distribution	more uniform	different size	different size
Note	particle	particle	Honey comb & particle

3.3.5 Sand

The builders sand used in this project is common construction sand from Bunnings, Hamilton as shown in the figure.

Figure 22: Image of sand

3.3.6 Cement

The cement is ageneral purpose cement, it complies with the requirements of type GP Cement in the New Zealand standard NZ1322: 2009- General purpose and blended cement.

3.4 Test Methods

3.4.1 Scanning Electron Microscopes (SEM) Analysis

Scanning electron microscopes (SEM) use high-energy electron focused beams to generate a variety of signals on the surface of solid specimens. Signals obtained from the interaction of electronic samples reveal information about the sample, including external morphology (texture), chemical composition, and the crystal structure and orientation of the material that makes up the sample. In most applications, data is collected through selected areas of the sample surface and a two-dimensional image that shows spatial variations in these properties. Areas from 1 cm to 5 microns can be used in traditional SEM technology to image in scan mode (magnification from 20X to approximately 30000X with a spatial resolution of 50 to 100 nm). The accelerated electrons in the SEM have kinetic energy, which is reduced by various signals when electricity interacts with the sample. These signals include secondary electrons (producing SEM images), backscatter electrons (BSE), diffraction backscatter electrons (EBSD, which can be used to determine the structure and direction of mineral crystals), photons (for elements), visible light and heat. Secondary electrons and backscatter electrons are commonly used in imaging samples: the primary function of secondary electrons is to show the surface characteristics of the supplies, and the reverse-scattering electrons can illustrate the composition comparison. X-rays are produced because electrons collide inelasticly with electrons in discrete shells in atoms in the sample. When excited electrons return to low-energy states, they produce X-rays with fixed wavelengths. As a result, each element in the mineral produces a specific X-ray.

Figure 23: Images of SEM & EDS machine

3.4.2 Energy Dispersive X-ray Spectroscopy (EDS) Analysis

EDS analysis means atom and element percentages of the samples, using energy dispersive X-ray analysis (EDXA). EDS is an important auxiliary instrument of SEM. Combined with an electron microscope, EDS can conduct a qualitative and quantitative analysis of element distribution in the microscopic region of materials within 1-3 minutes.

3.4.3 X-ray Fluoresce (XRF) Analysis

A typical X-ray fluorescence (XRF) instrument consists of an excitation source (X-ray tube) and a detection system. The X-ray tube produces an incident X-ray (a single X-ray) that excites the sample under test. Each element in the exciting sample emits a secondary X-ray, and the secondary X-ray emitted by different elements has specific energy characteristics or wavelength characteristics. The detection system measures the energy and amount of these emitted secondary X-ray. The instrument software then converts the information collected by the detection system into the type and content of various elements in the sample. The secondary X-ray produced when X-ray hit a substance are called X-ray fluorescence. Using the principle of X-ray fluorescence, every element after beryllium in the periodic table can be measured theoretically. In practical applications, effective element measurements range from element 9 (F) to 92 (U).

Figure 24: Images of the XRF machine

3.4.4 Compression Test (ASTM C109-2015)

The compressive of the cement paste will be evaluated through mechanical characterization of their strength.

The test will be in accordance with ASTM C109-2015.

By adding the proper load to the specimen until it breaks. This machine can test the load and compressive strength.

Figure 25: Images of compressive machine

3.4.5 Test of grinding

After the material fragments are placed in the grinding box, high-speed impact is carried out with the rotating parts, which is ground, cut, compressed, and eventually reduced to superfine crushing.

Figure 26: Image of grinding

3.5 Test process

3.5.1 Samples preparation of cement mortar

3.5.1.1 Cement with different materials

According to the calculation results in the figure below, a mixture of cement and fly ash or cement and rockpowder are prepared first.

Table 17: Test group setting (percentage)

Percentage Quantity By Weight				
Control Group				
Cement	100%			75%
Sand				
Group 1				
	Basalt Rock Powder 1	Basalt Rock Powder 2	Basalt Rock Powder 3	Basalt Rock Powder 4
Cement	90%	85%	80%	75%
Basalt Rock Powder	10%	15%	20%	25%
Group 2				
	Granite Rock Powder 1	Granite Rock Powder 2	Granite Rock Powder 3	Granite Rock Powder 4
Cement	90%	85%	80%	75%
Granite Rock Powder	10%	15%	20%	25%
Group 3				
	FA1	FA2	FA3	FA4
Cement	90%	85%	80%	75%
FA	10%	15%	20%	25%

Within groups 1, 2 and 3, there were four different proportional alternatives, 90%, 85 %, 80% and 75%.

ASTM C109 recommendation for 6-50*50*50 mm or 125 ml mortar cube specimens For 6 125 or 750 ml mortar, we need:

Cement=500 g

Sand=1500 g

Water=250 ml

W/C = 0.5

The calculation results are as follows:

Table 18: Test group setting (weight)

Control		C1			C2
Cement	g	500			375
Sand	g	1500			1875
Water	mL	250			250
Group 1					
		Basalt Rock Powder 1	Basalt Rock Powder 2	Basalt Rock Powder 3	Basalt Rock Powder 4
Cement	g	450	425	400	375
Basalt Rock Powder	g	50	75	100	125
Sand	g	1500	1500	1500	1500
Water	mL	250	250	250	250
Group 2					
		Granite Rock Powder 1	Granite Rock Powder 2	Granite Rock Powder 3	Granite Rock Powder 4
Cement	g	450	425	400	375
Granite Rock Powder	g	50	75	100	125
Sand	g	1500	1500	1500	1500
Water	mL	250	250	250	250
Group 3					
		FA1	FA2	FA3	FA4
Cement	g	450	425	400	375
FA	g	50	75	100	125
Sand	g	1500	1500	1500	1500
Water	mL	250	250	250	250

All the prepared materials are as shown in the figure below. There are 2 control groups and 12 experimental groups, with quantities of 7 days, 28 days and 90 days respectively in each group.

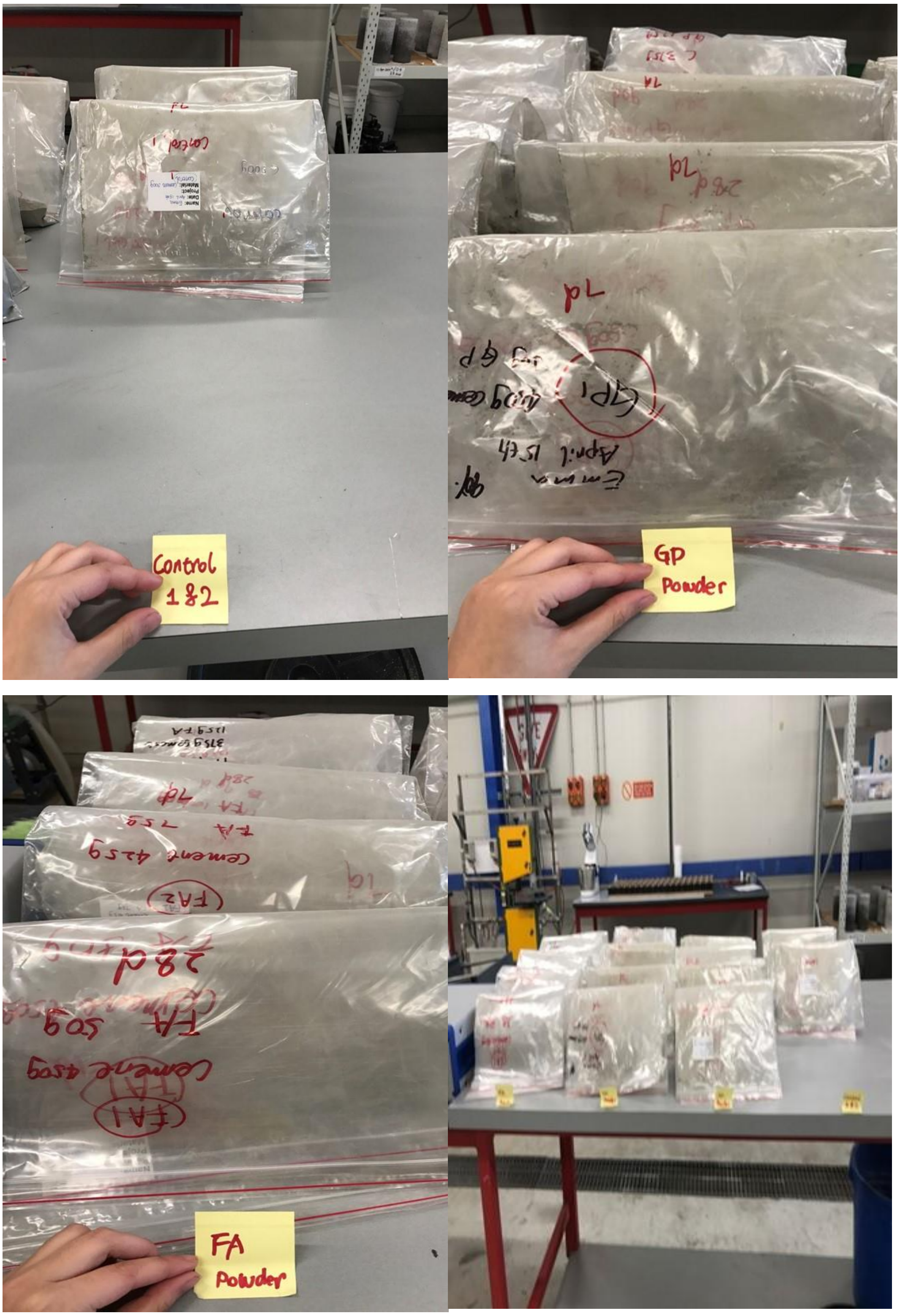


Figure 27: Samples preparation

3.5.1.2 Sand

Next, 42 bags of sand were weighed, and the net content of each bag was 1500g. Due to havimg 12 experimental groups, two control groups, and three different measurement times, we prepared 42 bags, as shown in the picture below, with green, blue and orange color labels to divide the measuring times.

