PROPERTIES OF 'GREEN' CONCRETE ENGINEERED FROM INDUSTRIAL WASTE MATERIALS: PAPER MILL BOILER ASH & WASTE FOUNDRY SAND

By

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I, Damian Anganoo, declare that

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ABSTRACT

The environmental impacts of cement manufacturing, coupled with the largescale consumption of natural resources, have placed concrete production techniques under scrutiny. In response, supplementary materials for green concrete production are being investigated. The South African pulp and paper industry generates large quantities of waste paper mill boiler ash (PMBA), whilst foundries are inundated with waste foundry sand (WFS) from metals production. Despite their high generation rates and the national landfill crisis, landfilling is the dominant disposal method. However, due to their inherent qualities and respective production processes, these materials may have potential for meaningful reuse in concrete.

This study investigated the properties of PMBA-integrated concrete and WFS-integrated concrete. PMBA partially replaced cement whilst WFS partially replaced fine aggregate. Replacements occurred in 5, 10, 15, and 20 percent by mass. Conventional concrete served as the control sample. Previous work of a similar nature left substantial gaps as testing was predominantly limited to mechanical strengths and occurred in international contexts. This study employed local waste materials to assess concrete workability, density, durability, mechanical strengths, and batch leaching tests to determine the pH value, ion conductivity and nitrates content in filtered concrete leachate. The following conclusions were drawn: A 10% replacement of cement, with PMBA, was identified as the overall optimum concrete mix as it achieved the highest density, the highest compressive and flexural strengths, a 'medium' degree of workability, a 'good' degree of durability in terms of oxygen permeability, 'excellent' degrees of durability against water sorptivity and chloride conductivity and a sufficient pH value to preserve the concrete passivation layer for steel protection.

Out of all WFS samples, the 5%WFS mix was found to be superior as it displayed a 'high' degree of workability, a suitable pH for protecting steel, 'excellent' degrees of durability against oxygen permeability, water sorptivity and chloride conductivity, and when compared to the control, exhibited a higher density and a lower compressive, flexural and tensile-splitting strengths.

In terms of leachate quality, ion conductivity assessments indicated that conventional concrete leachate exhibited a higher ion conductivity and leached more ionic species than all 'green' concrete samples. The leachates of all samples, except the 7-day WFS sample, exhibited nitrate contents which were low enough to meet the requirement for drinking water and the maximum contaminant level. Viability assessments, based on overall concrete performance, indicated all PMBA samples performed better than all other samples whilst the only 5%WFS sample performed better than the control sample.

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DEDICATION

This thesis is dedicated to my great one in the sky, my beautiful mother - Mrs. Priya Anganoo, who taught me that perseverance is key and will always be rewarded.

This thesis is further dedicated to my greatest inspiration and my concrete pillar of strength – my amazing aunt, Ms. Shayma Ramlakan.

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LIST OF SYMBOLS & ABBREVIATIONS

$\bar{x}_c$	Mean values of concrete control results
$\bar{x}_i$	Mean values of concrete test results
ASR	Alkali-silica reaction
AWM	Alternative waste management
C & CI	Cement & Concrete Institute
C_2S	Dicalcium silicate
C_3A	Tricalcium aluminate
C_3S	Tricalcium silicate
C_4AF	Tetracalcium aluminoferrite
CBD	Compacted bulk density

CC	Chloride conductivity
C_c	Coefficient of gradation
CH	Calcium hydroxide [$Ca(OH)_2$]
CSH	Calcium silicate hydrate [$C_3S_2H_3$]
C_u	Coefficient of uniformity
DEA	South African Department of Environmental Affairs
$eqNa_2O$	Alkali equivalent content
f_{cc}	Compressive strength
$f_{cc,28}$	28-Day compressive strength
$f_{cc,7}$	7-Day compressive strength
f_{cf}	Flexural strength
$f_{cf,28}$	28-Day flexural strength
$f_{cf,7}$	7-Day flexural strength
f_{ct}	Tensile-splitting strength
$f_{ct,28}$	28-Day tensile-splitting strength
$f_{ct,7}$	7-Day tensile-splitting strength
FM	Fineness modulus
GCT	Green concrete technology
GGBS	Ground granulated blast furnace slag
GHG	Greenhouse gas
H	Water [H_2O]
HCP	Hardened cement paste
ITZ	Interfacial transition zone
IWM	Industrial waste management
KZN	KwaZulu-Natal
LBD	Loose bulk density

MC	Moisture content
Ø	Diameter
OPI	Oxygen permeability index
PMBA	Paper mill boiler ash
PMS	Paper mill sludge
R	South African Rand
RD	Relative density
SA	South Africa
SANS	South African National Standard
SCM	Supplementary cementitious material
SHD/ρ_c	Saturated hardened density
Stats SA	Statistics South Africa
$t_{(v; a)}$	Critical statistic value
t_0	Test statistic for the null hypothesis condition
UIS	Umgeni Iron and Steel Foundry
UKZN	University of KwaZulu-Natal
W/B	Water-binder ratio
WFS	Waste foundry sand
WS	Water sorptivity
Δ	Change in property relative to the control

LIST OF UNITS

cm	Centimetre
hr	Hours
kg	Kilogram
L	Litre
mg	Milligram
MJ	Megajoule
mm	Millimetre
MPa	Megapascal
mS	MilliSeimens
N	Newton
s	Seconds
V	Volt
μm	Micron (micrometre)

1. CHAPTER ONE: INTRODUCTION

1.1 BACKGROUND

Globally, advancements in the sustainability crusade have prompted a detailed investigation into building materials, particularly concrete, which occupies an invaluable role in furthering the sustainability movement (Sabnis, 2012). Concrete is noted as the most widely used man-made substance on earth (Lekshmi, 2015). Currently, this composite material has no known alternative and with increasing infrastructural needs due to urbanisation, population growth, and economic growth, it becomes clear that concrete will remain ubiquitous (Domone & Illston, 2010). Accompanying this continuity is the environmentally-adverse process of cement manufacturing, coupled with the ongoing largescale consumption of natural resources (Moriconi, 2007; Colangelo et al., 2018). Accordingly, several authors such as Li (2011) and Mehta & Monteiro (2006), label the concrete industry as the largest consumer of natural resources in the world.

For these reasons, the concrete production process is thought to be unsustainable and the industry has been called upon to achieve a 'green' transition (Meyer, 2002). In response to this, the use of supplementary materials for concrete production is being researched extensively (Akinwale, 2018). Concrete is rather design-flexible; allowing for conventional constituents to be partially replaced with pre-determined, eco-friendly and abundantly-occurring materials, namely certain types of waste. This variant of concrete is termed 'green' concrete and arises from a concept known as 'green' concrete technology (GCT). Historically, this concept was found to have meaningful applications in industrial waste management (IWM) as the use of various industrial by-products have become a norm in the concrete industry, such as cements blended with ground granulated blast furnace slag (GGBS) from the iron and steel industry.

In all developed societies, industry remains an essential engine of progress; making waste production inevitable and IWM an incessant task (Makgae, 2011). According to the South African Department of Environmental Affairs (DEA, 2018), despite the landfill crisis in South Africa (SA), 90 percent of both industrial waste and total waste were landfilled in 2017. Evidently, landfilling is the dominant waste management option for industries in SA, however this system is not without its challenges, such as severely diminishing landfill capacities, scarcity of suitable land for landfill siting and extension, environmental degradation through greenhouse gas (GHG) landfill emissions and leaching, rising costs and increasing waste bans through continuously evolving legislative requirements (Garner, 2009; IWMSA, 2017; DEA, 2018). Goddard (1995) reasons that predicaments in a country's landfill situation could be taken as evidence of the unsustainability associated with current practices. As such, a pressing sustainability-driven issue is IWM by economic, environmentally-friendly, and lawful means (Abdul-Rahman, 2014; Aurecon, 2017).

It has long been acknowledged that due to their inherent qualities and the manufacturing processes that they arise from, certain industrial waste materials exhibit properties that render them favourable for reuse in concrete production. However, these valuable materials are still landfilled. Excellent examples of such waste materials are paper mill boiler ash (PMBA) and waste foundry sand (WFS).

PMBA is the biomass-derived waste ash arising from the pulp and paper industry. This landfilled ash is a by-product of the combustion of its organic parent material, waste paper mill sludge (PMS), with bituminous coal and additional waste variants (Byiringiro, 2014). As such, PMBA is often described as pulp and paper mill fly ash. In analysing various literature, it was found that due to the chemical composition of PMS and its combustion with bituminous coal, the major oxide contents present in the resulting PMBA are similar to the desired oxide contents in both cement and fly ash, namely silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3), and calcium oxide (CaO) (Naik & Kraus, 2003; Li, 2011; Bediako & Amankwah, 2015; Bajpai, 2015; Simão et al., 2018). Thus, PMBA has great potential as a supplementary cementitious material (SCM). The reuse of this ash is further warranted by its high production rates, its burden on landfills and its environmental implications, such as direct risks to the quality of soil and water. Additionally, several authors such as Likon & Trebše (2012), Singh (2014), and Marsland & Whiteley (2015), note that current methods of reuse, such as land application and landfill capping, are minor and infeasible.

WFS is the discoloured, uniformly sized waste sand generated in the foundry industry. This waste is a result of foundry sand moulds that have become unsuitable for reuse due to the repeated casting of metal (Mavroulidou & Lawrence, 2018). WFS masses are stockpiled in great quantities on the foundry site and are destined for landfills. This material is rich in silica, which is the dominant oxide in fine aggregate sand (Walker, 2013). Similar to PMBA, WFS is generated in large quantities which places a substantial strain on landfills. Moreover, due to the presence of heavy metals, this material may become a chemical hazard to health, agriculture, groundwater, and land (Penkaitis & Sigolo, 2012). The two variants of WFS occur as greensand and chemically-bonded sand. This investigation employed the latter.

This study explores the properties of two separate sets of concrete – PMBA-integrated concrete ('PMBA-concrete') and WFS-integrated concrete ('WFS-concrete'). PMBA partially replaced cement whilst WFS served as a partial fine aggregate replacement. In order to assess the influence of these test materials, all partial replacements varied in the order of 5, 10, 15, and 20 percent, by mass. Conventional concrete, which being concrete arising only from Portland cement, sand, stone and water, was employed as the control sample. PMBA was obtained from the Mondi Merebank paper mill located in KwaZulu-Natal (KZN). WFS was sourced from the Umgeni Iron & Steel (UIS) Foundry located in KZN.

1.2 PROBLEM STATEMENT

Internationally, GCT has been employed in the construction and waste management sectors of various countries (Agarwal & Garg, 2018). Nationally, SA has been slow in the implementation of sustainable practices (Aigbavboa et al., 2017). Accordingly, detailed studies dedicated to observing the properties of PMBA-concrete and WFS-concrete are rare, especially in SA. Internationally, past studies of a similar nature have been conducted, however substantial gaps exist in these studies as testing was typically limited to slump and mechanical strength tests. As such, it was uncommon for these past studies to subject concrete samples to density assessments, leaching tests, durability tests under South African climate conditions or to assess the protection afforded to reinforcements due to concrete alkalinity. More importantly, such past studies predominantly used PMS or PMS ash and have scarcely used PMBA – the former is the pure ash derived from the incineration of PMS alone, whilst the latter is a more realistic representation of the waste in the South African pulp and paper industry, in that it is the final product of the combustion of PMS with bituminous coal and other waste variants. Moreover, it may be reasoned that there is no immediate need to incinerate and reuse pure PMS in concrete as it is used in combustion to produce electricity and steam in pulp and paper manufacturing mills. However, the resulting PMBA is primarily landfilled, thereby warranting investigations for avenues of reuse.

In addition, Walker (2013) informs that various pieces of South African literature acknowledge the shortage of fine aggregate resources in the country; however, few have explored alternate sources of fine aggregate for concrete. Therefore, evaluations of various concrete properties arising from both test materials are required, whereby the optimum contents of PMBA and WFS must be identified.

1.3 SIGNIFICANCE OF RESEARCH

This study will provide a necessary evaluation of two sets of concrete, in terms of:

- The effects on concrete properties when cement is partially replaced with locally available PMBA; and
- The effects on concrete properties when fine aggregate is partially replaced with locally available WFS.

This evaluation extends past the point of workability and basic strength testing as the following testing is conducted: workability, density assessments, strengths in compression, flexure and splitting, assessments of the protection afforded to concrete passivation layer through pH value, testing of leachate quality (pH, nitrate content, ion conductivity) and standard South African durability assessments (oxygen permeability, water sorptivity and chloride conductivity). This study may serve as a preliminary resource to assist in the concrete industry's potential adoption of PMBA and WFS. Accompanying this adoption will be a variety of potential benefits in the economic, environmental, and social spheres, such as the:

- Advancement of concrete properties through GCT,
- Facilitation of IWM in the pulp & paper and foundry industries,
- Preservation of valuable landfill airspaces,
- Contributing to knowledge and narrowing of research gaps, and
- Environmental conservation through decreased cement manufacturing and sand mining.

In addition, this study provides a review on the properties of PMBA and WFS as they compare to cement and fine aggregate respectively.

1.4 RESEARCH QUESTIONS

The main research questions are:

- In comparison to conventional concrete, what effect does PMBA have on concrete properties when replacing cement by 5, 10, 15 and 20 percent by mass?
- In comparison to conventional concrete, what effect does WFS have on concrete properties when replacing fine aggregate by 5, 10, 15 and 20 percent by mass?

1.5 RESEARCH AIMS & OBJECTIVES

This research primarily aims to investigate the properties of two sets of concrete, each arising from the integration of local PMBA and WFS as partial replacements to cement and fine aggregate respectively.

To achieve the aim presented above, the following objectives are to be met:

- As part of a comprehensive literature review, document the relevant properties of cement, fine aggregate, PMBA and WFS and identify potential factors that may influence concrete.
- Investigate the effect of various contents of each test material (5%, 10%, 15% and 20%) on concrete workability, density, compressive strength, flexural strength, tensile-splitting strength, durability and the pH value, ion conductivity and nitrate content of the resulting leachate.
- Use knowledge gained from the literature review to explain the effect of the incremental additions of each test material on concrete and assess how the properties of PMBA and WFS achieves this effect.

1.6 LIMITATIONS OF RESEARCH

The limitations of the study were as follows:

- The study did not assess concrete properties arising from various types of cement as this was not related to the aim of the study. Cement was treated as a fixed variable and CEM II/B-S 42.5 N plus was used for all samples due to its availability at UKZN. This particular cement contains between 21 to 35 percent slag as extender. As such, the influence of ordinary Portland cement (i.e., no extenders) and cements containing other extenders has not been observed.
- The long-term deterioration of WFS-concrete due to ASR was not been investigated.
- The W/B ratio is known to have a substantial influence on concrete properties, particularly workability, strength and durability. This study did not evaluate influences arising from variations in W/B ratio as the point of focus were the influences of the test material.
- The long-term influence of alkali-silica reactions (ASR) due to the higher $eqNa_2O$ content of PMBA was not investigated.
- As per the norm in GCT studies, the test slumps were not modified to resemble the target slump so as to obtain an accurate evaluation on the impact on the water requirement.

- The factors that influence the long-term performance of concrete, such as creep, was not investigated in the study.
- The leaching tests conducted were not in accordance with SANS, but rather a variation of the ASTM D 3987 procedure. The variation was necessary to conduct the testing using available equipment. The modified procedure is explained in Section 3.4.7.
- Analyses to investigate the environmental and economic implications were not conducted in the study.

1.7 THESIS STRUCTURE

This thesis is segmented into five chapters and is structured as follows:

Chapter 1 leads the research topic by introducing the need for sustainable practices in the concrete industry and in waste management methods, as well as the potential solution of using waste materials in concrete for its improvement. Following this is an overview of the problems arising from each test material and the unsustainability of concrete production. Thereafter, a brief outline of the significance of the research, the research questions, aims, objectives, limitations of the research and thesis structure are provided.

Chapter 2 provides a comprehensive literature review on the research topic. This literature review includes reviews on the South African landfill crisis, the issues surrounding the heavy utilization of cement and fine aggregate, the merging of industrial waste and concrete, a background to ‘green’ concrete technology, a review of cement and fine aggregate properties and their influence in concrete, a review on the relevant properties of concrete, reviews of each test material and their potential influence on such concrete properties as based on their own properties and past studies.

Chapter 3 demonstrates the methodology by listing the materials used, discussing the concrete mix design and describing all test and analysis procedures employed.

Chapter 4 presents the results from the experimentation and the results from the statistical analysis. These results, per test material, are reviewed, explained and compared with the control sample. Knowledge is drawn from the literature review to explain results and both correlations and contradictions to past studies are discussed.

Chapter 5 concludes the research with a summary of the findings. Following this is a discussion on how the objectives of the study were met, the response to the research question, recommendations and the future scope.

1.8 CHAPTER SUMMARY

This chapter introduced the study by providing a background which speaks of the need for more sustainable measures to be implemented into the concrete industry, particularly the advent of producing ‘green’. The two test materials, namely PMBA and chemically-bonded WFS, were introduced. The problem statement, the significance of the research, research questions, aims and objectives, limitations of the research and the structure of the thesis were then discussed.

The next chapter will serve to provide theoretical insight into the research topic. This is done by discussing cement and fine aggregate technology and the ways in which concrete properties are influence by these materials. Afterwards, backgrounds to both waste materials are provided and their properties are discussed and compared to their conventional counterparts. Based on these properties and past study results, the potential effects of PMBA and WFS in concrete are examined.

2. CHAPTER TWO: LITERATURE REVIEW

2.1 INTRODUCTION

This chapter provides the theoretical framework for the investigation. This is achieved by discussing relevant literature relating to the following core topics:

- The need for sustainable practices in the waste management and concrete industries.
- The concept of GCT.
- The properties of the conventional materials being partially replaced.
- The properties of the test materials that are being investigated and how they compare to their conventional counterparts.
- The fresh and hardened state concrete properties that are being investigated, and the roles of cement, fine aggregate, PMBA and WFS in influencing these properties.

2.2 BRIDGING INDUSTRIAL WASTE MANAGEMENT & 'GREEN' CONCRETE

The integration of suitable industrial waste materials in concrete makes strategic sense, especially in the South African context. The country is subjected to growing unsustainability as raw materials for concrete production are depleting whilst demand and associated environmental impacts are rising, waste-driving factors are progressing and the landfill situation is deteriorating (Madzivhandila, 2018; Al-Mansour et al., 2019).

2.2.1 The Landfill Predicament

It is necessary to first review the landfill situation in the country as vast quantities of PMBA and WFS are landfilled, thereby contributing to the landfill crisis. According to Miller (2010), Mondi experiences a fine ash mass flow of 64 tonnes per day and Iloh (2018) states that annually, SA disposes approximately 500 000 tonnes of WFS. Nearly all quantities of PMBA and WFS are landfilled. On a larger scale, SA landfills approximately 90 percent of all industrial waste (Simelane, 2002; DEA, 2018). Gumbi (2015) reports that although the country is developing, the quantity of waste generated resembles that of developed countries. Tonnage reports by the South

African Waste Information Centre (SAWIC, 2020) reveal that increasing amounts of waste are sent to engineered landfills (Figure 2.1).

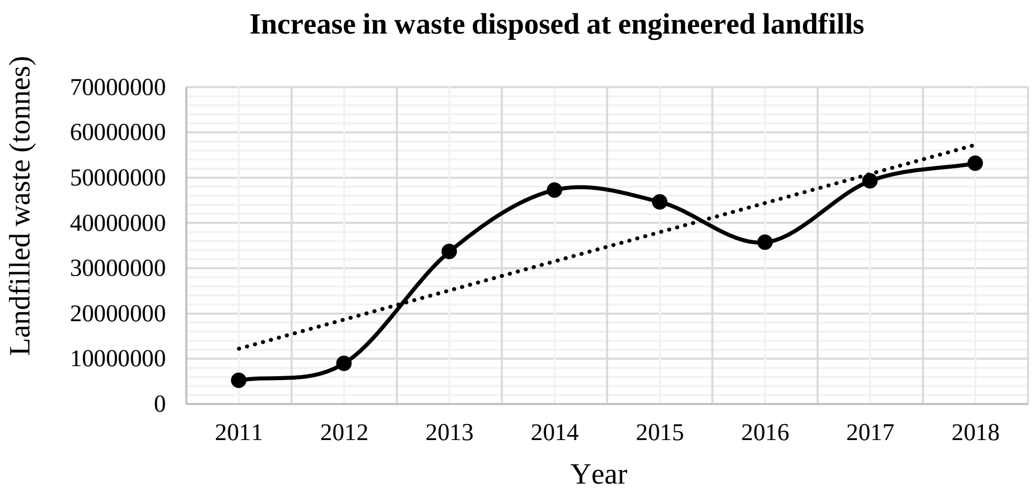


Figure 2.1: *Increase in waste sent to landfills (SAWIC, 2020)*

Naturally, rising landfilling rates have led to the reduction of landfill airspaces (i.e., the volume of space available for the disposal of solid waste in a landfill). Table 2.1 presents the estimated remaining airspaces across the major South African municipalities whilst Figure 2.2 displays trends in airspace depletion in major metropolitan municipalities.

Table 2.1: *Estimated remaining landfill airspaces in major municipalities (DEA, 2018)*

Metropolitan municipality	Estimated remaining airspace (years)
Ekurhuleni	36
eThekwini	29
City of Tshwane	18
City of Johannesburg	8
City of Cape Town	5

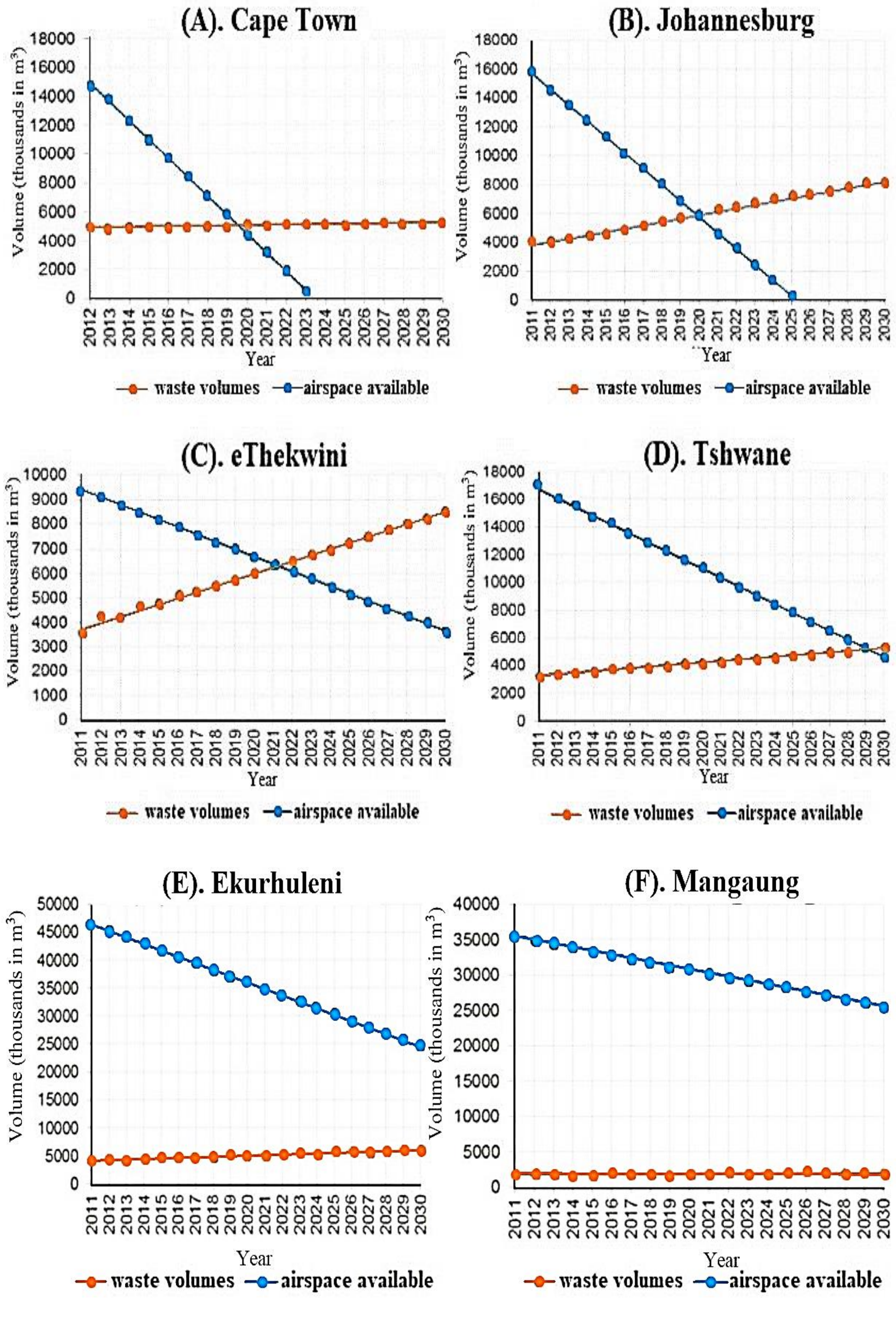


Figure 2.2: *Trends in declining airspaces and increasing waste volumes in major metropolitan municipalities in SA (SACN, 2014)*

According to the Institute of Waste Management of Southern Africa (IWMSA, 2017), the steadfast dependence on landfilling has led to certain sites rapidly approaching capacity. Consequently, without intervention, airspaces in certain municipalities in the country will diminish by the year 2030 (e.g., City of Johannesburg and City of Cape Town), whilst airspaces in other municipalities will have significantly depleted.

Additionally, South African waste regulations are evolving, followed by landfill bans on several waste materials. GreenCape (2020) informs that from 23 August 2021, a variety of waste materials will be banned, including hazardous e-waste, brine, batteries excluding lead acid, organic pollutant pesticides etc. Thus, it is uncertain as to whether the landfilling of certain types of waste materials will be permitted in future.

A further concern is the struggle to construct new landfills or extend existing sites. Gumbi (2015) states that in terms of landfilling, the most challenging task that South African waste management authorities are faced with are siting landfills. The scarcity of remaining suitable land, along with societal, economic, environmental, lawful and technical considerations, renders the task of siting landfills increasingly difficult (Kontos et al., 2005; Seyyedalipour et al., 2014).

For these reasons, the remaining landfill airspaces must be considered as a valuable resource and preserved accordingly. A step in the right direction would be to reduce quantities of PMBA and WFS from the waste stream, through means of redirection.

2.2.2 The Cement Predicament

In the South African concrete industry, cement production is the leading contributor of GHG emissions, with an average value of 94.7 percent of the total carbon dioxide equivalent emissions (CO_2-e) (Muigai et al., 2013). Sharma & Agrawal (2018) inform that the production of approximately one tonne of cement results in the release of nearly one tonne of carbon dioxide (CO_2). This is significant as SA has the cement production capacity of over twenty million tonnes per annum (Krüger, 2014). On average per year, SA produces 11.9 million tonnes of cementitious materials, 9 million tonnes of CO_2-e and consumes 9 million tonnes of cement (Muigai, 2014). Figure 2.3 displays the trends in cement production with the corresponding generation of CO_2-e in the South African concrete industry.

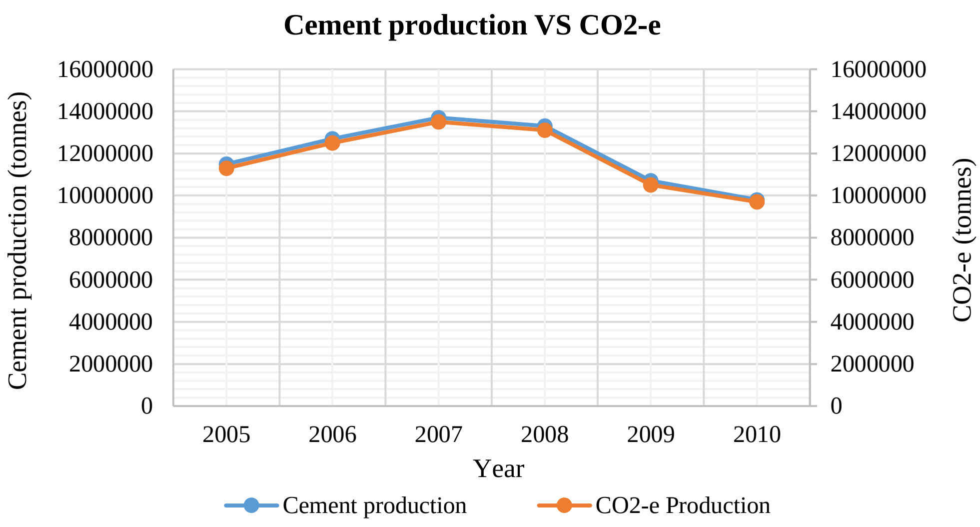


Figure 2.3: *The trends in cement production and the resulting CO2-e production in the South African concrete industry (Muigai et al., 2013)*

In 2009, SA ranked ninth in the top twenty GHG emitting countries in the world (Mwakasonda, 2012). Nationally, the cement sector contributes 1 percent to the country's total GHG emissions (Arp et al., 2018). Starting in the 1990s, South African cement manufacturers have attempted to reduce this contribution through partial clinker substitutions, however these emissions have still increased by 27 percent between 2000 and 2010 (WWF, 2018). This is largely due to the increasing demand for cement (Figure 2.4). In addition to GHG emissions, cement production emits air pollutants, namely dust, where roughly 164 kg of dust is emitted per tonne of cement produced (Babor et al., 2009).

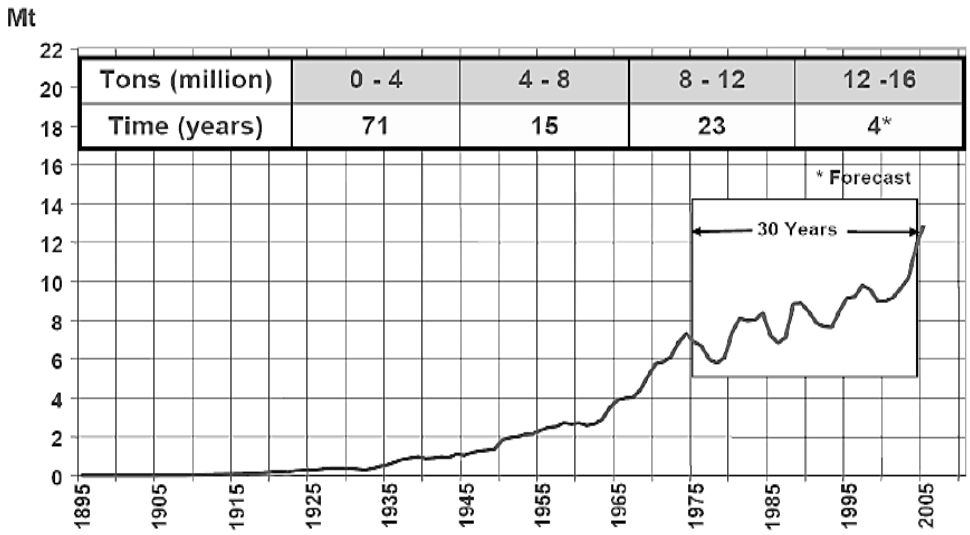


Figure 2.4: *Increasing trend in annual cement demand in SA (Ohanyere, 2012)*

In hand with cement production is the associated requirement for energy, whereby producing one tonne of cement consumes 4085 MJ of energy (Muigai, 2014). Moreover, between 2005 and 2010, South African cement production consumed a total of 37 billion MJ. Muigai (2014) further states that cement production accounts for 95 percent of the energy consumed in the South African concrete industry.

Placing aside the high levels of emissions and energy consumption arising from cement production, a separate concern is the requirement for raw materials to meet said production. In SA, between 2005 and 2010, an annual average amount of 19.1 million tonnes of raw materials (silica, limestone, clay, iron ore etc.) were required to meet the average 11.9 tonne-production of cementitious binders (Muigai, 2014). The harvesting of such raw materials also negatively impacts water regimes, land use patterns and air quality (Arp et al., 2018).

2.2.3 The Fine Aggregate Predicament

The United Nations Environment Programme (UNEP, 2019) describes fine aggregate as the unrecognised foundational material of economies as it is required for concrete, asphalt, pavements, glass and several other production processes.

Due to their prevalence in concrete, vast amounts of sand are harvested and consumed. Amponsah-Dacosta and Mathada (2017) inform that the demand for sand in the South African construction industry is intensifying, consequently leading to indiscriminate and excessive sand mining. This is accompanied by environmental losses such as the destruction of habitats. Naidoo (2008) states that over the years, the sales and value of South African fine aggregate have increased. More importantly, the rate of sand extraction has exceeded the rate of natural renewal (John 2009). In fact, Walker (2013) expressed concern for the shortage of fine aggregate resources in certain areas in the country, such as the Greater Cape Town area, whilst Davis et al. (1979) informs that the declining supply of Umgeni river sand in Durban has been stressed upon since the late seventies.

In addition to concerns over the high amounts of fine aggregate required, the production of CO_2-e and the energy consumption during the harvesting and preparation processes must be noted. Table 2.2 presents the rise in total aggregate production and consumption, along with the corresponding increases in $CO_{2\text{-}e}$ production and energy consumption from aggregate preparation. The Support Programme for Accelerated Infrastructure Development (SPAID, 2008) estimated that aggregates for concrete production occupy 30 percent of the total aggregates produced, hence, between 2005 and 2010, roughly 30 percent of 110 million tonnes of aggregate (i.e., about 33 million tonnes) was directed to the concrete industry (Muigai, 2014).

Table 2.2: *Trends in increasing aggregate production and consumption, with the resulting CO2-e production and energy consumption in the South African concrete industry (Muigai, 2014)*

Year	Aggregate production (tonnes)	Aggregate consumption (tonnes)	CO_2-e production (tonnes)	Energy consumption (GJ)
2005	94 684 000	28 400 000	230 000	2 650 000
2006	106 373 000	31 900 000	258 000	2 980 000
2007	113 118 000	33 900 000	275 000	3 170 000
2008	113 799 000	34 100 000	276 000	3 190 000
2009	114 714 000	34 400 000	279 000	3 210 000
2010	120 312 000	36 100 000	292 000	3 370 000
Average	**110 500 x 10^3**	**33 133 x 10^3**	**268 x 10^3**	**3095 x 10^3**

2.2.4 The Principles of Industrial Ecology & GCT

Sustainable development requires a balance between progression and preservation. This necessitates the improvement of the processes that must cyclically occur to maintain and develop everyday life, such as producing concrete for hard infrastructure and managing waste from essential industries. To assist in alleviating the landfill crisis, attention must be given to improving waste management practices in industries, such as redirecting PMBA and WFS towards useful applications. In the ideal case, this diversion must endeavor to ease the complications surrounding the production and utilization of cement and fine aggregate in concrete.

Jelinski et al. (1992) references an interesting notion, termed industrial ecology, which associates the industrial system with the biological ecosystem. El-Haggar (2007) explains that this biological system evolves through the flow of materials due to the system consuming what it produces, such that waste in one component becomes resources to another (e.g., fauna feeds on flora and microorganisms decay fauna waste and returns nutrients to flora). In mimicking this, one of the core principles of industrial ecology is to turn anthropogenic waste from one industry into raw materials for another industry to make use of (Frosch & Gallopoulos, 1989; O'Rourke et al., 1996; Brent et al., 2008).

By applying this ecological comparison to this study, each test material and concrete appear to share a mutual relationship. This is because PMBA and WFS require management and may be 'nutrient-rich' whilst concrete requires certain 'nutrients' to become more sustainable during phases of production. Furthermore, concrete is used "thick and fast" and has a long enough service life to allow for a sufficient form of waste management. Finally, once concrete has surpassed its design life, it can be demolished into rubble and processed to partially replace natural aggregates for further concrete production (Figure 2.5). This concept is in line with GCT. 'Green' concrete is a collective term used to describe concrete arising from environmentally-friendly materials or production methods. GCT was first developed in Denmark in 1998, and remains one of the most innovative concepts in the concrete industry. GCT largely involves the incorporation of supplementary cementitious materials (SCMs). Blended cements are a common example of this. Industrial waste materials such as fly ash (waste from coal combustion), GGBS (waste from ferrous-related manufacturing) and silica fume (waste from manufacturing silicon and ferrosilicon alloys) are famous for being sustainable cement extenders and have become a proclivity in concrete production (The Concrete Institute, 2013).

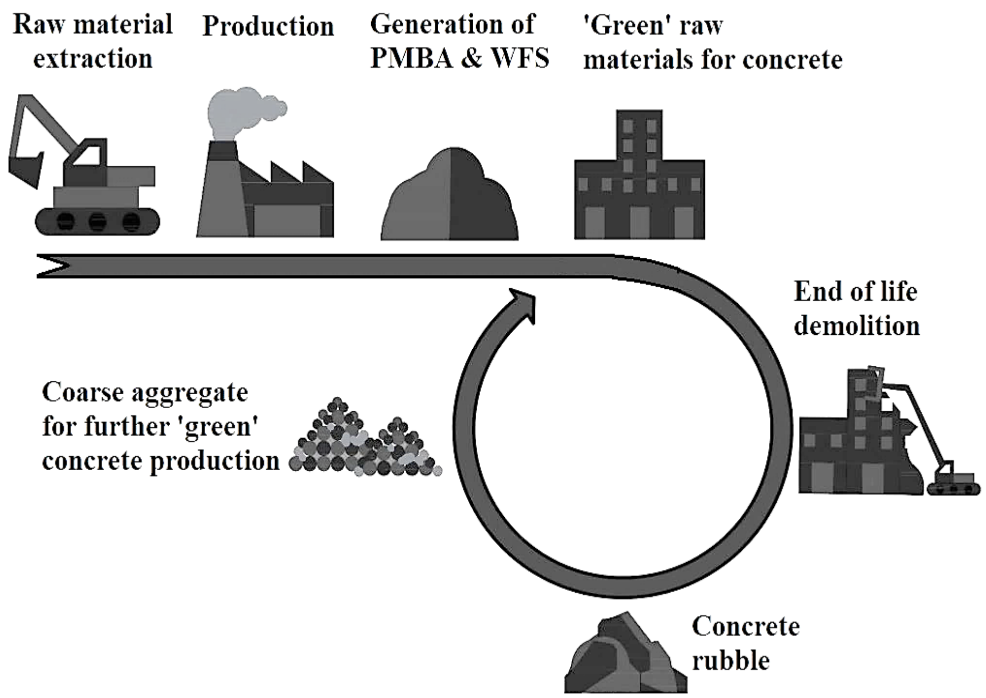


Figure 2.5: *Materials flow showing PMBA and WFS in 'green' concrete production*

Attwir & Kabir (2010) investigated various industrial waste materials as partial replacements to concrete constituents. Their results indicated superior concrete in terms of performance, environmental conservation and construction costs. These factors are major driving forces for the implementation of 'green' concrete in sustainable construction. Similarly, several researchers have observed the positive effect of waste from diverse industries in concrete applications. For these reasons, research is required to recognize additional industrial waste materials that can partially replace cement and aggregates. However, Allen & Behmanesh (1994) clarify that one of the challenges associated with industrial ecology will be conducting such research.

2.3 CONCRETE TECHNOLOGY

Conventional concrete fundamentally consists of approximately 12 percent cement, 80 percent aggregate, and 8 percent potable water (Mehta & Monteiro, 2006). These constituents amalgamate due to the chemical process called hydration, in which cement and water mix to form cement paste which then binds aggregates to form fresh concrete (i.e., rheological concrete that retains plasticity). The fresh state of concrete is transitory; however, fresh properties, particularly workability, are crucial for the effective handling and finishing of concrete. Once concrete has hardened, the material exhibits a wide range of new properties, particularly relating to strength and durability.

Due to its composite nature, the properties of concrete are largely influenced by its three constituent phases – hardened cement paste (HCP), aggregates and their interface. Since cement and fine aggregate are being replaced by PMBA and WFS respectively, the discussions that follow provide the necessary information on the inherent properties of these four materials and their influences on concrete. This would allow for a comparison between conventional and test material properties to be made, in order to predict, analyse and explain the performance of PMBA and WFS as partial replacements to cement and fine aggregate, respectively.

2.4 CEMENT

Cement is a binding agent and in hardened concrete, creates a rigid composite by forming a matrix to hold aggregates. South African Portland cements are grouped into five categories: CEM I (Ordinary Portland cement), CEM II (Portland-composite cement), CEM III (Blastfurnace cement), CEM IV (Pozzolanic cement), and CEM V (Composite cement). Portland cement serves as the base for all of these cement types. This is due to its ability to produce strong and durable concrete, to set at ordinary pressure and temperature conditions, and to be relatively cost-effective. This study uses cement type CEM II/B-S 42.5 N plus. The breakdown of this code is given in Table 3.1 in Section 3.2.3.

Fundamentally, Portland cement arises from an appropriate combination of a calcareous material (e.g., limestone) and an argillaceous material (e.g., clay or shale). These materials collectively provide the four major oxides required in Portland cement, namely lime (CaO), silica (SiO_2), alumina (Al_2O_3), and ferric oxide (Fe_2O_3).

2.4.1 Composition

In observation of Table 2.3 below, cement predominantly consists of CaO and SiO_2. These oxides work by forming the main hydrating compounds that promote strength. However, the chemical reaction involving these two oxides is difficult to achieve. It is the presence of Al_2O_3 and Fe_2O_3 that facilitates this reaction by creating a molten flux; allowing CaO and SiO_2 to partially dissolve and combine (Neville & Brooks, 2003). These four oxides collectively give rise to the four main compounds in cement, namely tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF).

These compounds, as presented in Table 2.4, form the major constituents in cement and play vital roles in achieving functionality. In terms of composition, the silicate compounds (C_3S and C_2S) are dominant, followed by the aluminate compounds (C_3A and C_4AF).

Table 2.3: *Chemical composition of Portland cement*

Reference	**Value**	**Oxide content (%)**							
		SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**Na_2O**	**K_2O**
Bediako & Amankwah (2015)	Minimum	18.40	3.10	0.16	58.10	0.02	0.00	0.00	0.04
	Average	21.02	5.04	2.85	64.18	1.67	2.58	0.24	0.70
	Maximum	24.50	7.56	5.78	68.00	7.10	5.35	0.78	1.66
Neville & Brooks (2010)		**LOI (%)**							
		2							
The Concrete Institute (2013)		**Alkali content (%)**							
		0.2 – 0.8							

Table 2.4: *Main compounds in Portland cement*

Compound	Oxide composition	Abbreviation	Content (%)			
			A[1]	B[2]	C[3]	D[4]
Tricalcium silicate	$3CaO.SiO_2$	C_3S	46-65	54.1	50	60-73
Dicalcium silicate	$2CaO.SiO_2$	C_2S	10-30	16.6	25	8-30
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A	5-12	10.8	12	5-12
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	6-12	9.1	8	8-16

[1]Newman & Choo (2003); [2]Neville & Brooks (2010); [3]Li (2011); [4]The Concrete Institute (2013)

2.4.2 Hydration

By the introduction of water, the main anhydrous compounds chemically react to form hydrated phases. This process is known as hydration. The various properties of hardened cement paste (HCP) are influenced by the characteristics of hydration, especially strength development, which is largely influenced by the hydration of the silicate compounds. The reactions of the silicate compounds are presented in Table 2.5 below. The HCP strength is crucial in influencing the strength of concrete.

Table 2.5: *Main hydration reactions in Portland cement (Li, 2011)*

Hydrating compound	Hydration reaction
C_3S	$2C_3S + 11H \rightarrow C_3S_2H_8 + 3CH$
C_2S	$2C_2S + 9H \rightarrow C_3S_2H_8 + CH$

$H = H_2O$; $CH = Ca(OH)_2$

2.4.3 Influence of Cementitious Properties on HCP and Concrete

Mehta & Monteiro (2006) informs that the desirable engineering properties of hardened concrete, such as strength and durability, are influenced by the properties of the HCP. The various properties of the HCP are in turn influenced by inherent cement properties.

These inherent properties include:

(A). Silicate compounds:

As illustrated in Figure 2.6 below, the strength of the HCP is mostly dependent on the hydration of the silicate compounds. It can be observed that C_3S is fast-reacting and contributes more towards early-age strength. Portland cements with higher C_3S contents exhibit greater strengths up until seven days (Motau, 2016). Conversely, C_2S reacts slowly and contributes more towards long-term strength. Due to their greater mobility, amorphous materials are generally more reactive than their crystalline counterparts. SiO_2 is required to be amorphous to be reactive. HCP strength increases with greater amorphousness and SiO_2 content.

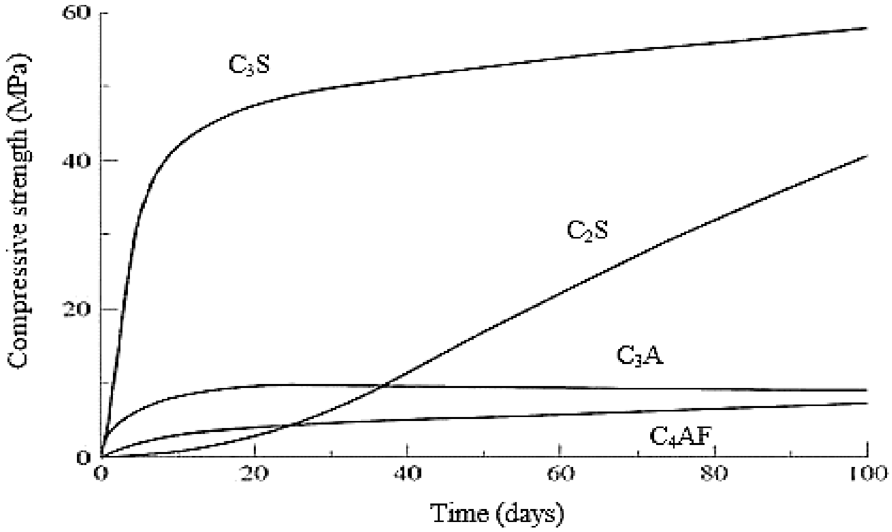


Figure 2.6: *Contribution to HCP strength by the hydration of silicates (Li, 2011)*

Silicate compounds take precedence over their aluminate counterparts because they are responsible for the formation of the primary binding agent, calcium silicate hydrate ($C_3S_2H_8$ – commonly referred to as C-S-H). According to Li (2011), approximately 50 to 60 percent of the structural component of cement is occupied by C-S-H, thereby contributing to most of the HCP strength. This is achieved by C-S-H gel occupying free spaces, reducing porosity and causing setting and hardening of the cement paste (Soroka & Stern, 1979).

C-S-H possesses small crystals which provide a large surface area with great potential for adhesion. Accordingly, C-S-H is responsible for adhering strongly to solids with low surface areas, fine and coarse aggregates and anhydrous cement particles. It is explained by Motau (2016) that with further hydration, C-S-H gel leads to additional strength gain by filling concrete pores, thus decreasing porosity. The hydration reactions that lead to the formation of C-S-H gel were shown in Table 2.5 above. Popovics (1992) suggests that higher contents of silicate compounds lead to improved strength development.

(B). Alkali equivalent content (eqNa_2O):

Later strength development is reduced when alkali oxides (K_2O and Na_2O) react with sulphur trioxide (SO_3) to produce soluble alkali sulphates. In this form, these alkali sulphates are represented by the alkali equivalent content (eqNa_2O), which is determined as the sum of the contents of 0.658K_2O and Na_2O. The alkali equivalent content dissolves into water and promotes early-age strength but reduces late strengths (Figure 2.7). In accordance with the Concrete Institute (2013), the eqNa_2O content generally ranges from 0.2 to 0.8 percent in Portland cement. CEM II/B-S 42.5 N plus exhibits a value of 0.6 percent (Spenner Zement, 2012).

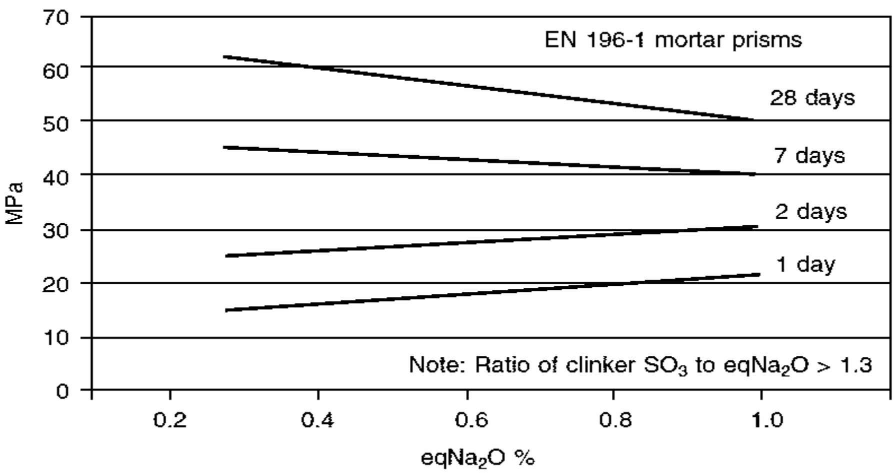


Figure 2.7: *Influence of eqNa_2O on strength development (Newman & Choo, 2003)*

(C). Cement fineness:

Portland cement is required to exhibit a certain degree of fineness in order to be effective. This is because said fineness is responsible for influencing various properties of both the HCP and concrete, such as strength, bleeding, expansion and setting times.

Cement fineness, which refers to the average particle size, is an important influence in early strength development. A physical property known as specific surface is an indication of said fineness, whereby finer cements display larger specific surface areas. Hydration initiates on the surface of cement particles, thus the total material available for hydration depends on the specific surface provided by these particles (Newman & Choo, 2003). Consequently, higher specific surface areas are necessary for rapid strength development. Mehta & Monteiro (2006) have found that increasing the specific surface from 300 to 500 m^2/kg will increase the one, three, and seven-day compressive strengths by 50 to 100 percent, 30 to 60 percent, and 15 to 40 percent, respectively. The influence of increasing cement fineness on compressive strength is shown in Figure 2.8.

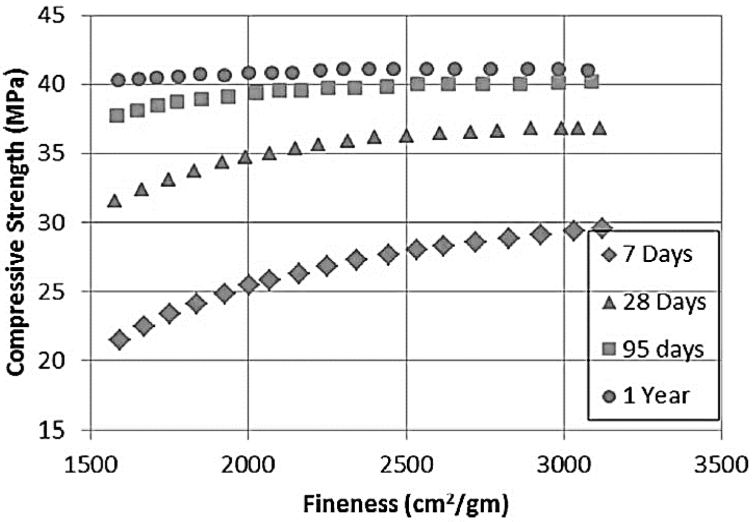


Figure 2.8: *The increase in compressive strength due to increasing cement fineness (Rafi & Nasir, 2014)*

Table 2.6 below displays the range of specific surface areas as obtained by different testing methods. As observed, there is an inconsistency in specific surface values given in literature. CEM II/B-S 42.5 N Plus exhibits a specific surface value of 370 m^2/kg (Spenner Zement, 2012).

Table 2.6: *Specific surface values of cement*

Specific surface (m^2/kg)	**Test method**	**Reference**
180 – 230	Wagner	Neville & Brooks (2010)
260 – 415	Lea and Nurse	
790 – 1000	Nitrogen adsorption	
349 – 545	Blaine fineness method	Ferraris & Garboczi (2012)
686 – 2000	Brunauer-Emmett-Teller	

(D). Soundness:

Once set, it is crucial that cement paste does not experience significant volume changes. This ability is referred to as soundness. Volume changes may occur due to four major phenomena – alkali-silica attack, delayed hydration of magnesia (MgO) and CaO, corroding steel, and sulphate attack.