Figure 28: Sand preparation setting

According to the amount in the table, sand, cement and fly ash, sand, cement and Basalt Rock Powder and sand, cement and Granite Rock Powder are mixed and put in their own plastic bags for later use. The material amount of each plastic bag can be used as six cubes.

3.5.2 Preparation of cement moulds

We chose to use wooden boards as the cement block models, and the specification of each small grid is 50mm*50mm*50mm. The picture of the model is as follows.

Figure 29: Images of models

The board is connected with screws in key parts. When the cement needs to be taken out, just loosen the screws.

3.5.3 Model making

In the experiment, sand, cement, and materials were mixed with a mixer. Firstly, mix the pulp for one minute, then turn to high speed for one minute, add 250 ml water, and later mix the paste normally for one minute. Secondly, use the shovel and other tools to clean up the remaining material on the mixer. Keep all the cement mixture in the blender bowl. Thirdly, stir again and set aside. Finally, load the cement into the wooden formwork evenly and expel any internal gas by shaking.

Figure 30: Mini mixture was used

Figure 31: Casting and compaction of the samples

For each filled wooden template, cover with plastic film to prevent water evaporation from the cement thereby ensuring normal hydration of the cement.

Figure 32: Image of normal temperature maintenance

The above process was repeated until the 14 experimental groups, a total of 70 cubes, were prepared and placed at room temperature to harden.

3.5.4 Curing

After the cement strength is established, remove the model and move the cubes into the water to continue hardening.The water level is above the cement cubes and placed at room temperature.

Figure 33: Water curing of the samples

The 7- and 28-day experimental groups were respectively cured in water for three days and one week, and then taken out and cured at room temperature.

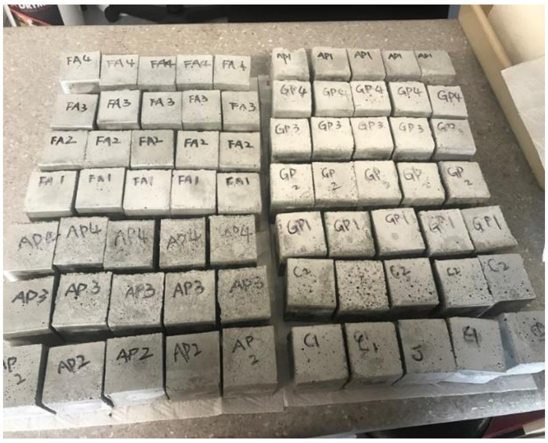


Figure 34: Samples at ambient curing

3.5.5 Flow test workability

Other same terms utilized to depict a newly prepared concrete is ‘consistency’, it will flow with it easily and they are measure of mobility or fluidity or the wetness of the concrete.

Therefore, in this experiment, the newly mixed cement is installed in a specific model and poured onto a vibrating machine. The workability can be judged by observing the diameter of the cement after the vibration.

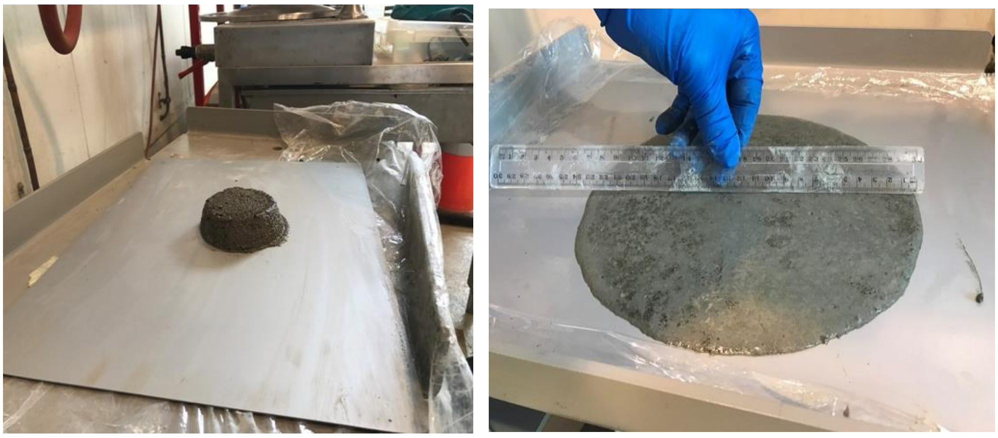


Figure 35: Workability (flow test)

3.5.6 Test of compressive strength

First, manually measure the weight of each cube and the surface area of the stressed surface to compare with the reference data given by the compressive machine, and to calculate the density of each sample Then, put all the cubes into the instrument to pressurize, and record the compression and stress levels.

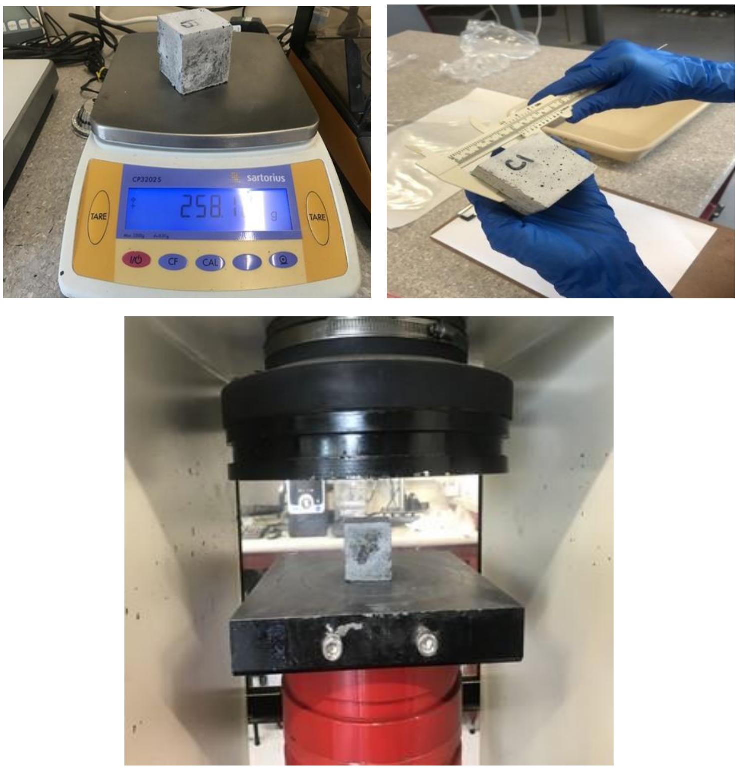


Figure 36: Measuring and compressive tests

3.5.7 Test of microstructure and chemical composition

Sample was grindedusing the grineded machine that shown section 3.4.5. Afterwards, the flux powder was added into the mixture and put it into a high-temperature box to melt into a sheet. Then the sample is placed in the XRF machine and the compound composition and its percentage are automatically analyzed.

Figure 37: XRF progress

Chapter 4: Results and Discussion

4.1 Introduction

This chapter shows the results of the tests described in Section 3. The effects of fly ash, granite rock powder and basalt rock powder on the workability, density, and 7- and 28-day compressive strength are presented and discussed. The microstructural analyses in terms of SEM and XRF are also performed to show the microstructural changes caused by the added mixtures.

The specimen have been tested following the steps outlined in Section 3. The main objective of this investigation is to compare the properties of cement with different mixtures and to quatify the effects of mixtures, especially the effects of replacement ratios of mixtures. The findings from this study are presented in the following sections.

4.2 Workability

Using the flow test, the workability of the cement can be judged by the diameter of the cement after vibration. The diameters of cement samples using the flow test are summarized in Table 19 and Figure 38.

For the control group (i.e. C1 & C2), the figure shows that the diameter of Sample C2 is slightly larger than that of Sample C1 due to the relatively high water-cement (w/c) ratio of Sample C2. Haach et al. (2011) also demonstrated that the w/c ratio is almost linearly correlated with cement workability. Compared with the control group, cement mortars with mixtures (i.e. fly ash, Grantie rock powder and Basalt rock powder) consistently have larger diameters except for the possible outlier of granite rock powder 4. The increase of workability can be attributed to that the substitution of part of the cement indicates less water for yielding a given workability, which also agrees with the finding of Mora et al. (1993). Moreover, for Samples 2 ~ 4 with mixtures, the diameter of cement appears to be gradually decreasing with the increase of quantity of mixtures. This may be attributed to the insufficient amount of water. As demonstrated by Haach et al. (2011), the cement with mixtures requires very high amount of water. Wang et al. (2003) explained that three forms of mixing water exist: free layer water, adsorpted layer water and filling water. Free layer water separates solid particles and thus increases the workability, while adsorpted layer water and filling water almost have no effect on workability. Insuffient amount of water may not be able to provide enough free layer water to maintain the workability. Therefore, both mixtures and sufficient water are key to increase the workability of cement.

Table 19: Workability of cement

Group	Diameters (cm)
C1	25.00
C2	22.00
Fly ash 1	24.00
Fly ash 2	23.50
Fly ash 3	23.00
Fly ash 4	25.50
Granite rock powder 1	24.25
Granite rock powder 2	23.00
Granite rock powder 3	22.25
Granite rock powder 4	16.75
Basalt rock powder 1	23.50
Basalt rock powder 2	22.75
Basalt rock powder 3	22.50
Basalt rock powder 4	22.00

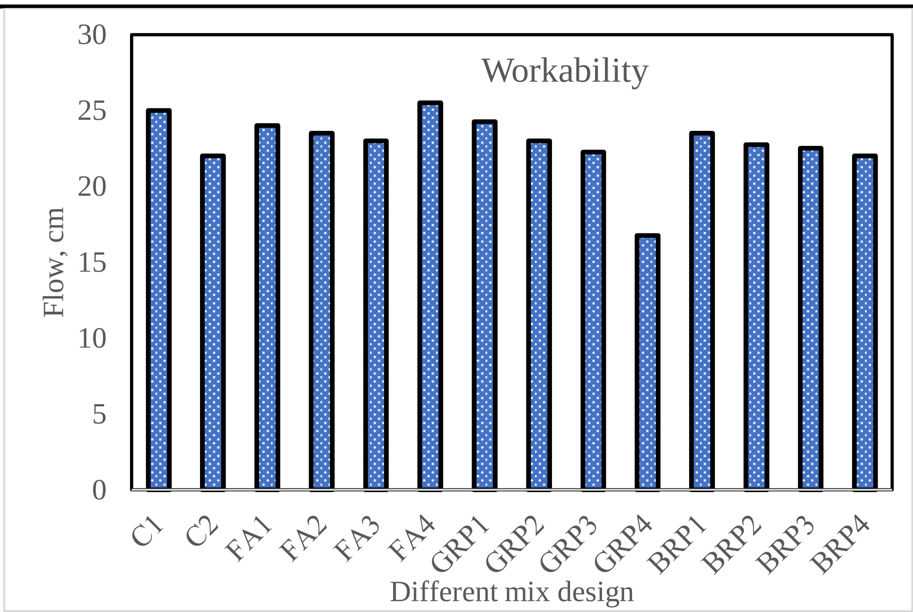


Figure 38: Workability of cement

4.3 Density

The mean and standard deviation of the density of samples are tabulated in Table 20 and Figure 39. It can be seen that the standard deviation of density is relatively small (about 2% of the mean value). As shown in Figure 39, density varies slightly between different samples. Specifically, Sample C1 with a high cement-sand ratio has a relatively larger density than Sample C2, while mixtures almost have no effects on the density of cement. These features also agree with those found by Krantz (1991).

Table 20: Mean and standard deviation of density

Group	Mean (kg/m^3)	Std. (kg/m^3)
C1	2.12	0.045
C2	2.00	0.061
Fly ash 1	2.01	0.044
Fly ash 2	2.06	0.052
Fly ash 3	2.04	0.030
Fly ash 4	2.04	0.049
Granite rock powder 1	2.09	0.129
Granite rock powder 2	2.01	0.069
Granite rock powder 3	2.06	0.066
Granite rock powder 4	1.97	0.042
Basalt rock powder 1	2.03	0.027
Basalt rock powder 2	2.05	0.017
Basalt rock powder 3	1.93	0.079
Basalt rock powder 4	2.07	0.042

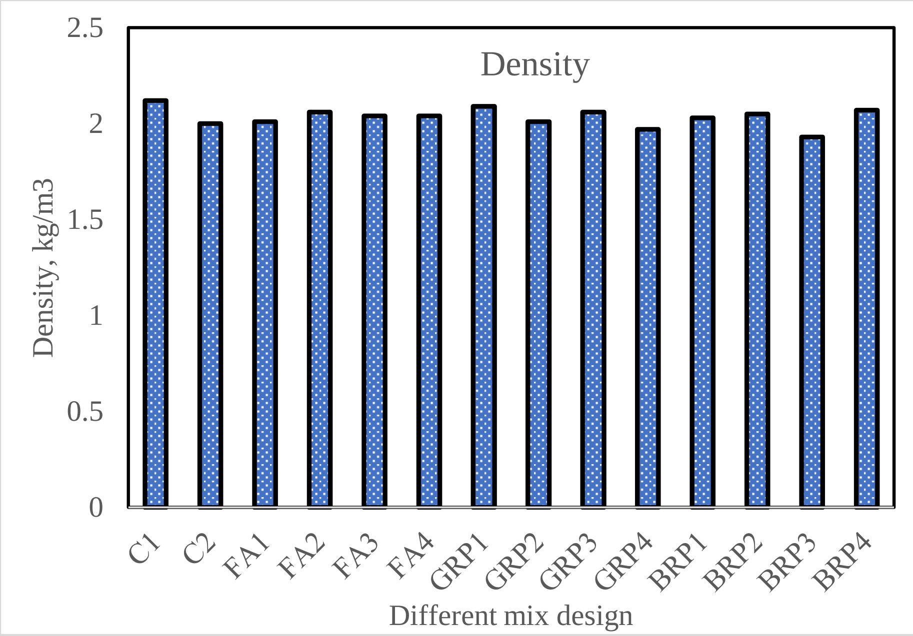


Figure 39: Mean values of density

4.4 Compressive strength at 7 days

Table 21 and Figure 40 show the 7-day compressive strength for all the groups. As shown in Figure 40, Sample C2 has a much smaller 7-day compressive strength than C1. This is due to the much lower cement-sand ratio of Sample C2. Consoli et al. (2009) also experimentally noticed that the cement amount greatly affects both the tensile and compressive strength of sand-cement mixture. This phenomenon can be explained by the fact that more cement can reduce the porosity of sand-cement mixture.

For the FA group, the 7-day compressive strength gradually decreases with the increase in the replacement ratio of fly ash. EI-Diamond et al. (2016) reported thatfor cement mortar with volcanic ash, the hydration reaction of cement is the main reaction within the first 7 days. After this, the volcanic ash reaction gradually dominates the whole cement hardening process. Therefore, the 7-day compressive strength decreases with the increase of replacement ratio. It can be seen that the 7-day compressive strength values of the samples in GR group are higher than Sample C1 in the control group. The compactness of the concrete is inversely proportional to the porosity of cement and the increases in porosity can thus lead to the reduction in compressive strength (Vijayalakshmi & Sekar, 2013). Similar to the strength variation in Group FA, the 7-day compressive strength in BA group gradually decreases with the increase of the replacement ratio of basalt rock powder. Some research (e.g. Bapat, 2012; Mehta, 1999 and Newman & Choo, 2003) has shown that the increase of rock powder can lead to a shortage of water that is available for the hydration of cement to produce calcium hydroxide, which is necessary for the pozzolanic reaction to take place. Therefore, a higher replacement ratio of basalt rock powder can result inrelatively lower strength.

Table 21: Mean and standard deviation of 7-day compressive strength

Group	**Mean (MPa)**	**Std. (MPa)**
C1	25. 40	1. 67
C2	16. 30	1. 57
Fly ash 1	23. 35	1. 59
Fly ash 2	19. 39	0. 69
Fly ash 3	19. 06	0. 49
Fly ash 4	14. 37	0. 66
Granite rock powder 1	23. 15	0. 6
Granite rock powder 2	18. 51	0. 98
Granite rock powder 3	20. 82	2. 02
Granite rock powder 4	18. 67	3. 77
Basalt rock powder 1	20. 34	1. 94
Basalt rock powder 2	19. 08	5. 56
Basalt rock powder 3	16. 79	0. 51
Basalt rock powder 4	13. 98	0. 61

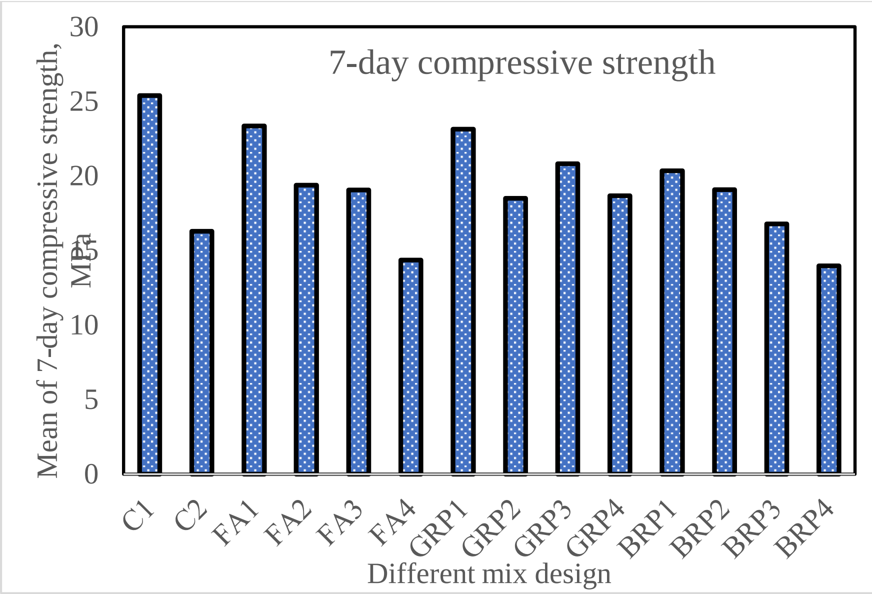


Figure 40: 7-day compressive strength

4.5 Compressive strength at 28 days

Table 22 and Figure 41 show the 28-day compressive strength for all the groups. It can be seen that Sample C2 has a much smaller 28-day compressive strength than C1, which is consistent with the comparison between 7-day compressive strength. The much lower cement-sand ratio of Sample C2 can still be attributed to this phenomenon based on the experimental findings by Consoli et al. (2009).