Cements that are rich in alkali hydroxyls tend to react with reactive silica in aggregates, causing an alkali-silica reaction (ASR). This process leads to the formation of alkali-silica gel, which swells and causes expansive forces in hardened concrete. This in turn results in severe durability losses via long-term cracking. To prevent ASR, the $eqNa_2O$ content of cement is required to be lower than 0.6 percent. Popovics (1992) shows that expansion due to ASR may be reduced by reductions in cement content, which may be achieved by the addition of pozzolanic material such as PMBA. Figure 2.9 below demonstrates the reduced concrete expansion because of decreasing cement contents.

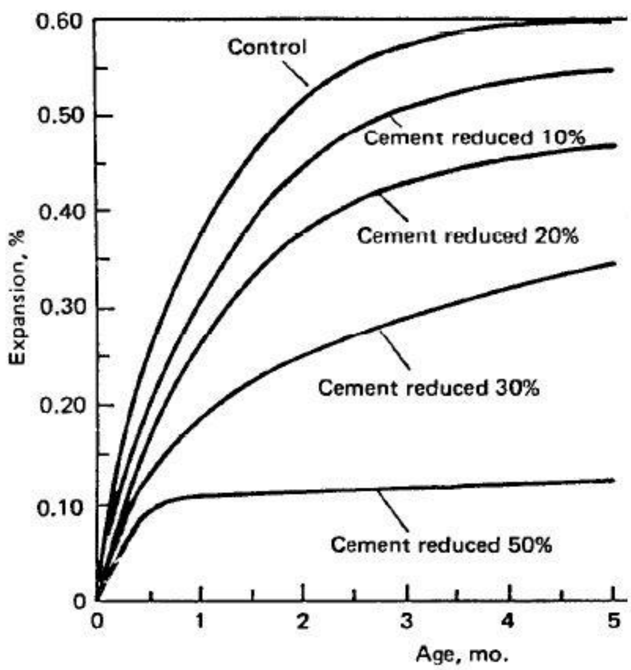


Figure 2.9: *Reduction in ASR-induced expansion through reduced cement content (Popovics, 1992)*

The autoclave expansion is an index of the potentially harmful, delayed expansion of hydraulic binder materials due to the late hydration of CaO or MgO (Klemm, 2005). Matalkah & Soroushian

(2017) have noted that the maximum autoclave expansion for Portland cement is 0.8 percent, whilst the general autoclave expansion is approximately 0.411 percent.

(E). CH from hydration:

The CH crystals, known as Portlandite, that form via hydration is believed to occupy 25 percent of the cement paste's structural component. CH serves a beneficial role by increasing concrete pH, thereby protecting steel reinforcement from corrosion and minimising the risk of spalling.

In contrast, CH may result in other forms of durability losses and so, must be kept as low as possible whist maintaining the alkaline environment. This is because CH may pose risks to the durability of concrete, such as in the form of ASR, carbonation via the reaction with CO_2 and sulphate attack via its reaction with sulphate. To control these durability losses, permeability is key and concrete needs to exhibit low permeability (Mehta & Monteiro, 2006). In addition to concerns over durability, the solubility of CH may lead to leaching issues in permeable concrete.

(F). SO_3 content:

The SO_3 content of cement is shown to have an influence on both strength and workability (Newman & Choo, 2003). As illustrated in Figure 2.10 below, greater SO_3 contents reduce slump, thereby increasing the water required to achieve a given consistency. In terms of strength, increasing contents of SO_3 lead to greater early-age strengths (Figure 2.10). Table 2.3 above shows that the average SO_3 content is 2.58 percent whilst CEM II/B-S 42.5 N plus shows a value of 2.9 percent.

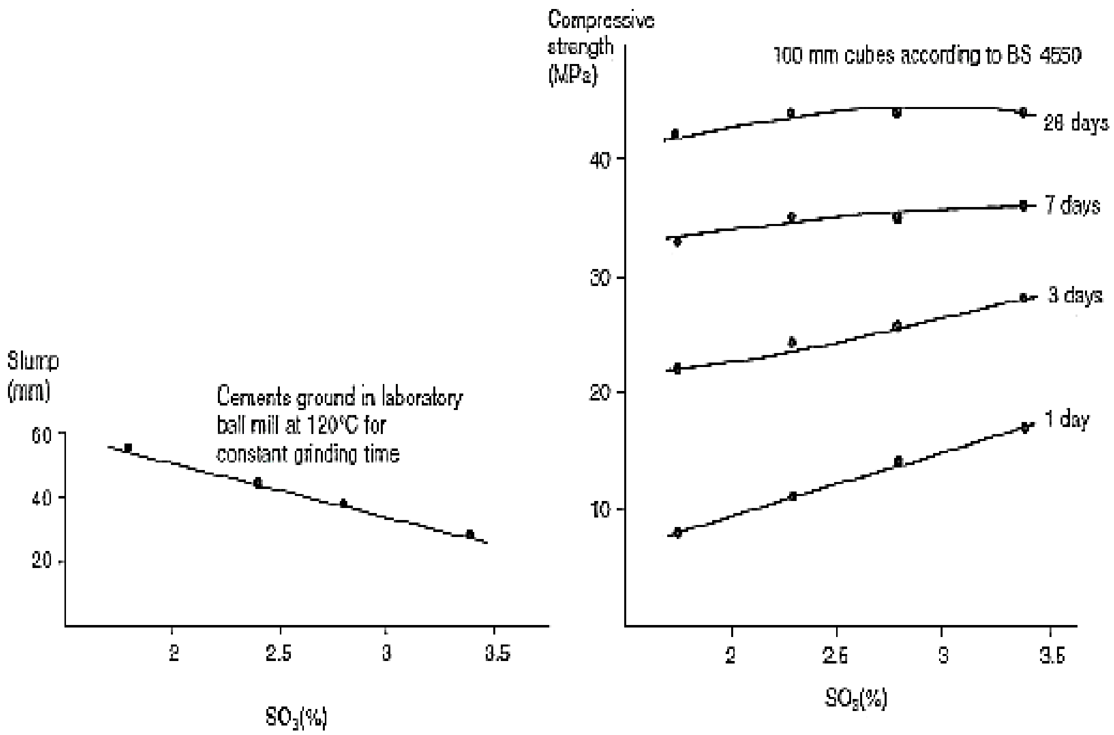


Figure 2.10: *Influence of cement SO_3 content on slump and compressive strength (Newman & Choo, 2003)*

2.4.4 Pozzolana & SCMS

Pozzolana are amorphous siliceous or siliceous and aluminous materials, of natural or artificial origin, that have no cementitious value but contain reactive silica and/or alumina (Mehta & Monteiro, 2014). These materials can form cementing compounds only when in the presence of moisture and whilst being in a finely-divided form. For this reason, pozzolanic materials are largely incorporated as SCMs.

Natural pozzolana consist of substances such as volcanic ash. Artificial pozzolana mainly consists of industrial by-products such as fly ash, silica fume, and GGBS. The artificial variants are widely used as cement extenders. Owing to its fly ash base, PMBA may have great potential to be a partial cement replacement. It is then crucial that pozzolana, especially fly ash, are reviewed because PMBA displays pozzolanic properties and its behaviour in concrete may depend on the influence from its fly ash nature (Bird & Talbert, 2008; Byiringiro, 2014; Cherian & Siddiqua, 2019). This is required to understand the potential effects of this waste material as a partial cement replacement. The advantages of pozzolana on concrete properties are discussed below. It should be noted that the use of pozzolana in blended cements surpasses the point of improved concrete properties. For example, Figure 2.11 demonstrates how blended cements reduce GHG emissions through reduced cement production and utilisation in India.

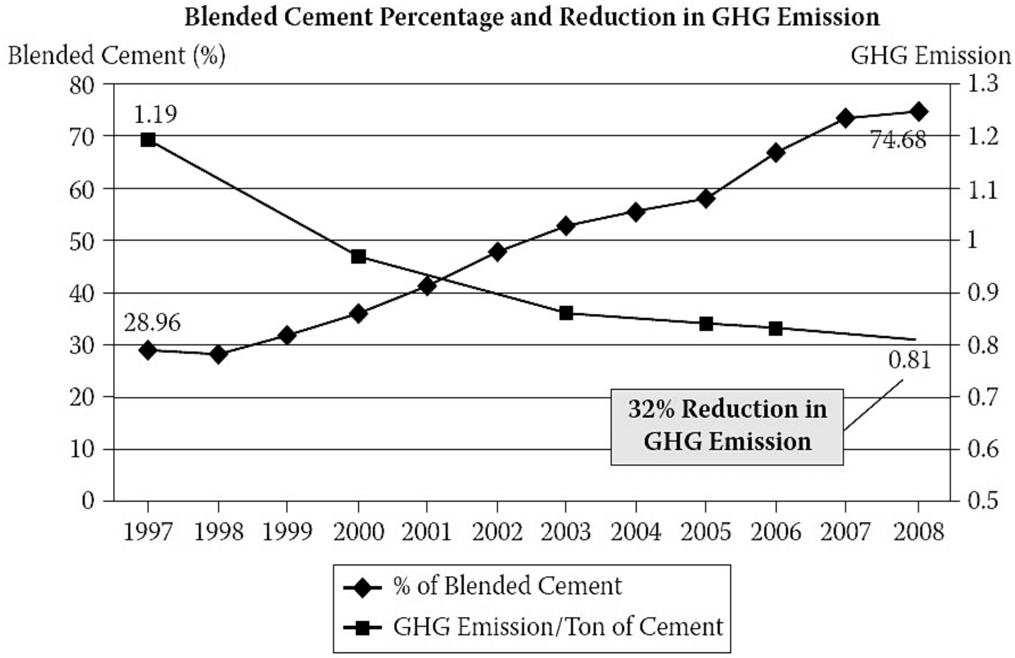


Figure 2.11: *Reduction in GHG emissions using blended cements (Sabnis, 2012)*

In terms of engineering properties, in addition to reducing the amount of cement required to obtain a particular strength, various authors, such as Alp et al. (2009), note that using pozzolanic materials lead to an enhancement of the major concrete properties, namely workability, strength and durability. Pozzolanic materials may be classified by the criteria provided in Table 2.7 below.

Table 2.7: *Classification of artificial pozzolana (Poernomo, 2011)*

Description	Unit	Artificial pozzolan class	
		F	C
SiO_2	Min (%)	54.90	39.90
$SiO_2 + Al_2O_3 + Fe_2O_3$	Min (%)	70	50
SO_3	Max (%)	5.0	5.0
Water content	Max (%)	3.0	3.0

Incandescent lost	Max (%)	12.0	6.0
Alkali as eqNa_2O	Max (%)	1.5	-

(A). Composition:

Table 2.8 below presents the chemical compositions of the main pozzolana used in SA. Various pozzolanic materials tend to share similar trends in chemical oxides. This similarity suggests that SiO_2 and Al_2O_3 dominate pozzolanic compositions. It is widely understood that amorphous SiO_2 improves reactivity which leads to greater concrete strength.

After investigating concrete arising from fly ash, GGBS and silica fume, Khalid et al. (2019) observed that both the highest workability and 28-day compressive strength was displayed in the silica fume-concrete sample (which had the highest content of SiO_2), followed by the fly ash-concrete sample (which had the second-highest content of SiO_2). This observation reinforces the understanding that SiO_2 is critical for strength development.

Table 2.8: *Typical chemical compositions of pozzolana (Walker & Pavia, 2010)*

Pozzolan	**Oxide content (%)**									
	SiO_2	**Al_2O_3**	**CaO**	**Fe_2O_3**	**SO_3**	**TiO_2**	**MnO**	**K_2O**	**MgO**	**P_2O_5**
FA	65.32	24.72	0.94	4.84	0.37	0.91	-	1.37	0.68	0.37
GGBS	34.14	13.85	39.27	0.41	2.43	0.54	0.25	0.26	8.63	-
SF	92.10	2.13	1.10	1.62	0.28	-	-	1.32	1.05	0.23
CC	51.37	45.26	-	0.52	-	-	-	2.13	0.55	-

FA – Fly ash; GGBS – Ground granulated blastfurnace slag; SF – Silica fume; CC – Calcined clay

(B). Pozzolanic reactions:

It was shown in Table 2.5 that hydration reactions produce CH. In the presence of moisture, pozzolanic materials then undergo a reaction with CH to form cementitious compounds, particularly C-S-H (Dunstan, 2011). This reaction is known as a pozzolanic reaction and is dependent on the contents of amorphous SiO_2 and Al_2O_3 and the specific surface of the pozzolanic particles. Table 2.9 below describes the pozzolanic reactions for siliceous and aluminous pozzolans. In comparison to hydration reactions, pozzolanic reactions are slow. This is because the latter may only occur once hydration produces quantities of CH (Motau, 2016). This may lead to a delayed strength development at earlier concrete ages.

Table 2.9: *Pozzolanic reactions (Dunstan, 2011)*

Pozzolan type	Pozzolanic reaction
Siliceous	$3CH + 2S \rightarrow C_3S_2H_3$
Aluminous	$3CH + A + 3H \rightarrow C_3AH_6$

$S = SiO_2$; $A = Al_2O_3$

(C). Influence on workability:

It is well-documented that most pozzolana improve workability. In the case of fly ash, workability is improved due to its glassy texture and spherical particle shape which reduces the water required to obtain a required consistency (Popovics, 1992). This is discussed in greater detail in Section 2.9.1 (C). Figure 2.12 below shows a comparison between the particles of cement and fly ash. One of the most important properties of pozzolana, particularly fly ash, is the 'fine-filler effect'. This property enables finer pozzolanic particles to occupy voids that occur between larger particles, thereby improving the packing density (Figure 2.13). Consequently, less water is required to fill voids, leading to a reduced water requirement (Fennis et al., 2009). This typically results in an increase in workability.

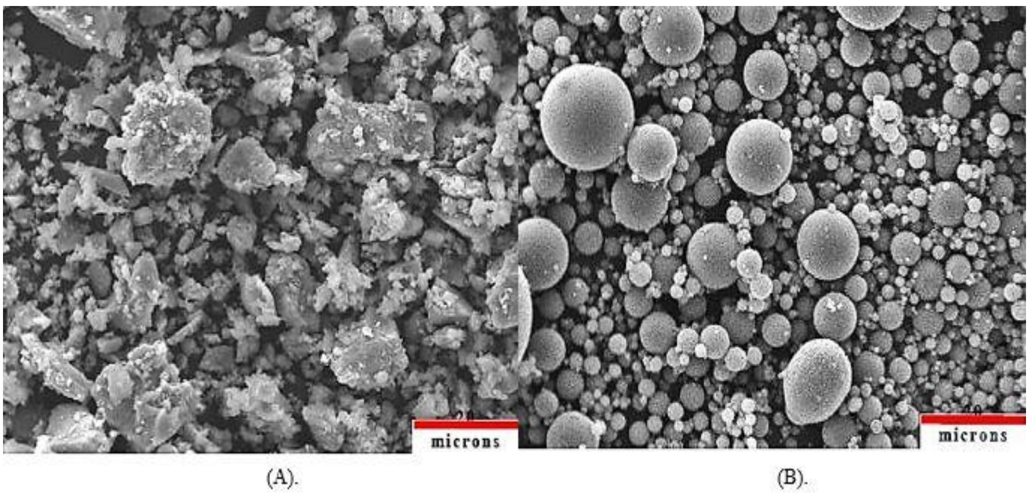


Figure 2.12: *Particle shapes of (A). cement & (B). fly ash (National Concrete Pavement Technology Center)*

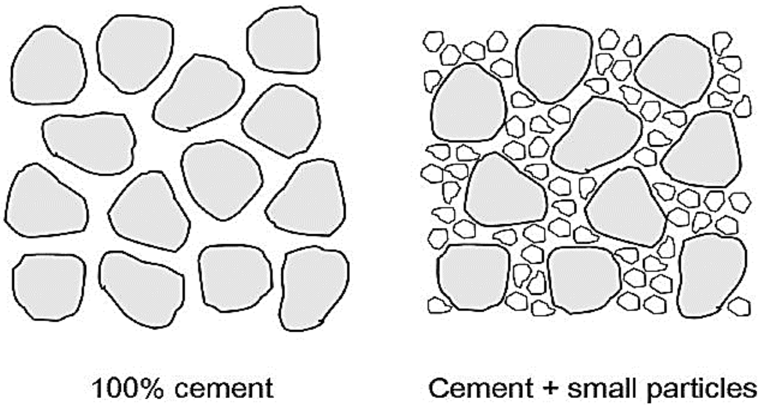


Figure 2.13: *Representation of the fine-filler effect (Fennis et al., 2009)*

(D). Influence on strength development:

The time difference between hydration and pozzolanic reactions causes an early delay in the strength development of concrete containing pozzolana. However, according to the studies of Dembovska et al. (2017), pozzolana impart superior strength with time. This characteristic is exhibited in Figure 2.14 below, which indicates that the strength of Portland cement concrete is higher at early ages whilst the strength of concrete arising from the additions of pozzolana are higher at later ages. Figure 2.15 shows that this trend occurs in fly ash concrete.

Strength enhancing properties of pozzolana include the amorphousness and its reactive SiO_2 content, specific surface and the fine-filler effect. This is discussed in greater detail in Section 2.11.3 (C).

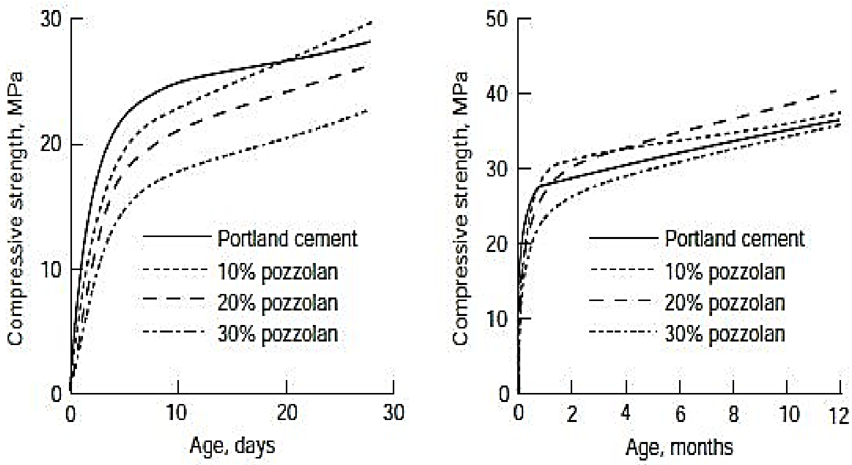


Figure 2.14: *Strength comparison between Portland cement and contents of pozzolana at different concrete ages (Mehta & Monteiro, 2006)*

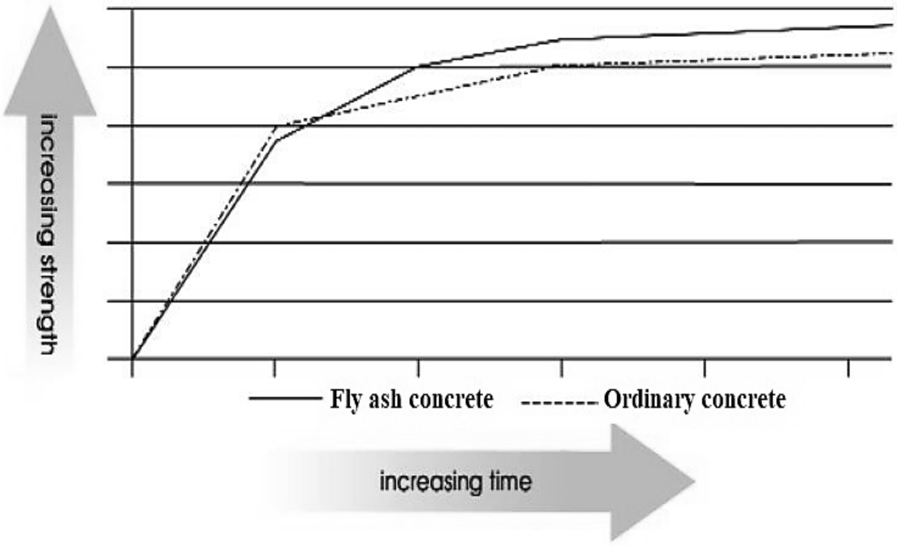


__Figure 2.15:__ Increase in strength due to fly ash (ACAA, 2003)

(E). Influence on durability:

Greater contents of pozzolana have shown to result in reductions in concrete expansion arising from ASR (Figure 2.16). Thus, promoting crack-reduction and durability.

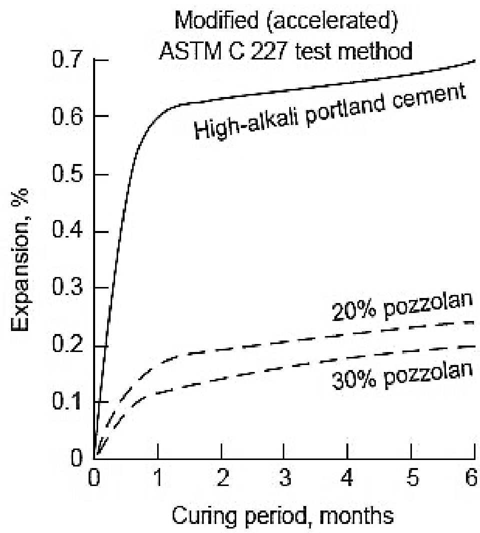


__Figure 2.16:__ Reducing expansion by pozzolana (Mehta & Monteiro, 2006)

As discussed in Section 2.4.3 (E), although CH maintains the pH of concrete for steel protection, it leads to a host of durability concerns and must be kept to a minimum. Due to the pozzolanic reactions consuming quantities of CH, its overall content is reduced. It is worth noting that pozzolana exhibits a property whereby its reactions may consume CH, however there is an adequate amount remaining to maintain concrete pH (Mehta & Monteiro, 2006).

Durability is further improved due to the fine-filler effect. This property improves packing density via the packing of voids, thereby refining the concrete structure and leading to improved resistance to mechanisms of concrete penetration, such as permeation. Figure 2.17 below shows a comparison between the permeability of fly ash concrete and that of conventional concrete. Evidently, concrete permeability is reduced via the integration of pozzolana such as fly ash.

As briefly discussed, fly ash provides a variety of benefits to concrete. Table 2.10 below summarises the effects of fly ash on the three major concrete properties – workability, strength and durability.

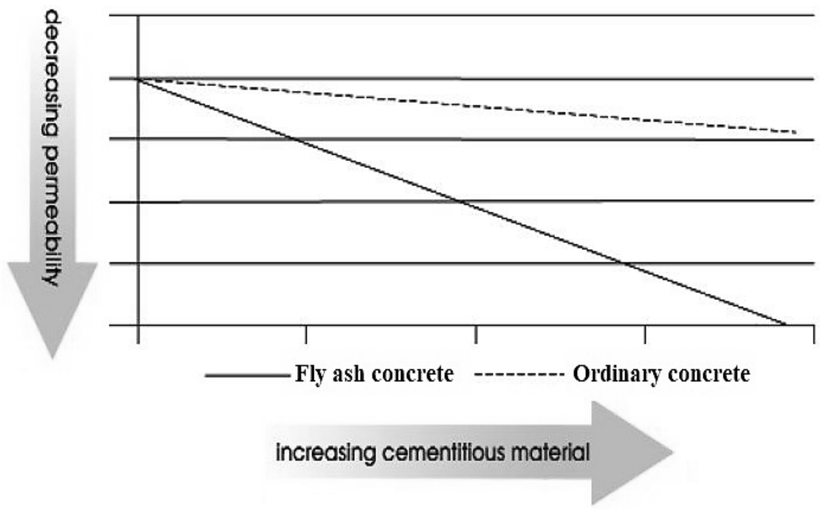


Figure 2.17: *Decrease in permeability due to fly ash (ACAA, 2003)*

__Table 2.10:__ Summary of the effects of fly ash on concrete properties (Owens, 2013)

Property	Effect
Workability	• Improves workability and reduces water requirement. • Slightly retards setting. • Improves adhesion in shotcrete.
Strength	• Slightly reduces rate of strength development. • Increases later-age strengths. • Reduces rate of heat generation caused by hydration.
Durability	• Reduces rate of chloride diffusion. • Reduces permeability by refining pore structure. • Prevents alkali-silica reaction. • Improves sulphate resistance. • Reduces thermal cracking.

2.5 PAPER MILL BOILER ASH (PMBA)

2.5.1 Background

PMS is the solid residual produced by wastewater treatment plants at pulp and paper mills (Lekha et al., 2017). This residual occurs as one of the major waste products to emanate from this industry. In order to produce electricity and steam and to manage the large volumes of this organic material, it undergoes combustion with bituminous coal, coal ash, bark, sawdust and other waste variants (Byiringiro, 2014). This combustion process occurs at 900° C in a multi-fuel boiler which uses fluidised bed combustion (FBC) technology. The resulting ash then occurs in a fine ash and a coarser variant (bottom ash). PMBA is the resulting fine ash.

Johakimu et al. (2016) explains that PMBA is dissimilar from ordinary, coal-based fly ash in that its quantity and its properties are primarily dependent on factors that are directly influenced by the pulp and paper mill, namely combustion conditions such as the presence of PMS quantities. Moreover, fly ash is commonly formed through pulverised coal combustion whilst PMBA forms from FBC (Miller, 2010). As such, traditional fly ash generated in coal-fired operations, such as in electricity generation, may significantly differ from PMBA. For this reason, research is required to assess meaningful management options, namely the applicability of this waste ash as an SCM. Currently, there are minor methods of reuse, however there exists no foremost sustainable solution, thus PMBA is still a major source of landfilled waste, an environmental hazard and a financial burden to the pulp and paper industry (Lekha et al., 2017; Donkor, 2019).

2.5.2 Classification in Accordance with National Waste Regulations

PMBA, as being categorised as ash from combustion, has been considered as hazardous waste. However, due its usefulness, on 02 June 2017, GN R 528 was published to exclude said ash from the definition of waste (DEA, 2018). In the Government Gazette No. 42990, published on 03 February 2020, Minister of Environment, Forestry and Fisheries of SA, Ms. B. Creecy, acknowledged this exclusion. Organisations that have applied for such an exclusion are Mondi, Sappi, Mpact and Kimberly-Clark.

2.5.3 Overview of the South African Pulp & Paper Industry

Since 1970, the growth rate experienced by the South African pulp and paper industry has surpassed the international average, consequently making SA the world's fifteenth largest producer of pulp and twenty-fourth largest producer of paper (FP&M SETA, 2014).

In terms of raw materials, the industry uses softwood (commonly pine) to produce bulk-required items like newsprint, magazines, and packaging whilst hardwood fibres (commonly eucalyptus) are used for high strength board and corrugated paper (Donkor, 2019). Table 2.11 below, presents the major producers in SA, along with their respective production capacities.

Table 2.11: *Five major producers in the South African pulp & paper industry (Donkor, 2019)*

Producer	Mondi SA	Sappi	Mpact	Nampak	Kimberly-Clark
Production Capacity (tonnes/year)	Pulp: 932 000 Paper: 1 233 000	Pulp: 1 510 000 Paper: 1 170 000	420 000	108 000	52 000

The industry comprises of various dedicated manufacturing mills that are predominantly situated in KZN and Gauteng (Figure 2.18). Figure 2.19 below shows the annual statistics of the production, imports, exports, and consumption of paper in SA. It is noted that consumption has often exceeded production.

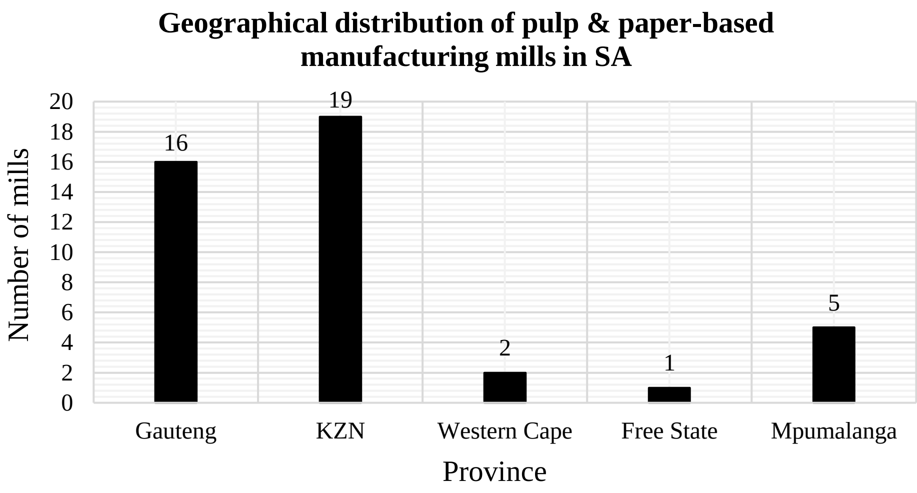


Figure 2.18: *Geographical distribution of pulp and paper-based manufacturing mills in SA (FP&M SETA, 2014)*

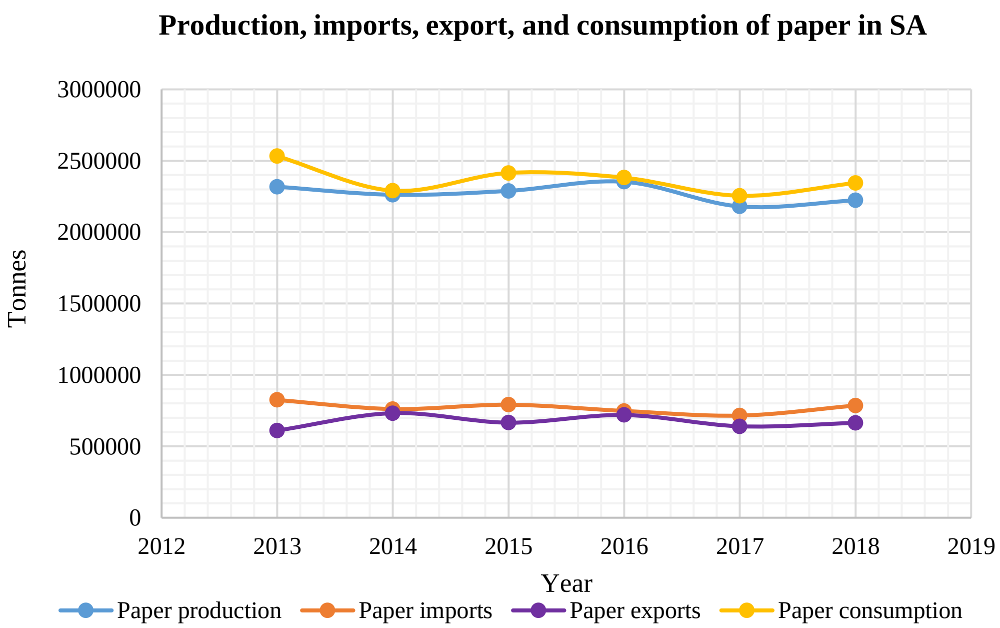


Figure 2.19: *Annual statistics on production, imports, exports and consumption of paper (Compiled from annual PAMSA reports)*

2.5.4 Characteristics of Production

(A). Production process:

The basic production process (Figure 2.20) begins with the processing of wood material into chips, which are then processed into pulp. The pulp is then refined to produce paper. This process results in the formation of the effluent stream, which comprises of waste streams from various operations, such as de-inking, washing, bleaching and papermaking. This effluent stream is then physiochemically-treated via filtration clarifiers and sedimentation, so as to separate the liquid and solid streams (Donkor, 2019). The suspended solids that are present in the effluent stream are then removed from primary clarifiers and are thickened and dewatered to form PMS. This material then undergoes combustion at 900° C with bituminous coal, coal ash, bark and other waste variants that arise in the pulp and paper industry. The fine ash that results from this combustion process is referred to as PMBA.

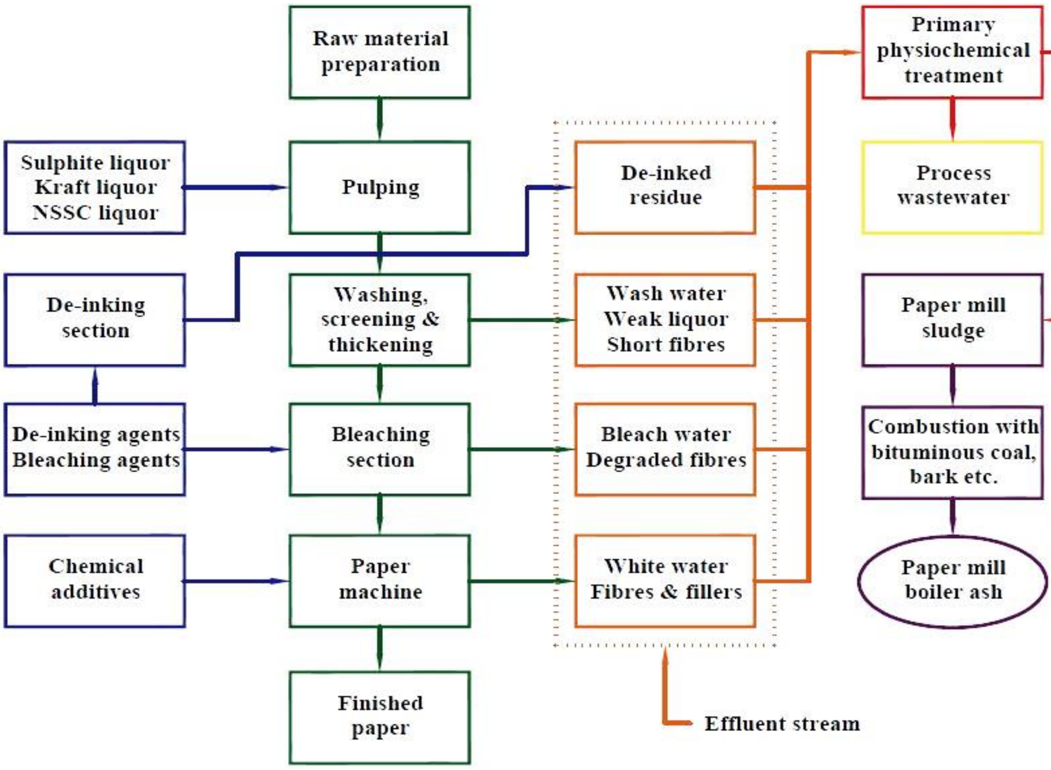


Figure 2.20: *Production process of PMBA (Modified after Donkor, 2019)*

(B). Production quantities:

In terms of PMS, various authors such as Donkor (2019) and Bajpai (2015) state that on average, approximately 50 kg (dry mass) is generated for every tonne of paper produced. Donkor (2019) has shown that annually, eleven South African pulp and paper mills generate nearly 70 000 dry tonnes of PMS (Table 2.12). According to statistics provided by FP&M SETA (2014), eleven mills merely constitute 26 percent of all pulp and paper manufacturing mills in the country. The production statistics for the total PMBA in the country are not readily available. However, Miller (2010) suggests that for PMBA produced at Mondi alone, the mass flow is 64 tonnes per day whilst PMS exhibits a mass flow of 231 tonnes per day.

Table 2.12: *PMS production based on eleven pulp and paper mills in SA (Boshoff et al., 2016; cited by Donkor, 2019)*

Company	Mill	PMS production (dry tonne/year)
Mondi	Richards bay	12 500
	Tugela	7000
Sappi	Ngodwana	15 000
	Enstra	7500
	Verulam	1500
Nampak	Kliprivier	1500
	Belville	1800
Kimberly-Clark	Enstra	6000
	Felixton	4000
Mpact	Springs	11 000
	Piet Retief	500
Total (dry tonne/year)		**68 300**

2.5.5 Properties of PMBA

Diverse manufacturing processes and wastewater treatment technologies in production mills lead to a variation in the properties of PMBA. Due to the lack of research pertaining to locally-available PMBA, its toxicity and physical, chemical, morphological and mineralogical properties have not been well-documented in SA. Internationally, a handful of researchers, specifically Naik

& Kraus (2003) and Cherian & Siddiqua (2019), have launched investigations into determining these properties.

Figure 2.21: *A typical sample of PMBA (m.indiamart.com)*

2.5.5.1 Physical properties

As shown in Figure 2.21 above, PMBA is a grey fine ash and the lightest component to arise from the pulp and paper mill combustion process. Table 2.13 below presents a summary of the physical properties of cement.

Table 2.13: *Summary of physical properties of PMBA*

Property	Value	Average	Reference
Relative density	2.32 – 2.76	2.45	Naik & Kraus (2003)
Autoclave expansion (%)	0.01 – 0.63	0.10	
Bulk density (kg/m^3)	150 – 1300	500	Cherian & Siddiqua (2019)
Particle size (μm)	150 – 250	-	
Specific surface area (m^2/kg)	4200 – 100 600	-	

(A). RD:

Relative density (RD) may be defined as the density of a substance, relative to the density of water. PMBA exhibits a lower RD (2.45) as compared to Portland cement, which is approximately 3.14. Naik & Kraus (2003) report that the RD of PMBA is similar to that of traditional fly ash, which Newman & Choo (2003) report as 2.30.

(B). Soundness:

Matalkah & Soroushian (2017) show that the autoclave expansion of Portland cement is 0.41 percent whilst the maximum value is taken as 0.8 percent. The average autoclave expansion of PMBA (0.10 percent) is lower than both Portland cement and the maximum limit. This suggests that HCP infused with PMBA may exhibit lower expansive tendencies than its conventional counterpart, thus reducing concrete cracking and improving durability. In addition, in reference to Figure 2.16 in Section 2.4.4 (E), ASR-induced expansions will likely decrease due to the reduced cement content as a result of integrating PMBA.

(C). Bulk density:

Bulk density is taken as the mass of a substance, per unit volume. It was found that for PMBA, increases in carbon content results in an increase in its bulk density (Cherian & Siddiqua, 2019). The general bulk density of Portland cement (1300 – 1400 kg/m^3) appears to be higher than the bulk density exhibited by PMBA, which ranges from 150 – 1300 kg/m^3 and averages 500 kg/m^3.

(D). Specific surface:

Various researchers have assessed the specific surface of cement, with Neville & Brooks (2010) reporting results ranging from 180 to 1000 m^2/kg, Ferraris & Garboczi (2012) reporting results that range from 349 to 2000 m^2/kg and Spenner Zement (2012) reporting a value of 370 m^2/kg for CEM II/B-S 42.5 N plus. As such, PMBA displays a significantly higher specific surface value than cement, with potential implications in pozzolanic reactivity and the fine-filler effect.

Table 2.14 below summarises the properties of PMBA and cement as discussed above.

Table 2.14: *Comparison of physical properties between PMBA and cement*

Property	PMBA	Cement
RD	2.45	3.14
Autoclave expansion (%)	0.10	0.41
Bulk density (kg/m^3)	500	1300 – 1400
Specific surface (m^2/kg)	4200 – 100 600	370[1]

[1] For CEM II/B-S 42.5 N

2.5.5.2 Chemical properties

Table 2.15 below presents a summary of the chemical properties of PMBA. Cherian & Siddiqua (2019) advise that the chemical properties of PMBA, its heavy metals content and the quantity of organic matter are largely due to the species of wood used in combustion and combustion conditions such as temperature. Mondi employs temperatures of approximately 800 to 900 ° C.

Table 2.15: *Summary of the chemical properties of PMBA*

Reference	Oxide content (%)									
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	TiO_2	MnO
Byiringiro (2014)	**32.58**	**35.83**	**22.41**	**1.11**	**1.55**	**-**	**0.43**	**4.93**	**1.16**	**-**
Vassilev et al. (2013)	28.90	31.60	13.20	5.12	5.4	1.42	13.20	2.67	-	2.77
Chowdhury et al. (2015)	19.60	50.70	8.20	2.10	6.50	2.10	2.80	-	-	-
Naik & Kraus (2003)	16.00	26.50	9.00	5.40	3.00	1.70	5.00	4.80	0.51	-
Abdullahi (2006)	10.53	31.80	28.00	2.34	9.32	6.50	10.35	-	-	-
Average	21.52	35.29	16.16	3.21	5.15	2.93	6.36	4.13	0.84	2.77

Reference	LOI (%)
Ahmed et al. (2001)	4 – 4.5
Khalid et al. (2012)	4.5
Cherian & Siddiqua (2019)	5
Johakimu et al. (2016)	4.2 – 6.7
Average	4.8

Reference	pH
Cherian & Siddiqua (2019)	11
Pöykiö et al. (2004)	12.6
Average	11.8

(A). Oxide contents

All values provided by Byiringiro (2014) are for PMBA sourced from Mondi Merebank. It is evident that Mondi's PMBA is rich in the desired major oxides, namely SiO_2 (36%), CaO (33%), and Al_2O_3 (22%). In comparison to the average major oxide contents in cement, PMBA exhibits a greater SiO_2 content, a lower CaO content and a greater Al_2O_3 content. The greater SiO_2 content may indicate more reactivity, leading to superior strength development.

Due to PMBA arising from the combustion of PMS with bituminous coal, a comparison may be drawn amongst the properties of PMBA, PMS ash, and traditional fly ash. Traditional fly occurs in two variants, class F and class C. Class F fly ash arises from the incineration of anthracite (high-grade coal) or bituminous coal (medium-grade coal), whilst the class C counterpart employs sub-bituminous coal (low-grade coal) or lignite (lowest-grade coal). Table 2.16 below presents a comparison of the major oxides present in these inter-related materials.

Table 2.16: *Comparison of major oxides in PMBA, class C fly ash, class F fly ash, Portland cement and PMS ash*

Material	Chemical constituent (%)						Reference
	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	LOI	
Mondi PMBA	32.58	35.83	22.41	1.11	4.93	4.80	Table 2.15
Class C fly ash	25.20	36.90	17.60	6.20	2.90	0.33	Scheetz & Earle (1998)
Class F fly ash	4.90	52.50	22.80	7.50	0.60	2.60	
Cement	64.18	21.02	5.04	2.85	2.58	2.00	Table 2.3
PMS ash	40.21	22.32	14.55	0.56	0.32	18.52	Amit & Islam (2016)

Certain pieces of literature refer to PMBA as pulp and paper fly ash. Analysis of Table 2.16 above showed the close relation between the major oxides of PMBA and class C fly ash. This is interesting as SA only produces class F fly ash (Heyns, 2016). It is possible that the difference may be attributed to the influence of PMS in the combustion process. Table 2.17 below provides the chemical criteria for fly ash classification and the performance of PMBA against said criteria. It is seen that due to the higher eqNa_2O content, PMBA may not be classified as fly ash. Moreover, the eqNa_2O content of cement is limited to 0.6 percent to prevent expansion due to alkali-aggregate reactions, thus it is noteworthy that PMBA exhibits an approximate value of 3.2 percent. However, fly ash generally tends to reduce this expansion (Popovics, 1992).

Table 2.17: *Chemical criteria for fly ash classification and the performance of PMBA against the criteria*

Requirement[1]	**Class F**[1]	**Class C**[1]	**PMBA**[2]
$SiO_2 + Al_2O_3 + Fe_2O_3$ (min %)	70.0	50.0	54.7
eqNa_2O (max %)	1.5	1.5	3.2
SO_3 (max %)	5.0	5.0	4.9
LOI (max %)	6.0	6.0	4.8
[1]ASTM C618 (2003a); cited by Xie (2009)		[2]Table 2.15	

(B). LOI:

Loss on ignition (LOI) serves to indicate the amount of carbon present in PMBA. According to literature, PMBA displays an average LOI of 4.8 percent. Table 2.3 informed that cement shows an LOI of 2 percent. The difference in LOI between PMBA and fly ash is attributed to the organic nature of PMS. In terms of aesthetics, a higher carbon content of PMBA leads to darker concrete (Xie, 2009).

(C). pH value:

PMBA is highly alkaline due to the addition of CaO during the pulping process. Byiringiro (2014) found that PMBA from Mondi has a CaO content of approximately 33 percent. The average pH value, based on values in literature, was found to be 11.80.

(D. Hydrophilic nature:

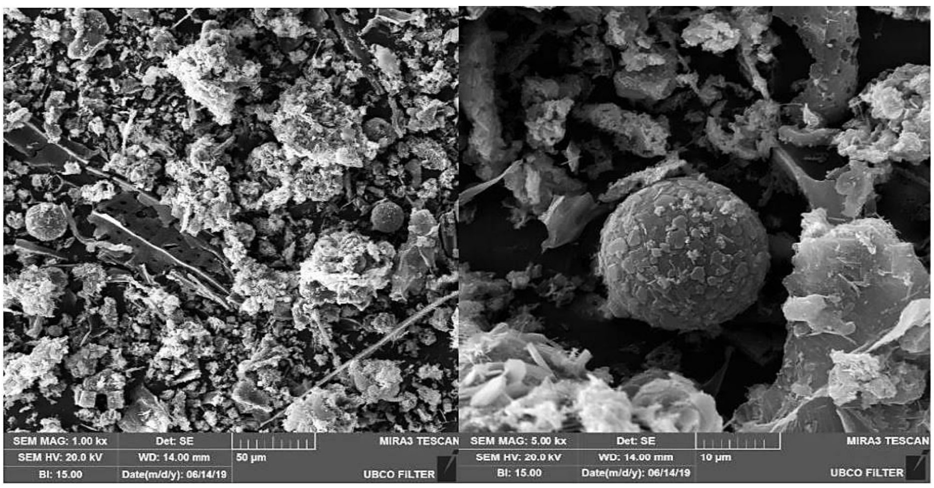
PMBA is hydrophilic in nature (Cherian & Siddiqua, 2019). Moreover, cement is also hydrophilic, thus the integration of PMBA may see the formation of a hydrophilic-hydrophilic relationship, which may improve the bonding of cement and PMBA.

2.5.5.3 Morphological & mineralogical properties

The particle characteristics of both cement and pozzolana hold a great influence over concrete properties, similarly PMBA-concrete may be largely influenced by the particles of PMBA.

Cherian & Siddiqua (2019) conducted analysis using a scanning electron microscope (SEM) and observed that PMBA consists of a mix of particles that are angular and spherical in shape, which is taken as the cause of its high specific surface. Figure 2.22 (B) below shows a spherical particle.

Naik & Kraus (2003) performed mineral analysis for PMBA using X-ray diffraction (XRD). The results indicate that PMBA is a glassy material largely consisting of amorphous SiO_2, Al_2O_3 and Fe_2O_3. There also exist crystalline phases such as quartz (SiO_2), Portlandite (CH), CaO, C_3S and C_3A. Cherian & Siddiqua (2019) explain that the aforementioned amorphous constituents, coupled with these crystalline components, allow PMBA to possess major cementitious properties. Xie (2009) suggests that this dual amorphous-crystalline nature is due to rapid cooling of burned coal.



(A) (B)

Figure 2.22: *(A). PMBA particles at 50 μm and (B). Spherical PMBA particle at 10 μm (Cherian & Siddiqua, 2019)*

2.5.5.4 Toxicity

The toxicity will be reviewed in terms of the contents of heavy metals and more importantly, the mobility of such metals with the corresponding risk of leaching.

In accordance with Pöykiö et al. (2005), the following metals must be given priority due to their risk to the environment: cadmium (Cd), copper (Cu), lead (Pb), chromium (Cr), zinc (Zn), nickel (Ni), cobalt (Co), arsenic (As), vanadium (V), and barium (Ba). In the past, the trace metal contents of PMBA (and wood ash at large) have been investigated for soil application. Various authors recognize the presence of trace metals in these materials; however, the concentrations of such metals vary. Table 2.18 below presents a summary of the findings of three such authors, accompanied by a comparison between the concentrations of trace metals with total concentration threshold (TCT) limits. It is evident that that barium, lead, copper and zinc are above TCT0 levels.

Table 2.18: *Trace metals content of PMBA compared with TCT limits*

Metal	Trace metal content (mg/kg)					
	Muse & Mitchell (1995)	**Pöykiö et al (2016)**	**Serafimova et al. (2011)**	**TCT0**	**TCT1**	**TCT2**
Molybdenum, Mo	15	3.8	-	40	1000	4000
Cadmium, Cd	< 2	2.9	1.11	7.5	260	1040
Barium, Ba	588	745	-	62.5	6250	25 000
Lead, Pb	72	28.7	99.7	20	1900	7600
Vanadium, V	-	92.7	-	150	2680	10 720
Chromium, Cr	75	66.9	23	46 000	800 000	-
Cobalt, Co	14	6.6	-	50	5000	20 000
Nickel, Ni	16	32.4	16.1	91	10 600	42 400
Copper, Cu	67	-	-	16	19 500	78 000
Zinc, Zn	183	295.3	133	240	160 000	640 000
Arsenic, As	-	13	11.3	5.8	500	2000

In terms of leaching and environmental protection, it is not the concentration of trace metals that are imperative, but the ease at which these metals can be mobilized (Cherian & Siddiqua, 2019). Pöykiö et al. (2005) investigated the mobility of trace metals in PMBA by determining their mobility factors. Their findings are presented in Table 2.19 below. Higher mobility factors indicate that potentially toxic metals are more mobile in the environment, thereby increasing the risk of leaching and contaminating soil and water resources.

It is noteworthy that the concentration of Cd is lower when compared to other trace metals in PMBA, however due to its high mobility, it is acknowledged as one of the most potentially toxic metals in the material (Cherian & Siddiqua, 2019). Highly mobile trace metals may become problematic when PMBA is landfilled as they may be transported into receiving media (Pöykiö et al., 2005). Fortunately, Cherian & Siddiqua (2019) point out that these metals are not easily leachable as they are held in the amorphous aluminosilicate matrix. Moreover, the high alkaline nature of PMBA tends to assist in retaining metals.

Table 2.19: *The measure of mobility of potentially toxic metals in PMBA (Pöykiö et al., 2005)*

Metal	Mobility factor (%)	Environmental risk
Cadmium, Cd	65	↑
Copper, Cu	20	
Zinc, Zn	17	
Nickel, Ni	12	
Lead, Pb	11	
Chromium, Cr	5	

2.5.6 Complications Associated with PMBA

In the 2018 risk assessment conducted on PMBA produced at the Mondi Merebank mill, environmental manager, Mr. R. Gafoor, suggests that this ash is a potential risk to soil, surface water, groundwater and air. Alternate uses of PMBA, such as land application and landfill capping, are questionable due to its high mineral content, the risk of soil contamination, economic reasons, the large and frequent quantities generated, the risk to health, crops, livestock, and the pollution of both terrestrial and aquatic environments (Likon & Trebše, 2012; Singh, 2014; Marsland & Whiteley, 2015). Despite digitization, the generation of this ash is likely to increase as the annual international rate of paper production is predicted to rise to 550 000 000 tonnes by 2050, resulting in an increase in PMS production by 48 to 86 percent (Faubert et al., 2016).

2.6 FINE AGGREGATE

Worldwide, natural silica sand is employed as the most common source of conventional fine aggregate (Newman & Choo, 2003). In the technical sense, according to SANS 1083 (2017), fine aggregate is a material comprising of aggregate particles of which 90 percent of mass must pass through a sieve of square apertures of size 4750 μm and is retained on a sieve of size 75 μm. The South African requirements for fine aggregate material are presented in Appendix B. The various types of fine aggregate depend on the environments from which they arise, may it be fluvial, glacial, coastal etc. The most frequently used natural sands are sourced from fluvial (river-based) environments (Li, 2011). These river sands typically consist of well-sorted, clean and rounded particles. By traditional proportioning practices, coarse aggregate is the most occurring material in typical concrete mixes, followed by fine aggregate.

2.6.1 Composition

Fine aggregate sand predominantly consists of quartz (SiO_2), with this oxide generally occupying more than 90 percent. This is followed by quantities of Al_2O_3. The chemical compositions of various local sands are presented in Table 2.20 below. This investigation employs a river sand.