As shown in Figure 41, the 28-day compressive strength of the FA group are almost the same for all the samples in FA group. Therefore, the replacement ratio of fly ash seems to only affect the 7-day compressive strength, but almost has no influence on the 28-day compressive strength. It can be also seen that the 28-day compressive strength values of the samples in GR group are higher than Sample C1 in the control group due to the relatively higher compactness of the cement samples with granite rock powder (Vijayalakshmi & Sekar, 2013). The figure also shows that the 28-day compressive strength in GR group gradually decreases with the increase of replacement ratio although the 7-day strength remains almost the same. This may be due to the fact that the addition of materials increases the volume of the mixture and the ratio of slurry to available water, which is necessary for cement hydration and subsequent pozzolanic reactions, ultimately resulting in lower strength.

Comprared with the 28-day compressive strength of Group FA, the 28-day compressive strength of Group BA is consistently higher. As explained by Varma and Gadling (2017), early strength development of cement mixed with fly ash may be delayed because fly ash has a relatively low surface area that can affect pozzolanic reaction. The rock powder has a higher surface area than fly ash, resulting in faster pozzolanic reaction. Moreover, as shown by the SEM images, fly ash is spherical, while the surface of rock powder is irregular and uneven. These factors can explain the higher 28-day compressive strength of Group BA than those of Group FA. Compared with fly ash, a big advantage of basalt rock powder is to gain strength quicker. Kiattikomol et al. (2001) found that at normal temperatures, the pozzolanic reaction of cement containing fly ash is late to begin, and its contribution to strength mainly occurs in the late-term stages (e.g. 28 days). Similar to the strength variation in Group GR, the 28-day compressive strength gradually decreases with the increase of the replacement ratio of basalt rock powder, that is, a higher replacement ratio of basalt rock powder can lead to relatively lower strength.

Table 22: Mean and standard deviation of 28-day compressive strength

Group	Mean (MPa)	Std. (MPa)
C1	32.36	2.97
C2	17.72	1.52
Fly ash 1	24.30	0.62
Fly ash 2	22.20	1.99
Fly ash 3	22.66	0.72
Fly ash 4	24.92	1.99
Granite rock powder 1	30.03	0.85
Granite rock powder 2	23.83	2.92
Granite rock powder 3	22.52	1.42
Granite rock powder 4	21.78	1.65
Basalt rock powder 1	29.49	3.99
Basalt rock powder 2	25.02	2.00
Basalt rock powder 3	24.34	5.20
Basalt rock powder 4	22.49	2.90

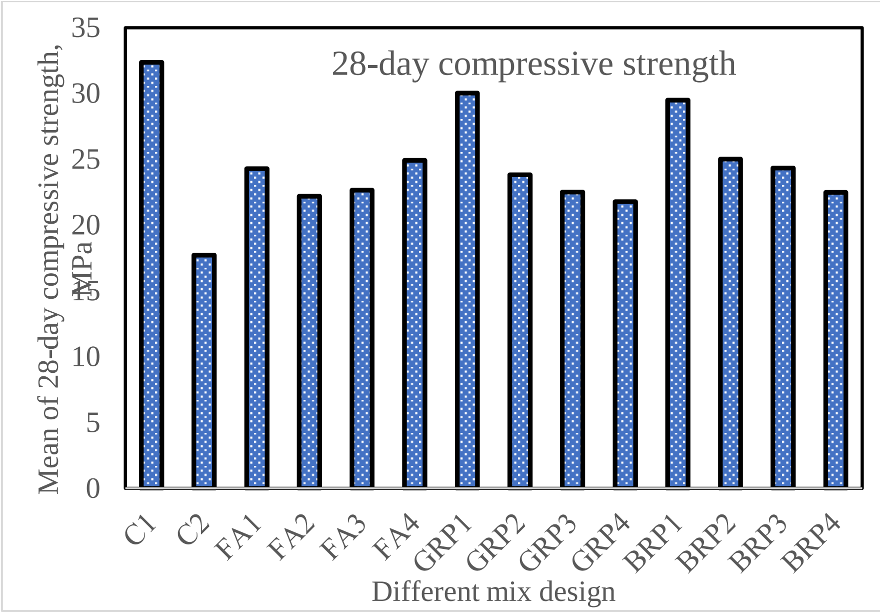


Figure 41: 28-day compressive strength

4.6 Strength development

Figure 42 shows the compressive strength development from 7- to 28-day compressive strength for all the groups. It can be seen that Sample C1 has a great strength increase from 7 to 28 days, while only a very slight compressive strength increase of Sample C2 can be observed. This may be due to that a lower cement-sand ratio results in not only a smaller 7-day compressive strength but also a reduced strength development compared with a higher cement-sand ratio.

For the FA group, the gained compressive strength from 7 to 28 days gradually increases with the replacement ratio of fly ash and consequently the 28-day compressive strength almost remain the same. Payá's trials (Payá et al., 1997) also found that the rate of stress growth of cement witha higher replacement ratio (i.e. 30-45%) appears to be greater than that of cement with a lower replacement percentage (i.e. 15%), and strength development depends largely on the fly ash/cement ratio. The replacement ratio of FA group is between 10% and 25%, which is consistent with the ratios adopted by Payá et al. (1997). As pointed by Payá et al. (1997), for the early strength (< 14 days), cement with the lowest replacing percentage gains the highest strength, which is consistent with the current results.

The GR group shows that the increase in the compressive strength from 7 to 28 days ranges from 10 to 30%, depending on the replacement ratio. In contrast with the FA group, a lower replacement ratio of granite rock powder generally corresponds to a higher strength development, which differs from the trend shown in FA group. However, it can be seen that there is a turning point in the strength gain of rock powder. It may be attributed to that for samples with a low substitution ratio, the free water of hydration reaction and the pozzolanic reaction is enough. However, with the increase of the replacement ratio, the quantity and workability of cement decrease, leading to the reduction of calcium hydroxide. When the displacement ratio reaches that for granite rock powder 3 or 4, the pozzolanic reaction is transformed into a stage of insufficient calcium hydroxide. At this time, due to excess rock powder, calcium hydroxide is constantly consumed. Although a high replacement ratio can lead to a decrease in the total amount of calcium hydroxide provided by cement, the lack of calcium hydroxide will promote the deepening of cement hydration reaction. This may be the main reason for the turning point of the cement strength increase rate for the GR group. For the BA group, the compressive strength development from 7 to 28 days appears to be almost the same for all the replacement ratios. This leads to that the variations of the 7- and 28-day compressive strength of the BA samples are consistent with those of the replacement ratio of basalt rock powder.

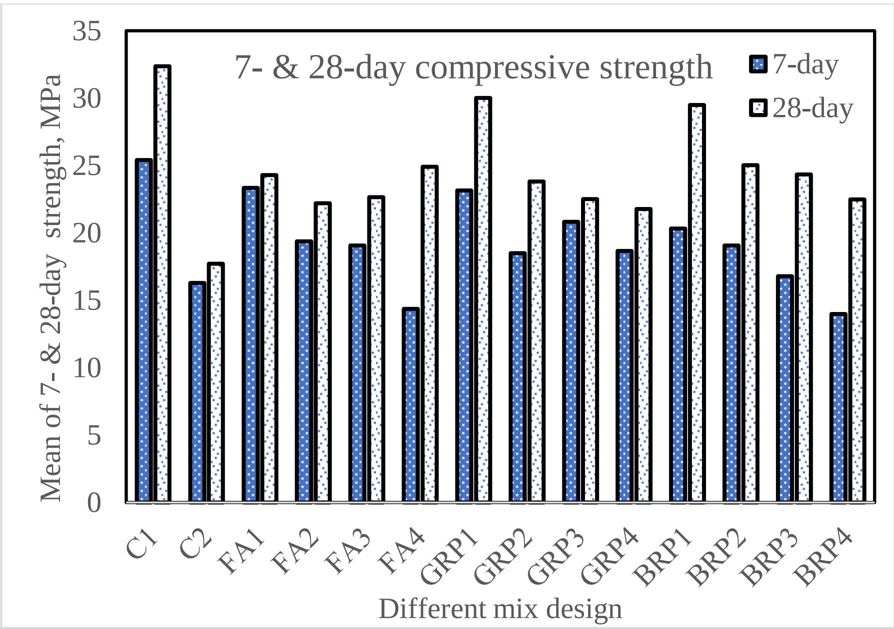


Figure 42: Strength developement

4.7 Microstructural analysis

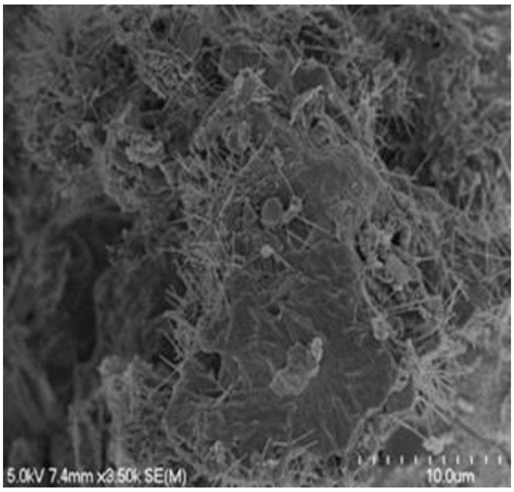
4.7.1 SEM

Figure 43 shows the microstructures of cement from the control and FA groups. It can be seen that Sample C1 (see Figure 43 (a)) seems that intermediate-size particles are lapped and jointed together by many needle hydrates, while Sample C2 shown in Figure 43 (b) exihits more stand-alone clusters, which appears to be the shape of sand. This is due to that Sample C2 was prepared with a much larger sand-cement ratio than C1. The contribution of these needle hydrates to the compressive strength of cement is significant, which can also explain that Sample C1 has greater 7- and 28-day compressive strength than C2.

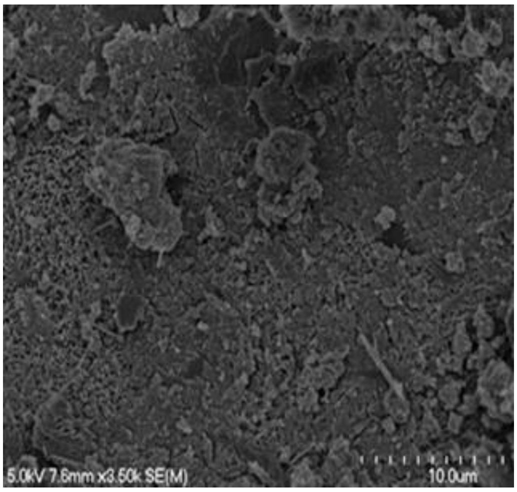
As shown in Figure 43 (c), the microstructure of Sample Fly ash 1 appears to be similar to that of Sample C1, but smaller clusters can be observed due to the presence of very small fly ash particles. With the increase of the replacement ratio of fly ash, the distribution of needle hydrates almost remains the same, however, some stand-alone fine particles co-exist, as shown in Sample Fly ash 2. This may be due to the fact that limited amount of water is available for the hydration of cement and fly ash and the remaining fly ash will just fill in the pores alone without contribution to the the compressive strength of cement. The same phenomenon can be found for Sample Fly ash 3. Due to the relatively smaller magnification of Sample Fly ash 4, this feature is not clear enough.

Figure 44 presents the the microstructures of cement from the control and GR groups. The SEM images of cement containing granite powder as shown in Figure 44 (c) and (d) are very compacted than these of controlling mortar inplicated in Figure 43 (a) and (b). What's more, mortars' SEM images with powder of granite have less pores at athe inter-facial bond among the fine aggregates and cement that that of C1 and C2 samples. Nevertheless, along with the increase of replacing ratio of rock power of granite, the clusters in Sample GR3 and GR4 (see Figure 44 (c) and (d)) appear to become smaller and more pores can be observed, which indicates that the connections between clusters are weaker than Samples GR1 and GR2. This may also result in the decrease in the compressive strength of cement with the increase of the replacement ratio of granite rock power.

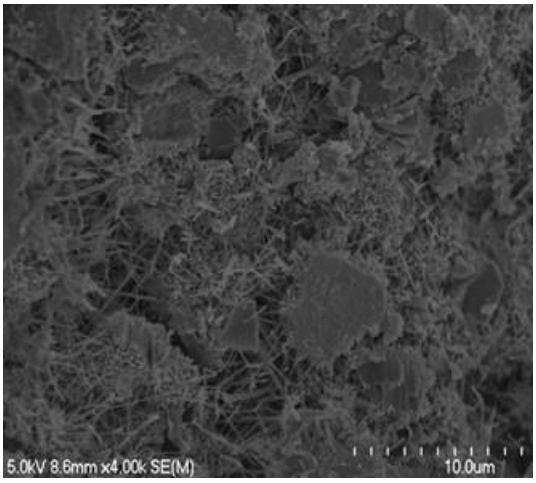
Figure 45 shows the the microstructures of cement from the control and BA groups. Compared with the SEM images of C1 and C2, it could be found that certain particles of basalt are covered with seams of minor amount of products of hydration. Certain amount of needles of ettringite grows in vacant place in paste, also coming out. As for BA3 Samples and BA4 with powder of basalt rock, the basalt particles surface would be coated by C-S-H, resulted from the reacting of CaO, basalt and other products of hydration.



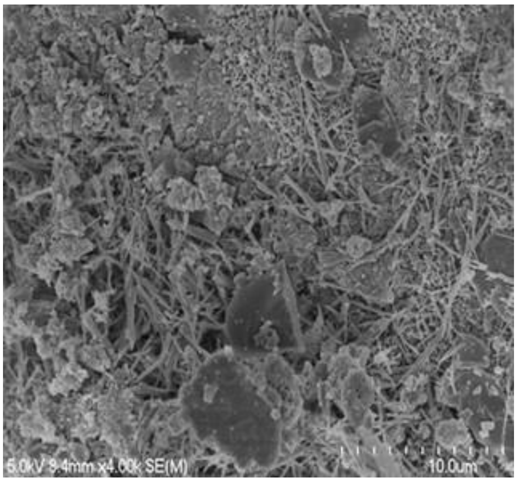
(a) C1 (3.5k)



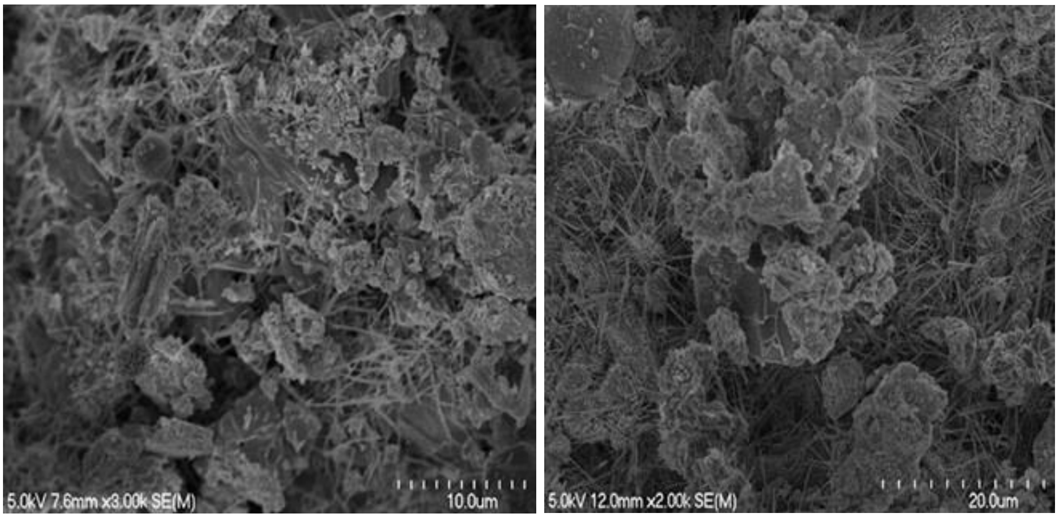
(b) C2 (3.5k)



(c) Fly ash 1 (4k)

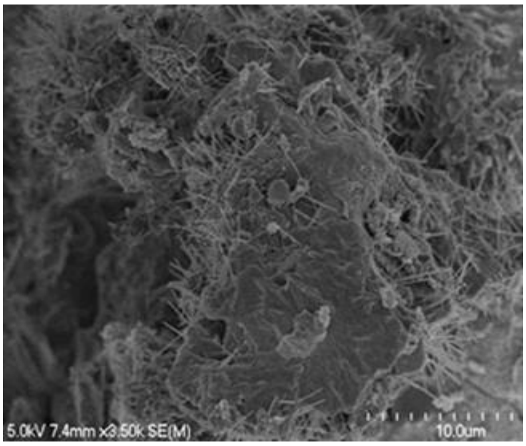


(d) Fly ash 2 (4k)

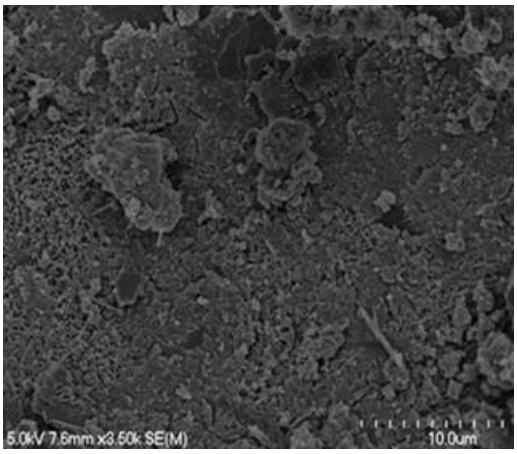


(e) Fly ash 3 (3k) (f) Fly ash 4 (2k)

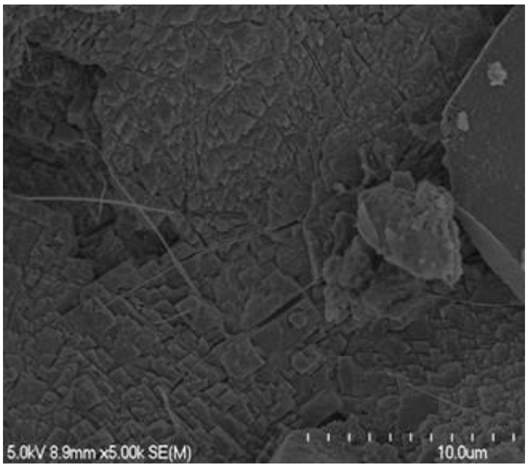
Figure 43: SEM of cement with fly ash



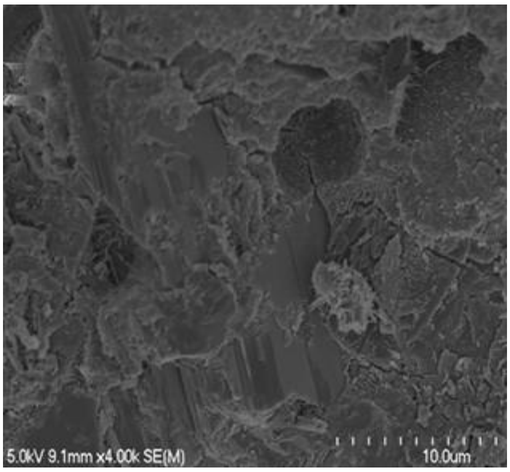
(a) C1 (3.5k)