Table 2.20: *Chemical composition of various local sands (Banganayi et al., 2017)*

Sample	Oxide content (%)									
	SiO_2	Al_2O_3	K_2O	SO_3	TiO_2	Na_2O	MgO	CaO	Cr_2O_3	P_2O_5
A[1]	92.02	4.24	1.63	0.55	0.23	0.16	0.07	0.06	0.05	0.03
B[2]	95.98	2.62	0.40	0.19	0.18	0.14	0.10	0.11	-	0.02
C[3]	96.20	2.09	0.44	0.33	0.06	0.10	0.07	0.24	0.05	0.02

[1]River sand; [2]Coastal sand; [3]Quartzite-blasted sand

2.6.2 Influence of Fine Aggregate Properties on Concrete

(A). Gradation:

The gradation of sand involves the particle size distribution, which has the largest influence on concrete workability, mainly due to its influence on packing density (Li, 2011). Sieve analysis is used to obtain an indication of aggregate grading, which ranges from poorly graded to well/continuous graded (Figure 2.23). For concrete production, well graded fine aggregate is desired. This is because such soils consist of a variety of particle sizes, such that smaller particles fill up voids between larger particles in concrete. This results in a well packed structure, which improves packing density, workability, concrete density, durability, strength and abrasion resistance whilst reducing both bleeding and shrinkage (Johansen & Andersen, 1991; Li, 2011; Owens, 2013). Conversely, poorly graded sands, such as uniformly graded sands, result in voids which reduces the abovementioned properties. Figure 2.23 further shows the difference in void presence in uniformly graded and well graded sands. In addition, well packed structures provide more economical concrete due to the reduced cement utilisation as less cement is required to fill interstices. However, Loseby et al. (2016) suggests that greater packing densities may reduce strength and durability due to overlapping in the interfacial transition zones (ITZ). ITZ is further discussed in Section 2.8.

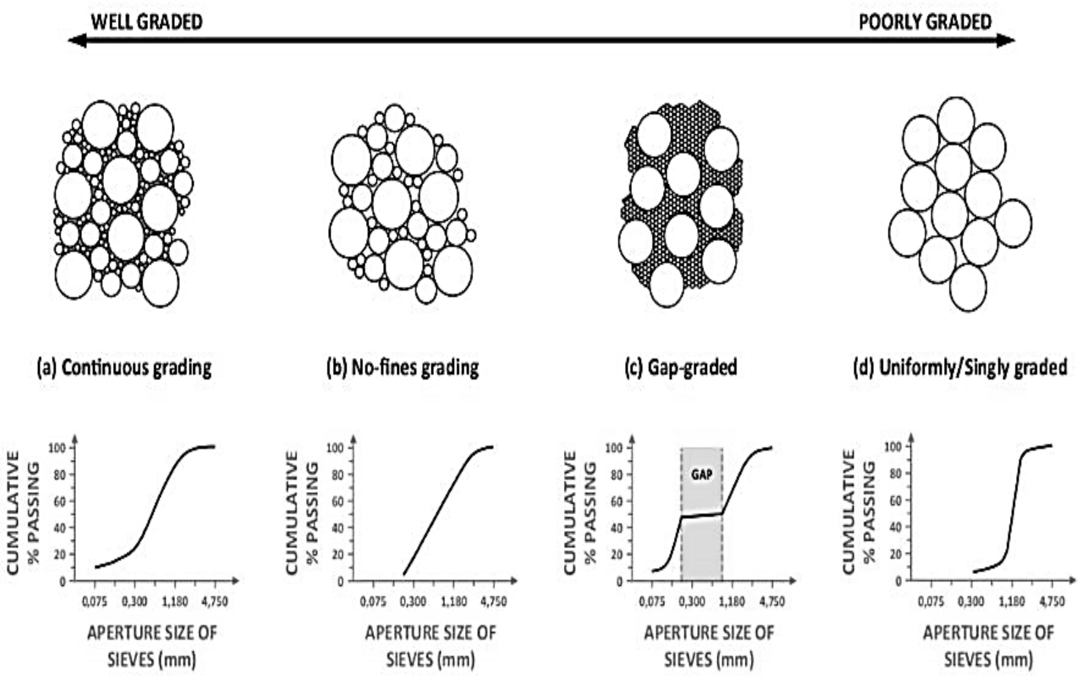


__Figure 2.23:__ Types of soil gradation (Walker, 2013)

In accordance with the Unified Soil Classification System, the coefficient of uniformity (C_u) is a measure of the uniformity of particle sizes whilst the coefficient of gradation (C_c) is used to classify the grading quality of soil. To determine if a soil is well graded, C_u and C_c must first be obtained as follows:

$$C_u = \frac{D60}{D10} \tag{2.1}$$

$$C_c = \frac{D_{30}^2}{D60 \times D10} \tag{2.2}$$

Where D_{60}, D_{30}, and D_{10} are particle diameters corresponding to 60, 30 and 10 percent finer, respectively. A sand sample is classified as well graded if C_u is equal to or greater than six ($C_u \geq 6$) and with C_c ranging from one to three ($1 \leq C_c \leq 3$) (Das & Sobhan, 2014).

The fineness modulus (FM) of an aggregate is determined by sieve analysis and is used to assess overall fineness or coarseness. FM is taken as the summation of the cumulative percentage of soil that is retained on each standard sieve, divided by one hundred. Table 2.21 demonstrates soil classification based on FM. Fine sands display lower FM values whilst coarser sands display higher values. Rangaraju et al. (2013) showed that very fine sands tend to reduce concrete workability by increasing the stiffness and water demand of the mix. On the other hand, very coarse sands produce concrete that exhibit segregation and bleeding. SANS 1083 (2006) requires that FM should range between 1.2 and 3.5. In terms of concrete strength, Walker (2013) suggests that finer sands would prove beneficial. Similar to certain pozzolana, fine aggregate has the ability to exhibit its own filler effect under certain conditions. Jaturapitakkul et al. (2011), replaced cement by 10 to 40 percent with river sand that was ground into three different particle sizes. Their observation indicated that compressive strength increased as the sand fineness increased and concluded that the fine-filler effect was responsible.

Table 2.21: *Fineness classification of fine aggregate (Walker, 2013)*

Very fine	FM < 1.0
Fine	1.0 < FM < 2.3
Medium	2.4 < FM < 2.9
Coarse	2.9 < FM < 3.5
Very coarse	FM > 3.5

Due to the fact that there exists no optimal grading for a particular application of concrete, grading limits have been developed to ensure that the required plastic properties of concrete will be achieved. Table 2.22 provides these limits as in accordance with SANS 1083 and the cement and concrete institute (C & CI).

Walker (2013) explains that outer limits are recommended for all fine aggregates used in concrete, whilst preferred limits are recommended for producing high-quality concrete and for concrete that is: pumped, used in sliding formwork or for high-quality off-shutter finishes required on concrete of 20 to 30 MPa.

Table 2.22: *Grading limits for fine aggregate (Walker, 2013)*

Sieve size (mm)	**SANS 1083 limits**	**SANS 1083 Suggested outer limits**	**SANS 1083 preferred limits**	**C & CI limits**
4.750	90 – 100	85 – 100	90 – 100	90 – 100
2.360	-	60 – 100	75 – 100	75 – 100
1.180	-	40 – 100	60 – 90	60 – 90
0.600	-	30 – 75	40 – 60	40 – 60
0.300	-	15 – 45	20 – 40	20 – 40
0.150	5 – 25	5 – 20	10 – 20	10 – 20
0.075	0 – 5	0 – 12	3 – 6	5 – 10
FM	1.20 – 3.50	1.00 – 3.65	2.00 – 3.00	-

(B). Particle characteristics:

The particle shapes of fine aggregate, as indicated in Figure 2.24, have a larger influence on workability than those of coarse aggregates. The difference in particle shapes imply that different surface areas are exposed to moisture. Accordingly, due to their smaller surface areas, spherical and cubical particles improve workability by reducing the water required to achieve a certain consistency. Since concrete durability is related to lower water content, Quiroga & Fowler (2004) extends the importance of particle shape by stating that since spherical and cubical particles reduce water requirement, the resulting concrete becomes more durable. In terms of strength enhancement, Li (2011) and Walker (2013) explain that spherical, angular and cubical shapes are advantageous.

It is accepted that smooth textures reduce water requirement by providing a smaller surface requiring wetting, thereby improving workability. However, the influence of texture on workability is not as prominent as the influence provided by grading or particle shape. Texture does however play a significant role in strength; whereby rougher textures tend to improve bond strength and increase compressive and flexural strength.

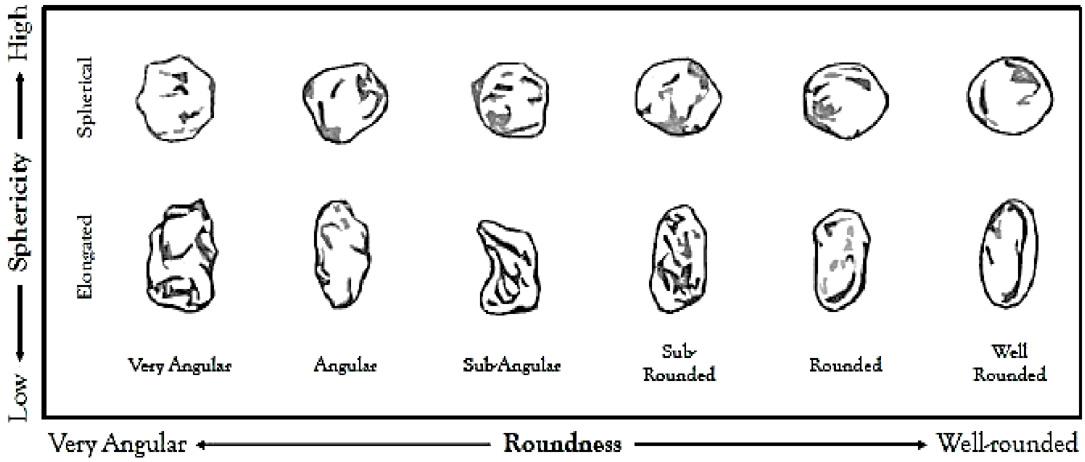


Figure 2.24: *Aggregate particle shape chart (Walker, 2013)*

In addition to particle size and surface texture, the RD of fine aggregate must be considered as it influences the settlement and bleeding mechanism in fresh concrete. Settlement involves the downward movement of denser particles, resulting in the upward displacement of water which escapes concrete as bleed water. Bleed water may reduce the evaporation of water from concrete which prevents plastic shrinkage. However, in reinforced concrete, upward-moving water gets trapped under reinforcement, resulting in voids which become zones of weakness (Owens, 2013). Moreover, where settlement is restrained, such as segments containing reinforcements, cracks tend to occur. Thus, settlement and bleeding are dependent on the RD of cement and aggregate particles as settlement increases with greater particle RD values. The Concrete Institute (2013) informs that conventional aggregates exhibit RD values ranging from 2.6 to 2.95.

(C). Presence of potentially harmful substances:

Particles passing the 75 µm sieve is regarded as fines (i.e., dust content). Moderate amounts of fines prove beneficial by occupying voids and aiding workability. However, excessive amounts of fines tend to reduce workability and strength via the weakening of the cement-aggregate bond (The Concrete Institute, 2013). The presence of clay materials within fine aggregate is a further concern due to its ability to cause swelling or local shrinkage. For natural sands, SANS 1083

(2017) states that the maximum dust content is 5 percent by mass, whilst the maximum clay content is 2 percent by mass.

2.7 WASTE FOUNDRY SAND (WFS)

2.7.1 Background

The foundry industry makes use of sand to create temporary moulds and cores for the casting of metals that are both ferrous (iron and steel) and non-ferrous (aluminium, brass, copper etc.). To be used as a moulding material, foundry sand is first treated with one of two binders, namely bentonite clay or synthetic resin (Iloh et al., 2019). The foundry sand arising from the clay binder is referred to as ‘greensand’ whilst the resin-infused variant is referred to as ‘chemically-bonded sand’ (Mavroulidou & Lawrence, 2018).

The fundamental casting process involves molten metal being poured into these temporary moulds until solidification. Permanent metallic moulds may be used, however SA employs sand moulds for approximately 90 percent of metals casting, largely due to the low-priced foundry sand exhibiting high resistance to heat damage, and its synergic relationship with both natural and synthetic binders (Nyembwe, 2016; Madzivhandila, 2018). Foundry sand is repeatedly used until rendered inapt for further use, thus becoming WFS, which is black in colour due to combustion and mixing with additives.

WFS constitutes up to 90 percent of the total waste emanating from a typical foundry, and with nearly all quantities being landfilled, a serious waste management problem occurs. (Nyembwe, 2016; Iloh et al., 2019). In addition to consuming large volumes of landfill airspace, environmental risks such as leaching are of further concern. The sample of WFS used in this study was obtained from Umgeni Iron & steel (UIS) and is of the chemically-bonded variant, which used furan resin as the primary binder.

2.7.2 Classification in Accordance with National Waste Regulations

Whilst various countries, such the United States, have declassified WFS as hazardous, SA currently maintains the classification (Iloh et al., 2019). However, in the month of July of 2020, the South African Institute of Foundrymen (SAIF) had applied, to the DEA, for the exclusion of WFS as a hazardous material.

2.7.3 Overview of the South African Foundry Industry

South African foundries collectively form one of the greatest industries in the manufacturing sector (Iloh et al., 2019). The foundry industry occupies a pivotal role in society by producing complex metallic elements that cannot be produced by other processes of forming metals (Nyembwe, 2016). This industry serves a variety of industries, namely those involving construction and engineering, the automotive industry, mining, energy, agriculture etc (Figure 2.25). Table 2.23 below, shows that there are 170 foundries in the country, with more than half being ferrous foundries.

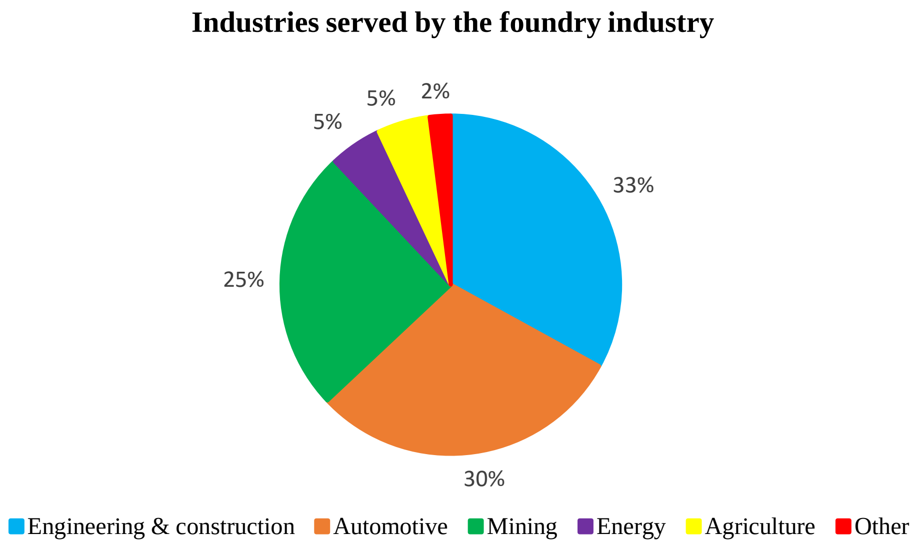


Figure 2.25: *Industries served by the South African foundry industry (Davis, 2015)*

Table 2.23: *Number of foundries by foundry type (Madzivhandila, 2018)*

Foundry type	Number of foundries in 2011	Number of foundries in 2015
Ferrous	74	88
Non-ferrous	70	54
High pressure die-casters	31	23
Investment casting	5	5
Total	**180**	**170**

In eThekwini alone, the number of foundries have increased from eight in 2003 to nineteen in 2013 (Robbins & Velia, 2016). However, the industry has experienced an overall decline in the number of total foundries (Figure 2.26) and production (Table 2.24). Additionally, Figure 2.26 shows that the majority of foundries are largely situated in the three highest economically-active provinces, which being Gauteng, KZN and Western Cape. Madzivhandila (2018) adds that these three provinces exhibit the highest foundry activities.

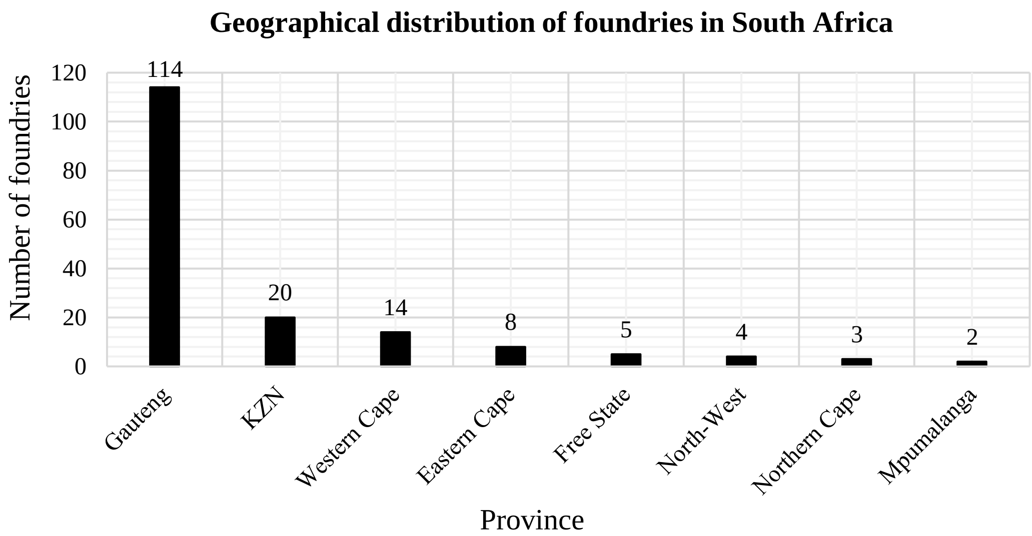


Figure 2.26: *Geographical distribution of foundries in SA (Davis, 2015)*

Table 2.24: *Annual trends in metals production in the foundry industry (Davis, 2015)*

<table>
<tr><th rowspan="2">Metal</th><th colspan="4">Production (tonnes)</th></tr>
<tr><th>2003</th><th>2007</th><th>2012</th><th>2013</th></tr>
<tr><td>Aluminium</td><td>66 000</td><td>77 800</td><td>21 000</td><td>22 000</td></tr>
<tr><td>Brass</td><td>9000</td><td>8200</td><td rowspan="2">14300</td><td rowspan="2">9100</td></tr>
<tr><td>Bronze</td><td>6000</td><td>7600</td></tr>
<tr><td>Zinc</td><td>3000</td><td>4200</td><td>1400</td><td>900</td></tr>
<tr><td>Grey iron</td><td>110 000</td><td>147 000</td><td>161 000</td><td>155 000</td></tr>
<tr><td>Ductile iron</td><td>100 000</td><td>86 000</td><td>59 000</td><td>47 000</td></tr>
<tr><td>White iron</td><td>85 000</td><td>145 600</td><td>54 000</td><td>28 500</td></tr>
<tr><td>Steel</td><td>123 000</td><td>179 100</td><td>118 000</td><td>106 000</td></tr>
<tr><td>Stainless steel</td><td>4000</td><td>4900</td><td>5800</td><td>6500</td></tr>
<tr><td>Total (tonnes)</td><td>506 000</td><td>660 400</td><td>434 500</td><td>375 000</td></tr>
</table>

2.7.4 Characteristics of Production

(A). Production process:

Silica-based sand is primarily used as virgin foundry sand; however, chromite, zircon, and olivine-based sand may be used. This sand is selected by assessing its physiochemical properties via routine testing, such as for permeability, refractory ability etc.

To form a mould for molten metal, a binder material and additives are introduced to virgin sand to improve cohesiveness and sand properties. The resulting sand is known as foundry sand. As mentioned, the two main types of binders are bentonite clay binder and synthetic resin binder, with each binder giving rise to the two types of foundry sand variants. The greensand variant arises from high-quality silica sand, the addition of 4 to 10 percent clay, 2 to 5 percent water, and approximately 2 to 5 percent carbonaceous sea coal additive (Madzivhandila, 2018). These additions provide the necessary bond strength of greensand, which is referred as so because of its moisture content relative to dry sand. Chemically-bonded sand is formed by a synthetic resin binder, such as furan, phenolic ester, and phenolic urethane (Nyembwe, 2016).

Sand moulds and sand cores are formed based on the desired shape of the metal to be produced. All sand cores are formed using chemically-bonded sand and are used to line the interior of sand moulds, to create interior contours of the casting (Nyembwe, 2016). Molten metal is then poured at a controlled rate and once solid, all materials that are not a part of the casting must be removed.

This removal process is referred to as fettling and involves the physical separation of the sand mould from the casting, via shakeout tables, vibratory screens, and tumbling drums (Nyembwe, 2016). Any residual sand is removed, and any surplus metal is trimmed and the casting is cleaned and inspected. The sand that has been removed is then processed and reused to create moulds and cores. This process is repeated until the foundry sand is no longer fit for purpose due to mechanical, thermal, and chemical stresses. Once foundry sand no longer meets the required foundry specifications, it is termed WFS.

The basic production of WFS is illustrated in Figure 2.27 below.

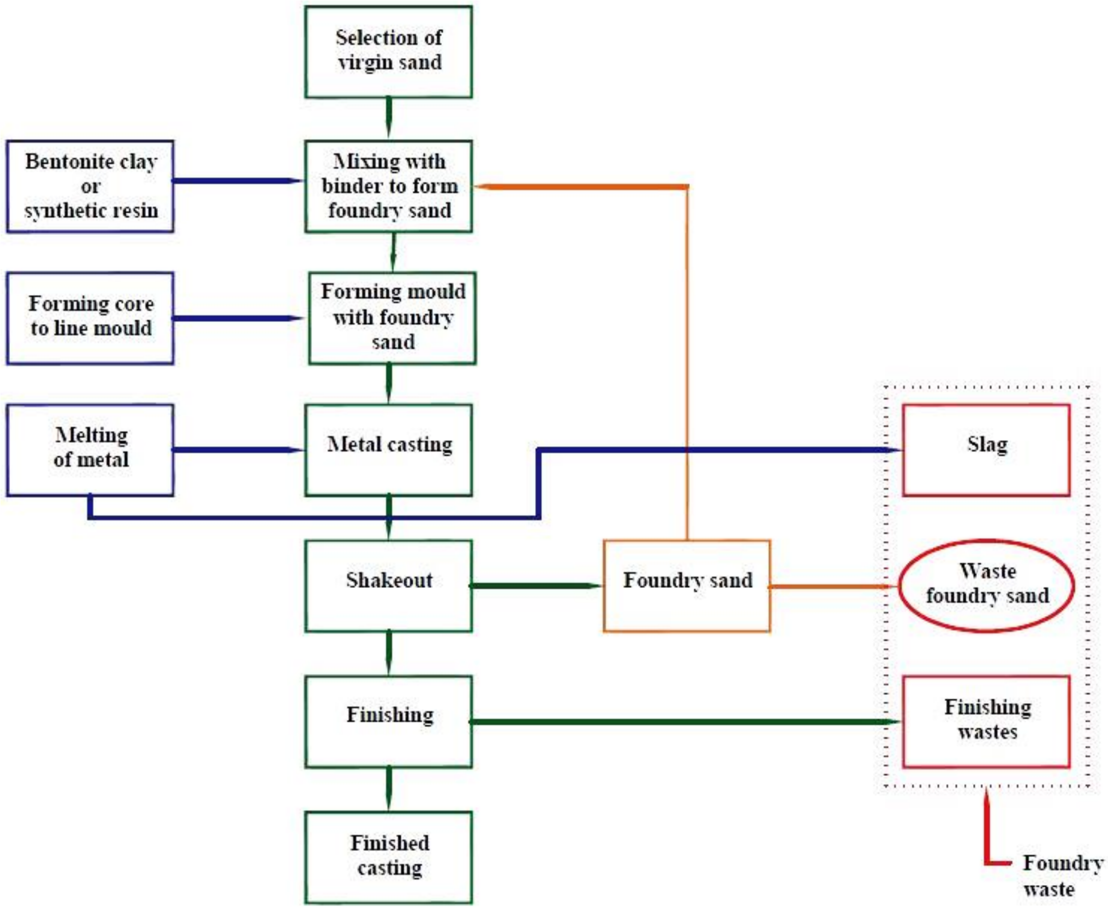


Figure 2.27: *Production of WFS (Modified after Bastian & Alleman, 1998)*

(B). Production quantities:

It is estimated that annually, SA disposes approximately 500 000 tonnes of WFS, with silica-based WFS constituting 350 000 tonnes (Iloh, 2018). In the UIS foundry, as per the 2018 statistics provided by UIS metallurgist, Mr. X. Matebese, this single site generates an average of nearly 270 tonnes of WFS per month (Table 2.25 below).

Madzivhandila (2018) conducted a survey on the characteristics of WFS generated at four South African foundries. The results, as presented in Table 2.26, display the generation of WFS, the disposal costs, and the distances to landfills for these four foundries. The conclusions drawn are that the cost of disposing WFS can become a significant burden to foundries and the cost per tonne is heavily influenced by the distance to the disposal site.

Table 2.25: *WFS production at UIS foundry in 2018*

Month	**WFS produced (tonnes)**
January	213
February	371
March	397
April	278
May	224
June	126
July	251
August	400
September	110
Total (tonnes)	**2370**
Average (tonnes)	**263**

Table 2.26: *WFS generation at four foundries in SA (Madzivhandila, 2018)*

Foundry	**WFS generated**	**Unit**	**Dumping cost (R / tonne)**	**Distance to dump-site (km)**
1	470	Tonne/month	300 – 900	20
2	250 – 300	Tonne/month	N/P	N/P
3	200	Tonne/month	N/P	15
4	7500 – 8500	Tonne/year	38.50	3

N/P – Not provided

2.7.5 Properties of WFS

The properties of WFS are largely dependent on whether the WFS is of the greensand or chemically-bonded variant. The properties of WFS from the UIS foundry, as presented in the subsequent tables, were provided by UIS metallurgist, Mr. X. Matebese (2020). Due to the inclusion of additives and the combustion process, WFS is black in colour (Figure 2.28).

Figure 2.28: *(A). Typical WFS sample (Siddique & Sandhu, 2013) & (B). On-site stockpiling of WFS (Sahare et al., 2019)*

2.7.5.1 Physical properties

Table 2.27 below provides both a summary and a means to compare the physical properties of WFS from the UIS foundry with greensand and chemically-bonded sand from other foundries in SA. Samples GS1 and GS2 are greensands from the Isando foundry and Guestro Casting & Machining, respectively. Samples CS1, CS2, and CS3 are chemically-bonded sands from Forbes Bros. Founders, Johannesburg Foundry, and Thomas Foundry, respectively.

Table 2.27: *Summary of physical properties of WFS from the UIS foundry and greensands and chemically-bonded waste sands from other foundries in SA*

Property	UIS WFS[1]	Greensand[2]		Chemically-bonded sand[2]		
		GS1	GS2	CS1	CS2	CS3
Total clay (%)	0.5	13	10	0	0	0
Relative density	2.65	2.5	2.3	2.6	2.6	2.8
LBD (kg/m^3)	1540	1247	1165	1387	1221	1437
CBD (kg/m^3)	1890 (general value)[3]					
Fineness modulus	3.26	1.2	1.0	1.4	3.2	0.5
Finer than 75 µm (%)	-	13	26	3	2	4
Specific surface (m^2/kg)	13	-	-	-	-	-

Sintering point (°C)	1450	-	-	-	-	-
Moisture content	Nil	0.4	1.9	8.3	0.5	0.2

[1]Matebese (2020); [2]Iloh et al. (2019); [3]Singh (2012)

(A). Clay content:

It must first be reiterated that the sample of WFS used in this study is of the chemically-bonded variant. This is evident as the clay content is practically zero, signifying the absence of the bentonite clay binder. This absence is also noticed in the chemically-bonded samples, namely CS1, CS2, and CS3. The WFS from the UIS foundry contained a 0.5 percent clay content, which meets the 2 percent maximum requirement as set out in SANS 1083 (2017). Evidently, greensand does not meet this requirement as GS1 and GS2 had clay contents of 13 percent and 10 percent, respectively.

(B). RD:

Chemically-bonded sand is shown to have higher RD values compared to greensand. This may be attributed to the inclusion of the porous sea-coal additive during the formation of greensand. The waste foundry sand from the Umgeni Iron & Steel (UIS WFS) was found to have a 2.65 RD, which is in keeping with the conventional fine aggregate range of 2.6 to 2.95. In addition, this value correlates with the RD value of Umgeni river sand and many South African river sands (Davis et al., 1979). As such, actions of settlement and bleeding and the difference in the densities of WFS-concrete and conventional concrete, due to the influence on RD, may be minor.

(C). Density:

On average, chemically-bonded sands exhibited higher loose bulk densities (LBD), with the UIS foundry sample having the highest LBD (1540 kg/m^3). The LBD of UIS WFS is in keeping with the range of LBD values required for normal-weight concrete, which Illoh et al. (2019) report as 1200 to 1750 kg/m^3. The LBD of conventional fine aggregate Umgeni river sand is approximately 1320 kg/m^3, thus the UIS WFS displayed a higher LBD than conventional fine aggregate. Singh (2012), reports that the compacted bulk density (CBD) of WFS is approximately 1890 kg/m^3 which is, as expected, higher than that of Umgeni river sand (1400 kg/m^3). A possible reason for UIS WFS exhibiting high density values may be due to the prevalence of rounded particles (Illoh et al., 2019).

(D). FM:

As discussed in Section 2.6.2 (A), greater FM values indicate coarser particles. Mavroulidou & Lawrence (2018) report that chemically-bonded sands are generally coarser than their greensand counterpart. The UIS WFS displayed a FM of 3.3, which was higher than all other WFS samples in Table 2.27, thus indicating a coarser material. SANS 1083 (2017) specifies that the FM for fine aggregate may range from 1.2 to 3.5, thus, UIS WFS is compliant in this regard. This FM value is less than that of Umgeni river sand (FM of 3.4), indicating that said river sand is coarser. The difference in FM, whilst slight, may indicate that UIS WFS may exhibit its own filler effect, which was reported by Mavroulidou & Lawrence (2018).

SANS 3001-AG1 (2014) classifies material passing the 75 μm sieve as dust content, which in accordance to SANS 1803 (2017), cannot exceed 5 percent. Evidently, both greensand samples displayed higher dust contents and did not meet this requirement, whilst all chemically-bonded samples were compliant. This advocates that the UIS WFS is expected to meet this requirement as it is a chemically-bonded sand. This is important as excessive dust content have been found to reduce concrete strength by weakening the cement-aggregate bond and increasing water demand (Newman & Choo, 2003). Moreover, Popovics (1992) mentions that an excessive fines content reduces workability and durability whilst increasing concrete shrinkage. The reduced fines content of chemically-bonded sands may improve workability as compared to greensands.

As per SANS 1083 (2017), 90 to 100 percent of fine aggregate must pass through the 4750 μm sieve, whilst 5 to 25 percent must pass through the 150 μm sieve. According to Iloh et al. (2019), all samples met the criterion involving the 4750 μm sieve but failed to satisfy the second criterion. However, light must be shed on this criterion as Umgeni river sand is a widely-used fine aggregate material in KZN, however as per sieve analysis, even this material did not meet this requirement as observed in Table 4.1 in Section 4.2. Figure 2.29 shows the particle size distribution curves for GS1, GS2, CS1, CS2, and CS3.

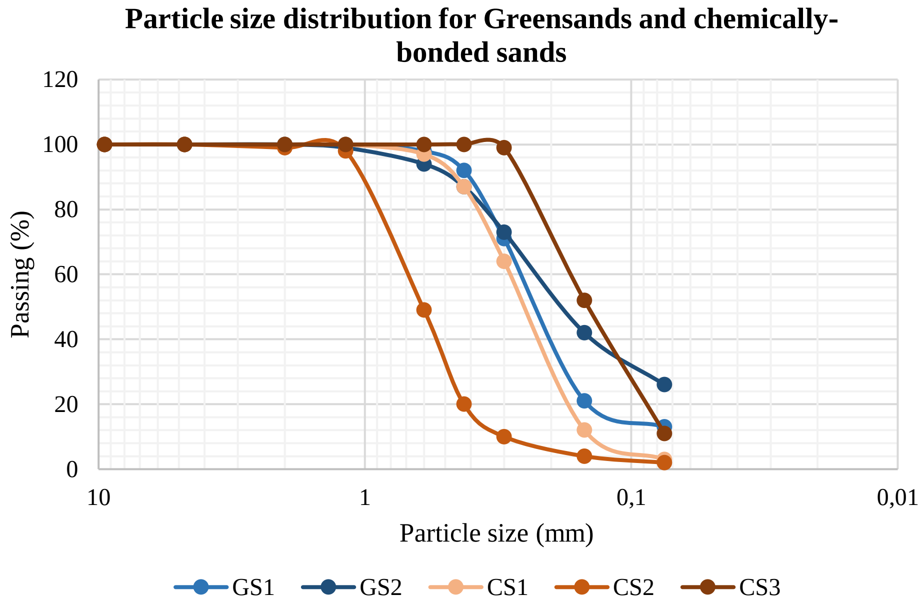


Figure 2.29: *Particle size distribution curves for the two types of WFS (Iloh et al., 2019)*

(E). Moisture content:

It is seen in Table 2.27 that the moisture contents of WFS are relatively low. Iloh (2018) advises that, compared to natural sand, WFS exhibits a low capability to absorb water.

(F). Gradation:

Table 2.28 below presents values relating to the gradation of GS and CS samples. It is shown that only GS2 may be categorised as being well graded. A possible reason for WFS not being categorised as well graded may be due to the fact that foundries largely require moulding sand that consists of uniformly sized particles (Mavroulidou & Lawrence, 2018). It is clear that chemically-bonded sands exhibit lower C_u values than greensands, indicating a greater tendency for chemically-bonded sands to be more uniformly graded.

Table 2.28: *An evaluation of WFS gradation (Iloh et al., 2019)*

WFS sample	WFS type	C_u	C_c
GS1	Greensand	5.27	2.03
GS2		7.87	1.66
CS1	Chemically-bonded sand	2.00	0.89
CS2		2.33	1.20
CS3		2.25	0.84

2.7.5.2 Chemical properties

In analysis of Table 2.29, past research has largely shown that, in order of occurrence, WFS predominantly consists of SiO_2, followed by Al_2O_3 and Fe_2O_3. Additionally, it appears that greensands contain higher levels of Al_2O_3 as compared to its chemically-bonded counterpart.

Table 2.29: *Summary of chemical properties of WFS from the UIS foundry and greensands and chemically-bonded sands from other foundries in SA*

Sample	Oxide content (%)									
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**MgO**	**K_2O**	**Na_2O**	**CaO**	**P_2O_5**	**MnO**
UIS WFS	**97.12**	**1.70**	**0.67**	**0.16**	**0.12**	**0.07**	**0.04**	**0.04**	**0.009**	**0.004**
GS1	82.68	8.10	3.54	-	1.48	1.15	-	-	-	-
GS2	73.00	11.90	6.33	-	2.16	-	1.36	1.92	-	-
CS1	88.82	3.22	2.82	-	-	2.53	1.03	-	-	-
CS2	89.32	2.01	3.26	-	-	-	2.87	-	-	-
CS3	68.93	6.23	8.31	-	-	3.18	-	-	-	-
Average	83.31	5.53	4.16	0.16	1.25	1.73	1.33	0.98	0.009	0.004

Sample	LOI (%)
UIS WFS	**0.33**
GS1	4.80
GS2	15.58
CS1	3.39
CS2	4.35

CS3	3.88
Average	5.4
Sample	**pH**
UIS WFS	**7.20**
GS1	8.88
GS2	8.87
CS1	9.34
CS2	9.89
CS3	9.52
Average	8.95

(A). Oxide contents:

Traditionally, fine aggregate is required to be chemically-inactive and a filler material. For this reason, compared to its physical properties, its chemical properties do not have a significant influence on the properties of concrete. This may be the cause for the lack of literature relating to the ways in which the chemical properties of both fine aggregate and WFS influence concrete. Walker (2013) informs that SiO_2 is the main oxide in fine aggregate. In comparing the SiO_2 contents of ordinary fine aggregate and UIS WFS from Tables 2.20 and 2.29 respectively, it is seen that the UIS WFS consists of 97.12 percent silica, which is greater than the silica contents in river sand (92.02 percent), coastal sand (95.98 percent) and quartzite-blasted sand (96.20 percent).

(B). LOI:

Evidently, UIS WFS shows the lowest LOI value (0.33 percent) compared to the other WFS samples presented in Table 2.29 above. This indicates it has the lowest content of carbon.

(C). pH value:

Matebese (2020) informed that UIS WFS exhibited a pH value of 7.20, which was the lowest in comparison to pH values exhibited by other WFS samples as listed in Table 2.29 above. However, the pH value of UIS WFS was lower than that of conventional river sand, which Verma (2015) observed to be an average of 7.50. This may indicate that WFS-concrete may display decreased pH values.

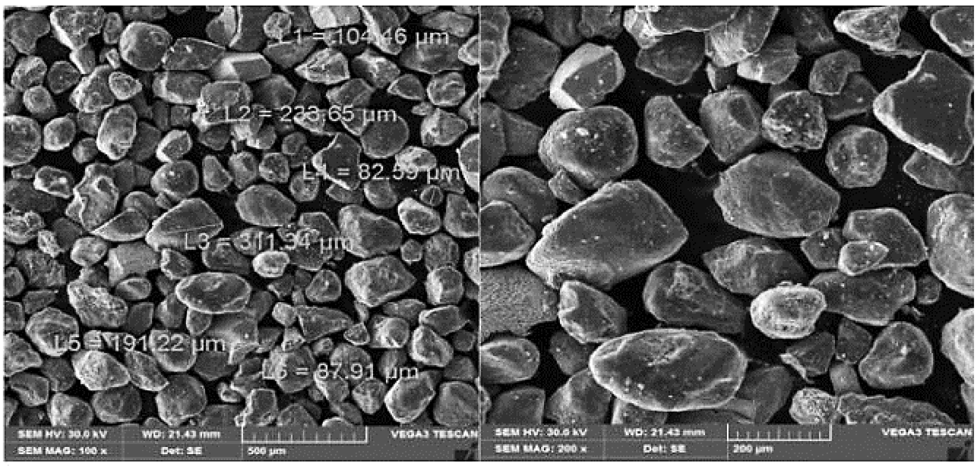
2.7.5.3 Morphological & mineralogical properties

Table 2.30 below provides a summary of the morphological properties of WFS.

Table 2.30: *Summary of morphological properties (Matebese, 2020)*

Property	UIS WFS
Approximate average grain size (µm)	339
Coefficient of angularity	1.83
AFS grain fineness number	44.18

SEM analysis conducted by Illoh et al. (2019) reveal the presence of various particle shapes present in both chemically-bonded sand (Figure 2.30) and greensand (Figure 2.31). In comparison to greensand, it appears that chemically-bonded sand consists of cleaner and smoother particles. It can be observed that both chemically-bonded sand and greensand largely consist of a mix of sub-angular, cubical and sub-rounded particles. Several authors, such as Bhimani et al. (2013), Jadhav et al. (2017) and Mavroulidou & Lawrence (2018), have made similar observations with respect to WFS particle shape. By conducting XRD analysis to determine the mineralogical characteristics of both variants of WFS, Illoh et al. (2019) found that the dominant crystalline phase was quartz (SiO_2).



(A) (B)

Figure 2.30: *(A). Chemically-bonded WFS particles at 500 µm and (B). Spherical sub-rounded and elongated sub-rounded particles at 200 µm (Illoh et al., 2019)*

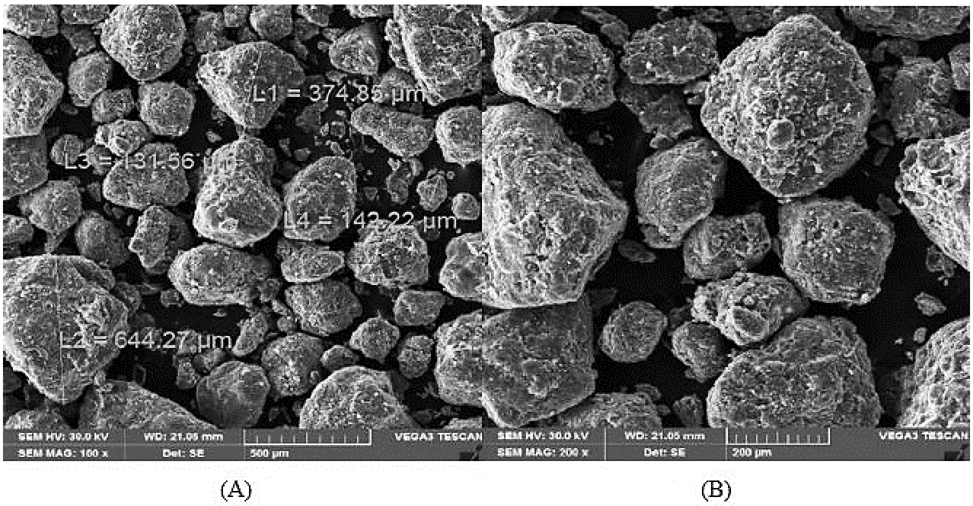


Figure 2.31: *(A). Greensand particles at 500 μm and (B). Spherical to sub-rounded particles at 200 μm (Illoh et al., 2019)*

2.7.5.4 Toxicity

The contents of trace metals present in UIS WFS, as provided by Matebese (2020), is shown in Table 2.31 below. Accompanying this is a comparison of the trace metals concentration with TCT levels. Evidently, the concentration of all trace metals in WFS are within standard limits.

Table 2.31: *Trace metals content of UIS WFS compared with Total Concentration Threshold (TCT) limits (Matebese, 2020)*

Metal	Trace metal content (mg/kg)			
	UIS WFS	TCT0	TCT1	TCT2
Boron, B	57	150	15 000	60 000
Molybdenum, Mo	1.79	40	1000	4000
Cadmium, Cd	0.04	7.5	260	1040
Antimony, Sb	0.04	10	75	300
Barium, Ba	44	62.5	6250	25 000
Mercury, Hg	0.33	0.93	160	640
Lead, Pb	9.74	20	1900	7600
Vanadium, V	4.37	150	2680	10 720
Chromium, Cr	24	46 000	800 000	N/A

Manganese, Mn	180	1000	25 000	100 000
Cobalt, Co	1.19	50	5000	20 000
Nickel, Ni	10.43	91	10 600	42 400
Copper, Cu	11.53	16	19 500	78 000
Zinc, Zn	21	240	160 000	640 000
Arsenic, As	0.61	5.8	500	2000
Selenium, Se	0.94	10	50	200

2.7.6 Complications Associated with WFS

WFS may pose a chemical hazard to health, agriculture, groundwater and land. The sand may contain elevated amounts of metals which serve as potentially toxic elements such as chromium, nickel, cobalt, copper, zinc etc. (Penkaitis & Sigolo, 2012). Fortunately, it is shown in Table 2.31 above that the UIS WFS employed in this study contain trace metals that are within standard limits.

In a 2014 risk assessment report, the Environmental Protection Agency (EPA) mentioned that the reclamation of this waste sand is expensive due to the high energy inputs required. This leads to the disposal of vast amounts of WFS. In SA alone, approximately 500 000 tonnes of WFS are disposed (Iloh, 2018). Additionally, due to expensive disposal fees and the high generation rate, WFS masses are typically stockpiled in enormous quantities at the foundry itself, and are then landfilled in portions. Matebese (2020) advises that in 2018, for the months of January to October, the cost involved with landfilling WFS was approximately R 386 000. In addition, WFS stockpiles considerably minimises working space and facilitates contaminant leaching, thereby creating complications to working conditions and obstacles to production (Mavroulidou & Lawrence, 2018).

2.8 INTERFACIAL TRANSITION ZONE (ITZ)

Concrete fundamentally consists of three phases – bulk cement paste, aggregate and the paste-aggregate interface. This interface is commonly referred to as ITZ and represents the region between the bulk cement paste and the aggregate (Figure 2.32 below). Due to its high porosity and relatively smaller size, which ranges from 10 to 50 μm in thickness, the ITZ serves as a major limitation to the mechanical performance of concrete (Li, 2011).

The ITZ is often described by many authors as the weakest link in the concrete chain. The ways in which the ITZ limit the behaviour of concrete may be observed in Figure 2.33 and Table 2.32 below. Figure 2.33 shows the results from the uniaxial test conducted on cement paste, aggregate, and concrete. Evidently, cement paste and aggregate exhibit linear elastic relationships, whilst concrete shows inelastic behaviour. As such, the influence of the ITZ causes concrete to deform more than the cement paste and aggregates. This is attributed to porosity, which is the reason the ITZ is considered the weakest phase in concrete (Li, 2011). Due to ITZ being more porous than the bulk cement, at any point its strength is dependent on the voids present, even for low W/B mixes (Mehta & Monteiro, 2006). Table 2.32 highlights the differences in permeability amongst cement paste, aggregate and concrete. Evidently, concrete is much more permeable than both of its fundamental constituent phases.

For this reason, the fine-filler effect provided by pozzolana may strengthen the ITZ. This proposition is further reinforced by Newman & Choo (2003), who explain that strengthening of the ITZ can be achieved by integrating pozzolana that are finer than cement. Thus, it is expected that PMBA-concrete may exhibit increased strength, partly due to the strengthening of the ITZ.

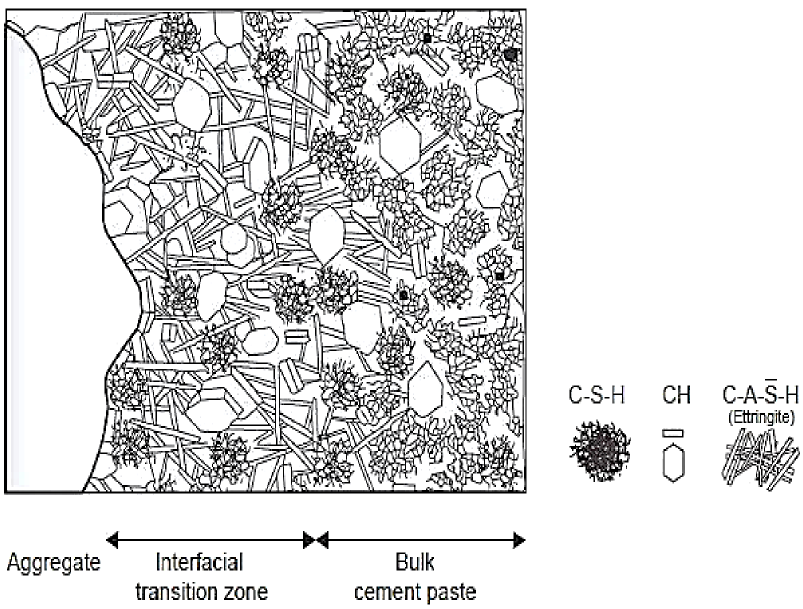


Figure 2.32: *Phases of concrete (Mehta & Monteiro, 2006)*

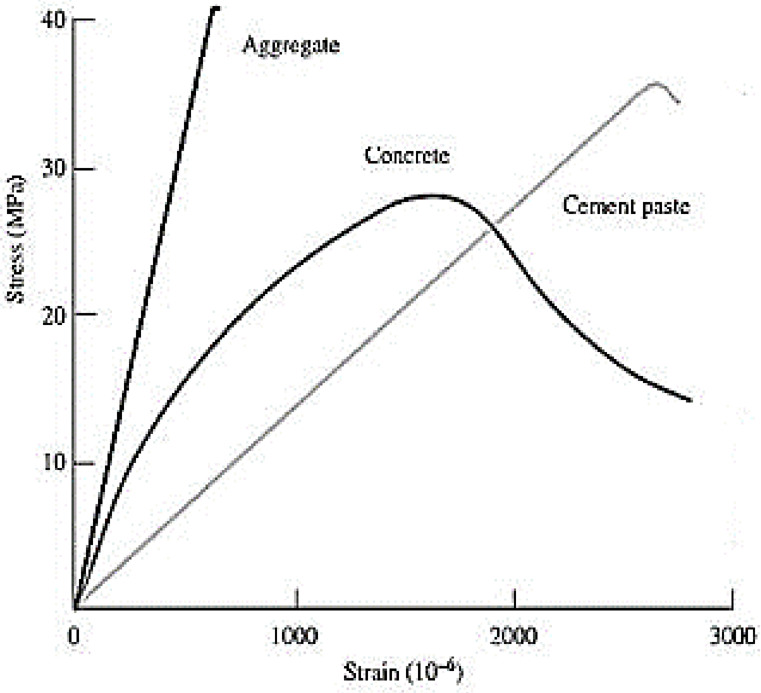


Figure 2.33: *Limited mechanical behaviour of concrete due to ITZ (Li, 2011)*

Table 2.32: *Increase in concrete permeability due to ITZ (Li, 2011)*

Material phase	**Permeability coefficient (10^{-12} cm/s)**
HCP	6
Aggregate	1 – 10
Concrete	100 – 300

2.9 WORKABILITY

When concrete has been designed and mixed, it is then required to be handled, transported to site, placed, compacted, and finished. Workability may be defined as the ease at which the abovementioned actions can be carried out without individual constituents separating from the mix. It can be said that this fresh state property is synonymous with two aspects; cohesiveness and consistency. Cohesiveness determines the ability to withstand constituent segregation and bleeding whilst consistency describes the ease at which fresh concrete may flow.

Whilst there is no test that can directly measure workability, the slump test is widely employed to provide an adequate indication. This test, as discussed in Section 3.4.1, assesses more so the consistency of fresh concrete by determining slump. When designing a concrete mix, a suitable slump is selected based on workability requirements. Figure 2.34 illustrates the apparatus required to conduct the slump test. The test itself involves issuing fresh concrete into a conical mould in three increments, uniformly tamping the concrete as increments are issued, and removing the mould. The distance by which the fresh concrete has settled, due to self-weight, is the slump. This settling action of fresh concrete may be categorised as zero slump, true slump, shear slump, or collapse slump (Figure 2.35). Shear slump occurs when fresh concrete is not uniformly tamped or when cement content is too low. The slump test is adequate for a range of 5 to 175 mm slumps.

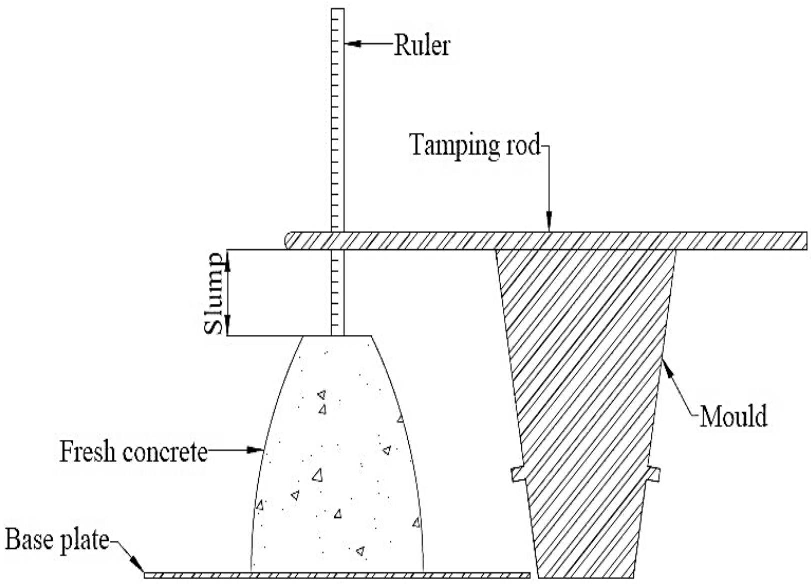


Figure 2.34: *Schematic of the slump test apparatus*

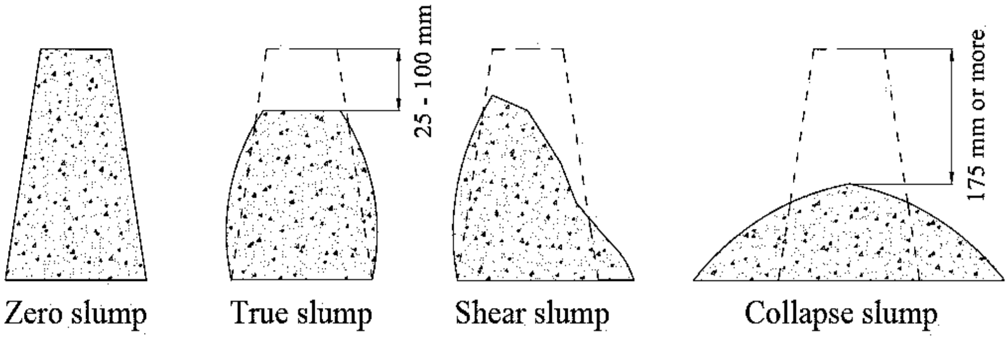


Figure 2.35: *General slump types*

Depending on the slump, workability may be classified as ranging from very low to high (Table 2.33). There is no universal requirement for workability, instead it is matched to the appropriate handling requirements. For common concrete applications, a medium level of slump is desired. This is because if slump is too low, concrete is too cohesive and does not flow well, becoming difficult to place and consolidate. Additionally, if slump is too high, cohesiveness is too low and individual constituents tend to segregate. The slump obtained is required to be within limits of the specified slump (Table 2.34 below).

Table 2.33: *Classification of the degree of workability by slump number (Li, 2011)*

Slump (mm)	Degree of workability	Typical application
0 – 25	Very low	• Roads vibrated by power-operated machines (compaction with hand-operated machines may be permitted at the more workable end).
25 – 50	Low	• Roads vibrated by hand-operated machines (manual compaction in roads using irregular/rounded shaped aggregate may be permitted at the more workable end). • Mass concrete foundations without vibrated/lightly reinforced sections with vibration.
50 – 100	Medium	• Manually compacted flat slabs using crushed aggregate. • Normal reinforced concrete. • Manually-compacted and heavily-reinforced sections with vibration.
100 – 175	High	• Congested sections that are not suitable for vibration

Table 2.34: *Slump tolerance (AfriSam, 2012; presented by Naicker, 2014)*

Specified slump (mm)	Tolerance (mm)
Slump ≤ 50	- 15 to + 25
50 < Slump ≤ 100	± 25
Slump > 100	± 40

Table 2.33 above classifies workability based on a slump of up to 175 mm. As in accordance with BS 8500, Table 2.35 below provides a further indication of concrete application as based on slump.

Table 2.35: *Concrete application based on slump range (Naicker, 2014)*

Target slump (mm)	Slump range (mm)	Application
20	10 – 40	Kerbs and pipework bedding
70	50 – 90	Normally specified for most concrete works
130	100 – 150	Thin sections and trench-filled foundations where a high flow is required
180	160 – 210	Specialist works
220	≥ 220	

2.9.1 Relevant Factors Influencing Workability

The term 'relevant factors' refers to factors that relate to the materials of interest in this particular study, namely cement, pozzolana and fine aggregate. The properties of fine aggregate and cement influence workability in two main ways – by influencing cohesiveness and consistency through particle characteristics and by governing the water required for a given workability. The following factors, as they relate to cement and fine aggregate, influence workability:

(A). Fine material content:

An excessive amount of cement or fine aggregate may result in high cohesiveness, making concrete sticky and handling difficult and producing a lower slump value, thereby reducing workability. However, an inadequate amount of fine material may result in excessive slumps, leading to bleeding and segregation of particles (The Concrete Institute, 2013).

Walker (2013) informs that generally, a higher workability relates to low cohesiveness, whereby such concrete allows for easier handling, however bleeding, plastic shrinkage and loss of strength may be experienced due to the higher content of free water. Conversely, lower workability involves higher cohesiveness, leading to difficult handling. The cement content exhibits less of an influence when compared to that of fine aggregate (Neville & Brooks, 2010). However, workability will be reduced for cements with low sulphate and high alkali contents.

(B). Fine aggregate characteristics:

Generally, very fine or very coarse sands are unfavourable for workability. This is because finer sands increase water requirement whilst coarse sands produce harsh mixtures that are prone to segregation (Walker, 2013). Additionally, due to their lower surface areas, cubical, sub-rounded and rounded particles may improve workability by acting as a miniature ball bearing mechanism which reduces friction between particles. As such, these particles are able to easily roll over each other with relative ease, thereby improving flow (Walker, 2013). Angular sands increase the water requirement for a given consistency, thereby decreasing slump (Newman & Choo, 2003). In terms of texture, particles that have rougher surfaces provide a larger surface area that requires wetting, which increases the amount of water required, consequently reducing workability (Walker, 2013).

(C). Pozzolana (fly ash):

Fly ash consists of finely divided, spherically-shaped particles with a glassy texture (Mehta & Monteiro, 2006). The American Coal Ash Association (ACAA, 2003) explains that the glassy particle texture reduces the surface requiring wetting, thereby reducing water requirement. Spherical particles exhibit the ball bearing mechanism as mentioned above (Newman & Choo, 2003). In addition, workability may improve by the fine-filler effect. This may occur through the filling of voids. As a result, less water is required to fill voids, leading to a reduced water requirement (Fennis et al., 2009). Berry & Malhotra (1980) have found that water requirement reduced by 7 percent when 30 percent of cement was replaced with fly ash.

2.9.2 Potential Influence of PMBA & WFS on Workability

(A). PMBA:

Wong et al. (2015) reported that concrete arising from PMS ash, as a cement replacement, showed a noticeable reduction in workability, which was likely attributed to the hydrophobic nature of the ash. This is because a share of the mix water becomes locked in as a result of PMS ash attaching to water particles, thereby forming a film which covers the surfaces of a portion of water particles (Wong et al., 2015). This prevents mix water from wetting constituents, ultimately causing a reduction in workability. However, it can be argued that since Cherian & Siddiqua

(2019) report that PMBA is hydrophilic, the ash may have the ability bond easily with water and facilitate wetting (Cherian & Siddiqua, 2019). This results in a reduced water requirement and an improvement of workability.

The presence of glassy, spherical particles may exhibit a ball bearing effect, which is noted to be displayed by pozzolan such as fly ash (Carlson et al., 1937; Popovics, 1992; ACAA, 2003; Awang et al., 2015). This effect, as mentioned in Section 2.9.1 (C), reduces particle friction and lubricates the mix; making the mix more workable. In addition, the fine-filler effect may fill voids, thereby reducing the water requirement.

Due to the lack of research involving PMBA-concrete, the ways in which PMBA influences the properties of concrete, including workability, are not well documented. Various researchers, such as Ahmad et al. (2013) and Raghuwanshi & Joshi (2017), have investigated PMS ash as a partial cement replacement, with the general trend of decreasing workability with ash content. This was attributed, by both of the aforementioned authors, to its high fineness. Hence, it is possible that PMBA may result in a reduction in workability as it displays a high specific surface (4200 – 100 600 m^2/kg) as compared to the relatively low 370 m^2/kg specific surface of CEM II/B-S 42.5 N plus (Spenner Zement, 2012; Cherian & Siddiqua, 2019).

(B). WFS:

As compared to natural sand, WFS shows a reduced capacity to absorb water, indicating its ability to increase slump (Iloh, 2018).

Soil gradation is considered one of the more important factors that influence workability, however the difference in gradation between conventional fine aggregate and UIS WFS may not cause a significant change in workability as both materials were classified as being poorly graded. This is because both exhibited similar soil coefficient values (i.e., C_u and C_c) and similar FM values.

In addition, the prevalence of the glassy cubical, sub-rounded and rounded particles of WFS, as reported by Illoh et al. (2019), may improve workability. This is suggested by Walker (2013), who commented on the particle characteristics of fine aggregate and their influence on workability.

Past studies inconsistently report the effects of WFS on workability. Mavroulidou & Lawrence (2018) investigated the replacement of fine aggregate with 10, 30, 50, 70 and 100 percent WFS. Their results showed that slump increases and remains constant for replacements of 10, 30 and 50 percent WFS, and thereafter decreases. Pandey et al. (2015) reported that workability improved with increasing additions of WFS. Similarly, Etxeberria et al. (2010) investigated both chemically-bonded WFS and greensand as fine aggregate replacements. They conclude that concrete arising from the chemically-bonded variant showed the highest degree of workability. In contradiction, several researchers have observed losing workability with increasing WFS contents. Khatib et al. (2010), Sowmya & Chaitanya Kumar (2015) and Jadhav et al. (2017) have reported that slump decreases with greater amounts of WFS.

2.10 SATURATED HARDENED DENSITY (SHD)

The SHD of concrete is given as its mass to volume ratio and, in accordance with SANS 6251, is assessed immediately after curing. This procedure is detailed in Section 3.4.2. Concrete may be classified in accordance with density (Table 2.36). The porosity of concrete has a major influence on various crucial hardened state properties, such as strength and durability. Hardened density is an important parameter as it is oppositely related to porosity, thereby giving an indication of concrete porosity (Mehta & Monteiro, 2006).

Table 2.36: *Classification of concrete based on density (Li, 2011)*

Classification	Density (kg/m^3)
Ultra-lightweight concrete	< 1200
Lightweight concrete	1200 – 1800
Normal-weight concrete	2400
Heavyweight concrete	> 3200

2.10.1 Relevant Factors Influencing SHD

(A). Pozzolana

It was found by various researchers, such as Amankwah et al. (2014), that due to pozzolana having a lower relative density than cement, SHD will decrease when increasing contents of pozzolana replace cement. While this notion is held by several researchers, it is interesting to note that Motau (2016) investigated the partial replacement of cement with pulverised pozzolana and fly ash, in increments of 5, 10, and 20 percent, and observed that SHD for both mixes increased between a 5 and 10 percent replacement, followed by a decline. No explanation was given for the increase in density as witnessed in the aforementioned replacement interval. Conversely, research conducted by Iffat (2015) showed that denser concrete has less voids, resulting in greater strengths and durability. To this effect, it is possible that, through the fine-filler effect of fine pozzolana, the integration of PMBA may lead to reduced porosity and a densification of the microstructure, however it is unknown if this may improve SHD. In support of this notion, is Bremseth (2010), who commented that fly ash increases concrete density by increasing cementitious compounds, reducing both bleed channels and water demand, and filling in voids.

(B). Aggregates

Denser constituents tend to produce denser concrete and due to their prevalence in concrete, the maximum sizes and densities of aggregates are generally responsible for influencing hardened density. Accordingly, well graded and denser aggregates will naturally produce denser concrete (Iffat, 2015). The quality of sand gradation is important as uniformly graded sands result in voids, thereby reducing density.

2.10.2 Potential Influence of PMBA & WFS on SHD

(A). PMBA:

Cement exhibits an RD of approximately 3.14 whilst the average RD of PMBA was 2.45, hence PMBA-concrete may exhibit lower densities compared to conventional concrete. Contrariwise, the fine-filler effect of PMBA may refine the pore structure, thereby reducing porosity and increasing density.

Past studies involving the integration of PMS ash have generally reported a decrease in density (Ahmad et al., 2013) whilst fly ash was shown to improve density (Tao & Dong, 2017).

(B). WFS:

As discussed in Section 2.7.5.1 (C), based on values in literature, WFS exhibits a higher density than conventional fine aggregate. For this reason, the addition of WFS may result in improved SHD values. However, poorly graded fine aggregates result in a reduced packing density, consequently decreasing concrete density through void creation. As such, WFS may also result in reduced concrete densities. Moreover, Iloh (2018) mentions that certain binders used in WFS production, such as wood flour, sawdust and clay, reduce concrete density.

2.11 MECHANICAL STRENGTH PROPERTIES

Concrete strength is the specified property in concrete design and quality control (Mehta & Monteiro, 2006). In this study, test mixes were not designed to meet a specified strength, rather it was the influence of each test material on strength that was under investigation.

Strength properties are so crucial that they are valued by designers over other concrete properties (Mehta & Monteiro, 2006). The significance of strength testing is due to the fact that obtaining strength data, through testing, is relatively easy and various other properties may be deduced from strength data, such as permeability and modulus of elasticity (Li, 2011). Due to the heterogeneity of concrete, the properties of strength tend to depend on several factors, such as porosity, the degree of cement hydration, the W/B ratio etc. The two main strengths may be categorised as compressive and tensile. The former is generally assessed using the uniaxial compressive strength test whilst the latter is assessed indirectly by the flexural strength test and the tensile-splitting strength test.

2.11.1 Compressive Strength (f_{cc})

Compressive strength is taken as the general index of concrete strength in structural design. This implies that compressive strength is an indication of both the quality of hardened concrete and its ability to withstand load. As such, this form of strength is widely regarded as the most common performance attribute of concrete. In fact, it is common practice to use compressive strength as a quantitative measure of other concrete properties (Abd elaty, 2013). Compressive strength may be used as a criterion for concrete classification as shown in Table 2.37 below.

Table 2.37: *Concrete classification based on compressive strength (Li, 2011)*

Classification	Compressive strength (MPa)
Low-strength concrete	< 20
Moderate-strength concrete	20 – 50
High-strength concrete	50 – 150
Ultra-high-strength concrete	> 150

In SA, the determination of compressive strength involves applying a uniaxial compressive load on concrete cubes until failure. The testing procedure is described in Section 3.4.3. Mindess et al.

(2003) state that a compressive strength of 35 MPa is typical of structural concrete whilst Naicker (2014) describes structural concrete as displaying a strength of 30 MPa. Table 2.38 below further describes concrete applications as based on compressive strength.

Table 2.38: *Concrete applications based on compressive strength (Naicker, 2014)*

Compressive strength (MPa)	**Applications**
10	Unreinforced foundations, blinding
20	Reinforced foundation, slabs, driveways, light duty floors
30	Structural slabs and beams, pre-cast items, heavy duty floors

2.11.2 Tensile Strength: Flexural (f_f) & Tensile-splitting

In relation to compressive strength, tensile strength is significantly lower. This difference is due to the direction of cracking, whereby tensile loads cause cracks to propagate orthogonal to the load. In this scenario, concrete offers less resistance (Newman & Choo, 2003). As such concrete is highly susceptible to tensile-induced cracking. For this reason, the determination of tensile strength becomes important. During direct tensile strength tests, it proves difficult to apply a true axial tensile load as secondary stresses are caused by the devices that hold the specimen in place (Mehta & Monteiro, 2006). For accuracy, these stresses may not be ignored, therefore direct tensile tests are infrequent. Tensile strength is instead assessed by indirect means, namely by flexural and tensile-splitting tests.

The flexural strength of concrete is critical for structural elements that are subjected to bending actions, as in the cases of concrete roads, airport pavements etc. Mindess et al. (2003) indicate that a 6 MPa flexural strength is typical of structural concrete. A minimum 28-day flexural strength of 4 MPa is required for minor roads in SA (SAPEM, 2013). Flexural strength, commonly referred to as the modulus of rupture, provides an indication of the ability of unreinforced concrete to resist failure due to tensile forces arising from bending. In SA, the test commonly involves a two-point load being applied at third points on a standard concrete beam until failure. The flexural strength test, generally referred to as the two-point load test, is discussed in Section 3.4.4.

Tensile-splitting strengths are usually assessed by applying compressive line loads on two diametrically opposed lines of a standard cylindrical sample (Li, 2011). The test procedure is described further in Section 3.4.5. By referring to the work of Popovics (1998), Naicker (2014) explains that tensile-splitting strength differs from flexural strength. This is because tensile-splitting strength is indicative of the tensile strength that occurs anywhere in the plane under tension, whilst flexural strength provides the tensile strength that occurs at the beam's tension surface. Structural concrete generally exhibits a tensile-splitting strength of 3 MPa (Mindess et al., 2003).

2.11.3 Relevant Factors Influencing Concrete Strength

As mentioned, compressive strength may be used to quantify additional concrete properties. The work of Akinpelu et al (2017) show that compressive strength and tensile strength share a somewhat proportional relationship whereby, tensile strengths increase with compressive strength at decreasing rates. This is because the relationship between the two strengths is largely determined by factors that influence the properties of the cement matrix and the ITZ (Li, 2011). The following factors are discussed as they are potentially influenced by either PMBA or WFS:

(A). Porosity

Porosity is the most important strength-influencing factor (Mehta & Monteiro, 2006). The cement matrix and the ITZ experience certain levels of porosity. In terms of the cement paste, the hydration products occupy a smaller volume than that of the original dry cement. The resulting residual space are termed capillary pores, which represents approximately 18.5 percent of the original dry cement volume (Newman & Choo, 2003).

There exists a general relationship between concrete strength and capillary porosity, whereby strength increases with decreasing concrete porosity (Figure 2.36). This is because pores or voids in the cement paste serve as sources of weakness.

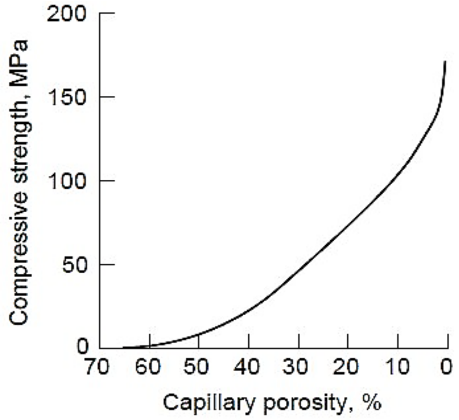


Figure 2.36: *Influence of porosity on compressive strength (Mehta & Monteiro, 2006)*

(B). Water-binder ratio (W/B ratio)

The influence of the W/B ratio on strength properties can be linked with porosity. This is because the W/B ratio is the main influence in the number and sizes of capillary pores. If the mix contained more water than was required for complete hydration, the resulting capillary pores will exceed the 18.5 percent volume mentioned above. Accordingly, higher W/B ratios generates greater concrete porosity (Figure 2.37A). In consequence, compressive strength decreases at all ages of concrete (Figure 2.37B).

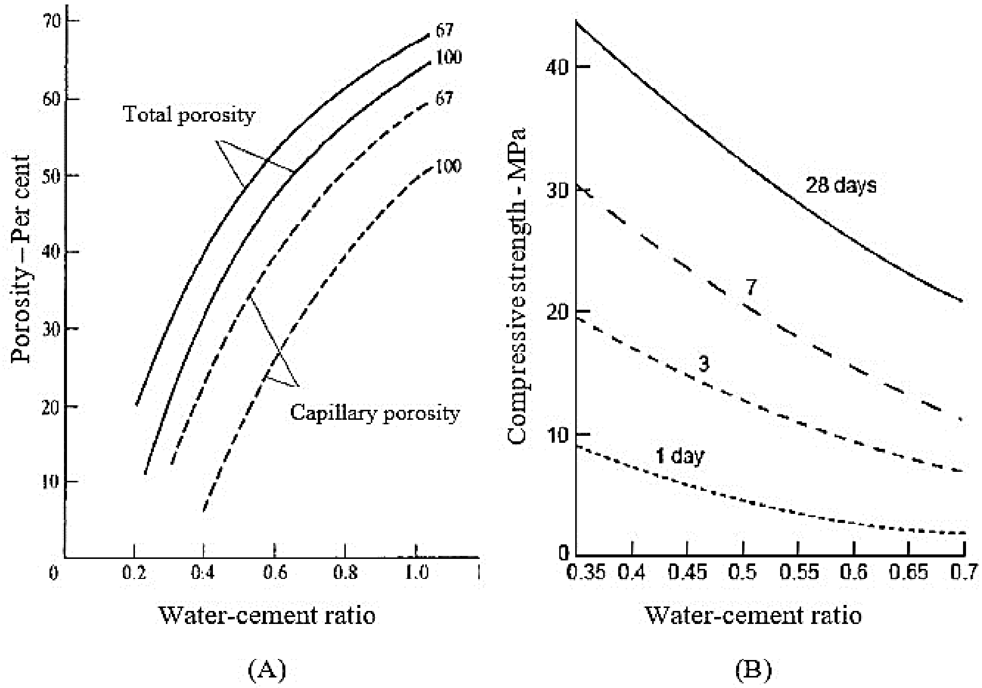


Figure 2.37: *(A). Influence of W/B ratio on porosity (Neville & Brooks, 2010) & (B). Influence of W/B ratio on compressive strength (Mehta & Monteiro, 2006)*

(C). Pozzolana

After investigating the influence of various pozzolana on the properties of cement paste, Walker & Pavía (2010) concluded that the amorphousness of pozzolana (mainly amorphous SiO_2) is the main influence in pozzolanic reactivity. In turn, a major aspect of strength development relates to the rate of pozzolanic reactivity, whereby higher rates contribute to enhanced strength development.

A larger specific surface improves pozzolanic reactivity by providing a greater surface for pozzolanic reactions to occur. In contradiction to Walker & Pavía (2010), are Yazici & Arel (2012), who state that the fine-filler effect is more effective than the pozzolanic characteristics in terms of enhancing the properties of concrete. Yazici & Arel (2012) further reinforce this concept by partially replacing cement with fly ash samples of varying specific surface areas, and concluded that compressive and tensile-splitting strength increases as the fineness increases.

As discussed, the addition of pozzolana reduces early-age concrete strength but improves strength development thereafter. This trend is noted by various authors, such as Harison et al. (2014), who implemented fly ash as an SCM and found that 7-day strengths were typically lower than that of conventional concrete, however 28-day strengths were observed to be higher. A possible reason for this is the fact that pozzolanic reactions are delayed as these reactions may only occur once the reactions of hydration produce CH, leading to slower early-age strength development.

Lastly, CH is not a significant contributor to concrete strength, however its reaction with pozzolana forms C-S-H which acts as the main strengthening element in hardened cement paste. Thus, pozzolana produces a strong gel phase from a weak crystalline phase (Owens, 2013).

(D). Fine aggregate characteristics

Li (2011) advises that strength is influenced by both coarse and fine aggregate characteristics, such as density, particle size, shape, and texture. In terms of fine aggregate, angular sands tend to improve mechanical performance whilst well-graded sands improve compressive strengths. The Concrete Institute (2013) suggests that coarser particles allow for the accumulation of trapped bleed water, which weakens the ITZ, thereby causing reductions in strength.

In addition, the gradation of fine aggregate once again exerts an influence on concrete properties. The voids that arise from less dense packing, as a result of poor gradation, may lead to significant decreases in concrete strength. Hence, a more uniformly graded sand may produce weaker concrete.

2.11.4 Potential Influence of PMBA & WFS on Strength

(A). PMBA:

In terms of strength development of the cement paste, PMBA may result in lower early-age strengths as pozzolanic activity is limited to CH from hydration, along with the ability of fly ash to retard the reaction with C_3S. This lower paste strength may result in lower early age concrete strengths. However, Newman & Choo (2003) advise that concrete strength development improves in the middle stage and greatly increases thereafter. The improvement in strength may be attributed mainly to the fact that PMBA consists largely of amorphous phases with a higher reactive SiO_2 content than cement, has a large specific surface compared to cement and may exhibit the fine-filler effect.

The large specific surface of PMBA (4200 – 100 600 m^2/kg) is one of the more crucial factors that may contribute to concrete strength development. PMBA has a greater specific surface than cement (370 m^2/kg). Pozzolanic reactions occur on the surface of pozzolanic particles. The high specific surface of PMBA points to a relatively higher pozzolanic reactivity through PMBA providing a greater surface for reactions to occur; thereby enhancing strength development. Additionally, as in the case of fly ash, the particle characteristics of PMBA may allow the material to exhibit the fine-filler effect.

In terms of the chemical nature of PMBA, due to pozzolanic reactivity being dependent on the content of reactive SiO_2 and Al_2O_3, strength development of PMBA-concrete will be largely influenced by these oxides. Walker & Pavía (2010) indicate that pozzolans with higher SiO_2 contents displayed greater strengths than pozzolans with lower contents. In comparing the SiO_2 contents, PMBA shows a larger content (35.83 percent) than the maximum SiO_2 content in cement (24.50 percent).

Figure 2.10 in Section 2.4.3 (F), illustrated that strengths tested after seven days are reduced as the SO_3 content in the binder material increased. Table 2.3 in Section 2.4.1 indicated that the average SO_3 content in Portland cement is 2.58 and a maximum of 5.35, whilst Byiringiro (2014) reports an SO_3 content of 4.93 in Mondi's PMBA. This may indicate that increasing quantities of PMBA may result in reduced strengths at later ages.

Finally, it was discussed in Section 2.5.5.2 (B) that PMBA displays a higher LOI than cement and fly ash. LOI is indicative of carbon content and Kearsley & Wainwright (2003) observed that increasing levels of carbon in fly ash resulted in reduced strengths. Accordingly, it is possible that the strength of PMBA-concrete may decrease with increasing quantities of PMBA.

Various studies have shown the benefit of using fly ash to improve strengths. Elsageer et al. (2009) showed that compressive strength improved for up to a 45 percent replacement. Anandan & Manoharan (2015) observed that compressive, flexural and tensile-splitting strengths peaked at a replacement of 25 percent. Kosior-Kazberuk & Lelusz (2007) observed that the maximum compressive strength occurred at a replacement of 20 percent.

The integration of PMS ash has been reported to show increases in strength at lower replacements. Ahmad et al. (2013) found that compressive and tensile-splitting strengths increased at a 5 percent replacement. Kumar & Shetty (2016) observed that PMS ash reduced compressive strength but improved flexural and tensile-splitting strengths at a 5 percent replacement.

(B). WFS:

It was noted that WFS is largely uniformly graded, suggesting a lack of packing structure, leading to voids which may reduce concrete strength. In addition, the presence of sub-rounded and cubical shaped particles may further reduce strength. An insignificant improvement in strength may occur due to the UIS WFS being marginally finer than Umgeni river sand, thereby potentially exhibiting its own filler effect.

Past studies show a general trend whereby strength increases with smaller replacements and decreases with larger replacements of fine aggregate with WFS. Pathariya et al. (2013) found that compressive strength improved up until 40 percent whilst tensile-splitting strengths decreased. Sowmya & Chaitanya-Kumar (2015) noted that compressive, flexural and tensile-splitting strengths increase up until a 20 percent replacement. Jadhav et al. (2017) observed that compressive strength increases up until a 30 percent replacement whilst Pandey et al. (2015) concluded that a 10 percent replacement resulted in the highest compressive strength. Mavroulidou & Lawrence (2018) investigated replacement orders of 10, 30, 50, 70 and 100 percent and found that the highest compressive, flexural and tensile-splitting strengths arose from a 30 percent replacement.

2.12 DURABILITY

The durability of concrete refers to its ability to withstand its design environment and retain its quality and serviceability. This ability largely consists of concrete providing resistance to chemical attack, weathering action and abrasion. By this definition, durability may be viewed as being indicative of concrete performance as opposed to being an inherent property. This is because concrete that may be durable in a given environment may not be durable in another (The Concrete Institute, 2013).

Inadequate durability is a global problem. Reinforced concrete structures that exhibit loss of durability pose a risk to public and property. As such, concrete must be designed to account for durability, such as considering exposure to the environment, providing sufficient cover depth, allowing tolerable movement of concrete during its service life etc. In addition to its core roles of ensuring safety and serviceability, practices in achieving concrete durability may be used to advance sustainable development practices through reduced life-cycle costs by reducing premature deterioration. This is due to the fact that concrete repair costs are high and continuous, reaching 3 to 5 percent of the Gross National Product in certain countries (Loseby, 2014). Table 2.39 below provides examples of repair costs associated with loss of durability in reinforced concrete structures.

Table 2.39: *Cost of repairing and replacing concrete structures due to loss of durability (Kessy et al., 2015)*

Location	Cost/year (US$)	Description
USA	8.3 billion	For repair and replacement of bridges
Western Europe	5 billion	For repair and replacement of structures
Arabian Gulf	798 million	Due to the corrosion of steel

Alexander et al. (1999) concluded that in terms of durability, the surface layer of concrete is critical as it is most affected by deleterious processes, which in turn are governed by transport mechanisms relating to penetrability, such as permeation, absorption and diffusion. As a result, SA has developed and adopted the South African durability index (DI) approach, which assesses durability based on the ability of concrete to resist the transportation of harmful substances arising from its service environment (Gouws et al., 2001; Martin, 2012). Concrete is subjected to attack by aggressive agents such as oxygen, water, chlorides and atmospheric CO_2 that are transported into concrete, resulting in deterioration. Stanish et al. (2006) inform that the DI approach characterises the microstructure of the surface layer of concrete by evaluating the oxygen permeability index (OPI), water sorptivity (WS) and chloride conductivity (CC).

2.12.1 Oxygen Permeability Index (OPI)

In the context of concrete, permeability serves as a measure of the ability of the material to transfer gases and fluids through its pore structure. A higher capacity to transfer, the less durable the concrete. The OPI test is used to assess concrete permeability by measuring the rate of permeating oxygen through a standard concrete disk specimen. As reported by Griesel & Alexander (2004), this is achieved using a falling head permeator, whereby an oxygen pressure gradient is applied across the specimen and the pressure decay is measured over time. The test procedure is discussed in Section 3.4.6 (A). The general OPI test setup is illustrated in Figure 2.38 below.

Figure 2.38: *(A). Sample assembly & (B). Permeator setup (CoMSIRU, 2018)*

The OPI value is given as the negative logarithm of the Darcy coefficient of permeability (K). Based on said OPI value, durability may be classified in accordance with Table 2.40 below. This classification system dictates that greater OPI values indicate less permeable and more durable concrete. Naicker (2014) reports that OPI values are often in the range of 8 to 11.

Table 2.40: *Durability classification based on OPI (Alexander et al., 1999)*

Durability class	OPI (Log value)
Very poor	< 9
Poor	9 – 9.5

Good	9.5 – 10
Excellent	> 10

As reported by Nganga & Gouws (2013), the OPI has an important application in determining the cover depth of concrete that is required to achieve a certain service life. Carbonation depth is the distance from the concrete surface where CO_2 has reduced alkalinity (Breysse, 2010). Figure 2.39 below demonstrates that greater OPI values result in a reduced advancement of the carbonation depth, thereby improving resistance to corrosion and allowing for smaller cover depths to be employed. Factors influencing the OPI include the characteristics of the permeating agent, moisture conditions and the characteristics of the microstructure such as the tortuosity and the width of cracks and pores (Nilsson, 2003; Beuhausen & Alexander, 2008).

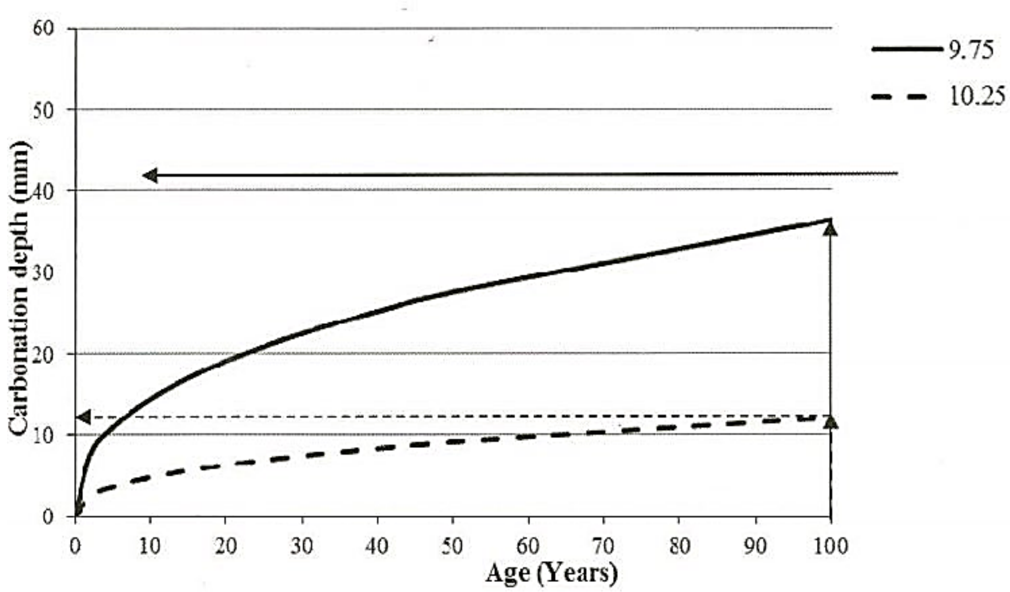


Figure 2.39: *Carbonation depth depending on OPI (Nganga & Gouws, 2013)*

2.12.2 Water Sorptivity (WS)

In concrete structures, capillary absorption is noted as the primary transport mechanism for water and occurs as a result of surface interactions between the pore wall and water (Hycrete, 2011; Naicker 2014). Alexander et al. (1999) defines sorptivity as the phenomenon arising from capillary absorption and is defined as the rate of movement of a wetting front through a porous material. Standard concrete samples are pre-conditioned at 50° C to ensure that all samples have uniform and low moisture contents. The sides of all samples are sealed to ensure the uniaxial absorption of water (Griesel & Alexander, 2014). The samples are placed on paper towels and exposed to water. The mass of water absorbed is measured at predetermined time intervals. In order to determine the effective porosity, the samples are vacuum-saturated in water.

The sorptivity is assessed as the slope from the straight-line plot of the mass of water absorbed against square root of time (Gouws et al., 2001). This process is discussed in detail in Section 3.4.6 (B). The general test setup is illustrated in Figure 2.40 below.

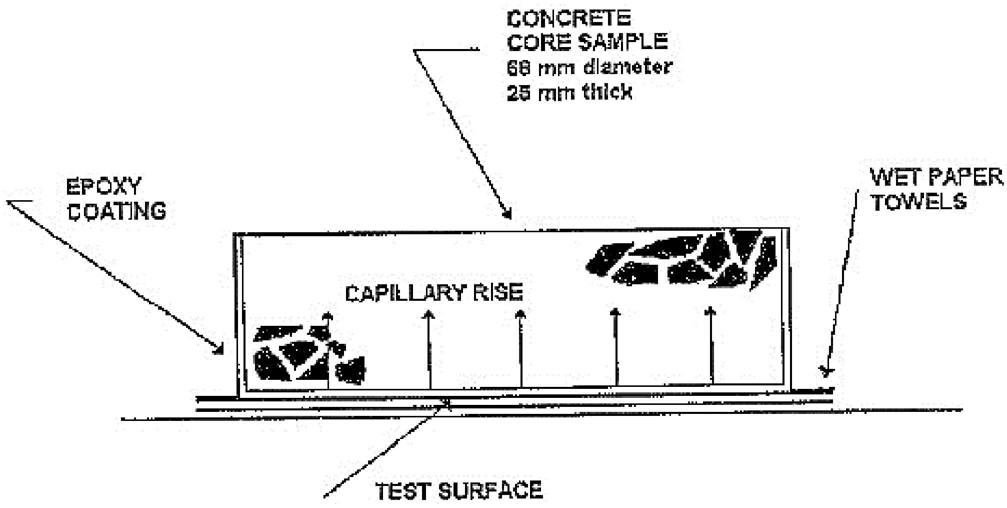


Figure 2.40: *WS test setup (Alexander et al., 1999)*

Naicker (2014) provides a background into the importance of WS by stating that out of all three transport mechanisms (i.e., permeation, absorption and diffusion), capillary absorption has the potential to cause the most damage as it is rapid, requires no pressure to occur and is the primary transport mechanism for the infiltration of not only water, but chlorides as well.

In addition, Hycrete (2011) refers to the work of Butler (1998), who observed that capillary absorption occurs at speeds that are a million times faster than pressure permeability. Table 2.41 demonstrates how concrete durability may be classified in terms of WS. Evidently, lower WS values indicate more durable concrete. Naicker (2014) reports that WS values typically range from 2 mm/$\sqrt{h}$ to 11 mm/$\sqrt{h}$.

The factors influencing sorptivity include the moisture state of concrete, large capillaries and the extent to which they are connected, the distribution and orientation of aggregates and the composition of the mix (Loseby, 2014; Iloh, 2018).

Table 2.41: *Durability classification based on WS (Alexander et al., 1999)*

Durability class	Sorptivity (mm/$\sqrt{h}$)
Very poor	> 15
Poor	10 – 15
Good	6 – 10
Excellent	< 6

2.12.3 Chloride Conductivity (CC)

Chloride may enter concrete via permeation, capillary absorption or diffusion; however, it is diffusion that is of particular concern as it is the main transport mechanism for chloride in marine environments (Gouws et al., 2001). Diffusion occurs as a result of a concentration gradient whereby ions, liquids or gases are transported through a porous material. Due to diffusion being a slow process, an accelerated test has been developed using an applied voltage (Alexander et al., 1999). The CC test, as arranged in Figure 2.41, involves applying 10 V to accelerate the movement of chloride ions through the pores of a pre-conditioned concrete sample. Pre-conditioning is vital for standardising the pore water solution and is achieved via vacuum saturation with an NaCl solution. By referring to observations made by Streicher & Alexander (1995), Naicker (2014) informs that diffusion and conductivity are linearly related. The CC test measures conductivity via the current flowing through the concrete sample. This procedure is discussed in Section 3.4.6 (C).

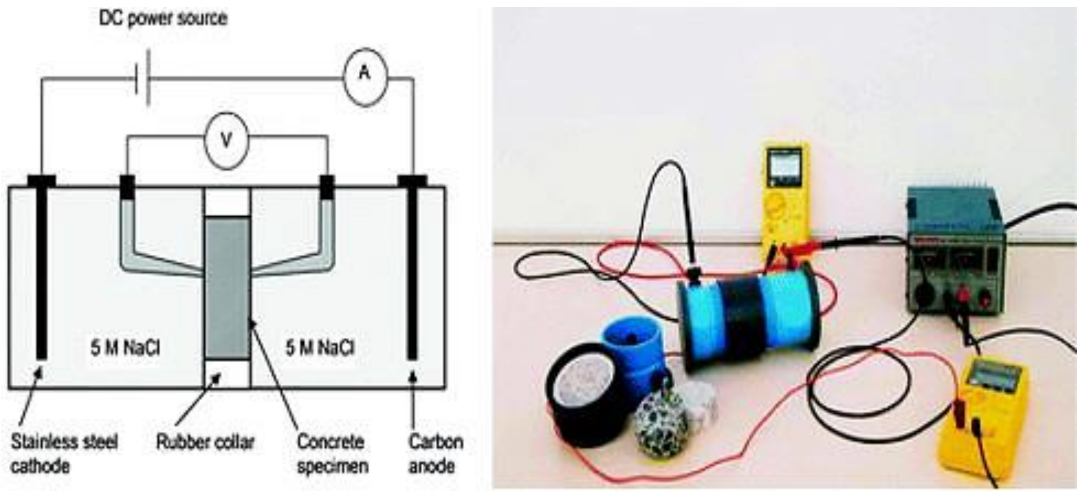


Figure 2.41: *CC test setup (Bjegović et al., 2016)*

The importance of assessing chloride conductivity lies primarily in steel protection. In considering all mechanisms that result in concrete losing durability, the corrosion of steel reinforcements is acknowledged as the most concerning. This is because corroding steel is the most common cause of loss of durability in reinforced concrete structures. In concrete, the CH that forms via the hydration process imparts a highly alkaline nature to concrete, with pH values ranging from 12.5 to 13.5 (Li, 2011).

This alkalinity is a desirable trait as it forms a thin film of iron oxide, called the passivation layer, on the surface of the reinforcement, which prevents steel corrosion by restricting the movement of ions near the surface of the steel. Li (2011) further states that chlorides may enter concrete from aggregates, from external sources such as marine environments and from the addition of calcium chloride. The chloride ions tend to break down the passivation layer at localised pits and promote metallic dissolution (Mackechnie & Alexander, 2001).

The consequent development of rust causes the volume of reinforcements to increase, resulting in swelling pressures that cause concrete to spall (Figure 2.42). This reduces the integrity of the reinforced concrete structure.

Figure 2.42: *Spalling of concrete due to corrosion of reinforcements (CivilDigital.com)*

In addition to chloride attack, carbonation is the other significant mechanism of corrosion and is noted as the principal cause for reductions in alkalinity. Carbonation is discussed in Section

2.13.1. Table 2.42 below demonstrates how concrete durability may be classified in terms of CC. Evidently, lower CC values indicate more durable concrete.

Table 2.42: *Durability classification based on CC (Alexander et al., 1999)*

Durability class	**CC (mS/cm)**
Very poor	> 2.50
Poor	1.50 – 2.50
Good	0.75 – 1.50
Excellent	< 0.75

The rate of diffusion is dependent on the properties of the diffusant, the concrete moisture content and temperature (Loseby, 2014).

This study employs the three standard DI tests to assess durability, however other indications of concrete durability include resistances to carbonation, sulphate attack, ASR, various causes of concrete expansion etc.

2.12.4 Relevant Factors Influencing DI Tests

The penetrability of concrete is a major influence on durability and occurs through permeation, sorptivity and diffusion. The movement of deleterious substances occur via the concrete pore structure; thus, most transport mechanisms are influenced by penetrability (Loseby, 2014). The following relevant factors are key in influencing durability, as assessed by the DI tests:

(A). Porosity

Permeability is noted as one of the most important factors relating to concrete durability. Naturally, increased permeability facilitates the transportation of deleterious substances through concrete. In turn, permeability is dependent on porosity, whereby increased concrete porosity results in a greater degree of permeability (Figure 2.43 below). The influence of porosity on CC is stressed by Shekhovtsova et al. (2014), who indicates that higher porosity facilitates chloride diffusion. Figure 2.44 provides an indication of the influence of porosity on permeating water. In order to produce durable concrete, it is important to achieve a low permeability.

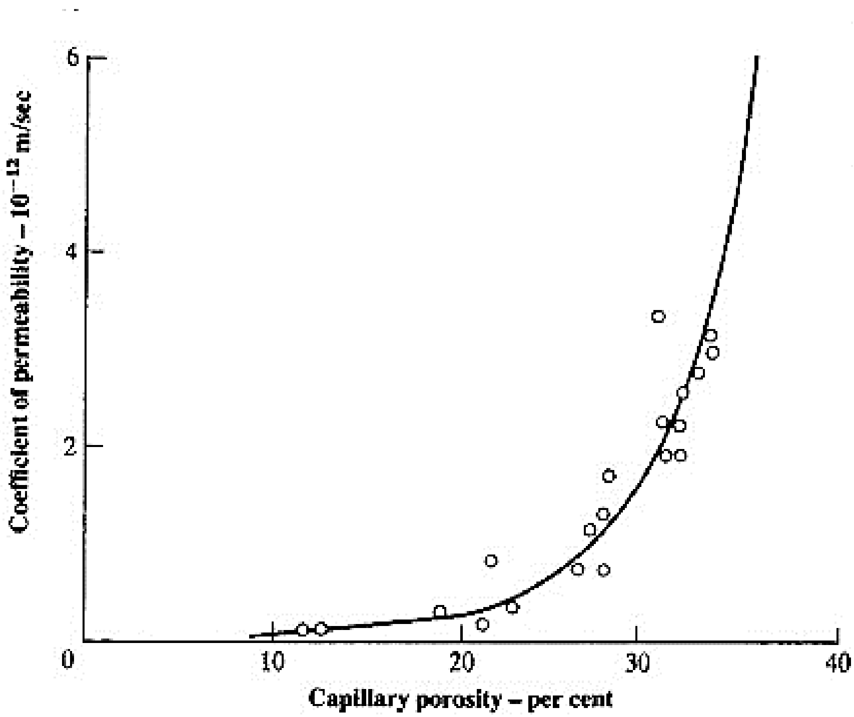


Figure 2.43: *Influence of porosity on permeability (Neville & Brooks, 2010)*

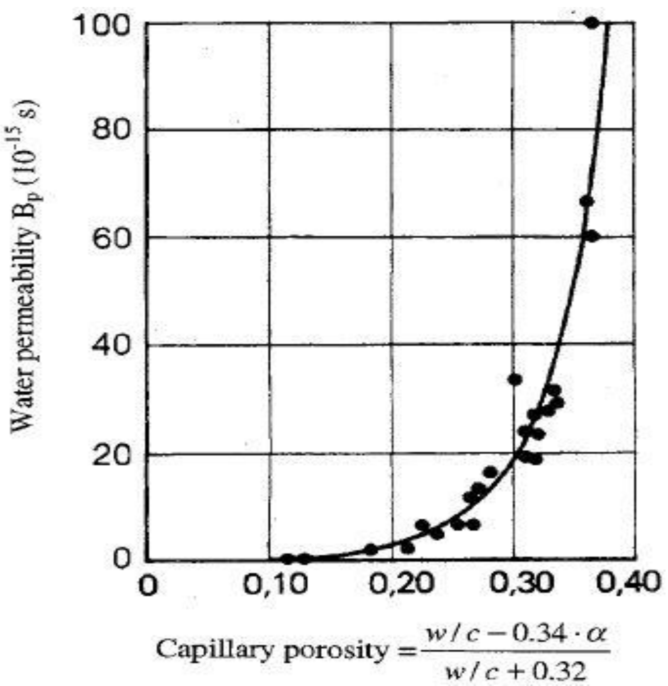
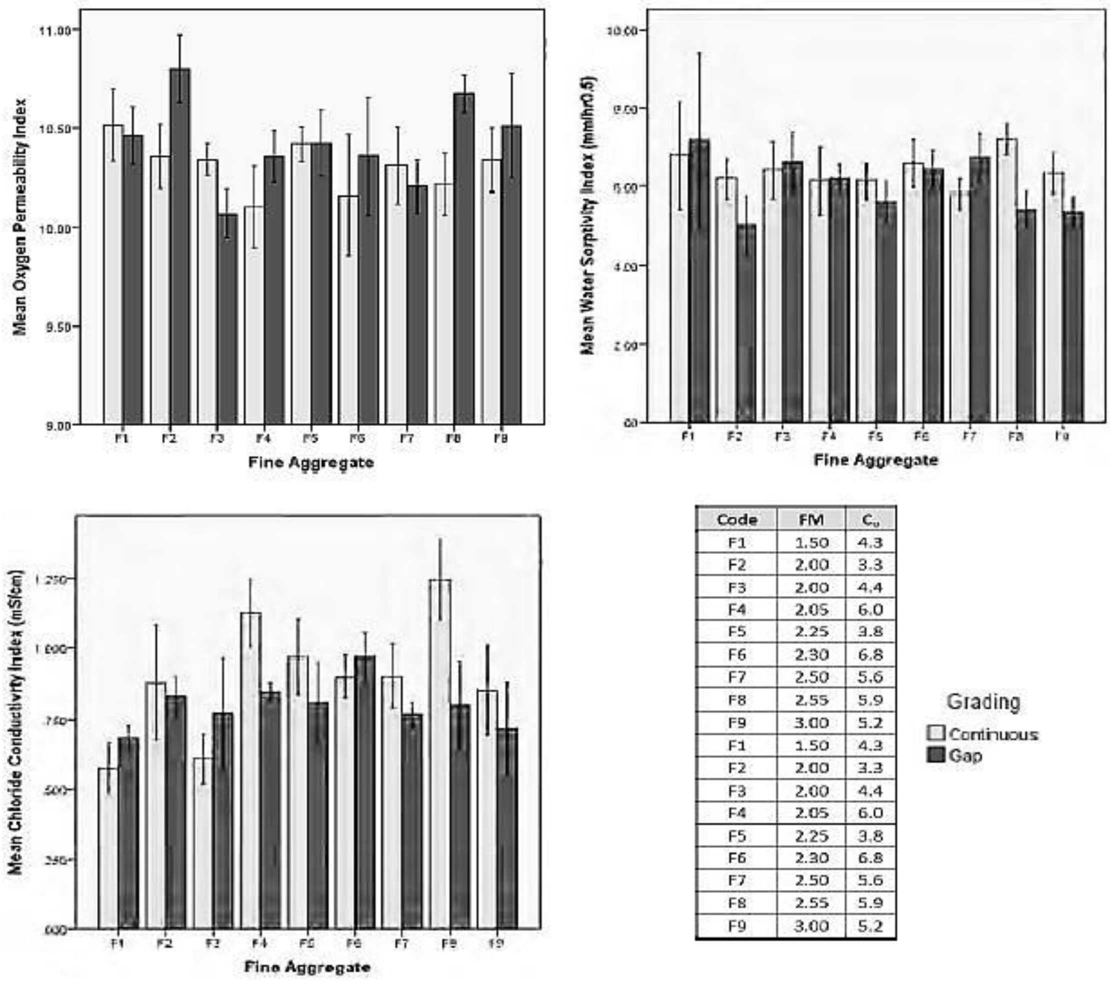


Figure 2.44: *Influence of porosity on water permeability (Ekström, 2001)*

(B). Fine aggregate characteristics

One of the major determinants of reduced concrete permeability is a finer pore network exhibiting less connectivity (Layssi et al., 2015). Authors such as Mehta & Monteiro (2006), suggest that finer particles present in fine aggregate tend to produce a finer network, reduce the porosity of the ITZ and decrease concrete permeability. This may be attributed to the fact that smaller particle sizes result in a lower degree of tortuosity, which restricts the penetration of substances. Moreover, smaller particles reduce the level of localised bleeding, leading to a less porous ITZ (Loseby et al., 2006). In addition, spherical and cubical particles reduce the water requirement, thereby reducing porosity. However, in terms of the three DI tests, Loseby (2014) investigated the influence of aggregate grading on penetrability by testing concrete arising from sands with FM ranging from 1.50 to 3.00 and C_u ranging from 3.3 to 6.8. He concluded that fine aggregate grading, as assessed by FM and C_u, does not appreciably influence concrete durability.

In terms of the influence of FM, Loseby (2014) observed that OPI values decreased for FM values between 1.50 and 2.05, increased for a FM of 2.25 and thereafter decreased with increasing FM. WS values decreased as FM increased from 1.50 to 2.50 and thereafter increased. CC values increased as FM increased from 1.50 to 2.05 and thereafter decreased up until a FM of 2.55, followed by a decrease in CC values. The increase in CC with FM was attributed to tortuosity, whereby increasing coarseness results in a lower tortuosity of the flow path through concrete. Consequently, as Ahmad et al. (2012) observed, decreases in tortuosity renders concrete more permeable, leading to increased CC values. Through further statistical evaluation, Loseby (2014) concluded that variations in FM had no meaningful influence on the three durability tests. In terms of C_u, no meaningful trend was observed, especially for the WS and CC tests. The OPI test provided a slight indication that OPI decreases as C_u increases. It is hypothesized by Loseby et al. (2016) that this occurs due to the increase in D_{60}, which causes higher degrees of bleeding at the surface of the aggregate, consequently making the ITZ more porous.



Code	FM	C_u
F1	1.50	4.3
F2	2.00	3.3
F3	2.00	4.4
F4	2.05	6.0
F5	2.25	3.8
F6	2.30	6.8
F7	2.50	5.6
F8	2.55	5.9
F9	3.00	5.2
F1	1.50	4.3
F2	2.00	3.3
F3	2.00	4.4
F4	2.05	6.0
F5	2.25	3.8
F6	2.30	6.8
F7	2.50	5.6
F8	2.55	5.9
F9	3.00	5.2

Figure 2.45: *Influence of aggregate grading on DI tests (Loseby, 2014)*

(C). Pozzolana

Pozzolana, especially fly ash, are noted for enhancing the microstructure of concrete, which is a major influence on the penetration of concrete and durability (Walker, 2014). Figure 2.17 in Section 2.4.4 (E) illustrated the general reduction in concrete permeability through the introduction of pozzolana. Ballim et al. (2009) demonstrates the ways in which various pozzolanic-cement blends influence the three DI tests. Their findings are presented in Figure 2.46 below. It is evident that cement blended with fly ash show improvements in OPI (for a W/B of 0.6), WS and CC, thereby indicating a more durable concrete. By referring to the work of Mackechnie (1996), Gouws et al. (2001) states that CC is highly sensitive to concrete pore structure, with the indication being that the integration of fly ash will reduce CC by refining pore structure.