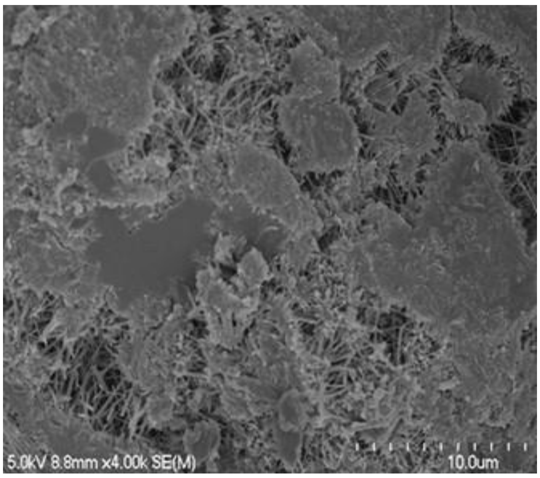
(b) C2 (3.5k)



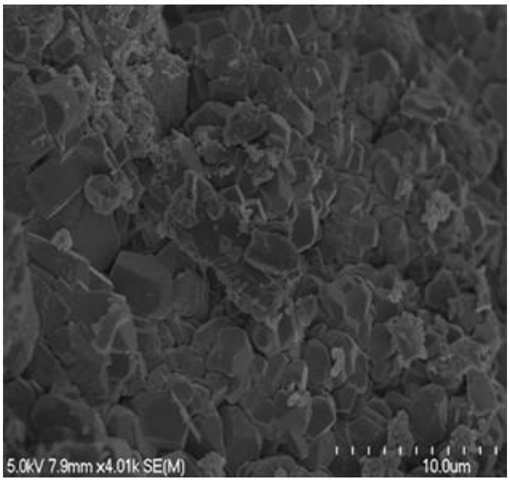
(c) Granite rock powder 1 (5k)



(d) Granite rock powder 2 (4k)

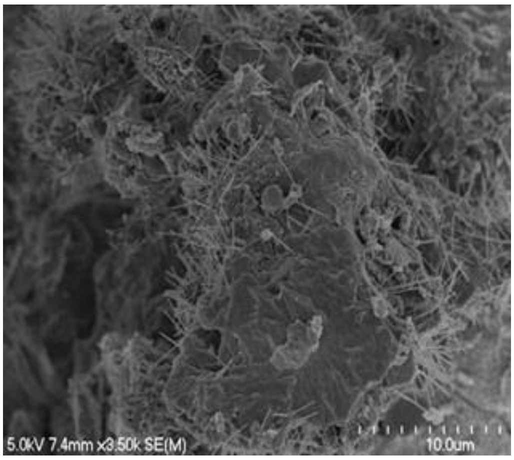


(e) Granite rock powder 3 (4k)

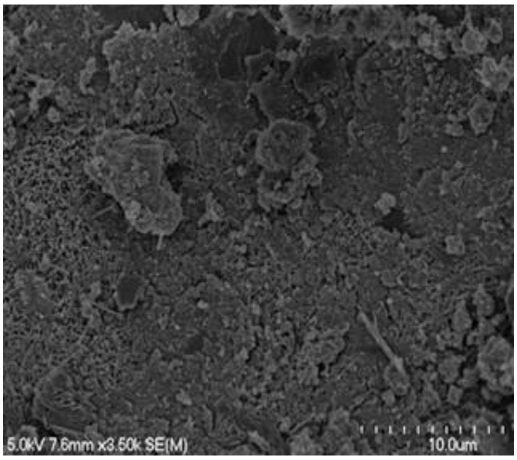


(f) Granite rock powder 4 (4k)

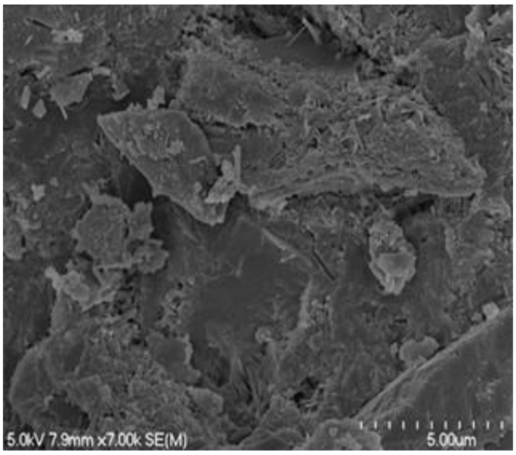
Figure 44: SEM of cement with granite rock powder



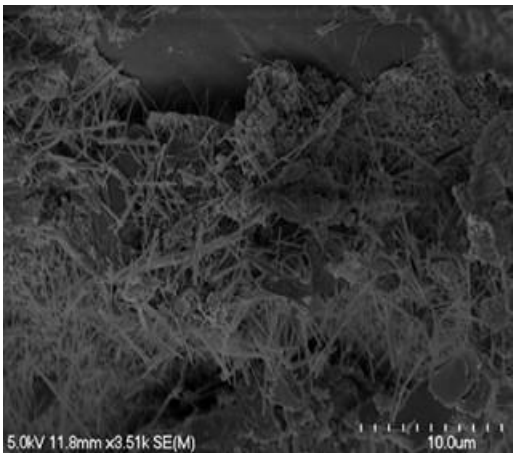
(a) C1 (3.5k)



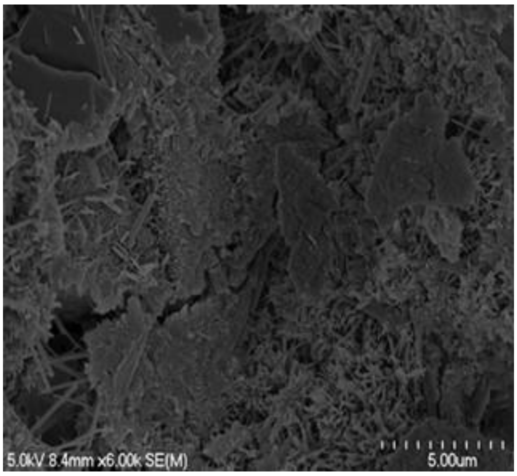
(b) C2 (3.5k)



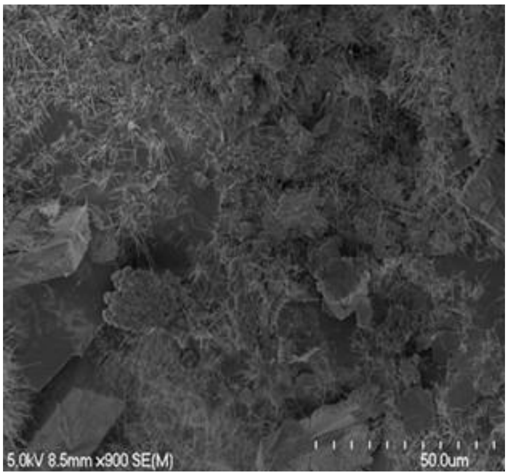
(c) Basalt rock powder 1 (7k)



(d) Basalt rock powder 2 (3.5k)



(e) Basalt rock powder 3 (6k)



(f) Basalt rock powder 4 (0.9k)

Figure 45: SEM of cement with the basalt rock powder

4.7.2 XRF

Table 23 summarizes the chemical composition of cement in the control and FA groups. Compared with the control samples (i.e. C1 & C2), Sample FA1 generally has similar chemical decomposition to Sample C1, which may be the basic reason that FA1 has the closest compressive shear strength to C1. The comparison of chemical composition between FA1 ~ 4 shows that the amount of CaO gradually deacreases with the increase of the replacement ratio of fly ash although the percentages of SiO_2 are very similar. As stated by Valls and Vazquez (2001), CaO along with SiO_2 and water are the essential crystalline mineral in the carbonation process in cement. This may be one of the primary reasons that the compressive strength of Group FA gradually decreases with increasing the replacement ratio of fly ash.

Table 24 tabulates the chemical composition of cement in the control and GR groups. Compared with the effect of fly ash shown in Table 23, granite powder seems to slightly increase the amount of SiO_2 due to the fact that the main chemical composition of granite rock is SiO_2. Similar to cement containing fly ash, cement with granite rock powder also exibits decreasing percentage of CaO with the increase of granite rock powder. This can also be attributed to the observation that the compressive strength of cement with granite powder also gradually decreases with increasing the replacement ratio of granite powder.

Table 25 lists the chemical composition of cement in the control and GR groups. Similar to cement containing fly ash and granite rock powder, the cement with basalt rock powder consists mainly of SiO_2, Al_2O_3 and CaO with minor contents of Fe_2O_3, MgO and Na_2O, indicating its siliceous nature. Moreover, the content of CaO still gradually decreases with the increase of the replacement ratio of basalt rock powder, which is also the main reason that the compressive strength reduces with increasing the amount of basalt rock powder regardless of the slight increase of the content of SiO_2 and Fe_2O_3.