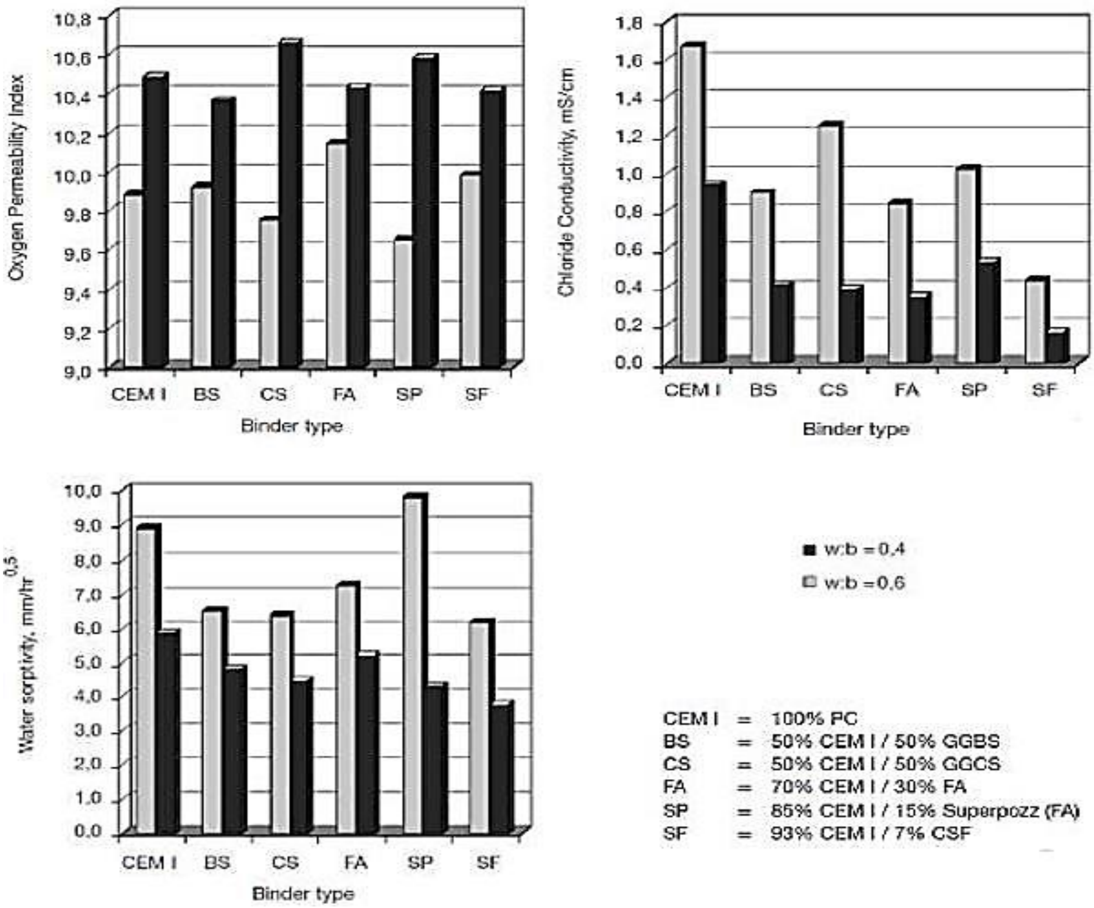


Figure 2.46: *Influence of pozzolana on DI tests (Ballim et al., 2009)*

In addition, Figure 2.16 in Section 2.4.4 (E) depicts how pozzolana improves durability through reduced concrete expansion.

(D). Moisture content

Mukadam (2014) reported that concrete with greater moisture contents experience reduced permeability. This is due to the ability of free water, known as capillary water, to block the paths of transporting substances such as gas. In addition, Mukadam (2014) states that sorptivity is also influenced by moisture content, whereby greater moisture contents typically show reduced absorption by the concrete cover, suggesting that capillary absorption is facilitated by low moisture states. These statements are further supported by Burmeister (2012) who states that greater contents of moisture will assist in preventing gases from being transported through concrete, however high moisture contents also lead to the facilitation of migrating soluble ions.

2.12.5 Potential Influence of PMBA & WFS on Durability

(A). PMBA

In reference to Figure 2.46 above, Ballim et al. (2009) found that fly ash results in improvements in the OPI, WSI and CCI. This is likely due to the fine-filler effect, which leads to reduced penetrability. This suggests that due to the fly ash nature of PMBA, durability may improve accordingly. These results were based on a 30 percent integration of fly ash. The findings of Zulu & Allopi (2014) indicate that for contents of fly ash exceeding a 30 percent replacement, the resulting OPI values show a decrease whilst both WS and CC increase at 7 and 28-days. Thus, suggesting that as fly ash content exceeds a particular limit, durability is reduced.

In terms of the additional indications of durability, CH may be linked to ASR, carbonation via the reaction with CO_2 and sulphate attack via its reaction with sulphate. Accordingly, due to pozzolanic reactions consuming quantities of CH, the resulting concrete may exhibit higher degrees of durability with respect to resistance against ASR, carbonation and sulphate attack.

The consumption of CH may also prove disadvantageous to durability via the reduction in concrete pH, potentially leading to steel corrosion and concrete spalling. Fortunately, Mehta & Monteiro (2006) inform that whilst pH value is reduced, there is still an adequate amount of CH remaining to maintain pH. For this reason, PMBA-concrete is expected to exhibit reduced pH values, however such a reduction may not be great enough to permit steel corrosion.

(B). WFS

Whilst the work of Loseby (2014) showed no meaningful relationship between aggregate grading and the DI tests, a basic indication of the influence of WFS on OPI, WS and CC may be obtained by referring to said work.

Section 4.2 shows that UIS WFS exhibited a FM value of 3.3 and a C_u value of 2.28. Hence, based on the findings of Loseby (2014), concrete arising from UIS WFS may see a decrease in OPI, an increase in WS and a decrease in CC. In terms of additional factors relating to durability losses, UIS WFS contains 0.5 percent clay material, which is lower than the 2 percent requirement, indicating that swelling arising from clay may not be a significant determinant of unwanted expansions. It was found that WFS exhibited greater bulk densities than conventional fine aggregate, which is noteworthy as The Concrete Institute (2013) states that the higher the aggregate bulk density, the lower the water requirement, which in turn results in lower levels of permeability. However, voids due to poor grading may reduce the durability of WFS-concrete.

Fortunately, Mavroulidou & Lawrence (2018) noted that the filler effect of WFS is responsible for the reduction in void spaces, whereby higher increments of WFS resulted in decreased levels of water absorption. This trend was observed for different W/B values as shown in Figure 2.47 below.

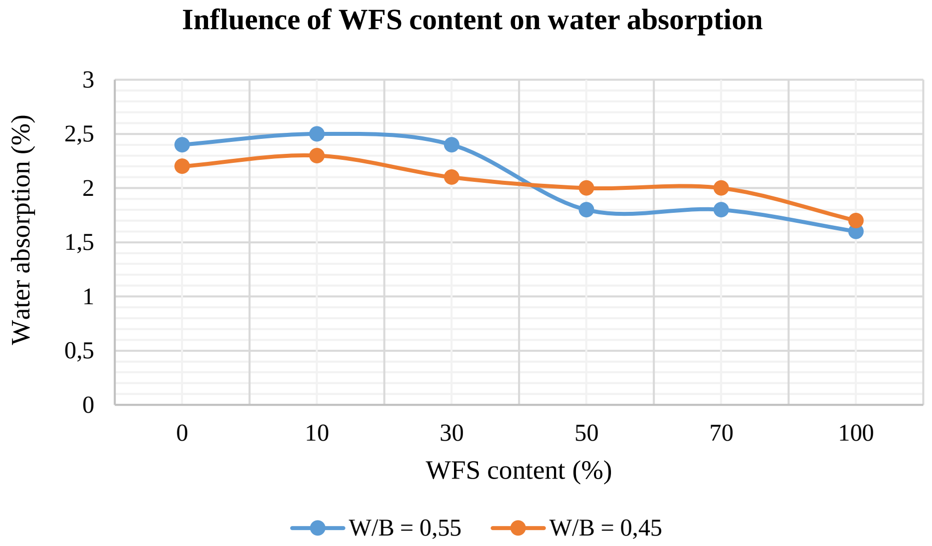


Figure 2.47: *Influence of WFS content on the water absorption of WFS-concrete (Mavroulidou & Lawrence, 2018)*

In terms of carbonation, the abovementioned investigation noted that for a W/B of 0.45, carbonation depths increased as WFS content increased. Conversely, for a W/B of 0.55 carbonation depths decreased as WFS content increased.

To investigate expansions due to ASR, said investigation deemed that concrete arising from a 100 percent replacement of conventional aggregate, with WFS, would constitute the worst-case scenario if the WFS sample was reactive, however no expansions were observed (Mavroulidou & Lawrence, 2018).

Sowmya & Chaitanya-Kumar (2015) investigated a separate determinant of durability in the form of resistance to acid attack, with the findings suggesting that the resistance to acid attack improves as WFS content increases.

2.13 LEACHING TESTS

The United States Environmental Protection Agency (U.S. EPA) defines leaching, in the environmental context, as "*the transfer of chemical species or compounds from a solid material into contacting water*". Accordingly, leaching tests are conducted, under laboratory conditions, to assess the amount of a substance that is released from a solid material into a predetermined amount of water. In field conditions, constituents that leach into contact water may contaminate surrounding soil, groundwater and surface water. The results from such leaching tests are crucial as they allow for an assessment of the leaching behaviour of a solid in field. This information is important to assess the quality of a specific leachate. In considering that hazardous industrial by-products are being utilised in this study, it is important to observe the leaching characteristics of PMBA-concrete and WFS-concrete.

In terms of concrete, leaching tests involves refining hardened concrete into concrete powder, which is then mixed with a specific content of deionised water to form a suspension. These samples undergo constant mixing in an orbital shaker. The suspension then undergoes filtration and the resulting liquid is subjected to a variety of testing at intervals of 24, 36 and 72 hours. The resulting liquid may be described as leachate. Leaching testing conducted in this study is a variant of the batch leachate test and provides information pertaining to concrete pH and the dissolved particles in the leachate.

2.13.1 pH Value

The leaching test involving the pH value of concrete offers insight into two factors:

- The protection afforded to steel reinforcements as provided by the alkaline nature of concrete.
- The quality of the leachate, as assessed by its pH value.

Neville & Brooks (2010) inform that when the pH value is lowered below 11.0, the protective passivation layer starts to break up, thereby leaving the steel exposed to corrosion. As per the work of Stojanović et al (2019), the leaching test for pH value provides an indication of the alkalinity of the concrete sample itself.

The pH value is taken as the negative logarithm of the hydrogen ion concentration. This value is directly influenced by the ratio of hydrogen ions and hydroxyl ions and is measured on a scale from zero to fourteen. A substance may be categorised as acidic (i.e., less than seven on the pH scale) if the hydrogen ion concentration is greater than the hydroxyl ion concentration. Conversely, due to a greater hydroxyl ion concentration, alkaline substances exhibit values greater than seven on the pH scale.

The two main mechanisms of reinforcement corrosion are carbonation and chloride attack. Carbonation occurs due to the reaction between atmospheric CO_2 and CH in the HCP, which forms calcium carbonate ($CaCO_3$). Carbonation causes a breakdown of the passivation layer by reducing the pH of concrete, due to the relatively lower pH value of $CaCO_3$ (approximately 8.5). Consequently, pits in the passive film cannot be repaired due to insufficient hydroxyl ions (Mackechnie & Alexander, 2001). It is important to note that carbonation is a growing concern as atmospheric CO_2 has seen a 50 percent increase in the last century (Owens, 2013). As discussed in Section 2.12.3, chloride attack occurs via contamination or ingress of chloride, which breaks down the passivation layer even if pH is kept above 11.0. In terms of resisting chloride attack, the performance of both PMBA and WFS was assessed via the CC test. The pH of PMBA-concrete and WFS-concrete was then determined in order to observe the effects of these test materials on the passivation layer.

In terms of leachate quality, a more neutral pH value is required so as to mimic the alkalinity of possible contact water. In accordance with SANS 214-1, the pH value for drinking water cannot occur outside the range of 5 to 9.7 pH units (Verlicchi & Grillini, 2020). Indeed, it is expected that leachate arising from concrete will not conform to drinking water standards as the pore water in concrete is naturally alkaline. As such, lower pH values will be seen as exhibiting a reduced potential to pollute contacting water and soil.

2.13.2 Ion Conductivity

The measurement of conductivity is a useful tool with applications in quality control. The determination of ion conductivity is low-cost and reliable; making it an avenue of interest for any good quality-monitoring program. Conductivity is a measure of the ability to pass ions, which is directly related to the ion concentration. The higher the ion presence, the higher the conductivity. Ion conductivity is measured in milliSiemens per centimetre (mS/cm).

Table 2.43 provides a set of conductivity values for various substances.

Table 2.43: Typical conductivity values for various substances (Radiometer Analytical)

Substance	Conductivity at 25°C (mS/cm)
Pure water	0.000055
Deionised water	0.001
Rainwater	0.05
Drinking water	0.5
Industrial wastewater	5
Seawater	50

It has been established that concrete durability is often compromised via the penetration of various aggressive substances into the concrete medium. Whether it be via carbonation, chloride ingress, sulphate attack, ASR or leaching; a common factor is observed – the movement of ions through the concrete microstructure. The ability of concrete to withstand the movement of ions may be attributed to its electrical resistivity, which in turn is said to be inversely proportional to ion conductivity (Madhavi & Annamalai, 2016).

Ion conductivity is largely influenced by the properties of the concrete microstructure, such as pore size.

2.13.3 Nitrate Content

The excessive presence of nitrate in water can become a major predicament, especially in rural areas. Gaskin et al. (2003) warn of the health problems associated with consuming water with a high nitrate content, such as methemoglobinemia which is commonly known as blue baby syndrome. Symptoms of this condition include a bluish tint on the skin, headaches, fatigue, seizures, vomiting, diarrhoea and difficulty breathing. Those who are susceptible include babies under the age of six months, the elderly and pregnant women.

Gaskin et al. (2003) further advise that U.S. EPA set a maximum nitrate contaminant level of 45 mg/L whilst drinking water standards in SA requires nitrate content to be less than 11 mg/L (Verlicchi & Grillini, 2020). The impacts of nitrate, as present in concrete leachate, are not well documented. This study investigates the nitrate content in leachate of conventional concrete, PMBA-concrete and WFS-concrete.

2.13.4 Relevant Factors Influencing Leachate Quality

The alkalinity of concrete is largely due to CH, however the more porous the concrete, the greater the water permeability, hence the more CH is leached out. In addition, the integration of pozzolana tends to reduce concrete pH due to pozzolanic reactions consuming a certain quantity of CH. Consequently, the leachate may exhibit reduced a pH value.

Ekström (2001), who performed an extensive investigation into the leaching of concrete, states that the main factor influencing leaching in concrete is the water permeability of concrete, which in turn largely depends on porosity (Figure 2.44 in Section 2.12.4 (A)). Accordingly, the leachate arising from less porous, more durable concrete is expected to experience a decreased ion content. In addition to water permeability, Halvorsen (1966) advises that the following factors influence leaching in concrete: the total amount of CH, the hardness of water, additives that are able to bind lime, the carbonation of CH and the amount of carbonic acid available to attack concrete. It may further be possible that fine material may reduce the occurrence of dissolved substances in concrete leachate due to the fine-filler effect.

2.13.5 Potential Influence of PMBA & WFS on Leachate Quality

(A). PMBA

In terms of the pH value of concrete, it is possible that PMBA may reduce the overall pH due to the consumption of CH during pozzolanic reactions. Accordingly, it is expected that the leachate would exhibit lower pH values. Contrariwise, the potential fine-filler effect of PMBA may reduce the amounts of CH that are leached out by containing paths of movement and reducing ion conductivity. This may preserve concrete pH.

Water permeability was noted as the main influence of leaching in concrete, which is largely influenced by porosity. As previously discussed, it is expected that PMBA will reduce porosity by the fine-filler effect, thereby reducing water permeability and decreasing ion conductivity and nitrate content of the leachate.

(B). WFS

The pH of UIS WFS was reported by Matebese (2020) to be 7.20, which is deemed to be twice as acidic as the pH value of river sand (Verma, 2015). It is possible that the difference in acidity may lead to a reduced pH value of WFS-concrete.

As mentioned in Section 2.12.5 (B), Mavroulidou & Lawrence (2018) observed that the introduction of WFS in concrete had led to a decreased water permeability, as a result of the filler effect. Naturally, a reduced water permeability may result in reductions in both ion conductivity and nitrate content of the leachate. It is also possible that the high presence of voids due to the poor grading may increase penetrability, resulting in greater ion conductivity and nitrate content in the leachate.

2.14 CHAPTER SUMMARY

This chapter provided the theoretical support which would allow for the interpretation of results as obtained in the experimental programme.

PMBA results from the combustion of PMS with bituminous coal, ash, bark and sawdust. This waste ash is not reminiscent of fly ash due to the difference in production processes. Accordingly, the properties of PMBA primarily depend on the content of PMS and combustion conditions (Johakimu et al., 2016). WFS results from sand moulds that have become unsuitable due to the repeated casting of metal. Key findings in this chapter relate to the differences between the properties of conventional materials and their respective test counterparts, and the influence of these properties on concrete.

Workability may improve with the integration of PMBA. The main properties of this waste ash that may achieve this are its hydrophilic nature and its spherical, glassy particles. However, its high specific surface, as compared to cement, may indicate that workability may be reduced as a result of fineness (Carlson et al., 1937; Popovics, 1992; ACAA, 2003). This was the case with PMS ash. Contrariwise, Fennis (2009) indicates that it is the fineness of the pozzolanic material that may improve workability due to the fine-filler effect, which fills voids, thereby reducing the water requirement. Accordingly, should PMBA improve workability, this may indicate that it behaves more like fly ash than PMS ash. Improvements in workability may also be observed in WFS-concrete. The properties of WFS that may be responsible for this are its reduced ability to absorb water as compared to conventional sand and the shapes of the WFS particles (cubical, sub-rounded and rounded). Past studies show an inconsistency when reporting the effects of WFS on workability. Some studies have shown that slump increases (Etxeberria et al., 2010; Pandey et al., 2015; Mavroulidou & Lawrence, 2019). Conversely, Khatib et al. (2010), Sowmya & Chaitanya Kumar (2015) and Jadhav et al. (2017) have reported that slump decreases with greater amounts of WFS.

Density may show improvements due to PMBA. This is due to the fine-filler effect, which was reported as one of the main properties exhibited by pozzolanic materials that allows them to enhance concrete properties (Newman & Choo, 2003; Mehta & Monteiro, 2006; Walker & Pavia, 2010). Alternatively, it was found that PMBA showed a lower RD value than cement, indicating that density may decrease indefinitely or at greater contents of PMBA. It is possible that WFS may improve concrete density as it exhibits a greater density than conventional fine aggregate. Conversely, a reduction in density may be observed as poor gradation may cause voids. Additionally, Iloh (2018) advised that certain binding agents in WFS may reduce density.

Mechanical strengths may improve with inclusions of PMBA. This may be due to its high fineness and highly amorphous constitution (especially SiO_2) which both improves pozzolanic reactivity and strength development. The fine-filler effect may also strengthen the ITZ, leading to reduced crack propagation, Additionally, the consumption of CH to create C-S-H will improve strength. Decreases in compressive strength may be observed as the content of PMBA increases. This may be due to its relatively higher LOI and SO_3 contents as compared to cement. Mechanical strengths may decrease with inclusions of WFS. This may be due to its poor gradation (which results in strength-reducing voids) and its particle shapes (sub-rounded and cubicle).

Durability, as assessed by OPI, WS and CC, may be improved with inclusions of PMBA. This is based on the findings of Ballim et al., (2009) who found that fly ash improved durability. This is likely due to the fine-filler effect of pozzolana, whereby concrete penetrability is reduced. PMBA may exert the same influence on durability. WFS may reduce durability by the creation of voids due its poor grading, facilitating the transport of deleterious substances into concrete. Alternatively, improvements in durability may be noticed due to the filler effect as witnessed by Mavroulidou & Lawrence (2018).

The pH value of concrete may be reduced due to the consumption of CH during pozzolanic reactions. This may indicate a less basic leachate and a reduced ability for concrete to maintain the passivation layer. However, it was reported that it is unlikely for the consumption of CH to result in the breakdown of the passivation layer as Mehta & Monteiro (2006) inform that adequate quantities of CH remain to keep pH above 11. WFS was reported to be twice as acidic as river sand, suggesting a possible reduction in pH value at greater replacements. Ion conductivity and nitrate content may see a decrease with the integration of PMBA. This may occur due to the fine-filler effect which may reduce concrete penetrability, thereby decreasing the content of substances that may leach out. It is possible that WFS may have the opposite effect, whereby the presence of voids increases penetrability, resulting in increased ion conductivity and nitrate content. Contrariwise, ion conductivity and nitrate content may see a reduction with WFS as a result of the filler effect reported by Mavroulidou & Lawrence (2018).

The next chapter discusses the methodology, provides the material properties, discusses the concrete mix design procedure and describes all testing procedures involved.

3. CHAPTER THREE: METHODOLOGY

3.1 INTRODUCTION

This study implements pre-determined quantities of PMBA in incremental additions, to produce PMBA-concrete. The same logic was applied to produce WFS-concrete. Several authors, such as Bajpai (2015), noted that the oxide contents in PMBA resembled the desired oxide contents in cement. Accordingly, it was decided that PMBA will serve as a cementitious material whilst the sandy test material will serve as a fine aggregate replacement for coherence. To assess and understand the influence of PMBA and WFS on their respective concrete properties, the methodological approach is designed to consist of two main sub-approaches – the literature review and the experimentation programme (Figure 3.1). In order to study the effectiveness of PMBA and WFS as partial replacements to cement and fine aggregate respectively, reviews of materials of interest, with their known influences on concrete, are required. To this end, the literature review in Chapter 2 provides an analysis of the following:

- The properties of Portland cement and fine aggregate and the ways in which said properties influence conventional concrete.
- The properties of each test material and how these properties compare with those of the materials being replaced, and how each test material may potentially influence concrete, based on both their own inherent properties and past study results.

The experimentation programme serves as a means to acquire the necessary raw data via laboratory testing. The raw data is refined into results and presented in graphical form. The knowledge gained from the literature review will allow for the interpretation of said results. The relevant information and testing standards, where applicable, have been provided and used in a South African context as this waste-reuse initiative occurs in a capacity that pertains to SA. As laid out in Table 3.8 in Section 3.4, the control concrete samples and all test concrete samples are subjected to various standard concrete tests to assess performance. The results from the test concrete samples are then compared with the results from the control concrete samples.

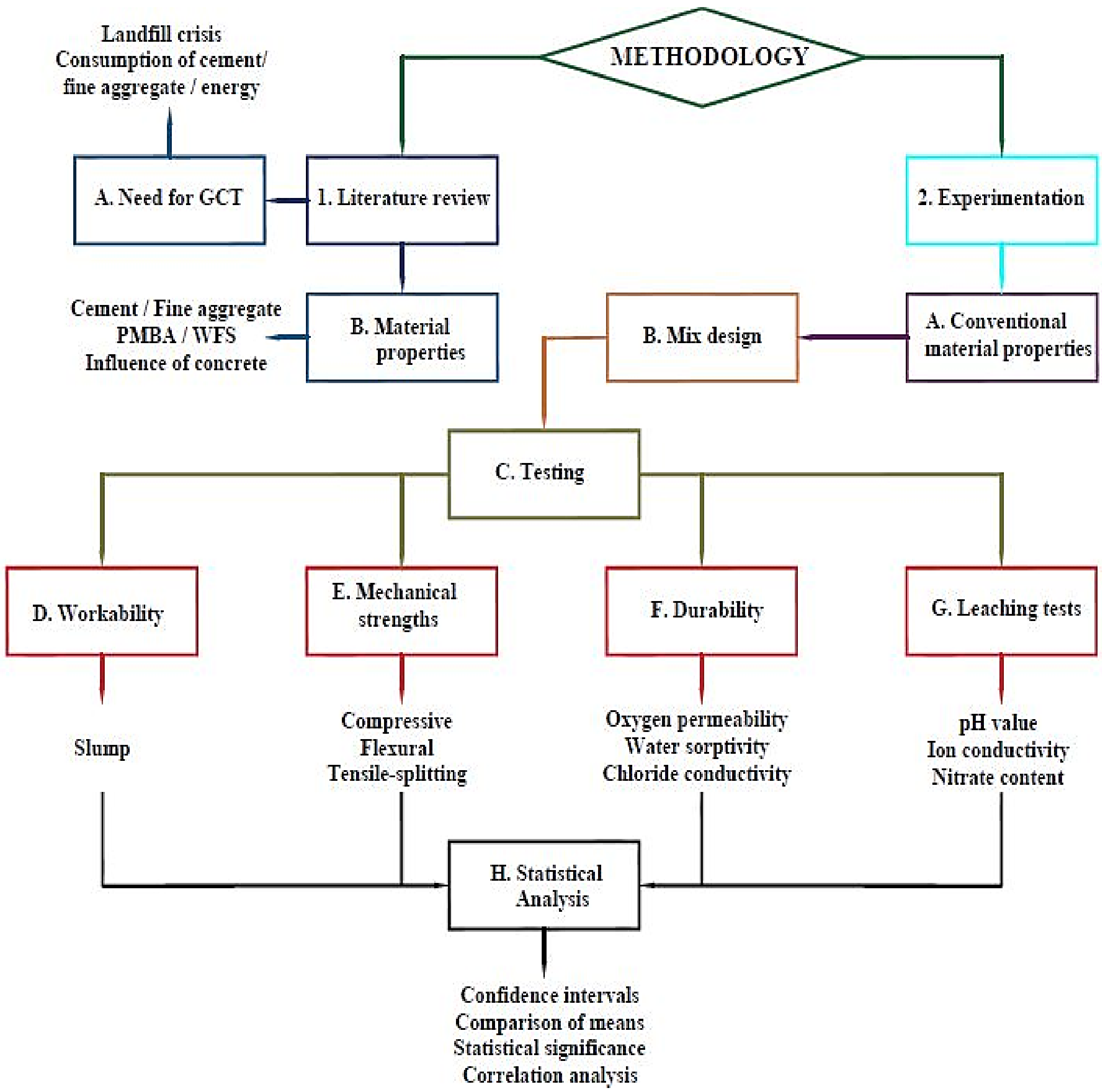


Figure 3.1: *Schematic of the fundamental research methodology*

3.2 MATERIALS

The term 'conventional concrete materials' will be used to refer to traditional concreting materials, which being Portland cement, aggregates, and potable water. In order to accurately assess the influence of PMBA and WFS on their respective concrete properties, the same conventional concrete materials were used throughout the experiment and no admixtures were used.

3.2.1 PMBA

PMBA was obtained from Mondi Merebank, situated on Travancore Drive, Merebank. The properties of PMBA produced at Mondi Merebank, as provided by Byiringiro (2014), are tabulated in Section 2.5.5.2. Figure 3.2 below shows a sample of PMBA as used in this study.

Figure 3.2: *A sample of PMBA as used in this study*

3.2.2 WFS

WFS was provided by UIS, located on Sea Cow Lake Road, Umgeni. The properties of said material, as tabulated in Section 2.7.5, were provided by UIS metallurgist, Mr. X. Matebese. Figure 3.3 below shows a sample of WFS as used in this study.

Figure 3.3: *A sample of WFS as used in this study*

3.2.3 Cement

As mentioned, Portland-Slag cement, CEM II/B-S 42.5 N plus, was employed as the conventional binding material in this research as it is readily available and widely used at UKZN. This is a common cement (i.e., non-masonry cement) and so is in accordance with SANS 50197-1 (The Concrete Institute, 2013). Moreover, this cement is produced with ground granulated blast furnace slag (GGBS) as an extender and so, is in accordance with SANS 55167-1 (The Concrete Institute, 2013). The cement sample used exhibited an RD value of 3.1.

Figure 3.4 below presents the cement used in this study whilst Table 3.1 provides a breakdown of the cement code.

Figure 3.4: *Portland-slag cement as used in this study*

__Table 3.1:__ Breakdown of Portland-Slag cement code (Source: The Concrete Institute, 2013)

Code:	**CEM II**	**B**	**S**	**42.5**	**N**
Description:	Common composite cement	Amount of extender: medium (21 to 35 %)	Type of extender: Slag	Strength class	Early age strength gain: Normal

In SA, this particular cement is commonly known as NPC original – Black and is widely used for civil engineering works involving general purpose applications. As per specifications provided by Natal Portland Cement (NPC) and InterCement South Africa, this cement exhibits the specifications as tabulated below.

__Table 3.2:__ Specifications of CEM II/B-S 42.5 N Plus cement (Source: InterCement South Africa, 2017)

Property	**Typical result**	**Specification requirement**
Setting time (minutes)	135	60 (minimum)
Soundness – Le Chatelier Expansion (mm)	1	10 (maximum)
Typical compressive strengths (MPa)		
2 Days	± 21	10 (minimum)
7 Days	-	No requirement
28 Days	± 50	≤ 62.5
Relative density	3.07	No requirement

3.2.4 Aggregates

Nineteen mm tillite stone was obtained from Flanders quarry in Canelands, KZN. This particular stone had an RD of 2.65, LBD of 1360 kg/m^3, and a CBD of 1446 kg/m^3. Density testing was done by the technical staff at the UKZN heavy structures laboratory whilst the FM value of the stone was provided by the quarry.

Umgeni river sand, procured by UKZN, served as fine aggregate. This sand displayed a FM of 3.40, RD of 2.65, LBD of 1320 kg/m^3 and a CBD of 1400 kg/m^3. Density testing was done by the technical staff at the UKZN heavy structures laboratory whilst FM was assessed using the sieve analysis method.

Both fine and coarse aggregates were air-dried prior to mixing. Figure 3.5 below shows samples of both the course and fine aggregates as used in this study.

Figure 3.5: *Aggregates used in this study – (A). Tillite stone coarse aggregate & (B). Umgeni river fine aggregate*

3.2.5 Potable Water

Ordinary tap water was used in this research. Care was taken to ensure all carrying containers were clean and free from impurities and that the hosepipe used was kept in a clean area so as to not contaminate the output end.

3.3 MATERIAL PROPORTIONING

The Cement & Concrete Institute (C & CI) mix design method is a South African concrete mix proportioning method, as based on the ACI Standard 211.1-91 (The Concrete Institute, 2013).

The following steps summarises the aforementioned mix design method as employed in this study:

- Selection of the W/B based on cement type.
- Selection of the water content based on the nominal stone size.
- Determination of the cement content using equation 3.2.
- Determination of the stone content using equation 3.3.
- Determination of the sand content based on the absolute volume and the quantities of water, cement and stone. This is followed by the conversion of the sand content from L to kg/m^3 by using the RD of sand.
- Adjustment of the mix based on the volume of control concrete samples required to be constructed.
- Design of the test mixes based on substitutions by mass.

This design process, as illustrated in Figure 3.6 below, involved applying the C & CI method to first determine the control concrete quantities, after which the test concrete quantities were obtained by determining 5, 10, 15 and 20 percent, by mass, of the replaced material. The incremental order of five was utilised as it is:

- Present in several related and unrelated GCT studies, such as in the works of Corinaldesi et al. (2010), Sowmya & Chaitanya-Kumar (2015), Srinivasan & Sathiya (2010) etc., and it is;
- Evident, based on past studies, that such an incremental order allows for the presence of sufficient enough quantities of test material to significantly influence concrete properties to provide passably clear results whilst being conservative in materials usage.

The control sample was conventional concrete and so consisted of zero percent test material. The subsequent samples with tests materials are called test samples. The specified slump for the control mix was 75 mm. The concrete mix quantities are presented in Table 3.7 in Section 3.3.8. All mix quantities were designed to account for the number of cubes, beams and cylinders that were necessary to comply with the required number of samples as stipulated in the respective SANS codes for strength and durability testing. Two separate mix sets were formulated in order to produce concrete arising from PMBA and concrete arising from WFS.

In order to cater for spillage and other losses, a 15 percent allowance was incorporated into the mix design. In total, nine mixes were designed – control, the PMBA mix set (5%PMBA, 10%PMBA, 15%PMBA, 20%PMBA) and the WFS mix set (5%WFS, 10%WFS, 15%WFS and 20%WFS).

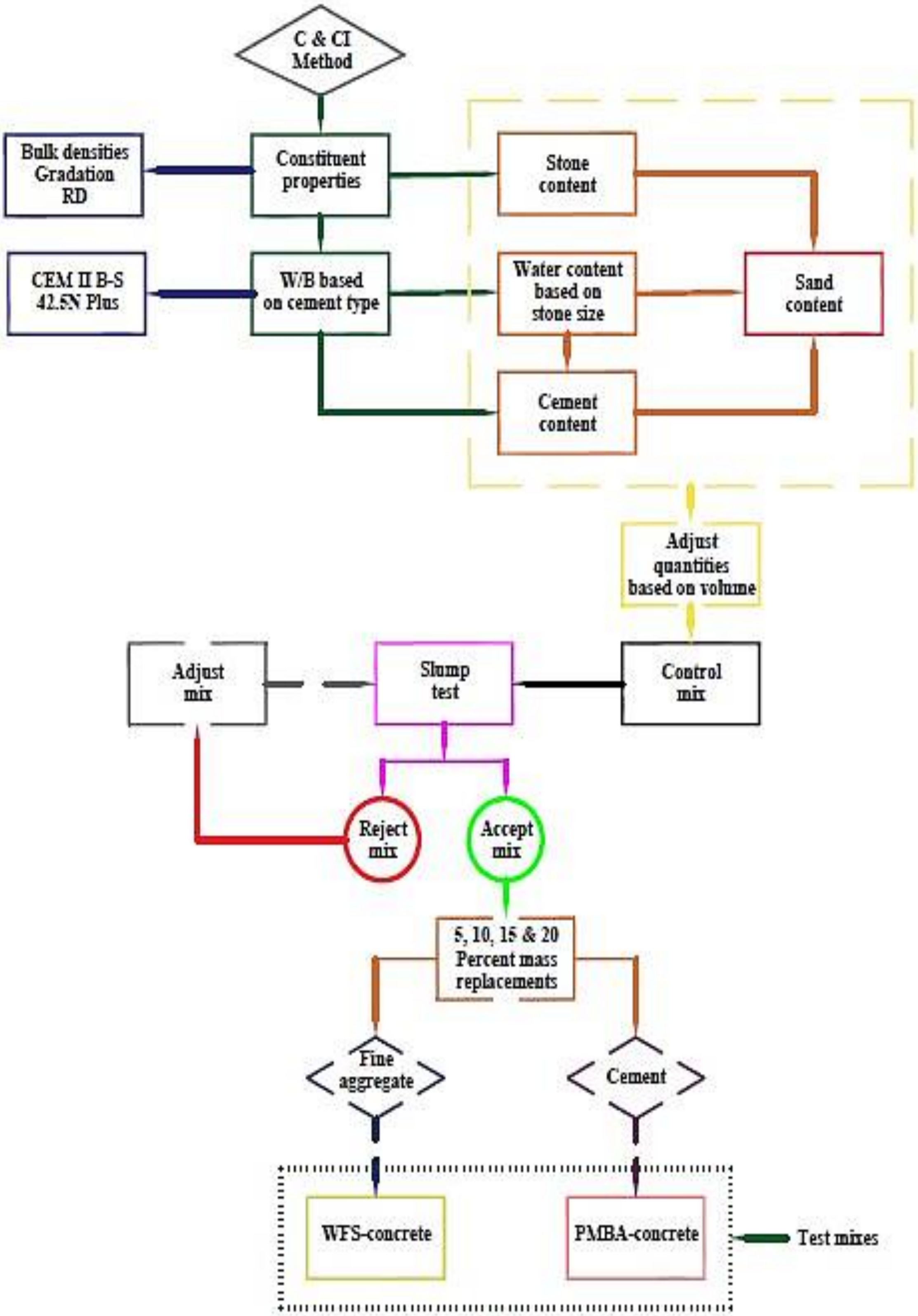


Figure 3.6: *C & CI concrete mix design method as employed in this study*

3.3.1 Properties of Conventional Constituents

In order to initiate the mix design process, the properties of conventional concrete constituents are to be determined. These properties include the RD values of cement and aggregates, the CBD and LBD of aggregates and the FM of fine aggregate. All values, with the exception of FM of the fine aggregate, were provided by the technical staff at the UKZN heavy structures laboratory.

(A). FM

FM is assessed by the sieve analysis procedure and indicates the fineness of aggregate. It is required in the C & CI design method to obtain the content of stone. The FM values of the Umgeni river sand and UIS WFS were determined using the standard B13 TMH1 method, as appearing in CSIR (1986). As per the aforementioned method, the FM is determined as per equation 3.1 below.

$$FM = \Sigma \text{ (Cumulative percentage retained)} \times 0.01 \qquad (3.1)$$

Umgeni river sand exhibited a FM of 3.4 whilst WFS showed a FM of 3.3. The detailed sets of results are presented in Section 4.2. Figure 3.7 below displays the standard set of sieves and the mass balance that was used in the determination of each FM values.

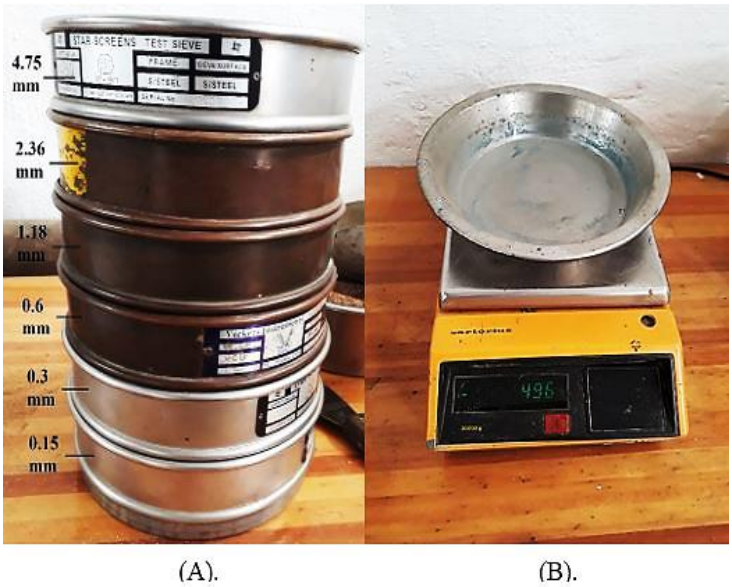


Figure 3.7: *(A). Sieve analysis equipment & (B). Mass scale*

(B). Densities: RD, CBD & LBD

Density values, namely RD, CBD and LBD, for cement and aggregates were either provided by the technical staff at the UKZN heavy structures laboratory or by the respective material supplier. The following Table presents these values as received. As per the C & CI method, the CBD and LBD values for cement are not required and so have not been determined.

Table 3.3: *Constituent density values as provided by the UKZN heavy structures laboratory*

Material	Property		
	RD	**CBD (kg/m^3)**	**LBD (kg/m^3)**
Cement	3.1	Not required for C & CI method	
Stone	2.65	1446	1360
Sand	2.65	1400	1320

3.3.2 Water-Binder Ratio (W/B)

This study primarily aims to determine the properties of PMBA-concrete and WFS-concrete relative to conventional concrete. For this reason, achieving a particular target strength or assessing varying W/B values or cement types were not given traditional priority. By using Figure 3.8, and based on cement type CEM II B-S 42.5N Plus, a W/B ratio of 0.53 was selected. By referring to the work of Addis & Owens (2011), Naicker advises that W/B ratios should range from 0.45 to 0.80.

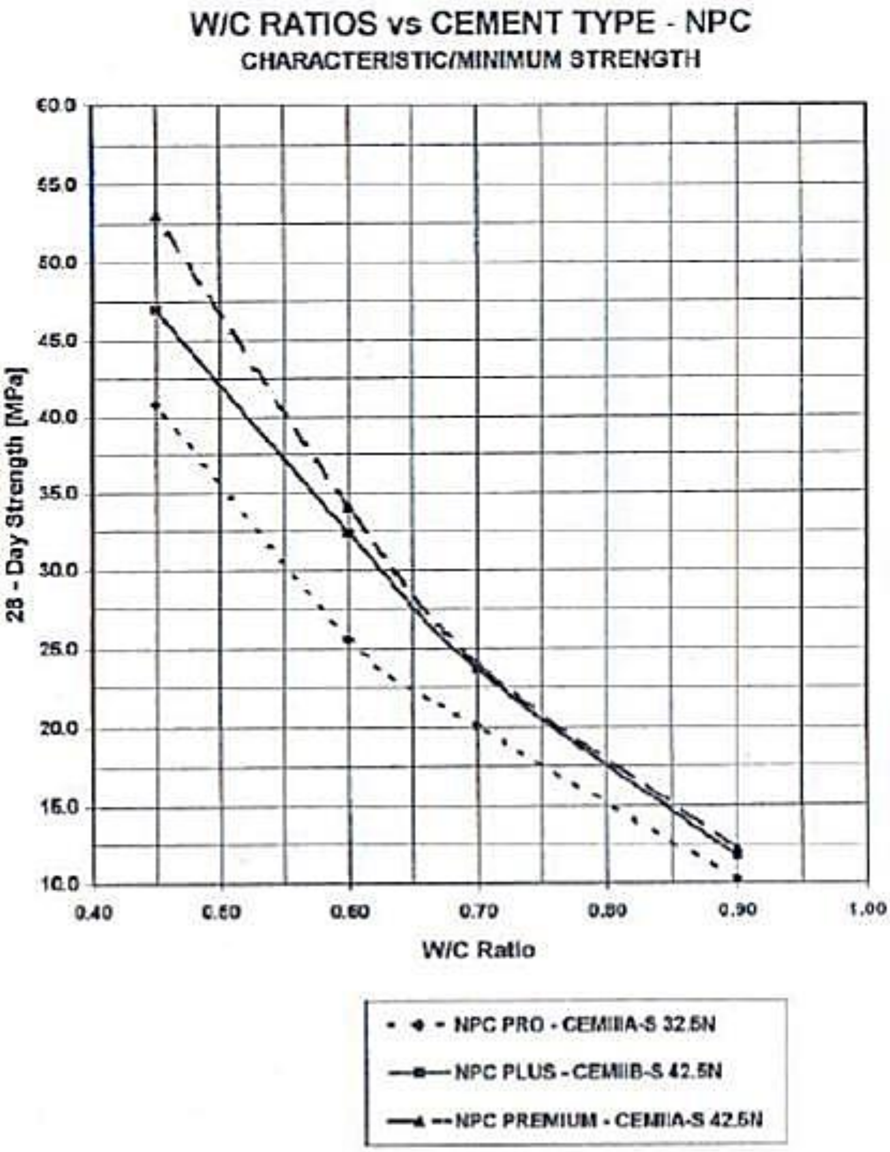


Figure 3.8: *W/B ratios VS 28-day strength (UKZN, 2009)*

3.3.3 Water Content (W)

The water content required is based on the nominal size of stone used. This study employed 19 mm stone. As presented in Table 3.4, the water content selected is 210 L/m^3.

Table 3.4: *Selection of water requirement based on nominal stone size (UKZN, 2009)*

Nominal stone size (mm)	Water requirement (L/m^3)
9.5	235
13.2	225
19.0	210
26.5	200
37.5	190

In order to accurately assess the properties of PMBA-concrete and WFS-concrete, the water content was kept constant for both the control and all test mixes. The influence each test material has on the water requirement was investigated by the slump test.

3.3.4 Cement Content (C)

The cement content required is computed by the manipulation of the W/B ratio, whereby cement required is determined using the following equation:

$$C = W \div \frac{W}{B} \tag{3.2}$$

Where, C = cement content (L/m^3)

W = water content (L/m^3)

$\frac{W}{B}$ = water-binder ratio

As discussed, it is the cement content that is partially replaced in increments of 5, 10, 15 and 20 percent by mass, with PMBA to produce PMBA-concrete.

3.3.5 Stone Content (St)

The content of stone is determined using the following equation:

$$St = CBD_{st} \times (k - 0.1FM) \tag{3.3}$$

Where, St = stone content (kg/m^3)

CBD_{st} = compacted bulk density of stone (kg/m^3)

k = factor based on degree of compaction (Table 3.5)

FM = fineness modulus of sand

The CBD value of stone was provided by the technical staff at UKZN. The k factor is determined using Table 3.5 below. In order to compact fresh concrete, a vibrating table was used. As per the UKZN guideline for the C & CI method, this method of vibration entails moderate vibration, which gave a k factor of 1.00. Sieve analysis was employed to determine the FM of sand, which was discussed in Section 3.3.1. Throughout the experimental programme, the content of stone was kept constant.

Table 3.5: *Values of k factors for the determination of stone content (UKZN, 2009)*

Stone size	**k Values**		
	Hand compaction	**Moderate vibration**	**Heavy vibration**
9.5	0.75	0.80	1.00
13.2	0.84	0.90	1.05
19.0	0.94	1.00	1.05
26.5	1.00	1.06	1.10

3.3.6 Sand Content (Sc)

The C & CI method prescribes that the sum of all conventional materials, in L, is to be approximately 1000 L. Accordingly, the sand content, in L, was determined as the sum of the contents of water, cement and stone in L, subtracted from 1000 L. As per equation 3.4, the sand content is then converted to kg/m^3 by multiplying by the RD of sand.

$$Sc = [1000 - (\frac{C}{RD_C} + \frac{St}{RD_{St}} + W)] \times RD_{sc} \qquad (3.4)$$

Where, Sc = sand content (kg/m^3)

C = cement content (L/m^3)

RD_c = relative density of cement

St = stone content (L/m^3)

RD_{st} = relative density of stone

W = water content (L/m^3)

RD_{sc} = relative density of sand

3.3.7 Lab Mix & Adjusted Mix

Four control mixes are computed, with mix 1 having 10 more litres of water than mix 2, which in turn has 10 more litres of water than mix 3 and so on. This is done to achieve the specified slump should the observed slump not be within the limits as stipulated in Table 2.34 in Section 2.9. In order to prepare the quantities obtained for use in the laboratory, the constituent quantities are multiplied by a mix factor as required to produce the necessary volume of concrete. This factor is shown below.

Concrete samples underwent testing at the curing ages of 7 and 28-days, where each test required six samples for both testing ages. In addition, 15 percent of the total volume was added for losses such as spillage. Thus, the following volume is applied to quantities, in kg/m^3, to construct the necessary number of samples as indicated by SANS 5863, SANS 5864 and SANS 6253:

$$\text{Volume per mix} = (6V_{cube} + 6V_{beam} + 6V_{cylinder}) \times (1.15)$$

$$= [6\,(0.15^3) + 6\,(0.1 \times 0.1 \times 0.5) + 6\,(\pi \times (0.075)^2 \times 0.3)] \times 1.15$$

$$= 0.094 \text{ m}^3$$

As an example, the following mix factor is applied to quantities in mix 4, in kg/m^3, to produce mix 4 in the laboratory, in kg. The information pertaining to the samples constructed is presented in Table 3.6 below.

$$\text{Mix factor for mix 4} = \text{Volume per mix} \times \left(\frac{\text{Water content for mix 1}}{\text{Water content for mix 4}}\right)$$

Table 3.6: *Sample details*

Mix ID	**Number of samples constructed**		
	Cubes	**Beams**	**Cylinders**
Control	6	6	6
5%PMBA	6	6	6
10%PMBA	6	6	6
15%PMBA	6	6	6
20%PMBA	6	6	6
5%WFS	6	6	6
10%WFS	6	6	6
15%WFS	6	6	6
20%WFS	6	6	6

Sample dimensions (mm)		
Cube	Beam	Cylinder
150 × 150 × 150	100 × 100 × 500	150Ø × 300

Constituent quantities for lab mix 1 are finalised, weighed on an appropriate mass scale (Figure 3.9A) and mixed using a rotating drum mixer (Figure 3.9B). The mix then undergoes the slump test, as detailed in Section 3.4.1, and is accepted provided that slump be within limits. If the mix exhibits an unacceptable slump, aggregate is added so as to create mix 2 and so on, until an appropriate slump is formed. All moulds are oiled with ordinary engine oil to facilitate concrete removal (Figure 3.10A). Fresh concrete is placed into the appropriate moulds (Figure 3.10B), compacted using a vibrating table and left to set (Figure 3.10C). Demoulding occurred after 24 hours. Hardened samples are marked with the appropriate mix ID using waterproof chalk. All samples are placed into curing tanks to initiate the curing process. As per standard concrete testing protocol, concrete samples were cured for 7 and 28-days at a controlled temperature.

(A). (B).

Figure 3.9: *Concrete mixing apparatus - (A). Mass scale & (B). Rotating drum mixer*

(A). (B).

(C). (D).

Figure 3.10: *(A). Mould lubricating oil, (B). Cube, beam and cylinder moulds, (C). Samples in moulds & (D). Demoulded samples submerged in the curing tank*

3.3.8 Test Mixes

The accepted mix discussed in Section 3.3.7 becomes the control mix, which is then used to obtain the quantities of the test mixes. Two sets of test mixes were investigated, with one arising from PMBA partially replacing cement and the other from WFS partially replacing fine aggregate.

Partial replacements for both mixes occurred at 5, 10, 15 and 20 percent by mass of the material being replaced. The use of these replacements was justified in Section 3.3. Once the control mix was accepted, the quantities of PMBA and WFS were obtained by applying the abovementioned percentage replacement order to cement and fine aggregate respectively. Both the water and stone contents were kept constant throughout both mixes. Table 3.7 below presents the quantities for the control and both test mix sets. The mix ID given in Table 3.7 describe the percentage of material replaced. For example, 5%PMBA signifies that 5 percent of cement was replaced with PMBA and 5%WFS indicates that 5 percent of fine aggregate was replaced with WFS.

Table 3.7: *Constituent quantities for the control and test concrete mixes*

Mix ID	**Material (kg)**				
	Coarse aggregate	**Fine aggregate**	**Water**	**Cement**	**PMBA**
Control	103	86	23	43	0
5%PMBA	103	86	23	41	2
10%PMBA	103	86	23	39	4
15%PMBA	103	86	23	37	6
20%PMBA	103	86	23	34	9
Mix ID	**Material (kg)**				
	Coarse aggregate	**Fine aggregate**	**Water**	**Cement**	**WFS**
5%WFS	103	82	23	43	4
10%WFS	103	77	23	43	9
15%WFS	103	73	23	43	13
20%WFS	103	69	23	43	17

3.4 EXPERIMENTATION PROGRAMME

The experimentation programme is developed to adhere to, where applicable, standards set out in the South African National Standards (SANS). The durability index testing was carried out by Contest Laboratories (PTY) Ltd whilst all other testing had been performed at the heavy structures laboratory and the environmental engineering laboratory at UKZN.