Table 23: XRF of cement with fly ash

Sample	C1	C2	Fly ash 1	Fly ash 2	Fly ash 3	Fly ash 4
SiO_2 (%)	55.03	54.44	53.75	53.51	54.12	53.92

Al_2O_3 (%)	12.79	13.07	12.82	13.06	13.52	13.54
TiO_2 (%)	0.43	0.49	0.45	0.48	0.49	0.48
MnO (%)	0.1	0.106	0.097	0.101	0.099	0.095
Fe_2O_3 (%)	4.15	4.53	4.10	4.26	4.18	4.08
MgO (%)	1.38	1.47	1.36	1.396	1.38	1.30
CaO (%)	14.35	14.20	15.11	14.96	14.63	13.37
Na_2O (%)	3.11	3.17	2.98	2.93	2.97	2.93
K_2O (%)	1.06	1.03	1.02	0.99	1.01	1
P_2O_5 (%)	0.096	0.1	0.10	0.10	0.11	0.11
SO_3 (%)	0.43	0.42	0.47	0.46	0.45	0.41
Sum (%)	99.65	100.53	99.82	99.61	99.62	98.52

Table 24: XRF of cement with granite rock powder

Sample	**C1**	**C2**	**Granite rock powder 1**	**Granite rock powder 2**	**Granite rock powder 3**	**Granite rock powder 4**
SiO_2 (%)	55.03	54.44	53.56	54.07	54.54	55.53
Al_2O_3 (%)	12.79	13.07	12.53	12.57	12.65	12.94
TiO_2 (%)	0.43	0.49	0.43	0.46	0.45	0.45
MnO (%)	0.10	0.11	0.098	0.10	0.10	0.10
Fe_2O_3 (%)	4.15	4.53	4.18	4.35	4.23	4.33
MgO (%)	1.38	1.47	1.41	1.47	1.41	1.46
CaO (%)	14.35	14.20	15.47	15.03	13.70	13.13
Na_2O (%)	3.11	3.17	2.99	2.99	3.07	3.11
K_2O (%)	1.06	1.03	1.10	1.13	1.16	1.20
P_2O_5 (%)	0.096	0.10	0.099	0.10	0.10	0.10
SO_3 (%)	0.43	0.42	0.47	0.46	0.41	0.40
Sum (%)	99.65	100.53	99.63	99.46	100.31	100.05

Table 25: XRF of cement with basalt rock powder

Sample	C1	C2	Basalt rock powder 1	Basalt rock powder 2	Basalt rock powder 3	Basalt rock powder 4
SiO_2 (%)	55.03	54.44	52.67	53.82	55.11	54.16
Al_2O_3 (%)	12.79	13.07	12.36	12.73	13.05	12.92
TiO_2 (%)	0.43	0.49	0.43	0.45	0.45	0.48
MnO (%)	0.10	0.11	0.099	0.10	0.10	0.11
Fe_2O_3 (%)	4.15	4.53	4.14	4.26	4.32	4.54
MgO (%)	1.38	1.47	1.38	1.43	1.43	1.50
CaO (%)	14.35	14.20	15.58	14.70	14.02	13.85
Na_2O (%)	3.11	3.17	2.95	3.07	3.14	3.13
K_2O (%)	1.06	1.03	1.09	1.15	1.22	1.22
P_2O_5 (%)	0.096	0.10	0.11	0.12	0.12	0.13
SO_3 (%)	0.43	0.42	0.48	0.45	0.43	0.41
Sum (%)	99.65	100.53	99.76	99.45	99.77	99.96

Chapter 5: Conclusions

The effects of Granite Rock Powder, Basalt Rock Powder,and fly ash on the compressive strength of cement with the substitution ratios of (10%, 15%, 20%, and 25%) were studied. Meanwhile, the microstructure and compound composition of the cement after replacement was observed. The microstructure and chemical composition of the three pozzolanic materials were also obtained in this process, and the effect on the workability of the cement was further evaluated. The following conclusions were obtained:

1. Cement mixed with pozzolanic ash is lighter than normal cement. The effect of the three materials on the density of cement is similar.
2. In addition to the replacement of 25% Granite Rock Powder samples, the other samples can increase cement workability, of which Granite Rock Powder 1, Basalt Rock Powder 1, FA1, FA4, are significantly higher than C1 and C2.
3. In the first 28 days, the compressive strength was higher than C2 (17.722 MPa), lower than C1 (32.357 MPa), the higher of which are Granite Rock Powder 1 (30.03 MPa) and Basalt Rock Powder 1 (29.485 MPa).
4. The fastest increase in strength is from Granite Rock Powder 1, Basalt Rock Powder1, FA4, and the FA group went up with the replacement ratio increase. Both Granite Rock Powder and Basalt Rock Powder have a tendency to decline first and then rise.

References

Abousnina, R. M., Manalo, A., Shiau, J., & Lokuge, W. (2015). Effects of light crude oil contamination on the physical and mechanical properties of fine sand. *Soil and Sediment Contamination: An International Journal*, 24(8), 833-845.

Ahmed, I., Jamkar, S. (2012). Effects of fly ash on properties of concrete as per Is: 10262-2009. IOSR *Journal of Mechanical and Civil Engineering (IOSR-JMCE)*, ISSN: 2278-1684, 4(2), 1-5.

American Coal Ash Association (2019). Retrieved from http://www.acaa-usa.org

Arikan, M., Sobolev, K., Ertün, T., Yeğinobali, A., & Turker, P. (2009). Properties of blended cements with thermally activated kaolin. *Construction and Building Materials*, 23(1), 62-70.

ASTM C 618 (2003). Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. *ASTM International,* West Conshohocken.

ASTM C 311(2000). Standard Test Method for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland Cement Concrete. Ann. *Book of ASTM Standards*, Section, 4.

Ay, N., & Ünal, M. (2000). The use of waste ceramic tile in cement production. *Cement and Concrete Research*, 30(3), 497-499.

Babu, K. K., Radhakrishnan, R., & Nambiar, E. K. K. (1997). Compressive strength of brick masonry with alternative-aggregate mortar. *CE and CR journal*, New Delhi, 25-29.

Badogiannis, E., Kakali, G., Dimopoulou, G., Chaniotakis, E., & Tsivilis, S. (2005). Metakaolin as a main cement constituent. Exploitation of poor Greek kaolins. *Cement and Concrete Composites*, 27(2), 197-203.

Bai, H. S. (2011). Use of crushed rock powder as replacement of fine aggregate in mortar and concrete. *Indian Journal of Science and Technology*, 4(8), 917-922.

Bapat, J. D. (2012). Admixtures in cement and concrete. Boca Raton: CRC Press.

Batayneh, M., Marie, I., & Asi, I. (2007). Use of selected waste materials in concrete mixes. *Waste management*, 27(12), 1870-1876.

Bediako, M., Gawu, S. K., Adjaottor, A. A., Ankrah, J. S., & Atiemo, E. (2016). Analysis of co-fired clay and palm kernel shells as a cementitious material in Ghana. *Case Studies Construction Materials*. 5, 42-52.

Bhanumathidas, N., & Mehta, P. K. (2001). Concrete mixtures made with ternary blended cements containing fly ash and rice-husk ash. *Special Publication*, 199, 379-392.

Chang, T. S., & Woods, R. D. (1992). Effect of particle contact bond on shear modulus. *Journal of geotechnical engineering*, 118(8), 1216-1233.

Chen, C., Habert, G., Bouzidi, Y., & Jullien, A. (2010). Environmental impact of cement production: detail of the different processes and cement plant variability evaluation. *Journal of Cleaner Production*, 18(5), 478-485.

China Investment Consulting (2019). Cement Production Data. Retrieved from http://www.ocn.com.cn/.

Chindaprasirt, P., & Rukzon, S. (2008). Strength, porosity and corrosion resistance of ternary blend Portland cement, rice husk ash and fly ash mortar. *Construction and Building Materials*, 22(8), 1601-1606.

Consoli, N. C., Cruz, R. C., Floss, M. F., & Festugato, L. (2009). Parameters controlling tensile and compressive strength of artificially cemented sand. *Journal of Geotechnical and Geoenvironmental Engineering*, 136(5), 759-763.

Davidovits, J. (1994). Global warming impact on the cement and aggregates industries. *World resource review*, 6(2), 263-278.

Eaton, J., & Murata, K. (1960). How Volcanoes Grow. Science, 132(3432), 925-938. Retrieved from http://www.jstor.org/stable/1706650.

El-Diadamony, H., Amer, A. A., Sokkary, T. M., & El-Hoseny, S. (2016). Hydration and characteristics of metakaolin pozzolanic cement pastes. *Housing and Building National Research Center Journal*, 14(2), 150-158.

Erdoğan, T. Y. (1997). *Admixtures for concrete*. Middle East Technical University Press. Ankara, Turkey.

Fairbairn, E. M., Americano, B. B., Cordeiro, G. C., Paula, T. P., Toledo Filho, R. D., & Silvoso, M. M. (2010). Cement replacement by sugar cane bagasse ash: CO2 emissions reduction and potential for carbon credits. *Journal of environmental management*, 91(9), 1864-1871.

Ganesan, K., Rajagopal, K., & Thangavel, K. (2008). Rice husk ash blended cement: assessment of optimal level of replacement for strength and permeability properties of concrete. *Construction and building materials*, 22(8), 1675-1683.

Gómez, M. I., Sánchez de Rojas, & M.Frías Rojas. (2013) Natural Pozzolans in *Eco-Efficient Concrete*. Woodhead Publishing Series in Civil and Structural Engineering. 105-122.

Guneyisi, E., Gesoglu, M., Ozturan, T., & Memerdas, K. (2012). Microstructural properties and pozzolanic activity of calcined kaolins as supplementary cementing materials. *Canadian Journal of Civil Engineering*, 39(12), 1274-1284.

Guneyisi, M., Sobolev, K., Ertün, T., Yeğinobali, A., & Turker, P. (2009). Properties of blended cements with thermally activated kaolin. *Construction and Building Materials*. 23, 62-70.

Haach, V. G., Vasconcelos, G., & Lourenço, P. B. (2011). Influence of aggregates grading and water/cement ratio in workability and hardened properties of mortars. *Construction and Building Materials*, 25(6), 2980-2987.

Hameed, M. S., & Sekar, A. S. S. (2009). Properties of green concrete containing quarry rock dust and marble sludge powder as fine aggregate. *ARPN J. Eng. Appl. Sci*, 4(4), 83-89.

Harteis, S.P., Alexander, D. W., Harris, M. L., Sapko, M. & Weiss, E.S (2016). Review of Rock Dusting Practices in Underground Coal Mines. Pittsburgh, PA: National Institute for Occupational Safety and Health.