Table 3.8: *Breakdown of experimentation programme*

Procedure	Description	Standard	Testing age (day)
Slump test	Workability	SANS 5862-1:2006	Casting day
SHD	Intrinsic property	SANS 6251:2006	28
Compressive strength test	Mechanical strengths	SANS 5863:2006	7 and 28
Flexural strength test		SANS 5864:2006	7 and 28
Tensile-splitting strength test		SANS 6253:2006	7 and 28
OPI	DI tests	SANS 3001-CO3-2:2015	> 28
WS[1]		-	
CC		SANS 3001-CO3-3:2015	
pH Value test	Steel protection (pH) / Leachate quality	Variation of ASTM D 3987	> 7
Ion conductivity test			
Nitrate content test			

[1]The WS test is yet to be formalised through SABS

3.4.1 Workability – Slump Test

The slump test was conducted in accordance with SANS 5862-1:2006. Figure 3.11 illustrates the basic apparatus required to conduct the slump test. Figure 3.12 shows the specifications of the slump test equipment whilst Figure 3.13 demonstrates how the slump test is carried out. The slump specified for the control mix was 75 mm. Equation 3.5 explains the determination of slump.

$$\text{Slump} = \text{height of slump mould} - \text{height of slumped sample} \tag{3.5}$$

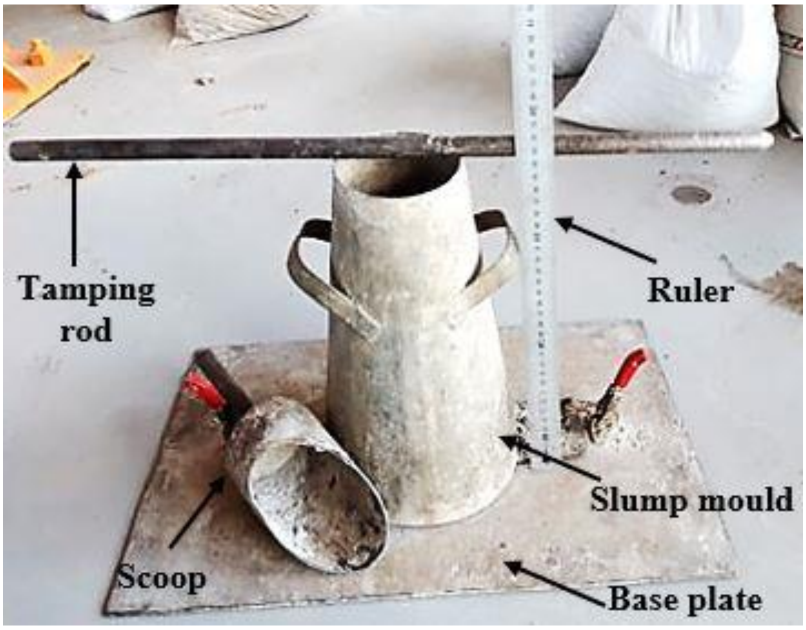


Figure 3.11: *Slump test apparatus*

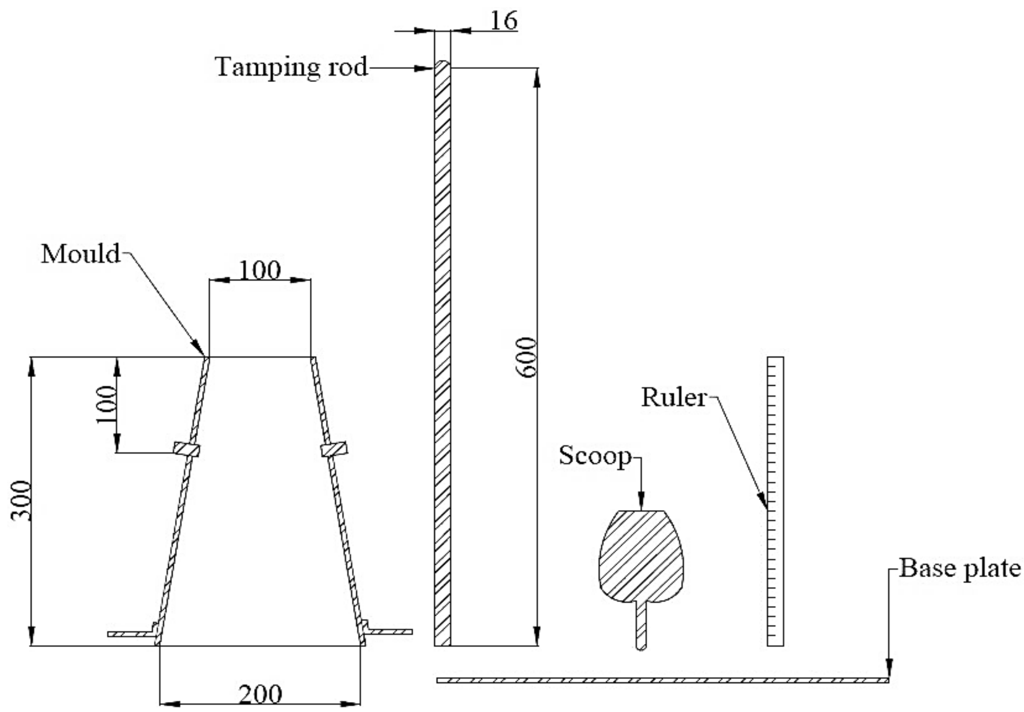


Figure 3.12: *Specifications for the slump test apparatus*

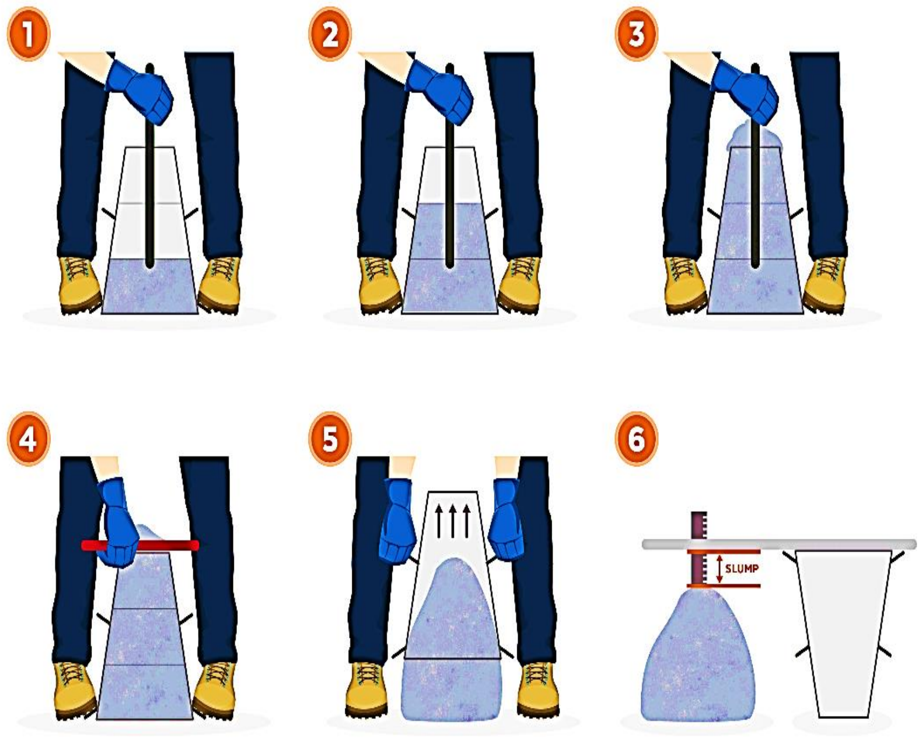


Figure 3.13: *Illustration of the slump test procedure (totalconcrete.co.uk)*

3.4.2 SHD Test

The test for SHD was conducted in accordance with SANS 6251:2006. Accordingly, SHD is computed, to the nearest 10 kg/m^3, by the following equation:

$$\rho_c = \frac{m}{v} \tag{3.6}$$

Where, ρ_c = SHD (kg/m^3)

m = mass of saturated sample (kg)

v = volume of saturated sample (m^3)

As per SANS 6251:2006, for each mix, three concrete cubes are tested and averaged density values are obtained. Figure 3.14 exhibits the mass scale used in the determination of SHD.

Figure 3.14: *Mass scale used in the computation of SHD*

3.4.3 Compressive Strength Test

The compressive strength testing was conducted as detailed in SANS 5863:2006. Accordingly, the compressive strength is computed as follows:

$$f_{cc} = \frac{F_c}{A_{cc}} \tag{3.7}$$

Where, f_{cc} = compressive strength (MPa)

F_c = maximum compressive load at failure (N)

A_{cc} = cross-sectional area of concrete cube on which F_c acts (mm^2)

A total of three cubes are required to produce three strength values and the average strength is determined. The average strength, as rounded to the nearest 0.5 MPa, serves as the final strength for the test. As required by SANS 5863:2006, compressive strength testing occurred at 7 and 28-days and the corresponding average strengths are determined. In this investigation, the averaged value for the 7-day test will serve as the seventh day compressive strength (f_{cc7}) and the averaged value for the 28-day test will serve as the twenty-eighth day compressive strength (f_{cc28}).

As per the aforementioned standard, there exists criteria whereby the averaged strength value is only deemed acceptable if the difference between the highest and lowest strength values do not exceed 15% of the averaged value. This acceptability check is presented in Appendix G. Figure 3.15 shows the apparatus for compression testing as used in this investigation.

Figure 3.15: *Compressive strength test machine as used in this study*

3.4.4 Flexural Strength Test

The flexural strength testing was executed as per SANS 5864:2006. Accordingly, the flexural strength is determined as per equation 3.8 below:

$$f_{cf} = \frac{F_f l}{bd^2} \tag{3.8}$$

Where, f_{cf} = flexural strength (MPa)

F_f = maximum two-point compressive load at failure (N)

l = length between axes of supporting rollers (mm)

b = width of sample (mm)

d = depth of sample (mm)

Similar to the compressive strength test, the averaged strength value for the 7-day test will serve as the seventh day flexural strength (f_{cf7}) and the averaged value for the 28-day day test will serve as the twenty-eighth day flexural strength (f_{cf28}). As per SANS 5864, the acceptability criteria, as stated in Section 3.4.3 applies. The assessment of this criteria is presented in Appendix G.

Figure 3.16 illustrates the arrangement of the two-point flexural strength test. Figure 3.17 shows the apparatus with a sample at failure.

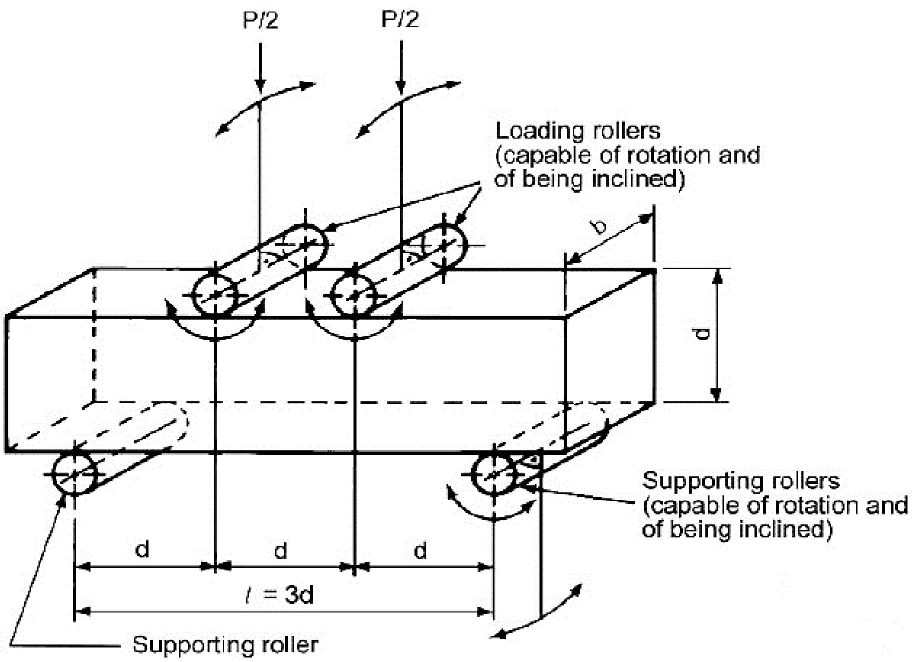


Figure 3.16: *Arrangement of the flexural two-point load test (SANS 5864, 2006)*

Figure 3.17: *Two-point flexural strength test apparatus with a sample at failure*

3.4.5 Tensile-splitting Strength Test

The tensile-splitting strength testing was conducted as detailed in SANS 6253:2006. Accordingly, the tensile-splitting strength is computed as follows:

$$f_{ct} = \frac{2F_t}{\pi l d} \tag{3.9}$$

Where, f_{ct} = tensile-splitting strength (MPa)

F_t = maximum compressive load at failure (N)

l = length of sample (mm)

d = cross-sectional dimension of the sample (mm)

The determination of the seventh day tensile-splitting strength (f_{cf7}) and the twenty-eighth day tensile-splitting strength (f_{cf28}) is done as per Sections 3.4.3 and 3.4.4. The acceptability criteria, as stated in Section 3.4.3 applies and the assessment of this criteria is presented in Appendix G.

Figure 3.18 illustrates the arrangement of the tensile-splitting strength test. Figure 3.19 shows the apparatus as used in this study.

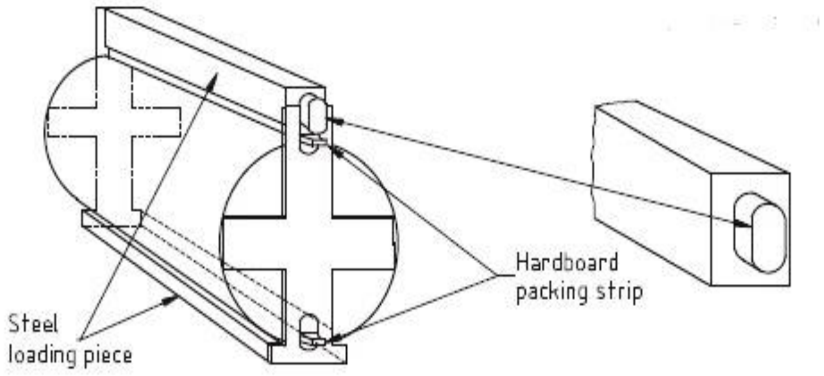


Figure 3.18: *Arrangement of the tensile-splitting strength test (SANS 6253, 2006)*

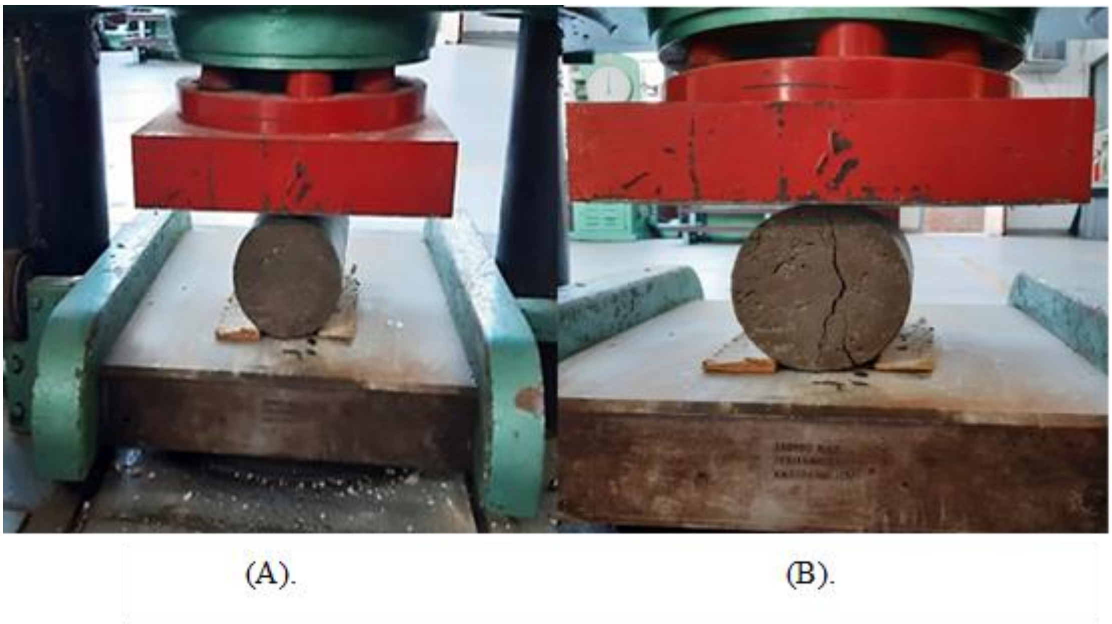


Figure 3.19: *Tensile-splitting strength test with (A). loaded sample & (B). failed sample*

3.4.6 Durability Tests

DI testing requires samples of a specific geometry, i.e., concrete discs of 70 mm (± 2 mm) diameter and 30 mm (± 2 mm) thick., which are created by coring though concrete cubes and cut into the specified geometry. Due to the unavailability of the specialized DI testing apparatus at UKZN, all phases of DI testing, including coring, were conducted by Contest (Pty) Ltd, situated in Westmead, KZN.

(A). OPI Test

The OPI testing was conducted as detailed in SANS 3001-CO3-2:2015. The OPI is determined, to two decimal places, as stipulated in equation 3.10 below. The OPI values for all four samples are determined and the recorded OPI becomes the average of all four OPI values. Figure 3.20 illustrates the arrangement of the permeability cell.

$$OPI_i = -\log_{10}(K_i) \tag{3.10}$$

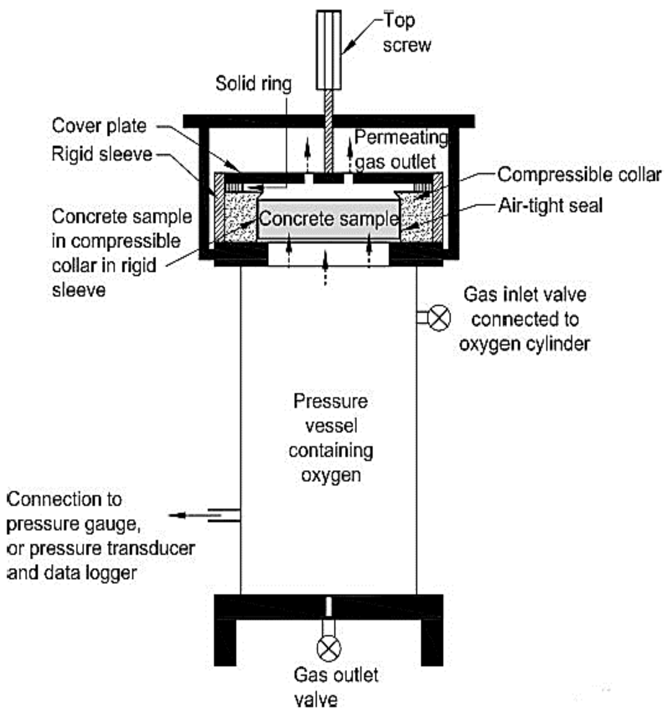


Figure 3.20: *Schematic showing the arrangement of the permeability cell (CoMSIRU, 2018)*

(B). WS Test

In considering that the WS test is yet to be formalized at the time of this investigation, the materials, apparatus and test procedure pertaining to this test will be discussed as below.

Test standard: To be formalized through SABS (CoMSIRU, 2018)

Materials: Four concrete discs (70 mm dia. ± 2 mm × 30 ± 2 mm thick) per test

Apparatus:

- Oven with a capacity to maintain 50° C (± 2° C)
- Vacuum saturation facility as arranged in Figure 3.21 below
- 20 mm deep stainless steel or plastic tray
- Absorbent paper towels arranged in ten layers
- Vernier caliper with the capacity to read to 0.02 mm
- Measuring sale with the accuracy to read to 0.01 g.
- Stopwatch
- Sealant
- Desiccator with a desiccant of anhydrous silica gel
- Tap water saturated with $Ca(OH)_2$ maintained at 23° C (± 2° C)

Procedure:

The samples as used in the OPI testing are immediately used in the WS tests. Paper towels are placed ten layers on the tray and saturated with water such that water is visible on the top surface. Calcium hydroxide is poured into the tray and the final water level is required to be a maximum of 2 mm up the sides of the samples. The sides of the samples are sealed and the mass is recorded as the dry mass (Ms_0). The samples are then placed with the test face down onto the wet paper and the stopwatch is started at time t_0. The samples are weighed at 3, 5, 7, 9, 12, 16, 20 and 25 minutes. The samples are then removed and the mass is recorded within 10 seconds of removal. The samples are placed in a vacuum saturated tank under a vacuum of -75 to -80 kPa for 3 hours (± 15 minutes). The vacuum saturated tank is then isolated and the water saturated with $Ca(OH)_2$ is introduced into the system until the water level is 40 mm above the tops of the samples. A vacuum of between -75 to -80 kPa is applied for 1 hour (± 15 minutes), after which air is allowed to enter and the samples are soaked for 18 hours (± 1 hour). The samples are removed, dried to a saturated surface dry condition and the vacuum saturated masses (Ms_v) are recorded. The mass of water absorbed is determined as follows:

$$M_{wti} = Ms_t - Ms_0 \tag{3.11}$$

Where, M_{wti} = mass gain (g)

Ms_t = mass of sample at time, t (g)

Ms_0 = mass of sample at initial time, t_0 (g)

A plot of the mass of water absorbed against the square root of time is constructed. The slope of the line of best fit is determined as per equation 3.12. WS is then computed as per equation 3.13.

$$F = \frac{\Sigma(\sqrt{t_i} - T)(M_{wti} - \bar{M}_{wt})}{\Sigma(\sqrt{t_i} - T)^2} \tag{3.12}$$

Where, F = slope of line of best fit (g/$\sqrt{h}$)

M_{wti} = mass gain according to equation 3.14 (g)

t_i = time corresponding to reading mass gain, M_{wti} (hours)

$T = \frac{\Sigma\sqrt{t_i}}{n}$

$\bar{M}_{wt} = \frac{\Sigma Mwti}{n}$

n = number of data points

$$WS = \frac{Fd}{Msv - Ms0} \tag{3.13}$$

Where, WS = water sorptivity of sample (mm/$\sqrt{h}$)

F = slope of line of best fit as per equation 3.15 (g/$\sqrt{h}$)

d = average sample thickness recorded to the nearest 0.02 mm (mm)

Ms_v = vacuum saturated mass to recorded to the nearest 0.01 g (g)

Ms_0 = mass of sample at time t_0 recorded to the nearest 0.01 g (g)

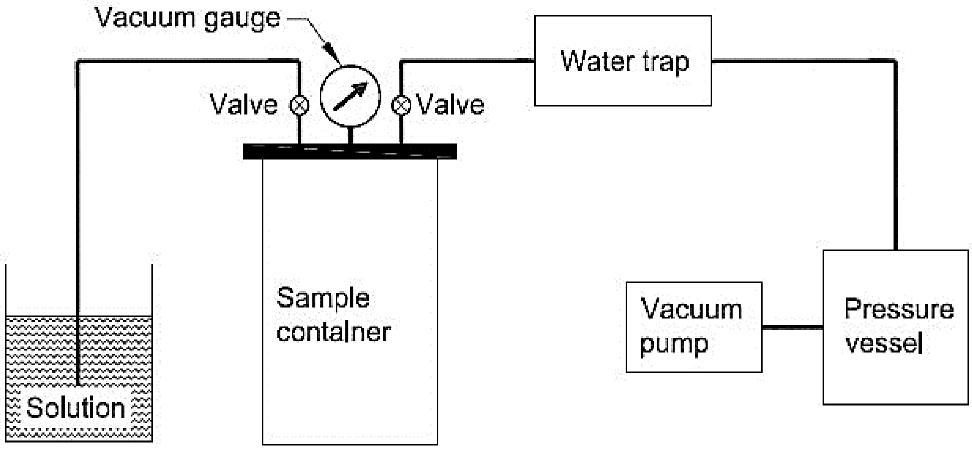


Figure 3.21: *Arrangement of vacuum saturation facility (CoMSIRU, 2018)*

(C). CC Test

The CC testing was conducted as detailed in SANS 3001-CO3-3:2015. Accordingly, CC is determined as follows:

$$\sigma = \frac{id}{VA} \tag{3.14}$$

Where, σ = chloride conductivity of the sample (mS/cm)

i = electric current (mA)

d = average thickness of sample (mm)

V = voltage difference (V)

A = cross-sectional area of sample (cm^2)

Figure 3.22 shows a schematic of the arrangement of the vacuum saturation facility.

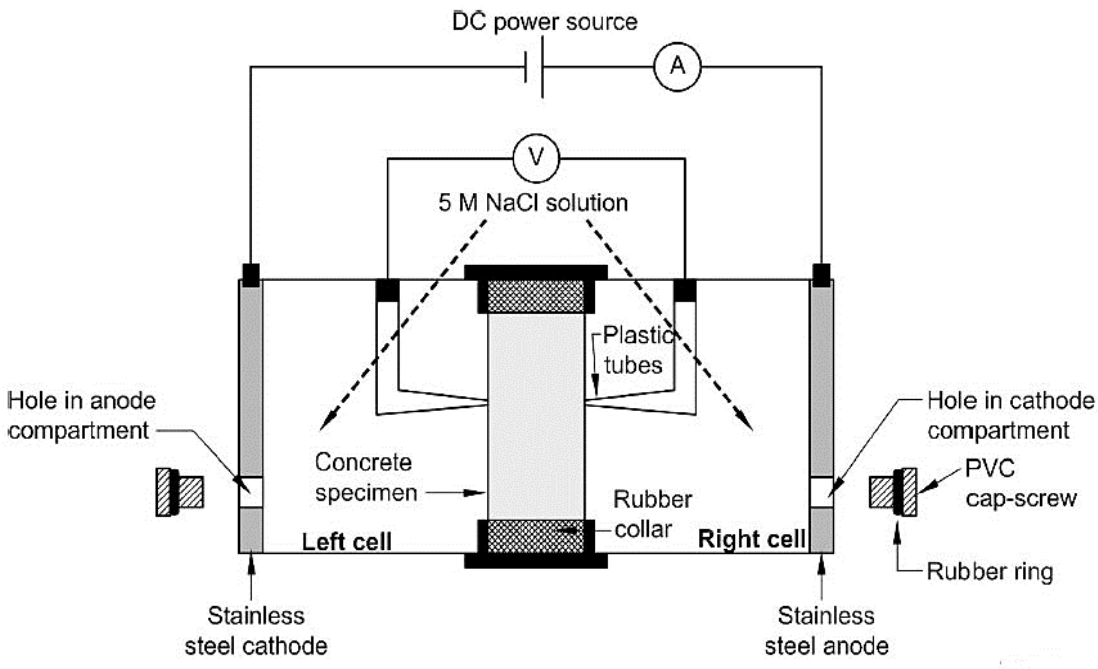


Figure 3.22: *Arrangement of the vacuum saturation facility (CoMSIRU, 2018)*

3.4.7 Leaching Tests

The leaching tests conducted in this investigation are a variation of the tests that are detailed in ASTM D 398. Accordingly, these tests are not formalized in SA. For this reason, the materials, apparatus and test procedure pertaining to this test will be discussed as below.

Test standard: Variation of ASTM D 3987

Material: One concrete cube per test

Apparatus:

- Hammer
- Oven capable of maintaining 130° C
- Sieve of size 300 µm
- Mass scale
- Digital scale
- Three crucibles
- Crucible tongs
- Laboratory spatula
- Measuring cylinder with a capacity of 1 L

- Funnel
- Three conical flasks, each with a capacity of 500 mL
- Stirrer plate and stirrer bar
- pH electrode, ion conductivity electrode and nitrate electrode with respective multimeters
- Squirt bottle with deionized water
- Tissue paper
- Cling wrap
- Plastic sheeting
- Three laboratory beakers, each with a capacity of 300 mL
- Cable ties
- Three closable containers
- Saline solution to store pH electrode

Procedure: The concrete sample is prepared by crushing and sieving to create fine powder. A standard 4-pound hammer is used to crush the cube and the resulting material is refined by into fine powder by passing through a 300 µm sieve. The process of crushing and sieving occurs until approximately 200 g of powdered concrete is produced. All three crucibles are handled with the crucible tong. The mass of each empty crucible ($M_{c)}$ is assessed on the digital scale and recorded. Using the laboratory spatula, approximately one to three scoops of powder is introduced into each crucible and the resulting mass is recorded as the wet mass of the sample including the crucible mass ($Ms_w + M_c$). Each crucible is then placed into the oven at a temperature of 130° C for 24 hours. The oven-dried mass is then recorded as the dry mass of the sample including the crucible mass ($Ms_d + M_c$). The wet mass (Ms_w) and the dry mass (Ms_d) of each sample is then determined by subtracting the respective crucible mass. The total solids content (TS) of each sample is then determined by the following equation:

$$TS = \frac{100M_{Sd}}{Ms_w} \tag{3.15}$$

Where, TS = total solids (%)

Ms_d = dry mass of sample (g)

Ms_w = wet mass of sample (%)

The TS values of all three powdered samples are determined and the average TS value, TS_{ave}, is computed and recorded. By using a representative sample of 100 g, equation 3.16 below is used to determine the total amount of sample for which 100 g is solid.

$$\frac{M_{T100}}{100} = \frac{100}{TS_{ave}} \tag{3.16}$$

Where, M_{T100} = total mass of sample for which 100 g is solid (g)

$TS_{ave} = \frac{TS_1+TS_2+TS_3}{3}$ (%)

By applying a ratio of 1 to 10 to indicate the ratio of sample used to the content of deionized water, i.e., 50 g of sample requires 500 mL of deionized water. However, the content of deionized water is to be reduced according to the content of moisture in the sample used. The equation to determine the amount of moisture in the total sample is as follows:

$$MS = M_{T100} - 100 \tag{3.17}$$

Where, MS = moisture in sample M_{T100} (mL)

M_{T100} = total mass of sample for which 100 g is solid (g)

A mass of 50 g of sample was introduced into each conical flask via a funnel. According to the 1 to 10 ratio discussed above, the corresponding content of deionized water should be 500 mL, from which the moisture in the sample is to be subtracted i.e., 500 – MS. This content of deionized water is filled in the measuring cylinder and poured into each conical flask. Each flask is then sealed with cling wrap, marked appropriately and fastened into the orbital shaker using cable ties. The samples were subjected to mixing in the orbital shaker and testing began at intervals of 24, 36 and 72 hours.

At the respective testing age, the contents of the conical flask are sieved into a container and the leachate is poured into a measuring beaker. All electrodes are gently washed with deionized water and patted down with tissue paper. The stirrer plate is placed under the respective electrode and the beaker containing the leachate is positioned on top of the stirrer plate. The stirrer bar is placed into the beaker and the stirrer plate is turned on. Each electrode is placed into the beaker and the pH value, ion conductivity and nitrate contents are assessed three times, with the electrodes being washed and wiped before and after each use. After testing, care was taken to submerge the tip of the pH electrode into the storage saline solution.

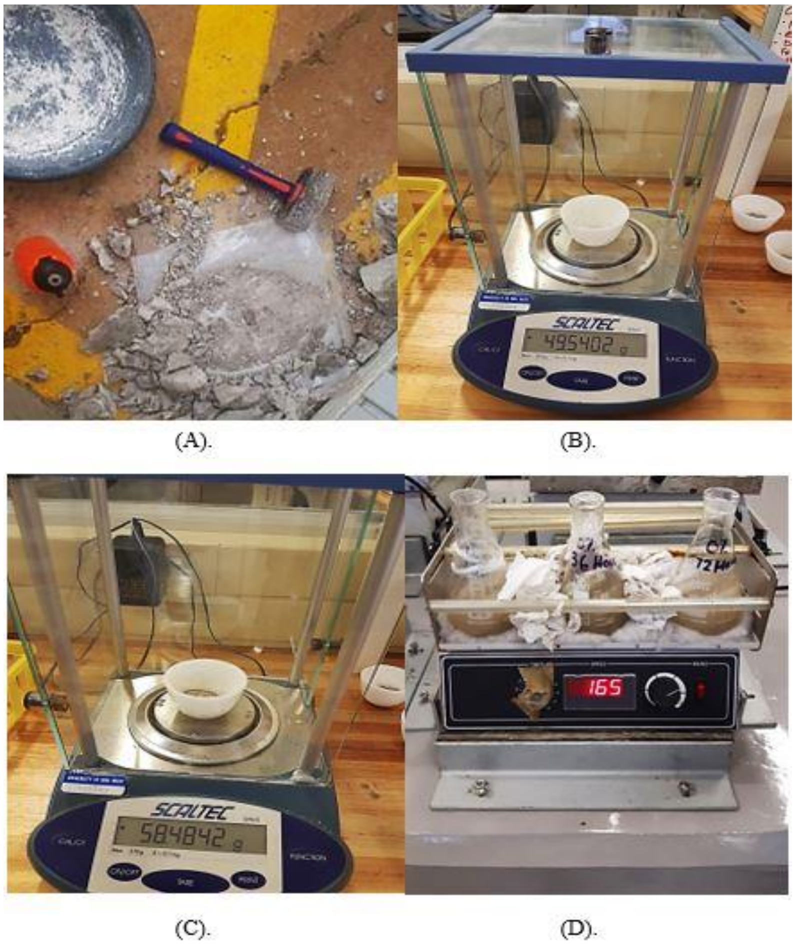


Figure 3.23: *(A). Producing powdered concrete, (B). Weighing crucible, (C). Weighing sample for moisture content test & (D). All three conical flasks in the orbital shaker*

Figure 3.23A above shows the creation of powdered concrete by way of physical breakdown. Figure 3.23B demonstrates the weighing of an empty crucible whilst Figure 3.23C shows the weighing of the powdered sample. Figure 3.23D demonstrates the prepared sample undergoing mixing in the orbital shaker.

Figure 3.24 below annotates all apparatus used in the leaching tests whilst Figure 3.25 provides a view of how pH content, ion conductivity and nitrate content are measured on their respective multimeters.

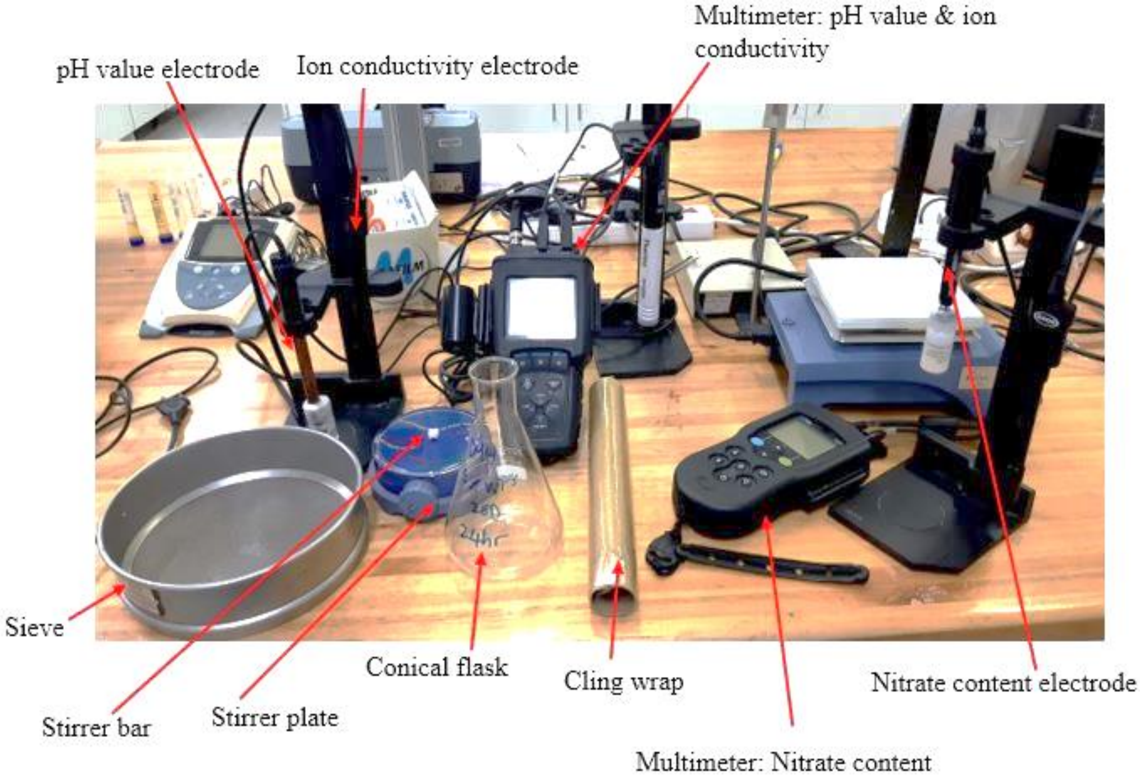


Figure 3.24: *Apparatus for the leaching test*

(A). (B).

Figure 3.25: *(A). Multimeter reading for pH value and ion conductivity & (B). Multimeter reading for nitrate content*

3.5 STATISTICAL ANALYSIS

Three main statistical analysis tools will be used, namely confidence intervals, comparison of means and correlation analysis. The analyses involving confidence intervals are based on the work of Newman & Choo (2003) for small sample sizes, whilst correlation analysis will be based on the work of Smith & Sam (2020). The raw data as pertaining to the statistical analysis is contained in Appendix J.

3.5.1 Confidence Intervals

Newman & Choo (2003) define the confidence interval as an interval within which, and with a specified probability called the confidence level, the population value might lie. It is common to employ a confidence level of 95 percent. Additionally, various researchers in the field of concrete technology, such as Matalkah et al. (2018), have used a confidence level of 95 percent in the course of their respective statistical analyses. For these reasons, a confidence level of 95 percent will be used in this investigation.

Assuming $X_1, X_2, X_3 \ldots X_n$ are results from a particular concrete test, the confidence interval for the population mean (μ), is given by the following expression:

$$\bar{x} \pm t_{(v;\,a)} \cdot \frac{S}{\sqrt{n}} \qquad (3.18)$$

Where, $\bar{x}$ = Sample mean; given as $\frac{1}{n}\sum_{i=1}^{n} Xi$

S = Sample standard deviation; given as $\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2}$

n = Number of samples

v = Degrees of freedom; given as n – 1

a = Significance level

$t_{(v;\,a)}$ = Critical value

The method for determining the confidence interval, as presented in Newman & Choo (2003), uses a t-distribution analysis as the sample size in this study is less than 30. Accordingly, the following sample table may be used to obtain the critical values.

__Table 3.9:__ Critical values of t-distribution (Newman & Choo, 2003)

a	**v**									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
0.05	6.31	2.92	2.35	2.13	2.02	1.94	1.89	1.86	1.83	1.81
0.025	12.71	4.30	3.18	2.78	2.57	2.45	2.36	2.31	2.25	2.23
0.01	31.82	6.96	4.54	3.75	3.36	3.14	3.00	2.90	2.82	2.76

The confidence intervals, where applicable, are shown for the results as presented in Chapter 4.

3.5.2 Comparison of Means

Statistical significance indicates the mathematical probability that a relationship or outcome arises due to something other than random chance. The comparison of means is a tool that Newman & Choo (2003) describe as providing the ability to compare the population means between two processes that are possibly in competition with each other. Comparison of means allows for determining if the differences between results of two separate mixes are statistically significant. In other words, a tool of this nature would be imperative in ascertaining whether a change in a concrete mix will result in an actual or non-random improvement to a particular property, such as strength.

If subscript i indicates test mixes and subscript c indicates the control mix, then $\bar{x}_i$ and $\bar{x}_c$ are the mean results from testing n_i and n_c samples from a test mix and the control mix respectively. Then, Newman & Choo (2003) explain that the confidence interval for a t-distribution sample statistic that allows for a comparison of the test and control population means, μ_i and μ_c, is expressed as follows:

$$(\bar{x}_i - \bar{x}_c) \pm t_{(v;\,a)}\, S\sqrt{\frac{1}{n_i} + \frac{1}{n_c}}$$

Where, $S = \sqrt{\frac{(n_i-1)S_i^2 + (n_c-1)S_c^2}{v}}$

v = Degrees of freedom; given as $n_i + n_c - 2$

The t-test for comparison of means requires the testing of the null hypothesis, i.e.,

$$H_O: \mu_i = \mu_c.$$

By obtaining a result that indicates the acceptance of the null hypothesis, it can be concluded that the difference between a test and control result is not statistically significant. In order for the null hypothesis to be accepted, the following condition must be true:

$$-t_{(v;a)} < t_0 < t_{(v;a)}$$

Where t_0 = test statistic for the null hypothesis; given as $\frac{\bar{x}_i - \bar{x}_c}{S\sqrt{\frac{1}{n_i}+\frac{1}{n_c}}}$

In this investigation, test results will be compared to those of the control in order to assess if the difference between them is significant. For the reasons stated in Section 3.5.1, a confidence level of 95 percent will be employed.

3.5.3 Correlation Analysis

Correlation relates to the association between two or more sets of variables. Smith & Sam (2020) conducted correlation analysis to ascertain the relation between concrete properties and the incremental integration of rice husk ash and fly ash as partial cement replacements. The statistical analyses employed in the abovementioned investigation was in the form of Pearson's product-moment correlation, as expressed by equation 3.20 below. This investigation uses said method of correlation analysis to assess the association between incremental amounts of test material on the resulting concrete properties. Pearson's product-moment correlation is limited to linear relationships; therefore, correlation analysis will only be conducted on results that exhibit linear relationships, namely the slump test results.

$$r = \frac{\sum XY}{\sqrt{[(\Sigma X^2)(\sum Y^2)]}} \tag{3.20}$$

Where, r = Pearson's coefficient of correlation

X = Value of deviations of concrete property from their mean value, given as $x - \bar{x}$

Y = Value of deviations of replacement order from their mean value, given as $y - \bar{y}$

In accordance with Pearson's coefficient of correlation, positive R values indicate a direct correlation whilst negative values indicate an inverse correlation. Moreover, Smith & Sam (2020) explain that the values of R give insights into the strength of correlation. This is represented in Table 3.10 below.

Table 3.10: *Strength of correlation as pertaining to Pearson's product-moment correlation (Smith & Sam, 2020)*

r	Strength of correlation
+ 1	Perfect direct correlation
- 1	Perfect inverse correlation
0.70 to 0.99	Fair direct correlation
- 0.70 to - 0.99	Fair inverse correlation
0.10 to 0.69	Weak direct correlation
- 0.10 to - 0.69	Weak inverse correlation
0	No linear correlation

3.6 CHAPTER SUMMARY

This chapter discusses the methodology as followed in this study.

The methodological approach taken was designed to meet all aims and objectives of the study. This consisted of reviewing the relevant properties of each test material and the relevant areas of concrete technology, in order to identify how concrete would be influenced by said properties. Accordingly, the key findings from the literature review will be used to discuss the findings of the experimentation programme.

The control mix was designed using the C & CI mix design method. Test samples were then obtained by replacing the appropriate material (cement and fine aggregate) with the respective test material (PMBA and WFS). All waste replacements occurred in 5, 10, 15 and 20 percent by mass of the replaced material. This order was chosen as it is widely employed in several GCT studies. Each sample underwent testing to assess workability, SHD, compressive strength, flexural strength, tensile-splitting strength, durability (oxygen permeability index, water sorptivity, chloride conductivity), and leachate quality (pH testing of concrete leachate, ion conductivity testing of concrete leachate and nitrate content of concrete leachate).

All tests, except the WS test, leaching tests and the FM assessments, were conducted in accordance with SANS. The FM assessments were however formalized and conducted in accordance with B13 TMH1. Due to limited equipment, a variation of the batch leaching test was performed after consulting with the laboratory technician at the environmental engineering laboratory.

In order to effectively represent results and to ascertain the difference in the results between two particular concrete samples, the comparison of means method will be used. To investigate the amount of association among the linear slump test results, Pearson's method of correlation analysis will be used.

The next chapter presents and discusses the results from the experimentation programme.

4. CHAPTER FOUR: RESULTS & DISCUSSION

4.1 INTRODUCTION

This chapter presents all results from the experimentation programme. Where applicable, the ‘green’ concrete samples will be compared with conventional concrete.

4.2 SIEVE ANALYSIS

Sieve analysis was performed on both fine aggregate materials with results indicating that conventional fine aggregate (Umgeni river sand) displayed a FM value of 3.4 whilst the WFS sample indicated a FM value of 3.3. Evidently, WFS is finer than Umgeni river sand. Both FM values are in accordance with SANS 1083 (2006), which requires that FM range between 1.2 and 3.5. In accordance with Table 4.1 and Table 4.2, both Umgeni river sand and WFS may be classified as coarse. The particle distribution curves for both Umgeni river sand and WFS are presented in Figure 4.1 below.

Table 4.1: *Sieve analysis results for conventional fine aggregate Umgeni river sand*

Sieve Size (microns)	Mass retained (g)	Mass retained (%)	Cumulative mass retained (%)	Cumulative mass passing (%)
4750	7	1.4	1.4	98.6
2360	20	4.0	5.4	94.6
1180	58	11.6	17.0	83.0
600	108	21.6	38.6	61.4
300	189	37.8	76.4	23.6
150	103	20.6	97.0	3.0
Pan	14	2.8	99.8	0.2
Total	**499**	**99.8**	**ΣCumulative Retained = 335.6**	
FM = 335.6 x 0.01 = 3.4				

__Table 4.2:__ Sieve analysis results for WFS

Sieve Size (microns)	Mass retained (g)	Mass retained (%)	Cumulative mass retained (%)	Cumulative mass passing (%)
4750	2	0.4	0.4	99.6
2360	9	1.8	2.2	97.8
1180	20	4.0	6.2	93.8
600	151	30.2	36.4	63.6
300	235	47	83.4	16.6
150	72	14.4	97.8	2.2
Pan	11	2.2	100	0.6
Total	**500**	**100**	**ΣCumulative Retained = 326.4**	
FM = 326.4 x 0.01 = 3.3				

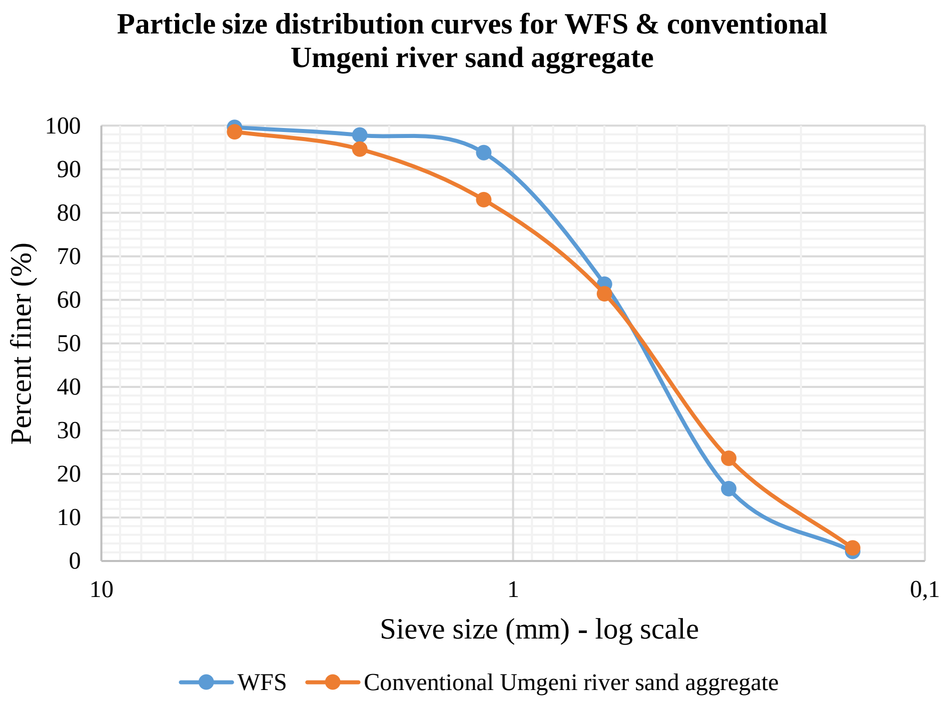
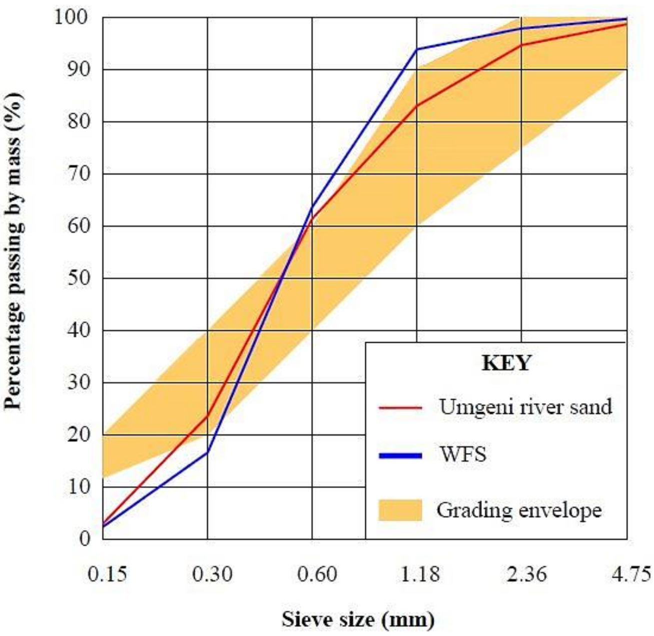
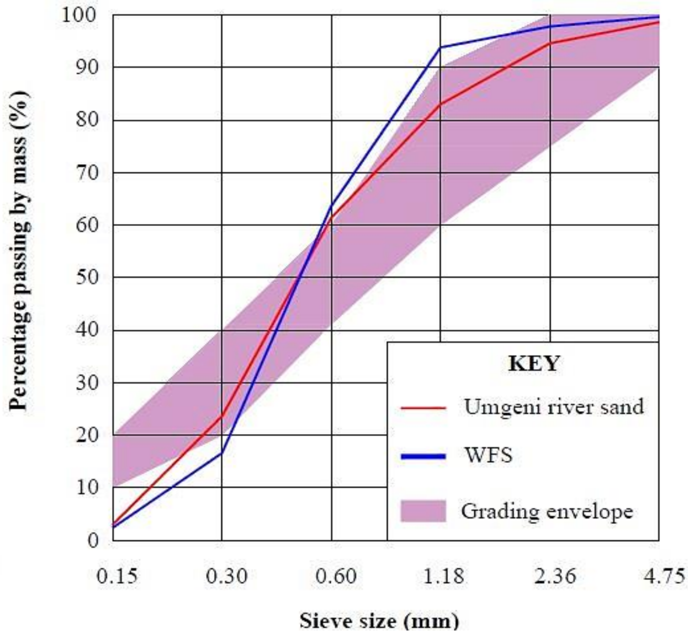


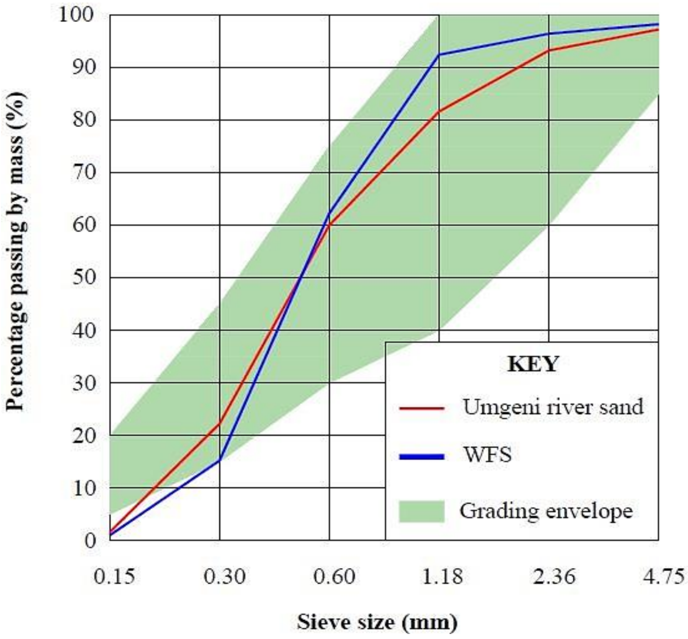
__Figure 4.1:__ Particle size distribution curves for conventional Umgeni river sand aggregate and WFS



(A).



(B).



(C).

Figure 4.2: *Characteristic curves of Umgeni river sand & WFS as compared to grading envelopes (A). C & CI limits, (B). SANS 1083 preferred limits & (C). SANS 1083 outer limits*

Figure 4.2 above depicts the way WFS and Umgeni river sand compares to grading limits for fine aggregate, as recommended by The Concrete Institute (2013) and SANS 1083 (2017). Evidently, the characteristic particle distribution curve for both WFS and Umgeni river sand do not lie within the proposed grading limits throughout, however Owens (2013) clarifies that sands having grading outside these limits may be adequate for concrete works if the concrete mix is designed well. As required by SANS 1083 (2017), both Umgeni river sand and WFS meet the requirement of 90 to 100 percent of sample passing the 4750 μm sieve. However, both materials failed to meet the requirement whereby 5 to 25 percent of sample is to pass the 150 μm sieve.

In terms of classifying gradation, equations 2.1 and 2.2 were used to determine said classification of the Umgeni river sand and WFS. As shown in Table 4.3 below, the results indicated that WFS may not be classified as well-graded as C_u did not exceed six and C_c did not lie between one and three. Lower C_u values indicate a more uniformly graded sand. It is expected that WFS showed a greater inclination to being uniformly graded as foundries require uniformly sized silica sand. Similarly, the conventional fine aggregate may not be classified as well graded as C_u was less than six. In comparison to Umgeni river sand, WFS shows a more uniform grading by virtue of having a lower C_u.

Table 4.3: *Classification of gradation*

Property	**WFS**	**Umgeni river sand**
D_{10}	0.25	0.20
D_{30}	0.37	0.35
D_{60}	0.57	0.60
C_u	2.28	3.00
C_c	0.96	1.02

4.3 C & CI Mix Design

As per Figure 3.8, a W/B ratio of 0.53 was selected, as based on cement type CEM II B-S 42.5 N Plus. Table 3.4 requires that, for 19 mm stone, the water requirement, W, is to be 210 L/m^3. In accordance with equation 3.2, the cement content is determined as follows:

$$C = \frac{210}{0.53} = 396 \text{ L/m}^3$$

The CBD of stone was provided as 1446 kg/m^3. For 19 mm stone and compaction by moderate vibration, the corresponding k factor is 1. FM for Umgeni river sand was determined as 3.4. Equation 3.3 dictates that the stone content is determined as follows:

$$St = 1446 \times (1 - 0.1[3.4]) = 954 \text{ kg/m}^3$$

The RD values of cement, stone and sand were provided as 3.1, 2.65 and 2.65, respectively. Equation 3.4 allows for the calculation of the sand content as shown below.

$$Sc = [1000 - (\frac{396}{3.1} + \frac{954}{2.65} + 210)] \times 2.65 = 800 \text{ kg/m}^3$$

The total volume required for the control concrete samples, including 15 percent for wastage, was computed in Section 3.3.7 as 0.094 m^3. The mix factors were determined as indicated in Section 3.3.7 and the appropriate slump was achieved using mix 4. Appendix D contains the full control mix design data.