Hasanbeigi, A., Morrow, W., Masanet, E., Sathaye, J. & Xu, T., (2012). Assessment of Energy Efficiency Improvement and CO_2 Emission Reduction Potentials in the Cement Industry in China. Lawrence Berkeley National Laboratory, Berkeley, CA.

Hendricks CA, Worrell E, Price L & Martin N., (1998). Emission reduction of greenhouse gases from the cement industry. In: *Fourth International Conference on Greenhouse Gas Control Technologies*, Interlaken, Austria, IEA GHG R&D Program.

Ilangovana, R., Mahendrana, N., & Nagamanib, K. (2008). Strength and durability properties of concrete containing quarry rock dust as fine aggregate. ARPN *Journal of Engineering and Applied Sciences*, 3(5), 20-26.

James, J., & Rao, M. S. (1986). Reaction product of lime and silica from rice husk ash. *Cement and Concrete Research*, 16(1), 67-73.

James, J., & Rao, M. S. (1986). Reactivity of rice husk ash. *Cement and Concrete Research*, 16(3), 296-302.

Kamau, J., Ahmed, A., Hyndman, F., Hirst, P., & Kangwa, J. (2017). Influence of Rice Husk Ash Density on the workability and strength of structural concrete. *European Journal of Engineering Research and Science*, 2(3), 36-43.

Khatri, R. P., Sirivivatnanon, V., & Yu, L. K. (2003). Effect of curing on water permeability of concretes prepared with normal Portland cement and with slag and silica fume. *Magazine of Concrete Research*, 49(180), 167-172.

Kiattikomol, K., Jaturapitakkul, C., Songpiriyakij, S., & Chutubtim, S. (2001). A study of ground coarse fly ashes with different finenesses from various sources as pozzolanic materials. *Cement and Concrete Composites*, 23(4-5), 335-343.

Krantz, R. W. (1991). Measurements of friction coefficients and cohesion for faulting and fault reactivation in laboratory models using sand and sand mixtures. *Tectonophysics*, 188(1-2), 203-207.

Kumarappan, N. (2013). Partial replacement cement in concrete using waste glass. *International Journal of Engineering Research and Technology*, 2, 2278-0181.

Lagerblad, B. (2012). Mechanism of carbonation. *Proceedings of the 18th International BaustofftagungIbausil*, 12–15 September.

Lavat, A. E., Trezza, M. A., & Poggi, M. (2009). Characterization of ceramic roof tile wastes as pozzolanic admixture. *Waste management*, 29(5), 1666-1674.

Le, H. T., & Ludwig, H. M. (2016). Effect of rice husk ash and other mineral admixtures on properties of self-compacting high performance concrete. *Materials & Design*, 89, 156-166.

Lei, Y., Zhang, Q., Nielsen, C. and He, K. (2011). An inventory of primary air pollutants and CO_2 emissions from cement production in China, 199045,147-154

Li, G., & Wu, X. (2005). Influence of fly ash and its mean particle size on certain engineering properties of cement composite mortars. *Cement and Concrete Research*, 35(6), 1128-1134.

Maekawa, K., Ishida, T., & Kishi, T. (2008). *Multi-scale modeling of structural concrete*. CRC Press.

Martin, N., Levine, M. D., Price, L., & Worrell, E. (1995). Efficient use of energy utilizing high technology: *An assessment of energy use in industry and buildings*. London: World Energy Council.

Mehta, P. K. (1999), Concrete technology for sustainable development. *Concrete International*, 21, 47-53.

Mehta, P. K., & Monteiro, P. J. (2006). *Concrete: microstructure, properties, and materials* (No. Sirsi i9780071462891).

Mora, E. P., Payá, J., & Monzó, J. (1993). Influence of different sized fractions of a fly ash on workability of mortars. *Cement and Concrete Research*, 23(4), 917-924.

Müller, H. S., & Haist, M. (2012). New types of high performance concretes–Potentials for innovations in concrete construction. *Innovative Materials and Techniques in Concrete Construction*, 43-58.

Nagaraj, T. S., & Banu, Z. (1996). Efficient utilization of rock dust and pebbles as aggregates in Portland cement concrete.

Newman, J., & Choo, B. S. (2003). Advanced concrete technology set. Oxford, England: Butterworth-Heinemann.

Ortiz, S. A. (1996). Avaliação da qualidade de embalagens de vidro. CETEA/ITAL.

Papadakis, V. G. (1999). Effect of fly ash on Portland cement systems: Part I. Low-calcium fly ash. *Cement and Concrete Research*, 29(11), 1727-1736.

Poon, C. S., Wong, Y. L., & Lam, L. (1997).The influence of different curing conditions on the pore structure and related properties of fly ash cement pastes and mortars. *Construction and Building Materials*, 11(7–8), 383–393.

Rangan, B. V., Hardjito, D., Wallah, S. E., & Sumajouw, D. M. J. (2004) On the development of fly ash based geopolymer concrete. *ACI Materials Journal*, 101(6), 467-472.

Rukzon, S., & Chindaprasirt, P. (2014). Use of ternary blend of Portland cement and two pozzolans to improve durability of high-strength concrete. *Journal of Civil Engineering*, 18(6), 1745-1752.

Rukzon, S., Chindaprasirt, P., & Mahachai, R. (2009). Effect of grinding on chemical and physical properties of rice husk ash. *International Journal of Minerals, Metallurgy and Materials*, 16(2), 242-247.

Saccani, A., & Bignozzi, M. C. (2010). ASR expansion behavior of recycled glass fine aggregates in concrete. *Cement and Concrete Research*, 40(4), 531-536.

Saeki, T., & Monteiro, P. J. (2005). A model to predict the amount of calcium hydroxide in concrete containing mineral admixtures. *Cement and Concrete Research*, 35(10), 1914-1921.

Sahu, A. K., Kumar, S., & Sachan, A. K. (2003). Crushed stone waste as fine aggregate for concrete. *Indian concrete journal*, 77(1), 845-848.

Schindler, A. K., & Folliard, K. J. (2005). Heat of hydration models for cementitious materials. *ACI Materials Journal*, 102(1), 24.

Schwarz, N., & Neithalath, N. (2008). Influence of a fine glass powder on cement hydration: Comparison to fly ash and modeling the degree of hydration. *Cement and Concrete Research*, 38(4), 429-436.

Schwarz, N., Cam, H., & Neithalath, N. (2008). Influence of a fine glass powder on the durability characteristics of concrete and its comparison to fly ash. *Cement and Concrete Composites*, 30(6), 486-496.

Shi, C., & Zheng, K. (2007). A review on the use of waste glasses in the production of cement and concrete. *Resources, Conservation and Recycling*, 52(2), 234-247.

Shi, C., Wu, Y., Shao, Y., & Riefler, C. (2004). Alkali-aggregate reaction of concrete containing ground glass powder. In Proceedings of the 12th *International Conference on AAR in Concrete* (pp. 789-795).

Soroka, I. (1979). Portland cement paste and concrete. *Macmillan International Higher Education.*

Su, K. F., Jiang, B., Lian, J. S., Qin, P. C., He, S. Z., & Chen, J. K. (2014). Effect of volcanic rock powder on performance of foamed concrete. *Advanced Materials Research*, 1033, 887-891.

Swapp, S (2019). Scanning Electron Microscopy (SEM). Retrieved from https://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html.

Thomas, J., & Jennings, H (2019). Retrieved from http://www.iti.northwestern.edu/cement/monograph/Monograph2_2_4.html.

Tironi, A., Trezza, M. A., Scian, A. N., & Irassar, E. F. (2013). Assessment of pozzolanic activity of different calcined clays. *Cement and Concrete Composites*. 37, 319-327.

Valls, S., & Vazquez, E. (2001). Accelerated carbonatation of sewage sludge–cement–sand mortars and its environmental impact. *Cement and Concrete Research*, 31(9), 1271-1276.

Varma, J., Monzo, J., Borrachero, M. V., Peris, E., & González-López, E. (1997). Mechanical treatments of fly ashes. Part III: Studies on strength development of ground fly ashes (GFA)-cement mortars. *Cement and concrete research*. 27(9), 1365-1377.

Varma, M. B., & Gadling, P. P. (2017). Additive to cement: A pozzolanic material-fly ash. *International journal of Engineering Research*. 3(5), 558-564.

Vijayalakshmi, M., & Sekar, A. S. S. (2013). Strength and durability properties of concrete made with granite industry waste. *Construction and Building Materials*, 46, 1-7.

Vitruve. (1960). Vitruvius: The ten books on architecture. Dover.

Wang, A., Zhang, C., & Sun, W. (2003). Fly ash effects: I. The morphological effect of fly ash. *Cement and Concrete Research*, 33(12), 2023-2029.

Wang, A., Zhang, C., & Sun, W. (2004). Fly ash effects: II. The active effect of fly ash. *Cement and concrete research*, 34(11), 2057-2060.

Wang, I.Q., Zhang, C.Z., & Tang, M.S. (1995). Filling of volcanic ash materials. Retrieved from http://www.doc88.com/p-0816642427133.html.

Wang, X. Y. (2014). Effect of fly ash on properties evolution of cement based materials. *Construction and Building Materials*, 69, 32-40.

Wang, X. Y., & Lee, H. S. (2010). Modeling the hydration of concrete incorporating fly ash or slag. *Cement and concrete Research*, 40(7), 984-996.

Wang, X.S. (2013). Magnetic properties and heavy metal pollution of soils in the vicinity of a cement plant, Xuzhou (China). *J. Appl. Geophys*. 98, 73-78.

World Business Council for Nagabhushana Sustainable Development. (2002). The cement sustainability initiative: Our agenda for action. Stevenage, Hertfordshire, UK: Earthprint.