4.4 WORKABILITY

Workability will be assessed by slump, whereby workability will be deemed to increase if slump increases. Table 4.4 below presents the results from the slump test for all samples, namely the control, PMBA and WFS samples.

The slump specified in the control mix was 75 mm whilst the slump observed was 60 mm. Accordingly, the control mix was accepted as the observed slump was within the ± 25 mm tolerance as set out in Table 2.34.

Moreover, the control slump was classified as having a medium degree of workability, indicating its suitability for normal concrete applications, along with the other applications as listed in Tables 2.33 and 2.35 in Section 2.9. All data used for correlation analysis of the slump tests are presented in Appendix J.

Table 4.4: Slump test results

Test material content (%)	PMBA			WFS		
	Slump (mm)	Degree of workability	Slump type	Slump (mm)	Degree of workability	Slump type
Control	60	Medium	True	60	Medium	True
5	75	Medium	True	130	High	True
10	95	Medium	True	170	High	Collapse
15	120	High	True	190	High	Collapse
20	140	High	True	230	High	Collapse

4.4.1 Influence of PMBA

Figure 4.3 below demonstrates the influence of increasing contents of PMBA on concrete slump. The results indicate that incremental additions of PMBA showed a positive effect on workability, whereby increasing PMBA contents increased the slump of the concrete mix. Table 4.5 below shows the analysis performed on the slump test results for PMBA-concrete.

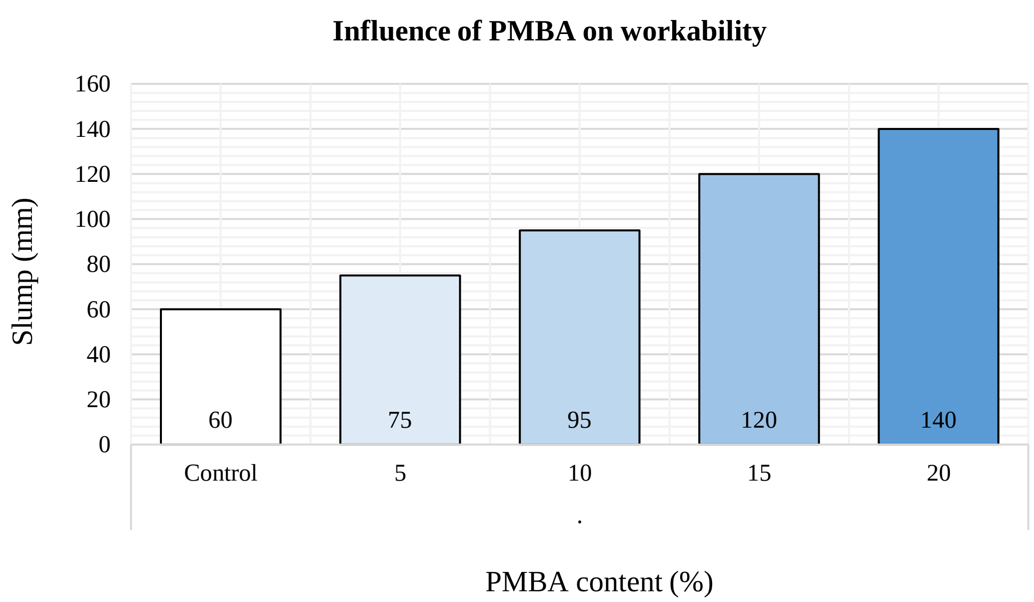


Figure 4.3: *Workability under the influence of incremental additions of PMBA*

__Table 4.5:__ Analysis of slump test results for PMBA-concrete

Mix ID	Δ (%)
5%PMBA	25
10%PMBA	58
15%PMBA	100
20%PMBA	133
r = 1	

Slumps ranging from 50 to 100 mm specify a medium degree of workability and is used for normal reinforced concrete applications. Delta (Δ) indicates the percentage change of each test sample in relation to the control. At a 5 percent replacement, the resulting slump of 75 mm was 25 percent higher than the control whilst a 10 percent replacement produced a slump of 95 mm, which was 58 percent higher as compared to the control. Therefore, these test mixes satisfy the handling requirements for normal concrete applications and are increasingly more workable than conventional concrete (as represented by the control sample).

Fresh concrete arising from the 15%PMBA and 20%PMBA mixes have displayed slumps of 120 mm and 140 mm respectively. In comparison to the control, the 15%PMBA mix showed a 100 percent increase in slump and the 20%PMBA mix showed a 133 percent increase. Due to their slumps exceeding 100 mm, these mixes are classified as having high degrees of workability and may have the requisite handling to be used for situations that require the specialized placement of concrete, such as in sections that are congested with reinforcements, situations where concrete has to flow a great distance, thin sections and trench-filled foundations where a high flow is required.

Pearson's coefficient of correlation (r), in conjunction with Table 3.10, revealed that the trend observed is a perfect direct correlation, thereby indicating that the content of PMBA and slump are strongly related. Accordingly, concrete displays higher degrees of workability when increasing quantities of PMBA replaces cement, thus showing a progressive reduction in the water requirement. A possible reason for the increasing slumps is the fly ash nature of PMBA. Similar to fly ash, PMBA has a glassy texture and contains spherical particles. These characteristics tend to improve workability whereby spherical particles behave as miniature ball bearings which reduce particle friction and applying a lubricating effect in the concrete mix. This causes a reduction in friction and an improvement in flow. Glassy textures improve workability by providing a smaller surface area requiring wetting, thereby reducing the water requirement. Moreover, the hydrophilic nature of PMBA may have promoted a more workable mix by facilitating wetting, leading to improved slump. These results are in accordance with claims made by Cherian & Siddiqua (2019). All PMBA samples showed plastic slumps.

For decades, various studies, such as those done by Carlson et al. (1937), Popovics (1992) and ACAA (2003), document the enhancement of workability through the integration of fly ash. Conversely, researchers such as Ahmad et al. (2013), Wong et al. (2015) and Raghuwanshi & Joshi (2017), have noted that PMS ash reduces workability. Due to the correlation between the influence of fly ash on workability and PMBA on workability, these results suggests that PMBA, in its capacity as a partial cement replacement, may behave more like fly ash as opposed to the pure ash arising from PMS.

4.4.2 Influence of WFS

Figure 4.4 below shows the effect that increasing contents of WFS has on concrete slump. The incremental addition of WFS as a partial fine aggregate replacement showed drastic increases in slump. All WFS mixes were classified as having a high degree of workability. Table 4.6 below shows the analysis of the slump test results for WFS-concrete.

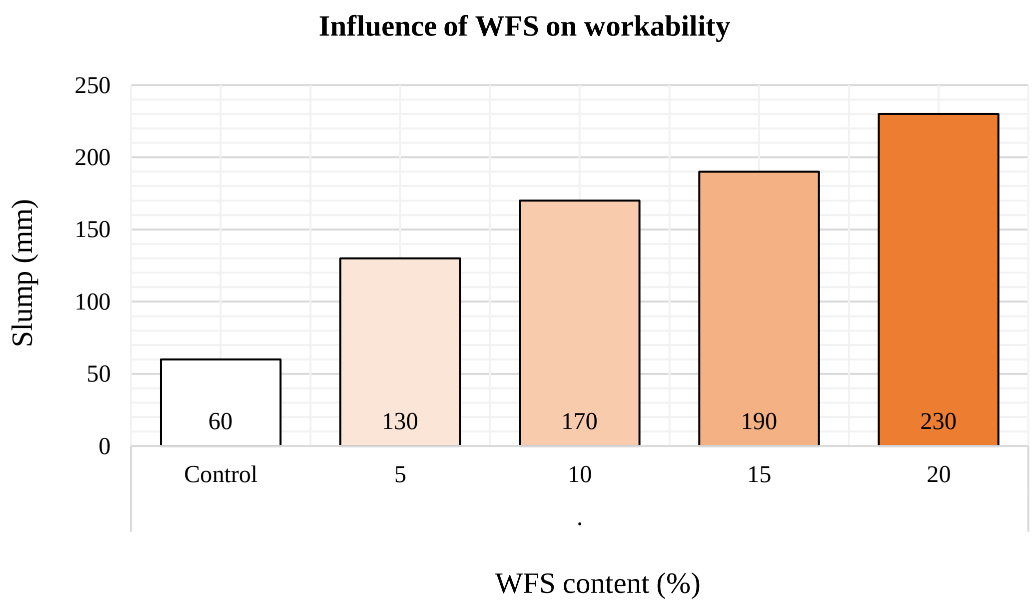


Figure 4.4: *Workability under the influence of incremental additions of WFS*

Table 4.6: *Analysis of slump test results for WFS-concrete*

Mix ID	Δ (%)
5%WFS	117
10%WFS	183
15%WFS	217
20%WFS	283
r = 0.98	

In this study, the smallest quantity of WFS occurred as a 5 percent replacement, which produced a plastic slump of 130 mm which was 117 percent greater than the control mix. A 10 percent replacement resulted in a 170 mm slump, which was 183 percent greater than the control. A 190 mm slump was observed for a 15 percent replacement, which was 217 percent greater than that of the control. The greatest degree of WFS integration occurred at a 20 percent replacement, which produced a slump of 230 mm, which being 283 percent greater than the control mix.

The 5%WFS mix meets the handling requirements to be used for sections being congested with reinforcements. Slumps over 150 mm are to be used for specialized works, such as being used as high tremie mixes. This is because such mixes may run the risk of aggregate segregation. Accordingly, the 10%WFS, 15%WFS and 20%WFS mixes may require the inclusion of additives to be used for structural work. These mixes may experience bleeding, plastic shrinkage and loss of strength due to the higher content of free water.

In consideration of Table 3.10, the r value of 0.98 suggests a fair direct correlation between WFS content and slump. A plausible explanation for all WFS mixes exhibiting high slumps may be due to the particle characteristics, which is often cited as the main determinant of workability. Due to their lower surface areas, the prevalence of cubical, sub-rounded and rounded particles may improve workability by reducing the water required to achieve wetting. Moreover, such rounded particles are able to easily roll over each other, reducing particle friction, which leads to a more workable mix. In addition, compared to natural sand, WFS was reported to exhibit a low capability to absorb water (Iloh, 2018).

The results resemble those of Pandey et al. (2015), who reported that slump improved with increasing additions of WFS. However, the results contradict the findings of Khatib et al. (2010), Sowmya & Chaitanya-Kumar (2015) and Jadhav et al. (2017), who have all reported that slump decreases with greater amounts of WFS. Further testing is required in order to establish whether greater contents of UIS WFS will continue exhibiting drastic increases in slumps.

4.5 SHD (ρ_c)

Appendix F contains the data collected during testing whilst the averaged 28-day SHD values are presented in Table 4.7 below. Appendices J contains all data used in the statistical analysis. The statistical analysis indicates that for tests requiring three samples, and with a significance level of 0.05 with 0.025 in each tail, the corresponding test statistic, as obtained from Table 3.9 is 2.78. The control sample exhibited a density of 2354 kg/m^3 which, in accordance with Table 2.36, may be classified as normal-weight concrete. In addition, said density exceeds 2300 kg/m^3, thus the control sample meets the requirement for classification as structural concrete (Mindess et al., 2003). A density of 2400 kg/m^3 is widely accepted as being the characteristic density of concrete. The observed density of the control concrete differed by the characteristic density by approximately 2 percent. The densities of test mixes will be compared to the density of the control.

Table 4.7: *28-day SHD results*

Test material content (%)	ρ_c (kg/m^3)	
	PMBA	WFS
Control	2354	
5	2365	2361
10	2400	2340
15	2387	2314
20	2382	2284

4.5.1 Influence of PMBA

Figure 4.5 demonstrates how SHD is influenced by increasing contents of PMBA. Evidently, all PMBA samples showed increased density when compared to the control, however 5 and 10 percent replacements showed positive trends in density, followed by a declining trend in SHD as a result of replacing cement with 15 percent and 20 percent PMBA. Table 4.8 displays the statistical analysis carried out on the SHD results. The 5%PMBA sample showed a density of 2365 kg/m^3, which was 0.5 percent greater than the control. For this mix, the test statistic for the null hypothesis (t_0) is determined to be 0.75, which lies within the region dictated by the critical value ($t_{(v;a)}$), which being -2.78 to 2.78. This indicates that the null hypothesis is valid and the difference in results is not statistically significant. The same logic will be applied hereafter to discuss the statistical significance in the difference between the respective test results and those of the control. The comparison of means analysis resulted in a 95 percent confidence interval which suggested that the 5%PMBA sample is denser than the control sample by a value between -29.62 kg/m^3 and 51.62 kg/m^3. From all concrete samples tested in this study, the greatest density was achieved by replacing 10 percent of cement with PMBA, where the resulting concrete exhibited a density of 2400 kg/m^3, which was 2 percent greater than the control. Moreover, the test statistic for the 10%PMBA sample is greater than the critical value, indicating that the SHD of said sample is greater than that of the control by a value that is statistically significant. Accordingly, the difference in the mean SHD values of the 10%PMBA and control samples are shown to lie in the 95 percent confidence interval of 14.07 kg/m^3 to 77.80 kg/m^3. Table 4.8 further shows the 95 percent confidence intervals for all samples. The 95 percent confidence interval for the population mean of the 10%PMBA sample was shown to be 2376.50 kg/m^3 to 2423.77 kg/m^3, whilst that of the control ranged from 2310.95 kg/m^3 to 2397.45 kg/m^3.

SHD exhibited a decline after a 10 percent replacement, whereby the 15%PMBA sample had a density of 2387 kg/m^3, which was still 1.4 percent greater than the control. Despite the SHD of the 15%PMBA sample decreasing, statistical analysis provided sufficient evidence to show that said SHD was greater than the control by a significant margin. This is indicated by the difference, in the SHD means of the 15%PMBA and control samples, nesting in the 95 percent confidence interval of 3.46 kg/m^3 to 63.07 kg/m^3. It was observed that a 20 percent replacement further reduced SHD by resulting in a value of 2382 kg/m^3, which was still 1.2 percent greater than the control, but not adequate enough to be considered statistically significant.

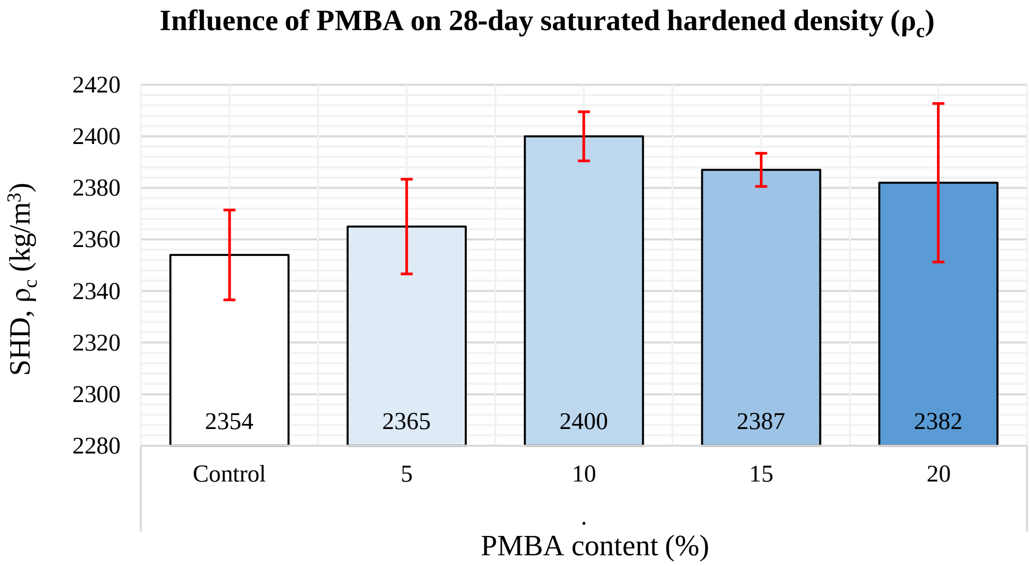


Figure 4.5: *SHD under the effect of incremental additions of PMBA*

__Table 4.8:__ Analysis of SHD results for PMBA-concrete

Mix ID	**Δ (%)**	**ρ_c (kg/m³)**	**Confidence interval (kg/m³)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (kg/m³)**	
			Lower	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (kg/m³)**	**Lower**	**Upper**
Control	-	2354	2310.95	2397.45	-	-	-	-
5%PMBA	0.5	2365	2319.62	2410.78	0.75	11.00	-29.62	51.62
10%PMBA	2.0	2400	2376.50	2423.77	4.00	45.93	14.07	77.80
15%PMBA	1.4	2387	2371.51	2403.43	3.10	33.27	3.46	63.07
20%PMBA	1.2	2382	2306.14	2458.80	1.39	28.27	-28.45	84.99

The increased SHD values of the test samples, when compared to the control, does not resemble trends witnessed in past studies involving pozzolana, such as in the work of Amankwah et al. (2014). It is commonly observed that SHD decreases with pozzolana. However, Ghazali et al. (2019) and Bremseth (2010) suggest that improvements in density are due to the additional C-S-H created by the pozzolanic reaction, which fills pores and through the reduction of bleed channels. These ideas are supported by statements made by Newman & Choo (2003), Mehta & Monteiro (2006) and Walker & Pavía (2010), who claim that fine pozzolanic materials improve concrete density by reducing porosity. However, it is uncertain that the densification of concrete microstructure, due to pozzolanic activity, results in increased SHD. Consequently, further investigation is warranted into cases where pozzolana, particularly fly ash and PMBA, increase SHD.

A possible reason for the expected decline in SHD, as associated with the 15 and 20 percent replacements, may be the difference between the higher densities of cement (bulk density of 1300 to 1400 kg/m³ and RD of 3.14) and the densities of PMBA (average bulk density of 500 kg/m³ and average RD of 2.45). It is widely acknowledged and proven by researchers such as Iffat (2015) and Amankwah et al. (2014), that the RD values of concrete constituents are highly influential on the density of concrete itself, implying that replacing a denser constituent (cement) with a less dense counterpart (PMBA) may result in a reduction in concrete density. The results suggest that replacement levels above 15 percent introduces sufficient quantities of PMBA such that the difference in densities became more influential in reducing SHD. This analysis supports the findings of al-Attar et al. (2019), who investigated high-volume fly ash concrete and found that replacing cement with 50, 60 and 70 percent fly ash causes a reduction in concrete density. The relatively lower density of fly ash was reported as the reason for the decreases in density.

The increasing-to-decreasing effect was also observed by Motau (2016), who replaced cement with fly ash in increments of 5, 10, and 20 percent, and found an increase in concrete density at a 10% replacement, followed by a decrease. No explanation was given for this increase.

4.5.2 Influence of WFS

Figure 4.6 below shows the variations in SHD as a result of increasing contents of WFS whilst Table 4.9 summarises findings from the statistical analysis. The results show that, from all WFS samples, the only enhancement to SHD occurred due to a 5 percent replacement, which resulted in a 0.3 percent improvement compared to the control sample. Statistical analysis reveals that despite the 5%WFS sample displaying this higher SHD, said SHD exhibited a test statistic of -0.92, which was within the critical range of -2.78 to 2.78. Thus, indicating that the difference in SHD between the 5%WFS and control samples is not statistically significant. Additionally, all WFS samples were found to exhibit SHD values that, when in relation to the control SHD, were statistically insignificant. The 95 percent confidence interval for the population mean of the 5%WFS sample was shown to be 2312.90 kg/m^3 to 2409.23 kg/m^3, whilst the control showed a range of 2310.95 kg/m^3 to 2397.45 kg/m^3.

The near linear decline in SHD observed after the 5 percent replacement may be attributed to the poor grading of the WFS. As discussed in Section 4.2, the C_u of WFS was lower than that of Umgeni river sand, indicating that the waste material exhibited a more uniform grading than the conventional material. It is expected that poorly graded fine aggregates are inefficient in producing a well packed structure, leading to voids and a subsequent reduction in SHD. Due to the decline in SHD, the difference in grading, although slight, may indicate that aggregate gradation becomes more influential as greater contents of WFS replaces conventional fine aggregate.

The type of binder used in WFS production may have also been influential in reducing SHD. Iloh (2018) advises that certain binders, such as wood flour, sawdust, and clay, are capable of reducing the SHD of WFS-concrete. Further research must be conducted to separately assess the influence of the furan resin binder type and greater contents of WFS on SHD.

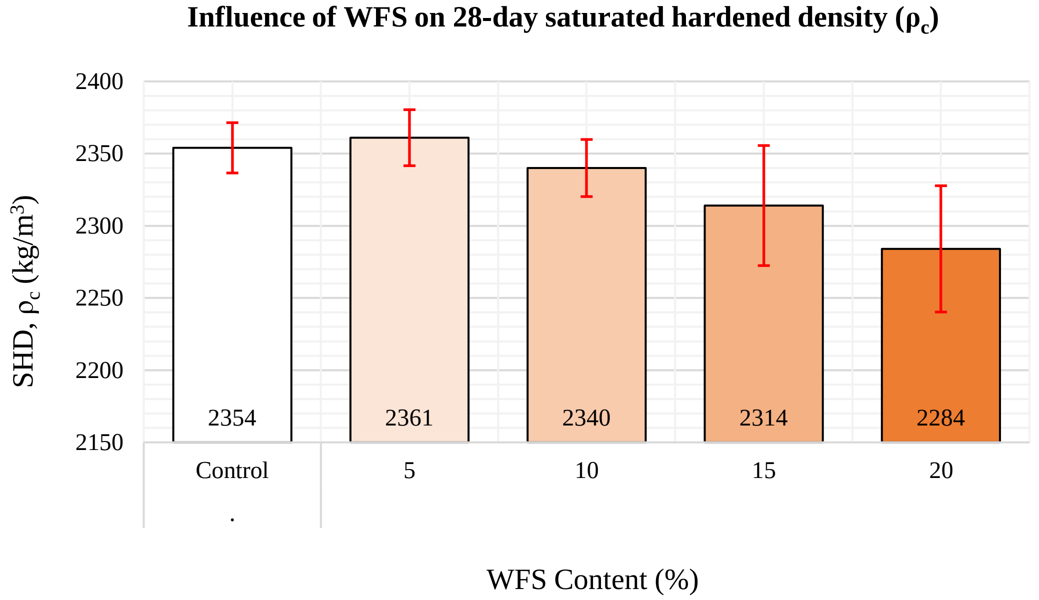


Figure 4.6: *Concrete density under the effect of incremental additions of WFS*

Table 4.9: *Analysis of SHD results for WFS-concrete*

Mix ID	**Δ (%)**	**ρ_c (kg/m^3)**	**Confidence interval (kg/m^3)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (kg/m^3)**	
			Lower	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (kg/m^3)**	**Lower**	**Upper**
Control	-	2354	2310.95	2397.45	-	-	-	-
5%WFS	0.3	2361	2312.90	2409.23	0.46	6.87	-34.99	48.72
10%WFS	-0.6	2340	2291.12	2389.28	-0.92	-14.00	-56.30	28.30
15%WFS	-1.7	2314	2210.32	2416.75	-1.56	-40.67	-113.02	31.68
20%WFS	-3.0	2284	2175.36	2392.50	-2.58	-70.27	-145.82	5.29

4.6 COMPRESSIVE STRENGTH (f_{cc})

Appendix G contains all the readings for all three mechanical strengths, the corresponding averaged strengths and the acceptability criteria as based on the comparison between 15 percent of the average strength and the difference between the highest and lowest strength.

Table 4.10 below presents the results obtained in the compressive strength tests. As seen, the control sample exhibited a 7-day strength of 23 MPa and a 28-day strength of 35 MPa. In accordance with Mindess et al (2003) and the classification system presented in Table 2.37, based on the 28-day strength, the control sample may be categorized as moderate-strength structural concrete and so, meets the strength requirement for reinforced beams and slabs, heavy duty floors, pre-cast items etc. The 95 percent confidence interval for the population mean of the 28-day control sample was shown to be 33.14 MPa to 37.08 MPa. For each mix, both the 7-day and 28-day compressive strengths showed similar fluctuation patterns.

Table 4.10: *Compressive strength results*

Test material content (%)	**f_{cc} (MPa)**			
	PMBA		**WFS**	
	7 Day	**28 Day**	**7 Day**	**28 Day**
Control	23.0	35.0	23.0	35.0
5	24.0	35.5	22.0	32.5
10	25.5	38.0	18.0	30.5
15	22.5	38.0	19.0	30.0
20	20.0	36.5	19.0	30.0

4.6.1 Influence of PMBA

Figure 4.7 below shows that all 28-day samples of PMBA-concrete displayed strengths exceeding 35 MPa, indicating their capacities to be used as structural concrete. Statistical analysis of the 7 and 28-day compressive strength results are displayed in Table 4.11. The 7 and 28-day compressive strengths exhibit similar variations as the content of PMBA increases. Both the 7 and 28-day strengths showed increased compressive strengths at a 5 percent replacement, whereby the former showed a 4.3 percent improvement and the latter showed a 1.4 percent improvement in relation to their respective controls. Despite said increases, neither value was shown to be statistically significant when compared to the control. The strength gain at both testing ages continued up until a 10 percent replacement, which resulted in a 25.5 MPa 7-day strength, which was 10.9 percent greater than the 7-day control. More importantly, at 10 and 15 percent replacements, the 28-day compressive strengths were both 38 MPa, which was 8.6 percent greater than the 28-day control. When compared to all mixes investigated in this study, these two mixes produced the highest compressive strength at both, 7 and 28 days. This is important as the 28-day compressive strength is the property of concrete that is generally specified and serves an indication of concrete quality. The 28-day 10%PMBA sample showed a 95 percent confidence interval of 32.17 MPa to 44.39MPa, whilst the 28-day control exhibited a range of 33.14 MPa to 37.08 MPa. The comparison of means analysis indicated a 95 percent confidence that the 28-day strength of the 10%PMBA sample was greater than that of the 28-day control by a value between -0.98 MPa to 7.32 MPa. However, it should be noted that despite achieving the highest compressive strengths, both the 7 and 28-day strength difference between the 10%PMBA and control samples were deemed statistically insignificant as their respective t_0 values were less than 2.78. In fact, with the exception of the 7-day 20%PMBA sample, all test concrete samples exhibited greater strengths than the control sample at both testing ages, however no strength difference (between the test and control samples) was sufficiently large to be considered statistically significant. The inclining strength trend observed at the 5 and 10 percent replacements may be credited to the fly ash nature of PMBA, which lends to the following:

- The fine-filler effect of PMBA, which potentially reduced concrete porosity. As discussed in Section 2.11.3 (A), porosity is the most important factor to influence strength. An indication of the fine-filler effect being a significant contributor to strength, specifically at 5 and 10 percent replacements, is that the densities of PMBA-concrete improved at the same replacements due to possible reductions in porosity; thus, potentially linking porosity, the fine-filler effect and density to compressive strength. Existing evidence shows that denser concrete typically displays improved strengths. The findings of Iffat (2015) proved that density and compressive strength are so closely related that density may be easily predicted from compressive strength via linear equations. The results in this study builds on such evidence by linking porosity as one of the main determinants in the density-strength relationship.
- The utilisation of CH that occurs during pozzolanic reactions, whereby the weak crystalline phase of CH is used to create the main strengthening agent in HCP (i.e., C-S-H), thereby replacing a weaker substance with a stronger one.
- The amorphous phases in PMBA, particularly SiO_2, which was observed by Naik & Kraus (2003) to constitute a large portion of the material. The amorphousness of a pozzolanic material is more influential to pozzolanic reactivity than other properties, whereby pozzolanic reactivity and strength development increases with amorphousness (Walker & Pavía, 2010).
- The high specific surface of PMBA, which improves pozzolanic reactivity, leading to enhanced strength development.

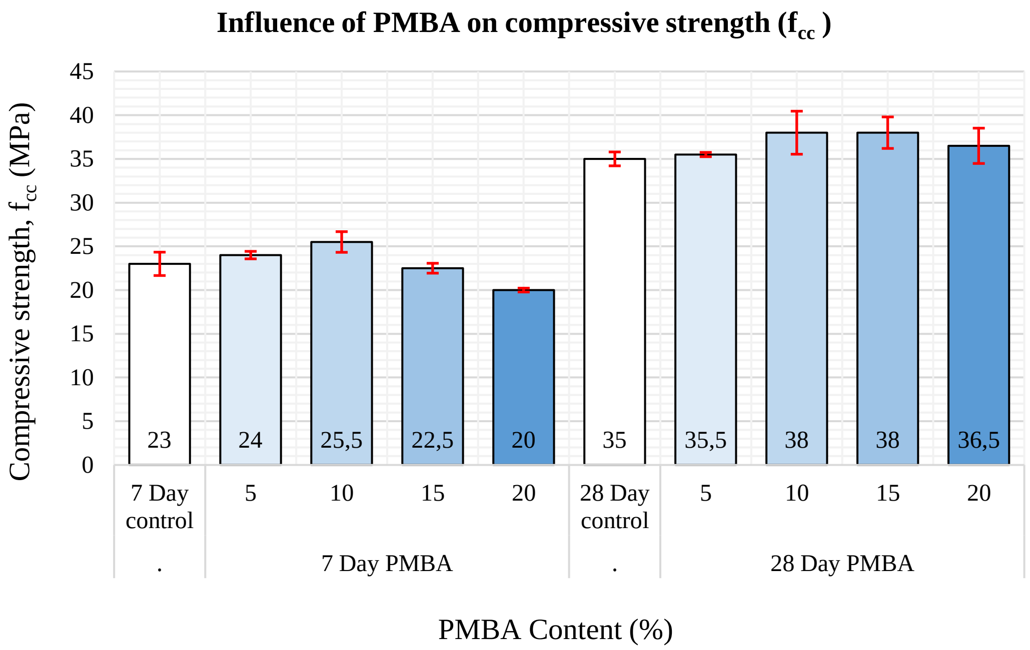


Figure 4.7: *Compressive strength under the effect of incremental additions of PMBA*

Table 4.11: *Analysis of 7and 28-day compressive strength results for PMBA-concrete*

7-Day statistical analysis			**Confidence interval (MPa)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (MPa)**	
Mix ID	**Δ (%)**	**$f_{cc,7}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	23.0	19.71	26.34	-	-	-	-
5%PMBA	4.3	24.0	22.88	25.01	1.14	0.92	-1.33	3.17
10%PMBA	10.9	25.5	22.32	28.19	2.17	2.23	-0.63	5.09
15%PMBA	-2.2	22.5	21.14	23.95	-0.57	-0.48	-2.81	1.85
20%PMBA	-13.0	20.0	19.59	20.67	-3.70	-2.89	-5.07	-0.72
28-Day statistical analysis			**Confidence interval (MPa)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (MPa)**	
Mix ID	**Δ (%)**	**$f_{cc,28}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	35.0	33.14	37.08	-	-	-	-
5%PMBA	1.4	35.5	35.09	36.31	1.24	0.59	-0.74	1.92
10%PMBA	8.6	38.0	32.17	44.39	2.12	3.17	-0.98	7.32
15%PMBA	8.6	38.0	33.48	42.42	2.50	2.84	-0.32	6.00
20%PMBA	4.3	36.5	31.25	41.27	0.92	1.15	-2.33	4.63

An interesting observation is that for a 15 percent replacement, the 7-day strength shows a decline whilst the 28-day strength remains constant and declines thereafter at a 20 percent replacement. A possible reason for this is that pozzolanic reactions only occur once hydration produces quantities of CH, thereby delaying pozzolanic reactions and reducing early-age strength gain, followed by increased strength gain at later ages (Motau, 2016). Additionally, it was discussed in Section 2.5.5.2 (B) that PMBA displays a greater LOI than both cement and fly ash., indicating a higher carbon content. It was shown by Kearsley & Wainwright (2003) that fly ash containing greater contents of carbon resulted in reduced strengths. As such, it is possible that the high carbon content in PMBA resulted in reduced strengths at higher replacements.

The results suggest that the delay in pozzolanic reactions may become more influential in reducing early-age strengths at higher contents of PMBA. This analysis gains further support by observing the 7-day strengths of the 15%PMBA and 20%PMBA mixes, which are below the 7-day control by 2.2 percent and 13 percent respectively, whilst all 28-day strengths are higher than the 28-day control. This is in line with Harison et al. (2014), who integrated fly ash as an SCM and found that 7-day strengths were typically lower than that of the 7-day control, however 28-day strengths were observed to be higher. It is noteworthy that after a 15 percent replacement, the 28-day strengths were both higher than the control but also declining.

4.6.2 Influence of WFS

Figure 4.8 below shows that the compressive strength of the 7 and 28-day controls are higher than those of all WFS samples. A 5 percent replacement showed the greatest 7 and 28-day compressive strengths when compared to the 10, 15 and 20 percent replacements. The statistical analysis, as presented in Table 4.12 below, indicates that the 7-day strength difference between the 5 percent and control samples is not statistically significant, however this is not the case for the 28-day counterpart.

The gradation of WFS may be a possible reason for the decreasing strength trend as WFS content increases. The voids that exist as a result of insufficiently packed structures may have acted as zones of weakness and reduced compressive strength accordingly. The results suggest that increasing contents of WFS leads to more voids. This analysis correlates with the results from the density assessments in Section 4.5.2, whereby density exhibited a decreasing trend as the content of WFS increased. This reinforced the concept that gradation becomes more influential with increasing contents of WFS. It must be noted that, with the exception of the 7-day 5%PMBA sample, all WFS samples at both testing ages exhibited a reduction in compressive strength such that, when compared to the control, was deemed statistically significant.

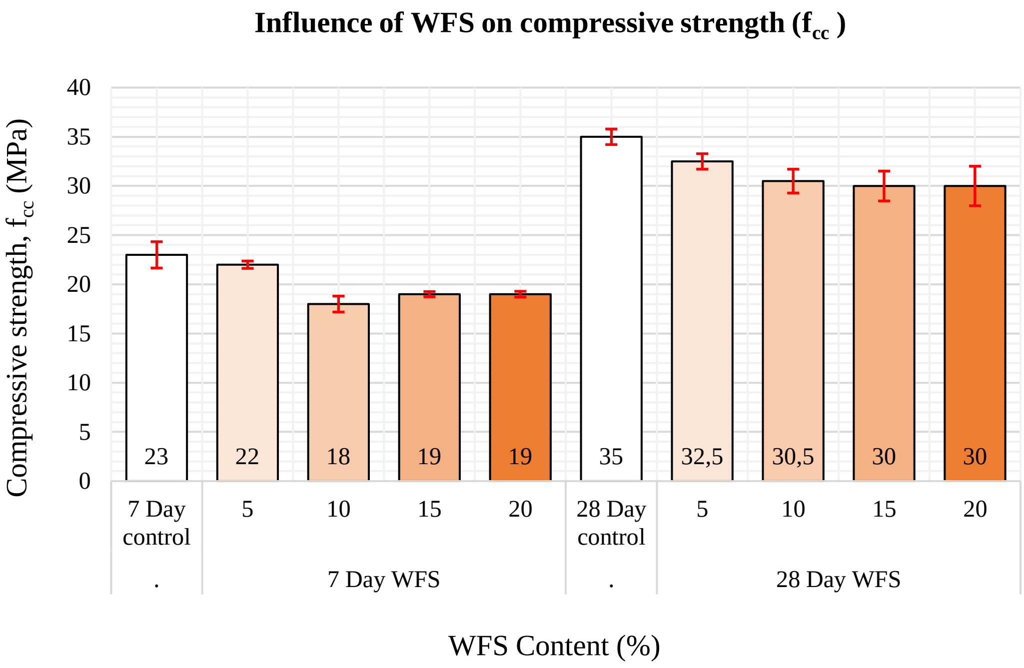


Figure 4.8: *Compressive strength under the effect of incremental additions of WFS*

Table 4.12: *Analysis of 7and 28-day compressive strength results for WFS-concrete*

7-Day statistical analysis			**Confidence interval (MPa)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (MPa)**	
Mix ID	**Δ (%)**	**$f_{cc,7}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	23.0	19.71	26.34	-	-	-	-
5%WFS	-4.3	22.0	20.86	22.74	-1.53	-1.23	-3.46	1.00
10%WFS	-21.7	18.0	16.17	20.19	-5.37	-4.85	-7.36	-2.34
15%WFS	-17.4	19.0	18.53	19.85	-4.88	-3.84	-6.02	-1.65
20%WFS	-17.4	19.0	18.27	19.74	-5.08	-4.02	-6.21	-1.82
28-Day statistical analysis			**Confidence interval (MPa)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (MPa)**	
Mix ID	**Δ (%)**	**$f_{cc,28}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	35.0	33.14	37.08	-	-	-	-
5%WFS	-7.1	32.5	30.33	34.22	-4.41	-2.83	-4.62	-1.05
10%WFS	-12.9	30.5	27.48	33.49	-5.54	-4.62	-6.95	-2.30
15%WFS	-14.3	30.0	26.19	33.73	-5.21	-5.15	-7.90	-2.41
20%WFS	-14.3	30.0	25.11	35.11	-4.00	-5.00	-8.47	-1.53

Whilst previous research did indicate a declining strength trend with increasing WFS content, said trend was usually preceded with increases in compressive strength, often up to a 30 percent replacement as found by Jadhav et al. (2007) and Mavroulidou & Lawrence (2018).

It is important to state that whilst increasing contents of WFS result in decreasing compressive strengths, all 28-day samples of WFS-concrete are classified as moderate-strength concrete. Additionally, all WFS samples showed 28-day strengths above 30 MPa, which Naicker (2014) notes as meeting the strength requirement for structural concrete. It must further be noted that, at both testing ages, no further reductions in compressive strength were observed at and beyond a 15 percent replacement. This finding opens up an avenue of research into the influence of greater contents of WFS on compressive strength, including investigating variations in FM.

4.7 FLEXURAL STRENGTH (f_{cf})

Table 4.13 below presents the results obtained in the flexural strength tests. The full data is laid out in appendix G. As seen, the control sample exhibited a 7-day strength of 2.45 MPa and a 28-day strength of 4.30 MPa. Thus, the control concrete meets the 4 MPa strength requirement for minor roads but fails to exhibit the 6 MPa strength that is generally displayed by structural concrete.

Table 4.13: *Flexural strength results*

Test material content (%)	f_{cf} (MPa)			
	PMBA		WFS	
	7 Day	28 Day	7 Day	28 Day
Control	2.45	4.30	2.45	4.30
5	2.40	4.20	2.30	4.05
10	2.65	4.85	2.15	4.05
15	2.50	4.20	1.95	3.35
20	2.45	4.45	1.90	3.35

4.7.1 Influence of PMBA

Figure 4.9 below shows that the general trend displays a reduction in strength at a 5 percent replacement, followed by an increase in strength at a 10 percent replacement to give the peak strength, and thereafter reductions in strength.

The 7-day 5%PMBA mix was 2.4 MPa which was 2 percent lower than the control. The corresponding 28-day mix was 4.2 MPa, which was 2.3 percent lower than the control. A 10 percent replacement saw a peak in strength, which resulted in the highest flexural strengths obtained in this study. The 7-day 10%PMBA strength was 2,65 MPa and the 28-day counterpart was 4,85 MPa. Each of these strengths were 8.2 percent and 12.8 percent greater than their respective controls, respectively. This indicates that a 10 percent replacement results in concrete that experiences an improved resistance to tensile forces on its tension surface. Table 4.14 shows that the 28-day strength arising from the 10%PMBA sample exhibited a 95 percent confidence interval of 3.94 MPa to 5.72 MPa, whilst the 28-day control ranged from 3.58 MPa to 4.99 MPa.

Interestingly, Table 4.14 further suggests that the 7-day strength difference between the 10%PMBA and control samples was recognised as being statistically significant, whilst the 28-day counterpart was not. Additionally, the 7-day 5%PMBA sample produced the only strength difference, relative to the control, that was statistically significant. The comparison of means analysis indicated that the 7-day strength of the 5%PMBA sample was greater than that of the 7-day control by a value that is between 0.04 MPa and 0.46 MPa. The inclining strength trend observed between the 5 and 10 percent replacements was followed by a decline in flexural strength. It is interesting to note that the aforementioned decline is much greater for the 28-day strength than the 7-day. This is indicated by the 28-day strength being 2.3 percent lower than the control, whilst the 7-day strength declined, but was still 2 percent higher than the control. The 7-day strength continues declining further at a 20 percent replacement; however, the 28-day strength displays increased strength, which was 3.5 percent greater than the control. To understand this unfitting increasing effect, further investigations into PMBA substitutions exceeding 20 percent replacements are required. It is possible that the increase in the 28-day 20%PMBA mix may be attributed to the PMS portion of PMBA as Nazar et al. (2014) integrated PMS ash into concrete and only observed that the first increase in flexural strength occurred at a 30 percent replacement.

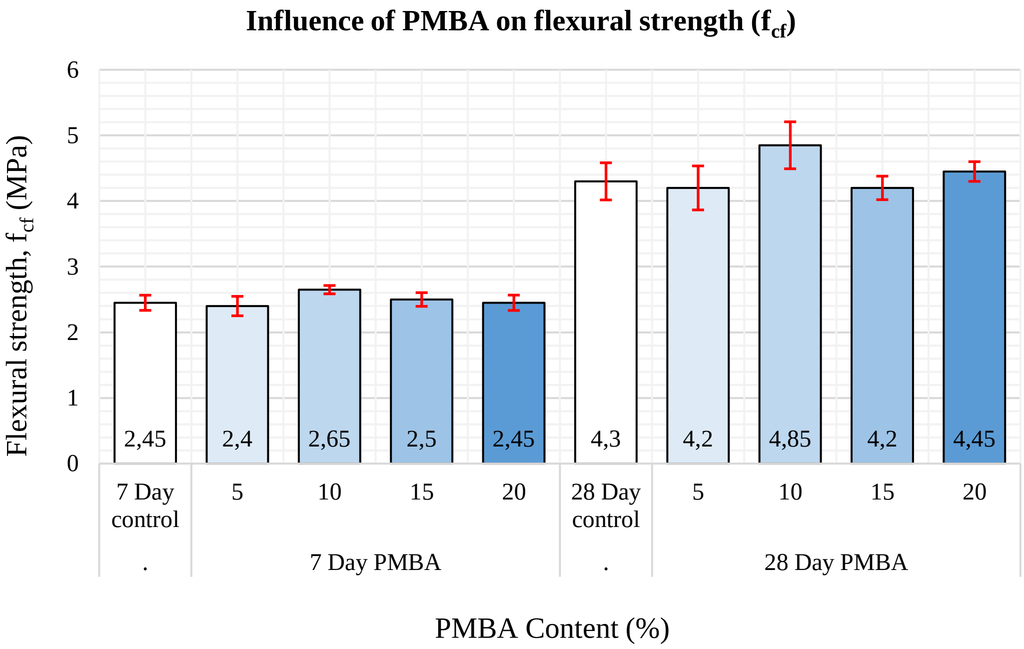


Figure 4.9: *Flexural strength under the effect of incremental additions of PMBA*

Table 4.14: *Analysis of 7and 28-day flexural strength results for PMBA-concrete*

<u>7-Day statistical analysis</u>			**Confidence interval (MPa)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (MPa)**	
Mix ID	**Δ (%)**	**$f_{cf,7}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	2.45	2.10	2.68	-	-	-	-
5%PMBA	-2.0	2.40	2.06	2.80	0.37	0.04	-0.26	0.34
10%PMBA	8.2	2.65	2.49	2.80	3.33	0.25	0.04	0.46
15%PMBA	2.0	2.50	2.23	2.75	1.08	0.10	-0.15	0.35
20%PMBA	0.0	2.45	2.18	2.76	0.81	0.08	-0.19	0.34
<u>28-Day statistical analysis</u>			**Confidence interval (MPa)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (MPa)**	
Mix ID	**Δ (%)**	**$f_{cf,28}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	4.30	3.58	4.99	-	-	-	-
5%PMBA	-2.3	4.20	3.39	5.06	-0.24	-0.06	-0.76	0.64
10%PMBA	12.8	4.85	3.94	5.72	2.07	0.55	-0.19	1.28
15%PMBA	-2.3	4.20	3.77	4.66	-0.34	-0.07	-0.60	0.47
20%PMBA	3.5	4.45	4.09	4.84	0.99	0.18	-0.33	0.70

In terms of application, all 28-day flexural strengths were greater than 4 MPa, indicating the satisfaction of the 4 MPa strength requirement associated with minor roads. However, none of the 28-day strengths resembled that of typical structural concrete. Both the 7-day and 28-day results display similar trends in strength fluctuation.

The fluctuations of flexural strength due to increasing amounts of PMBA is observed to be similar to the fluctuations arising from the integration of fly ash. Upadhyay et al. (2014) found that a 20 percent integration of fly ash resulted in peak strengths followed by a decline. Barbuta et al. (2017) observed that a 10 percent replacement gave the highest flexural strength, followed by a decline.

4.7.2 Influence of WFS

Figure 4.10 below shows the influence of increasing WFS contents on concrete flexural strength.

As indicated by the similar percentage changes in Table 4.15, both the 7 and 28-day flexural strengths displayed similar strength trends. At both testing ages, the highest flexural strength was observed to be the control whilst a 5 percent replacement gave the highest strength from all WFS samples. The 7 and 28-day strength differences between the control and the 5%WFS samples were shown to be statistically insignificant. Flexural strength appears to show consistency at the 5 and 10 percent replacements, followed by a strength decline along the 15 and 20 percent replacements. The aforementioned trend in strength reductions was adequate so as to be considered statistically significant when compared to the control samples. For instance, the lowest 28-day WFS flexural strength arose from the 20%WFS sample, whereby the comparison of means showed a 95 percent confidence interval of -1.50 MPa to -0.34. This indicates that the 28-day control exhibited a higher flexural strength than the 28-day 20%WFS sample, and by a value within the region of 0.34 MPa to 1.50 MPa.

In terms of application in minor roads, it is seen that only the 5%WFS and 10%WFS mixes meet the 28-day strength requirement of 4 MPa. The results are in contrast with past studies, such as the work of Sowmya & Chaitanya-Kumar (2015) who observed that flexural strength peaks for a 20 percent replacement. In addition, Mavroulidou & Lawrence (2018) found that flexural strength peaks for a 10 percent replacement. The flexural strength results are in correlation with the compressive strength and density results of WFS concrete. Thus, it is possible that the more uniformly graded WFS used in this study had led to the presence of more voids as compared to the control, thereby reducing flexural strength.

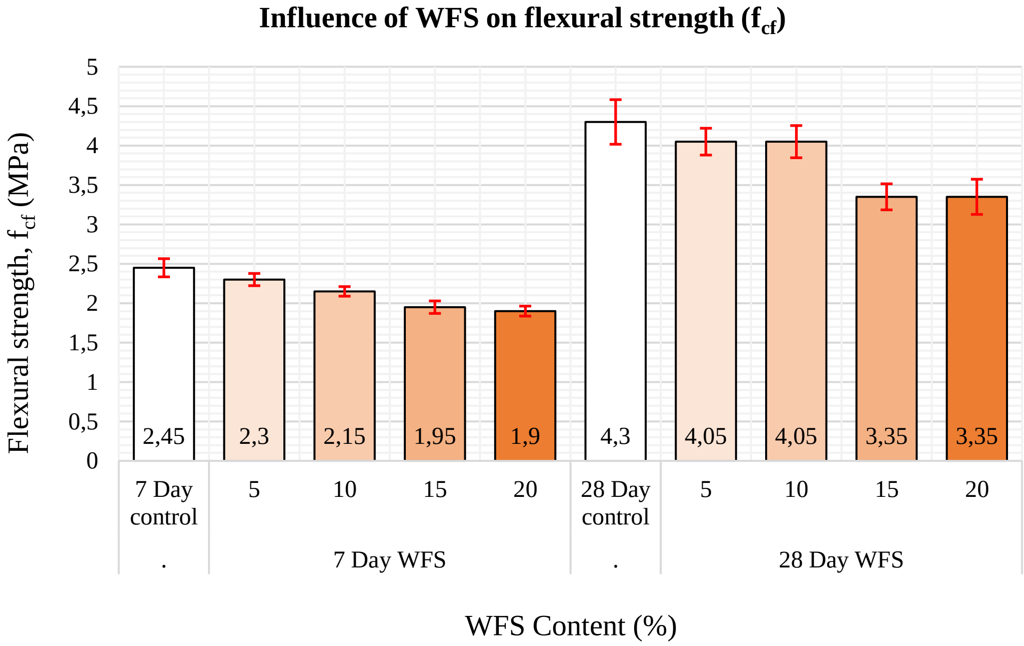


Figure 4.10: *Flexural strength under the effect of incremental additions of WFS*

Table 4.15: *Analysis of 7and 28-day flexural strength results for WFS-concrete*

<u>7-Day statistical analysis</u>			Confidence interval (MPa)		$t_{(v;a)}$ 2.78		Comparison of means (MPa)	
Mix ID	**Δ (%)**	**$f_{cf,7}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	2.45	2.10	2.67	-	-	-	-
5%WFS	-6.1	2.30	2.09	2.48	-1.33	-0.11	-0.33	0.12
10%WFS	-12.2	2.15	1.99	2.30	-3.27	-0.25	-0.46	-0.04
15%WFS	-20.4	1.95	1.77	2.17	-5.20	-0.42	-0.64	-0.20
20%WFS	-22.4	1.90	1.74	2.05	-6.49	-0.49	-0.70	-0.28
<u>28-Day statistical analysis</u>			Confidence interval (MPa)		$t_{(v;a)}$ 2.78		Comparison of means (MPa)	
Mix ID	**Δ (%)**	**$f_{cf,28}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	4.30	3.58	4.99	-	-	-	-
5%WFS	-5.8	4.05	3.64	4.49	-1.14	-0.22	-0.75	0.31
10%WFS	-5.8	4.05	3.53	4.55	-1.21	-0.24	-0.80	0.32
15%WFS	-22.1	3.35	2.93	3.75	-4.98	-0.94	-1.47	-0.42
20%WFS	-22.1	3.35	2.81	3.92	-4.41	-0.92	-1.50	-0.34

4.8 TENSILE-SPLITTING STRENGTH (f_{ct})

Table 4.16 below presents the results obtained in the tensile-splitting strength tests. The complete data is laid out in appendix G. The control sample exhibited a 7-day strength of 2.20 MPa and a 28-day strength of 2.70 MPa. Evidently, the 28-day strength does not resemble the strength of 3 MPa as generally displayed by structural concrete. The 28-day control exhibited a 95 percent confidence interval of 2.48 MPa to 2.89 MPa.

Table 4.16: *Tensile-splitting strength results*

Test material content (%)	f_{ct} (MPa)			
	PMBA		WFS	
	7 Day	28 Day	7 Day	28 Day
Control	2.20	2.70	2.20	2.70
5	1.70	2.55	2.15	2.45
10	2.20	2.70	1.65	2.55
15	2.15	2.70	1.45	2.40
20	1.80	2.55	1.65	2.75

4.8.1 Influence of PMBA

Figure 4.11 below shows the influence of increasing PMBA contents on tensile-splitting strength. A general trend can be observed at both testing ages whereby strength decreases at a 5 percent replacement, increases at a 10 percent replacement, and decreases thereafter. Table 4.17 shows that, relative to the control, the strength reduction experienced by the 28-day 5%PMBA and the 20%PMBA is much less than that of the 7-day values. A possible reason for this may be the delayed pozzolanic reaction. Moreover, it is only the differences between the strength of the 7-day control and the strengths of the 7-day 5%PMBA and 20%PMBA samples that are statistically significant. For instance, the 7-day control exhibited a greater tensile-splitting strength than the 7-day 5%PMBA sample by a value in the range of 0.12 MPa to 0.82 MPa. Similarly, it can be suggested, with 95 percent confidence, that the 7-day strength difference between the control and the 20%PMBA sample lies in the interval of 0.03 MPa to 0.69 MPa.

It must be noted that, similar to the control, none of the PMBA samples exhibited a tensile-splitting strength that is reminiscent of structural concrete. The lowest tensile-splitting strengths at both testing ages were observed at a 5 percent replacement. The 10 percent replacement resulted in the greatest strengths, whereby the 7-day strength of 2.2 MPa was the same as the 7-day control. Moreover, the greatest 28-day strength of 2.7 MPa occurred at the control and at 10 and 15 percent replacements. The 28-day 10%PMBA sample exhibited a 95 percent confidence interval of 2.31 MPa to 3.12 MPa, whilst that of the 28-day control ranged from 2.48 MPa to 2.89 MPa. It is interesting to note the trends, whereby the 5%PMBA and 20%PMBA samples show a resemblance in strength at both testing ages, whilst the strengths of the control and the 10%PMBA samples are equal at both testing ages.

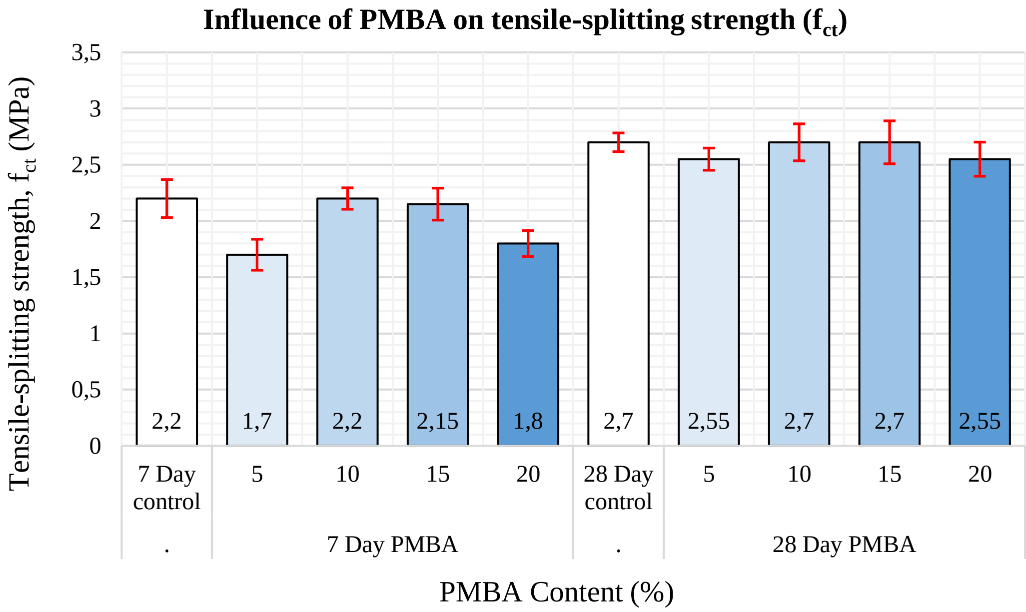


Figure 4.11: *Tensile-splitting strengths under the effect of incremental additions of PMBA*

Table 4.17: *Analysis of 7and 28-day tensile-splitting strength results for PMBA-concrete*

7-Day statistical analysis			**Confidence interval (MPa)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (MPa)**	
Mix ID	**Δ (%)**	**$f_{ct,7}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	2.20	1.77	2.61	-	-	-	-
5%PMBA	-22.7	1.70	1.37	2.06	-3.73	-0.47	-0.82	-0.12

10%PMBA	0.0	2.20	1.94	2.42	-0.06	-0.01	-0.32	0.31
15%PMBA	-2.3	2.15	1.80	2.51	-0.24	-0.03	-0.38	0.32
20%PMBA	-18.2	1.80	1.54	2.11	-3.07	-0.36	-0.69	-0.03
28-Day statistical analysis			**Confidence interval (MPa)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (MPa)**	
Mix ID	**Δ (%)**	**$f_{ct,28}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	2.70	2.48	2.89	-	-	-	-
5%PMBA	-5.6	2.55	2.32	2.80	-1.70	-0.13	-0.33	0.08
10%PMBA	0.0	2.70	2.31	3.12	0.25	0.03	-0.27	0.32
15%PMBA	0.0	2.70	2.22	3.17	0.06	0.01	-0.33	0.34
20%PMBA	-5.6	2.55	2.17	2.92	-1.4	-0.14	-0.42	0.14

In comparison to other PMBA samples, the results suggest that a 10 percent replacement provides greatest resistance to tensile forces at a given point in the tension field. This result is in line with investigations conducted on fly ash. Yerramala et al. (2012) and Barbuta et al. (2017) confirmed that tensile-splitting strength was maximised at a 10 percent replacement with fly ash. The results are in contrast with the investigations involving PMS ash. As indicated by Ahmad et al. (2013) and Raghuwanshi & Joshi (2017), it is instead a 5 percent replacement with PMS ash that results in the greatest strength. This may again suggest that PMBA shares more of a resemblance to fly ash than to PMS ash.

4.8.2 Influence of WFS

Figure 4.12 below shows the influence of increasing PMBA contents on concrete tensile-splitting strength.

The results suggest that tensile-splitting strength decreases at a 5 percent replacement. This was observed at both testing ages. However, Table 4.18 indicates that a 5 percent replacement, at both testing ages, did not warrant statistical significance in terms of their difference in strengths when compared to their respective controls. The 7 and 28-day results show a contradiction at a 10 percent replacement, whereby the former decreases whilst the latter increased. It is shown that, when compared to the 7-day control, the 7-day 10%PMBA exhibited a strength difference that was considered statistically significant. The 15 percent replacements resume the pattern of decreasing strength at both testing ages. Both the 7-day and 28-day strengths show an increase in strength at a 20 percent replacement. At a 7-day testing age, the 10, 15 and 20 percent replacements exhibited strength reductions, relative to the 7-day control, that were considered statistically significant. However, it is interesting that none of the 28-day test results indicated statistical significance in terms of said reductions in strength.

Incidentally, the 28-day strength arising from the 20 percent replacement showed the highest tensile-splitting strength from all samples tested in this study. Additionally, Table 4.18 shows that the only strength greater than the control was the aforementioned 28-day strength. This suggests that 20%PMBA may display a greater resistance to tensile forces than the control concrete. The 28-day 20%WFS sample exhibited a 95 percent confidence interval of 2.66 MPa to 2.86 MPa, whilst the 28-day control ranged from 2.48 MPa to 2.89 MPa. These results resemble the findings of Sowmya & Chaitanya-Kumar (2015), who observed that the 28-day tensile-splitting strengths decreased up until a 20 percent replacement, which improved strength. Their findings indicate that strength decreases afterwards, which may imply that the tensile-strength may decrease with greater contents of UIS WFS.

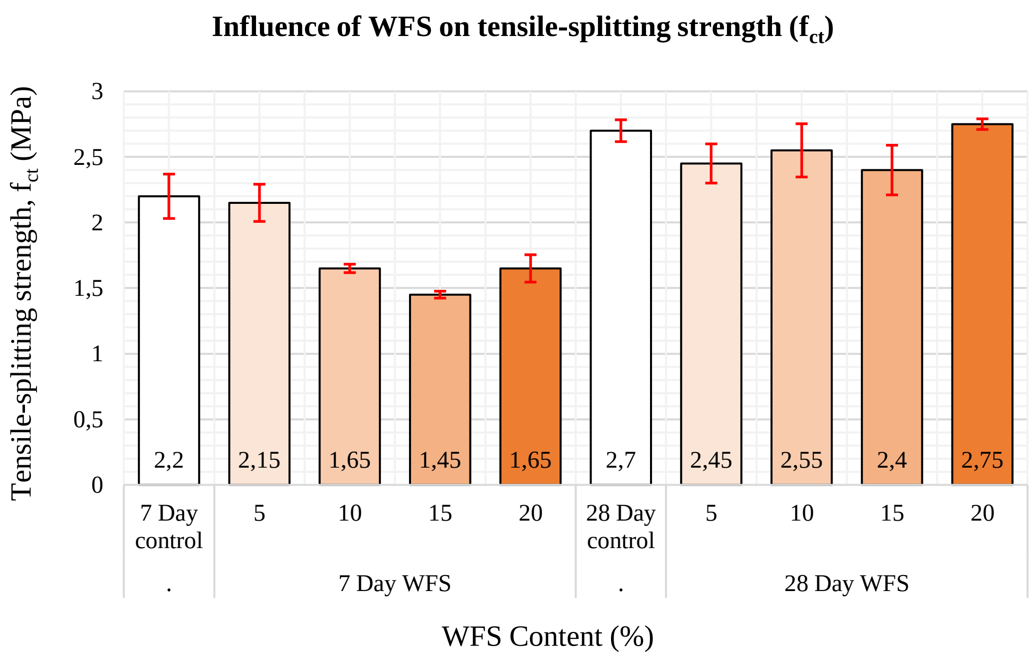


Figure 4.12: *Tensile-splitting strengths under the effect of incremental additions of WFS*

Table 4.18: *Analysis of 7and 28-day tensile-splitting strength results for WFS-concrete*

7-Day statistical analysis			**Confidence interval (MPa)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (MPa)**	
Mix ID	**Δ (%)**	**$f_{ct,7}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	2.20	1.77	2.61	-	-	-	-
5%WFS	-2.3	2.15	1.82	2.52	-0.13	-0.02	-0.37	0.34
10%WFS	-25.0	1.65	1.59	1.75	-5.23	-0.52	-0.80	-0.24
15%WFS	-34.1	1.45	1.39	1.53	-7.35	-0.73	-1.00	-0.45
20%WFS	-25	1.65	1.41	1.93	-4.50	-0.52	-0.84	-0.20
28-Day statistical analysis			**Confidence interval (MPa)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (MPa)**	
Mix ID	**Δ (%)**	**$f_{ct,28}$ (MPa)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (MPa)**	**Lower**	**Upper**
Control	-	2.70	2.48	2.89	-	-	-	-
5%WFS	-9.3	2.45	2.07	2.81	-2.50	-0.25	-0.52	0.03
10%WFS	-5.6	2.55	2.05	3.06	-1.05	-0.13	-0.49	0.22
15%WFS	-11.1	2.40	1.93	2.87	-2.37	-0.28	-0.62	0.05
20%WFS	1.9	2.75	2.66	2.86	1.43	0.08	-0.07	0.23

4.9 DURABILITY: OPI

Appendix H contains all the readings for all three DI tests, the corresponding averaged values and coefficient of variation (CoV). Table 4.19 presents the results from the OPI test, as provided by Contest (PTY) Ltd. As indicated by the classification criteria presented in Table 2.40, the greater the OPI value, the less permeable the concrete.

The control sample showed an OPI value of 10.31, which was classified as exhibiting an ‘excellent’ degree of durability in terms of permeability. In addition, the sample showed a 95 percent confidence interval of 10.03 log value to 10.59 log value. All other test samples will be assessed relative to the control.

Table 4.19: *OPI results*

Test material content (%)	PMBA		WFS	
	OPI (log value)	Durability category	OPI (log value)	Durability Category
Control	10.31	Excellent	10.31	Excellent
5	10.32	Excellent	10.32	Excellent
10	9.84	Good	9.91	Good
15	10.23	Excellent	9.89	Good
20	10.11	Excellent	10.11	Excellent

4.9.1 Influence of PMBA

Figure 4.13 shows that the 5%PMBA sample exhibited the highest OPI value of 10.32, which was 0.10 percent higher than the control. This indicates that a 5 percent replacement results in the least permeable concrete as compared to all PMBA samples. Since strength and density improved at a 5 percent replacement, a possible reason for the increase in OPI may be the fine-filler effect of PMBA, which may have packed voids, resulting in reduced permeability by blocking the migration of gases. Following the discussion presented in Section 2.12.1, by virtue of displaying a greater OPI value, the 5%PMBA sample may exhibit an improved resistance to carbonation-induced corrosion by reducing the advancement of the carbonation depth. However, it is important to state that since the test statistic in Table 4.20 is less than the critical value of 2.45, OPI difference, between the 5%PMBA and control samples, is not statistically significant. The 5%PMBA sample had a 95 percent confidence interval of 10.09 log value to 10.59 log value.

Contrary to expectations, a 10 percent replacement resulted in concrete that exhibited the lowest OPI value of 9.84, indicating that the 10%PMBA sample was the most permeable as compared to all PMBA samples. The OPI of this sample was 4.6 percent lower than the control, and exhibited a 95 percent confidence interval ranging from 9.57 log value to 10.11 log value, whilst the control ranged from 10.03 log value to 10.59 log value. Statistical analysis indicated that the difference in OPI, between the control and 10%PMBA samples, is statistically significant. In considering that the 10%PMBA sample showed an OPI value that was 4.5 percent less than the control, the sample may require increased cover depth in order to cater for carbonation. However, it should be noted that whilst this sample exhibited the lowest OPI, the concrete was still classified as having a ‘good’ degree of durability with respect to permeability. It is of interest that the 10%PMBA sample exhibited the greatest permeability. This is because both density and compressive strength peaked at a 10 percent replacement, both of which indicate reduced permeability. This suggests that the fine-filler effect of PMBA may not have been as influential in improving density and strength and that other factors, such as those relating to pozzolanic reactions (consumption of CH to produce C-S-H) and PMBA characteristics (higher reactivity due to increased amorphousness) may have been more responsible for strength gain.

Another interesting observation occurs at a 15 percent replacement, which resulted in a less permeable concrete as compared to the 10%PMBA sample. However, the 15%PMBA sample was classified as having 'excellent' durability. The decrease in OPI values appear more gradual at a 20 percent replacement, however the sample was still classified as having an 'excellent' degree of durability with respect to permeability. In relation to the control, the aforementioned decline in OPI was shown to be associated with statistical insignificance.

All test samples, except the 10%PMBA produced concrete having 'excellent' degrees of durability, with the 5%PMBA showing the best performance with respect to OPI testing. The 15 and 20 percent results contribute to the findings of Zulu & Allopi (2014), who investigated higher volumes of fly ash in concrete and concluded that greater contents of fly ash result in greater permeability. In addition, the results from this study establishes that further research is required into assessing the separate influences of the fine-filler effect and the amorphousness of pozzolana on OPI. These results contradict the results obtained when PMS ash was tested for permeability in concrete. Wong et al. (2015) showed that permeability decreased up until a 12 percent replacement with PMS ash, which resulted in the maximum oxygen permeability observed.

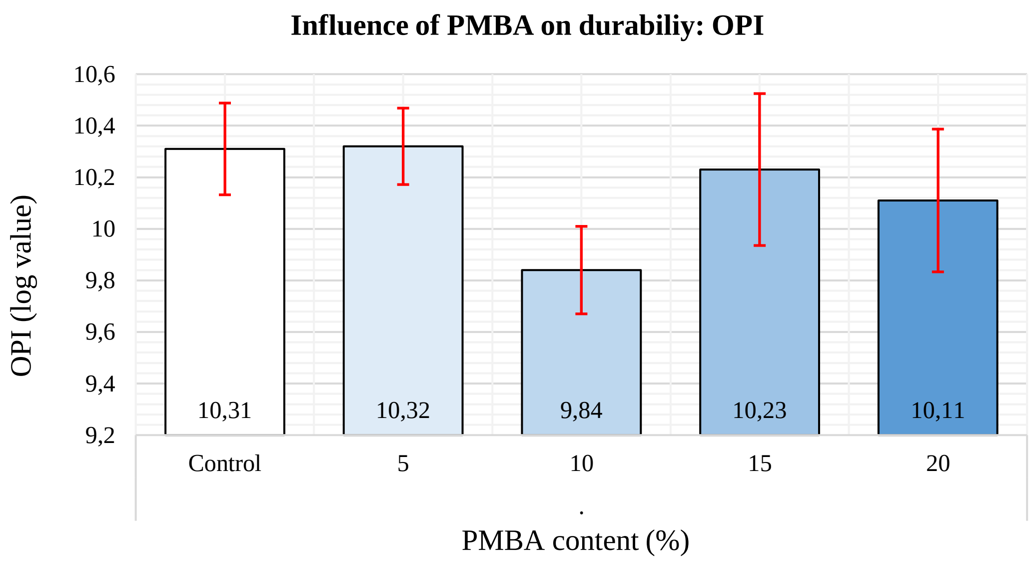


Figure 4.13: *OPI under the influence of incremental additions of PMBA*

Table 4.20: *Analysis of OPI results for PMBA-concrete*

Mix ID	**Δ (%)**	**OPI (log value)**	**Confidence interval (log value)**		**$t_{(v;a)}$ 2.45**		**Comparison of means (log value)**	
			Lower	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (log value)**	**Lower**	**Upper**
Control	-	10.31	10.03	10.59	-	-	-	-
5%PMBA	0.1	10.32	10.09	10.59	0.11	0.01	-0.27	0.30
10%PMBA	-4.6	9.84	9.57	10.11	-3.82	-0.47	-0.77	-0.17
15%PMBA	-0.8	10.23	9.76	10.70	-0.46	-0.08	-0.50	0.34
20%PMBA	-1.9	10.11	9.67	10.55	-1.23	-0.20	-0.61	0.20

4.9.2 Influence of WFS

Figure 4.14 shows that the 5 percent replacement resulted in the least permeable WFS-concrete. The results indicate that this was the only WFS sample with an OPI that was greater than the control (by 0.1 percent). In analysis of the density and compressive strength results of all WFS samples, it was shown that the 5%WFS sample exhibited the greatest density and strength. This may lend to the analysis that, at a 5 percent replacement, WFS may exhibit its own filler effect which reduces void spaces. This analysis supports the claims made by Mavroulidou & Lawrence (2018) who found that WFS is responsible for the reduction in concrete voids. Naturally, the 5%PMBA was classified as having 'excellent' durability against permeability. Table 4.21 shows that, despite the 5%WFS sample showing a greater OPI than the control, the difference in OPI between these two samples was shown to be statistically insignificant. The 5%WFS sample exhibited a 95 percent confidence interval of 10.26 log value to 10.38 log value, whilst the control showed a range from 10.03 log value to 10.59 log value.

A 10 percent replacement showed a decreased OPI value of 9.91, which was 3.9 percent lower than the control. This sample exhibited a 'good' degree of durability. When compared to the control, the aforementioned reduction in OPI was shown to be statistically significant. The decreasing trend was further extended, whereby a 15 percent replacement resulted in the most permeable WFS-concrete sample, and the resulting OPI difference when compared to the control was statistically significant. However, this sample was still classified as having a 'good' resistance to permeability. A replacement of 20 percent showed an increase in OPI, whereby the sample had 'excellent' durability against permeability. These results lend to the conclusions made by Iloh

(2018), who observed similar trends in the fluctuations of OPI and credited increases in OPI to the filler effect of WFS.

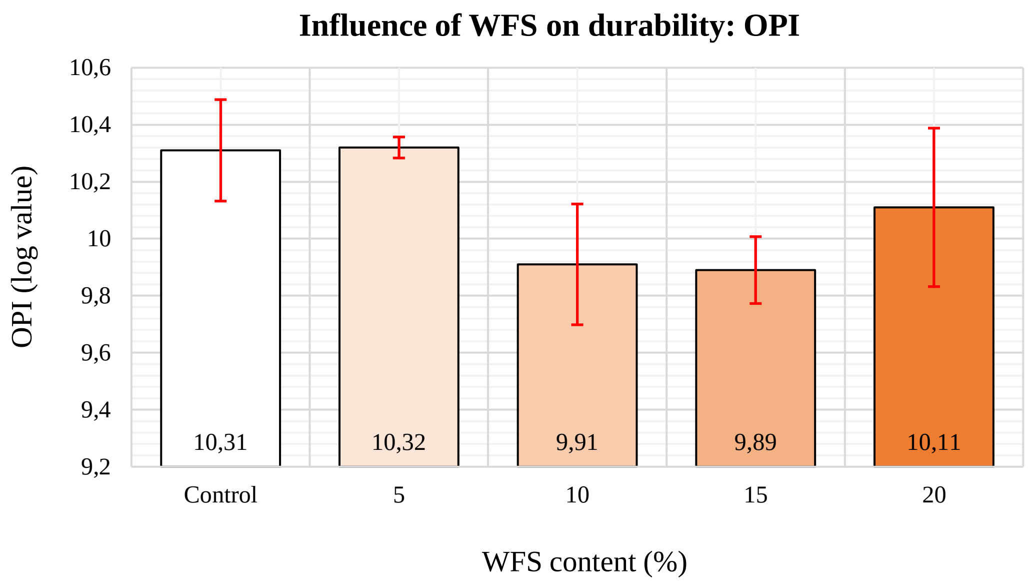


Figure 4.14: *OPI under the influence of incremental additions of WFS*

Table 4.21: *Analysis of OPI results for WFS-concrete*

Mix ID	**Δ (%)**	**OPI (log value)**	**Confidence interval (log value)**		$\mathbf{t_{(v;a)}}$ **2.45**		**Comparison of means (log value)**	
			Lower	**Upper**	$\mathbf{t_0}$	$\bar{x}_i - \bar{x}_c$ **(log value)**	**Lower**	**Upper**
Control	-	10.31	10.03	10.59	-	-	-	-
5%WFS	0.1	10.32	10.26	10.38	0.08	0.01	-0.22	0.23
10%WFS	-3.9	9.91	9.58	10.25	-2.87	-0.40	-0.74	-0.06
15%WFS	-4.1	9.89	9.71	10.08	-3.92	-0.42	-0.68	-0.16
20%WFS	-1.9	10.11	9.67	10.55	-1.22	-0.20	-0.61	0.20

4.10 DURABILITY: WS

As indicated in Table 2.41, lower WS values indicate a more durable concrete. As per Table 4.22 below, the control sample displayed a WS of 6.28 mm/$\sqrt{h}$, which was classified as having a 'good' degree of durability against sorptivity.

Table 4.22: *WS results*

Test material content (%)	**PMBA**		**WFS**	
	WS (mm /$\sqrt{h}$)	**Durability category**	**WS (mm /$\sqrt{h}$)**	**Durability Category**
Control	6.28	Good	6.28	Good
5	5.66	Excellent	4.97	Excellent
10	5.58	Excellent	5.92	Excellent
15	5.85	Excellent	5.62	Excellent
20	5.84	Excellent	5.80	Excellent

4.10.1 Influence of PMBA

Evidently, all PMBA-concrete samples resulted in improved WS when compared to the control. However, Table 4.23 indicated that although the abovementioned improvement occurred, no statistical significance was witnessed in the difference in WS values between the test and control samples. Figure 4.15 shows that a 5 percent replacement results in a WS value of 5.66 mm/$\sqrt{h}$. Table 4.23 further indicates that this reduction was 9.9 percent lower than the control, thereby indicating a more durable concrete. Accordingly, the 5%PMBA sample was classified as having an 'excellent' degree of durability against sorptivity.

From all PMBA mixes, the greatest improvement in WS occurred with a 10 percent replacement, which resulted in a WS of 5.58 mm/$\sqrt{h}$, which was 11.1 percent lower than the control. The 95 percent confidence interval of this sample ranged from 5.05 mm/$\sqrt{h}$ to 6.10 mm/$\sqrt{h}$, whilst the control ranged from 5.06 mm/$\sqrt{h}$ to 7.49 mm/$\sqrt{h}$. Naturally, this sample displayed an 'excellent' degree of durability in terms of WS. A possible reason for this is the fine-filler effect of PMBA and other factors that had improved the 10%PMBA density, which resulted in a refined pore structure with poorly connected pores, thereby reducing capillary absorption. Generally, greater moisture states decrease values of WS by reducing capillary absorption. However, it is unlikely that the moisture content (MC) contributed to the improved WS as the 10%PMBA concrete exhibited a relatively low MC of 6.03 percent (Figure 4.16 below).

A 15 percent replacement resulted in a downgrade in WS, by exhibiting a value of 5.85 mm/$\sqrt{h}$, which however was still classified as displaying 'excellent' resistance to sorptivity and was 6.8 percent lower than the control. The 20 percent replacement showed a slight improvement in WS, with a value of 5.84 mm/$\sqrt{h}$, which was 7 percent greater than the control.

The results show a correlation to the findings of Nath & Sarkar (2011), who integrated fly ash into concrete and observed that all test samples showed reductions in sorptivity when compared to the control. It is noteworthy that for the 15 and 20 percent replacements, variations in WS values are slight. This observation may add to the study of Zulu & Allopi (2014), who observed that variations in WS values are minor after a 30 percent integration of fly ash. These results contradict the results from investigations involving PMS ash, whereby Joshi & Pitroda (2018) observed a continued increase in WS as the content of PMS ash increased.

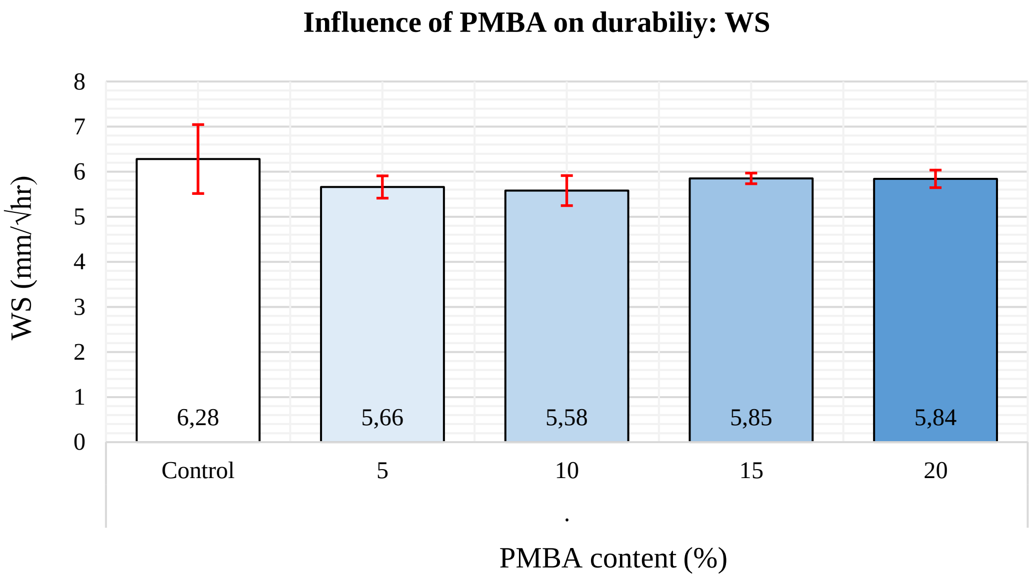


Figure 4.15: *WS under the influence of incremental additions of PMBA*

__Table 4.23:__ Analysis of WS results for PMBA-concrete

Mix ID	Δ (%)	WS ($mm/\sqrt{h}$)	Confidence interval ($mm/\sqrt{h}$)		$t_{(v;a)}$ 2.45		Comparison of means ($mm/\sqrt{h}$)	
			Lower	Upper	t_0	$\bar{x}_i - \bar{x}_c$ ($mm/\sqrt{h}$)	Lower	Upper
Control	-	6.28	5.06	7.49	-	-	-	-
5%PMBA	-9.9	5.66	5.27	6.06	-1.53	-0.62	-1.60	0.37
10%PMBA	-11.1	5.58	5.05	6.10	-1.68	-0.70	-1.72	0.32
15%PMBA	-6.8	5.85	5.67	6.04	-1.10	-0.43	-1.37	0.52
20%PMBA	-7.0	5.84	5.53	6.15	-1.12	-0.44	-1.41	0.53

Figure 4.16 below shows a trend whereby greater values of MC produce reduced WS values, and consequently a greater resistance to sorptivity. This analysis is supported by the work of Mukadam (2014). The exception to this trend appears to occur at a 10 percent replacement.

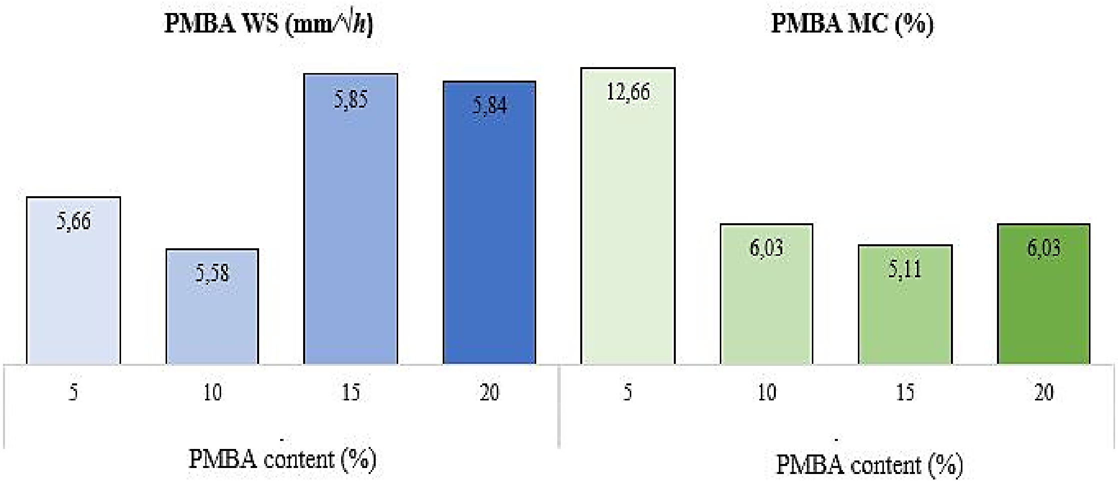


***Figure 4.16:** Comparison between the WS values and MC values of PMBA-concrete*

4.10.2 Influence of WFS

As per Figure 4.17, all WFS samples showed improved WS values compared to the control. The 5%WFS sample resulted in a WS of 4.97 $mm/\sqrt{h}$. Table 4.24 indicates that this improvement in WS is statistically significant in relation to the control. This is evident considering that the test statistic exhibited by the 5%WFS (i.e., -2.47) was shown to lie outside the critical region of -2.45 to 2.45. Table 4.24 further shows that the 5%WFS provided a WS value that was 20.9 percent lower than the control and was the best WS result observed in this study. Similar to PMBA, a possible reason for this improvement may be the fine-filler effect. This is further supported by the fact that the greatest WFS density result occurred at a 5 percent replacement. As shown in Figure 4.18 below, it may also be possible that the relatively high MC of the 5%WFS concrete may have reduced capillary absorption, thereby decreasing WS. This supports the understanding that MC and WS are related and further builds on the work of Mukadam (2014). The 5%WFS sample showed a 95 percent confidence interval of 3.80 mm/$\sqrt{h}$ to 6.14 mm/$\sqrt{h}$, whilst the control ranged from 5.06 mm/$\sqrt{h}$ to 7.49 mm/$\sqrt{h}$.

A 10 percent replacement showed an increased WS value, however the 10%WFS concrete was still classified as having an 'excellent' degree of durability and said increase was not statistically significant when compared to the control. Incidentally, the 10, 15 and 20 percent replacements did not provide WS values that satisfy the condition for statistical significance when compared to the control. A gradual decrease in WS was observed at the 15 percent replacement, followed by a gradual increase at the 20 percent replacement. Both samples were classified as having an 'excellent' degree of durability against sorptivity.

These results contradict the results obtained by Bhardwaj & Kumar (2018), who observed that sorptivity showed a continued decrease as WFS increased.

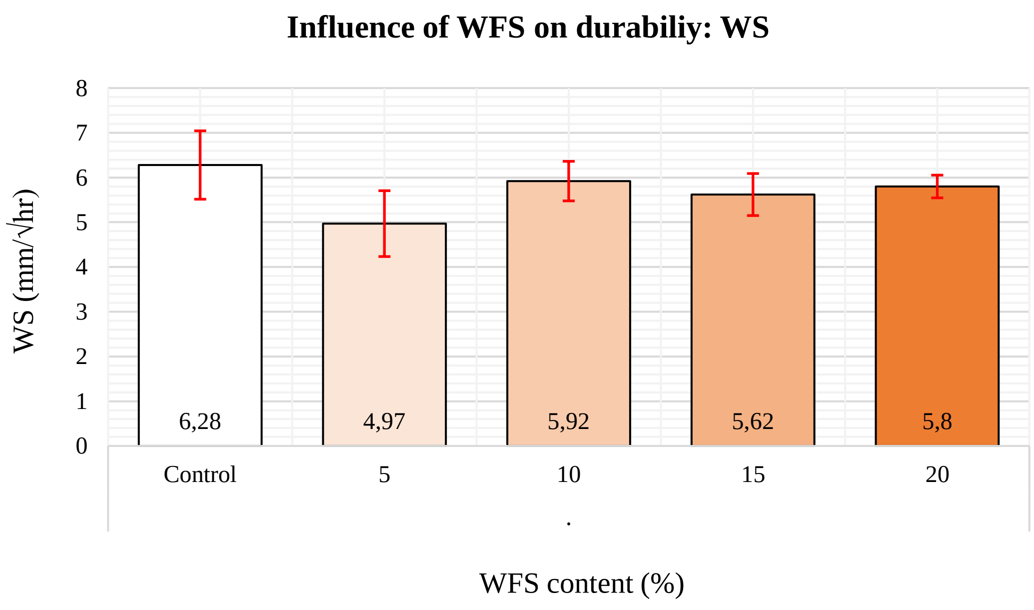


Figure 4.17: *WS under the influence of incremental additions of WFS*

Table 4.24: *Analysis of WS results for WFS-concrete*

Mix ID	Δ (%)	WS ($mm/\sqrt{h}$)	Confidence interval ($mm/\sqrt{h}$)		$t_{(v;a)}$ 2.45		Comparison of means ($mm/\sqrt{h}$)	
			Lower	**Upper**	t_0	$\bar{x}_i - \bar{x}_c$ ($mm/\sqrt{h}$)	**Lower**	**Upper**
Control	-	6.28	5.06	7.49	-	-	-	-
5%WFS	-20.9	4.97	3.80	6.14	-2.47	-1.31	-2.61	-0.10
10%WFS	-5.7	5.92	5.21	6.62	-0.82	-0.36	-1.44	0.72
15%WFS	-10.5	5.62	4.87	6.36	-1.47	-0.66	-1.76	0.44
20%WFS	-7.6	5.80	5.40	6.21	-1.18	-0.48	-1.46	0.51

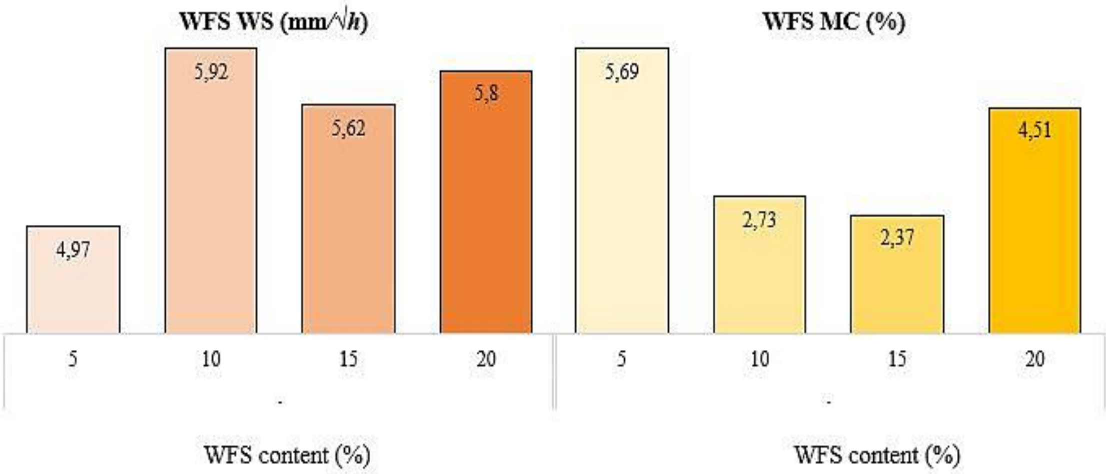


Figure 4.18: *Comparison between the WS values and moisture contents of WFS-concrete*

4.11 DURABILITY: CC

Table 4.25 presents the results from the CC test. As in the case of WS, lower values of CC indicate a more durable concrete. It was found that the control sample displayed a CC of 0.26 mS/cm, which was classified as having an 'excellent' degree of durability against chloride diffusion.

__Table 4.25:__ Chloride conductivity results

Test material content (%)	PMBA		WFS	
	CC (mS/cm)	**Durability category**	**CC (mS/cm)**	**Durability Category**
Control	0.26	Excellent	0.26	Excellent
5	0.26	Excellent	0.23	Excellent
10	0.24	Excellent	0.22	Excellent
15	0.27	Excellent	0.25	Excellent
20	0.26	Excellent	0.26	Excellent

4.11.1 Influence of PMBA

The 5 percent replacement produced concrete that displayed a CC value of 0.26 mS/cm, which was the same CC value as the control concrete. As compared to all samples tested in this investigation, the most improved CC value was achieved at a 10 percent replacement. This CC value was found to be 0.24 mS/cm which was 7.7 percent lower than the control. As discussed in Section 2.12.4 (C), CC is highly influenced by concrete pore structure and porosity. By extension, the fine-filler effect is responsible for refining the pore structure and reducing porosity, as indicated by the greatest density and strength occurring in the 10%PMBA sample. This analysis is in line with statements made by Mackechnie (1996) and Shekhovtsova et al. (2014), who informed of the importance of pore structure as an influence of CC. The 95 percent confidence interval for this sample ranged from 0.22 mS/cm to 0.28 mS/cm. Interestingly, the control sample shares the same a 95 percent confidence as the 10%PMBA sample. Accordingly, despite the 10%PMBA sample exhibiting the superior CC value, the difference in CC values between this sample and the control showed a lack of statistical significance. This is evident in Table 4.26, whereby the 10%PMBA sample produced a test statistic of -0.48, which was within the critical region of -2.45 to 2.45. Incidentally, none of the test samples proved to be statistically significant when compared to the control.

A 15 percent replacement saw an increase in CC, which was 3.8 percent greater than the control. The 20 percent replacement displayed a CC of 0.26 mS/cm, which resembled the control and the 5%PMBA sample. All PMBA strengths were classified as ‘excellent’ in resisting chloride conductivity. Accordingly, all PMBA samples are likely to exhibit improved resistances to chloride attack and increased capacities for steel protection.

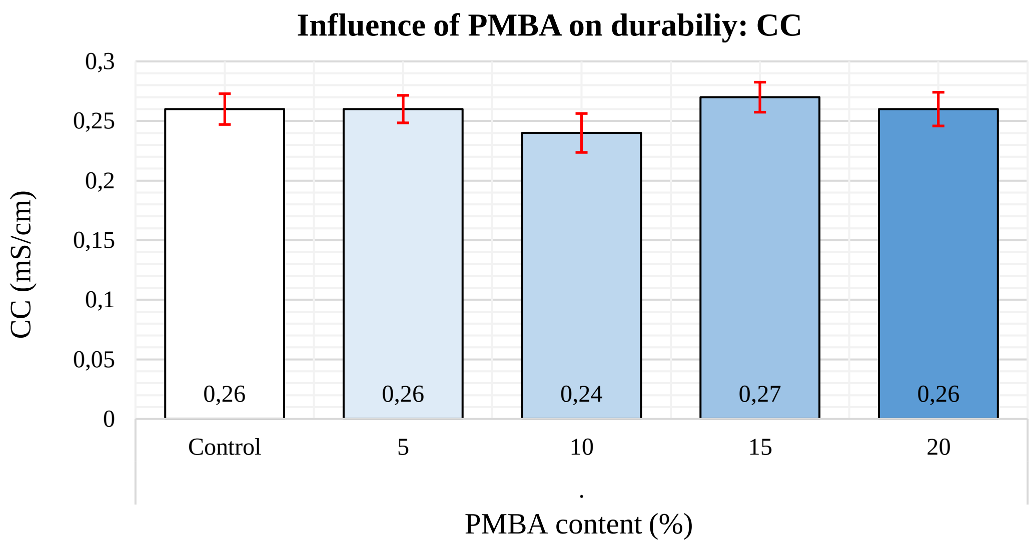


Figure 4.19: *CC under the influence of incremental additions of PMBA*

Table 4.26: *Analysis of CC results for PMBA-concrete*

Mix ID	**Δ (%)**	**CC (mS/cm)**	**Confidence interval (mS/cm)**		**$t_{(v;a)}$ 2.45**		**Comparison of means (mS/cm)**	
			Lower	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (mS/cm)**	**Lower**	**Upper**
Control	-	0.26	0.22	0.28	-	-	-	-
5%PMBA	0.0	0.26	0.24	0.28	0.58	0.010	-0.02	0.03
10%PMBA	-7.7	0.24	0.22	0.28	-0.48	-0.005	-0.03	0.02
15%PMBA	3.8	0.27	0.25	0.29	1.39	0.012	-0.01	0.03
20%PMBA	0.0	0.26	0.24	0.28	0.52	0.005	-0.02	0.03

4.11.2 Influence of WFS

The 5%WFS sample exhibited a reduced CC value of 0.23 mS/cm. which was 11.5 percent lower than the control. From all samples tested in this study, the best CC value was displayed by the 10%WFS sample. Table 4.27 shows that this sample exhibited a 95 percent confidence interval of 0.18 mS/cm to 0.26 mS/cm, whilst the control ranged from 0.23 mS/cm to 0.28 mS/cm. The

CC value of the 10%WFS sample was lower than that of the control sample by a value between 0.001 mS/cm to 0.07 mS/cm. As a result, the difference in CC values was deemed statistically significant as the test statistic for the 10%WFS sample (-2.53) was not within the critical region of -2.45 to 2.45. The 10%WFS sample was the only WFS sample to meet the condition of statistical significance. It is unclear as to whether the filler effect of WFS contributed to this enhancement as both density and strengths reduced at a 10 percent replacement.

At replacements of 15 and 20 percent, the resulting CC values were 3.8 and 0.0 percent lower than the control. All WFS samples showed 'excellent' degrees of durability against chloride diffusion, thereby indicating their ability to resist corrosion of reinforcements.

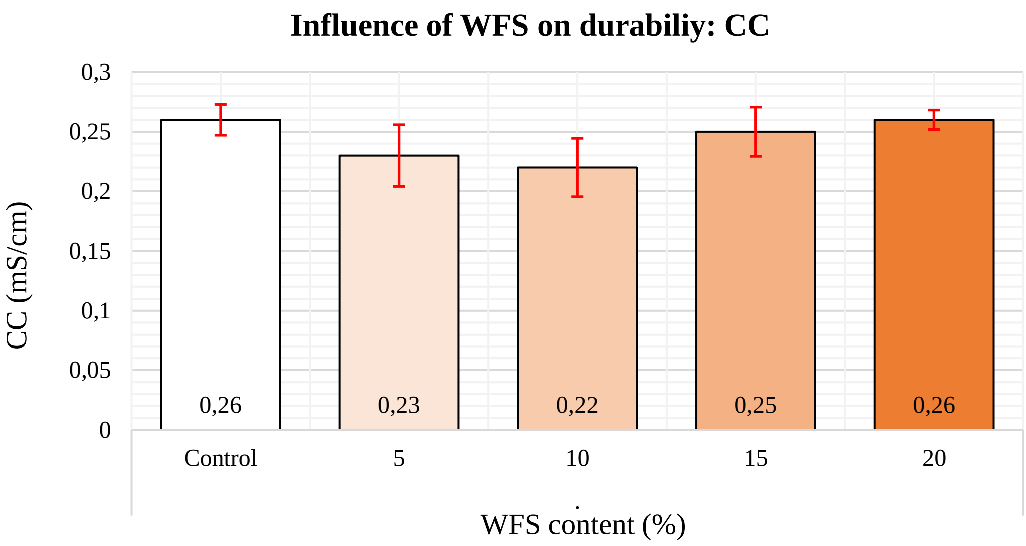


Figure 4.20: *CC under the influence of incremental additions of WFS*

Table 4.27: *Analysis of CC results for WFS-concrete*

Mix ID	Δ (%)	CC (mS/cm)	Confidence interval (mS/cm)		$t_{(v;a)}$ 2.45		Comparison of means (mS/cm)	
			Lower	Upper	t_0	$\bar{x}_i - \bar{x}_c$ (mS/cm)	Lower	Upper
Control	-	0.26	0.23	0.28	-	-	-	-
5%WFS	-11.5	0.23	0.19	0.27	-1.73	-0.030	-0.06	0.01
10%WFS	-15.4	0.22	0.18	0.26	-2.53	-0.035	-0.07	-0.001

15%WFS	-3.8	0.25	0.21	0.28	-0.62	-0.008	-0.04	0.02
20%WFS	0.0	0.26	0.25	0.27	0.65	0.005	-0.01	0.02

4.12 pH VALUE

Appendix I contains all raw data, the readings for all three leaching tests and the corresponding averaged values. Appendix J contains all raw data for the statistical analysis conducted on all three leaching tests. pH values were assessed at 7 and 28-days to identify the influence of each test material over time. The 7-day control showed a leachate having a pH value of 13.30 whilst a 28-day pH value was found to be similar, with a value of 13.36. Both of these values meet the requirement for maintaining the steel-protecting passivation layer by exceeding a pH value of 11. The 95 percent confidence interval for the 7-day testing indicated a pH value range of 12.96 to 13.64, whilst the 28-day counterpart showed a range of 13.26 to 13.46. In terms of leachate quality, the pH value for drinking water cannot occur outside the range of 5 to 9.7 pH units. As such, due to the inherent alkaline nature of concrete, leachate samples with lower pH values will be seen as exhibiting an improved quality. Table 4.28 presents the results from the pH tests.

Table 4.28: *pH value results*

Test material content (%)	pH Value			
	PMBA		WFS	
	7 Day	28 Day	7 Day	28 Day
Control	13.30	13.36	13.30	13.36
5	13.33	13.25	13.35	12.31
10	13.18	13.24	13.35	12.58
15	13.25	13.13	13.40	12.81
20	13.17	13.06	13.39	13.49

4.12.1 Influence of PMBA

As shown in Figure 4.21, the 7-day pH values did not show a specific trend, whilst the 28-day values exhibited a general decreasing trend. The 7 and 28-day values of PMBA concrete are in contrast. The highest 7-day pH value was observed at a 5 percent replacement. The 10%PMBA sample exhibited the lowest pH value of 13.18, which was 0.9 percent lower than the control, yet still higher than 11 to maintain the passivation layer. This was followed by more fluctuations in pH as the 15%PMBA showed an increased 7-day pH value of 13.25 whilst the 20%PMBA showed a reduced 7-day pH value of 13.17. Evidently, all 7-day pH values were above 11 so as to support the preservation of the passivation layer. However, when compared to the control, none of the 7-day pH values arising from test samples was shown to be statistically significant. This is evident in Table 4.29, whereby all 7-day test statistic values were within the critical region of -2.78 and 2.78. The 28-day pH decreased with increasing contents of PMBA. Due to the aforementioned decreasing trend, 20%PMBA produced the lowest 28-day pH value of 13.06, which was 2.25 percent lower than the control. Statistical analysis indicated that the 15%PMBA and 20%PMBA samples were lower than the control by values that met the criteria for statistical significance. This is evident as per Table 4.29, which shows that the 28-day test statistics that arose from the 15 and 20 percent replacements did not lie within the critical range. The decreasing trend may indicate that the later age pH values of concrete are reduced as the content of PMBA increases. This may be possible due to the consumption of CH. However, it is noteworthy that all 28-day pH values were above 11, thereby indicating the preservation of the passivation layer. This analysis supports claims made by Mehta & Monteiro (2006) who stated that whilst pozzolana reduces quantities of CH during its reaction, there is still sufficient quantities left to maintain concrete pH. In terms of leachate quality, the 28-day samples indicate that the addition of greater amounts of PMBA may produce a more environmentally-friendly leachate.

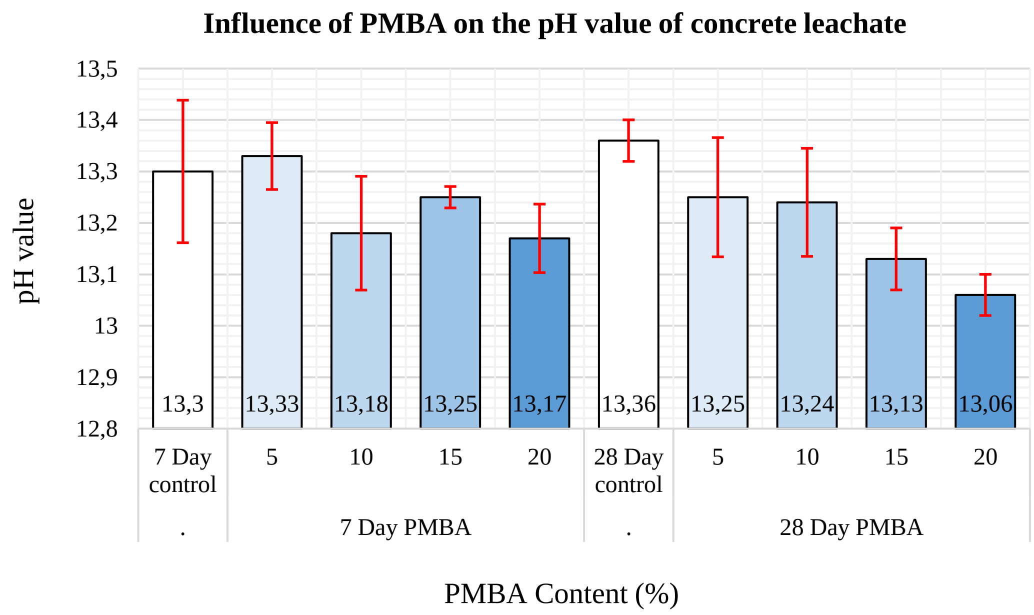


Figure 4.21: *pH of concrete leachate under the influence of incremental additions of PMBA*

Table 4.29: Analysis of pH values for leachate from PMBA-concrete

7-Day statistical analysis			**Confidence interval**		**$t_{(v;a)}$ 2.78**		**Comparison of means**	
Mix ID	**Δ (%)**	**pH value**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$**	**Lower**	**Upper**
Control	-	13.30	12.96	13.64	-	-	-	-
5%PMBA	-0.23	13.33	13.17	13.49	0.38	0.03	-0.21	0.28
10%PMBA	-0.90	13.18	12.91	13.46	-1.14	-0.12	-0.40	0.17
15%PMBA	-0.38	13.25	13.19	13.30	-0.66	-0.05	-0.28	0.17
20%PMBA	-0.98	13.17	13.00	13.33	-1.50	-0.13	-0.38	0.11
28-Day statistical analysis			**Confidence interval**		**$t_{(v;a)}$ 2.78**		**Comparison of means**	
Mix ID	**Δ (%)**	**pH value**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$**	**Lower**	**Upper**
Control	-	13.36	13.26	13.46	-	-	-	-
5%PMBA	-0.82	13.25	12.96	13.53	-1.55	-0.11	-0.31	0.09
10%PMBA	-0.90	13.24	12.98	13.50	-1.85	-0.12	-0.30	0.06
15%PMBA	-1.72	13.13	12.98	13.28	-5.49	-0.23	-0.35	-0.11
20%PMBA	-2.25	13.06	12.96	13.16	-9.04	-0.30	-0.39	-0.21

4.12.2 Influence of WFS

Figure 4.22 shows that pH value shows a general increase as the content of WFS increases. The 7 and 28-day results share the same trend; however, the 28-day pH values are significantly lower as compared to their 7-day counterparts whilst the 28-day control resembled 7-day results. This suggests that WFS may show more influence in reducing concrete and leachate pH values at later ages. This analysis suggests the scope for further research by testing concrete at greater curing ages. Due to the increasing effect, the lowest 7-day pH value arose from the 5%WFS sample whilst the highest resulted from the 20%WFS sample. It is of note that all 7-day WFS samples exhibited pH values that were greater than that of the 7-day control. However, Table 4.30 shows that all 7-day test statistic values were within the critical region, indicating a lack of statistical significance when compared to the 7-day control.

The 28-day results provide certain interesting observations. The 5, 10 and 15 percent replacements showed a 7.86, 5.84 and 4.12 percent decrease relative to the control, respectively. The 5%WFS sample exhibited a pH of 12.31, which was the lowest observed in this study. However, this value was still greater than the 11-pH unit value for required for steel protection. The pH difference between the 28-day control and 10%WFS samples indicate statistical significance between the two samples. Moreover, when compared to the control, statistical significance was also proven for the 15%WFS and 20%WFS samples. Figure 4.22 illustrates that pH value of the 20%WFS sample was the only 28-day sample that was greater than the pH value of the 28-day control. Statistical analysis indicates that the 28-day difference between the 20%WFS sample and the control was statistically significant. Moreover, the 28-day 20%WFS sample exhibited a 95 percent confidence interval of 13.39 to 13.59.

Due to discrepancy in pH values of the 7-day and 28-day test samples, it is evident that lower contents of WFS result in a more environmentally-friendly leachate at later ages.

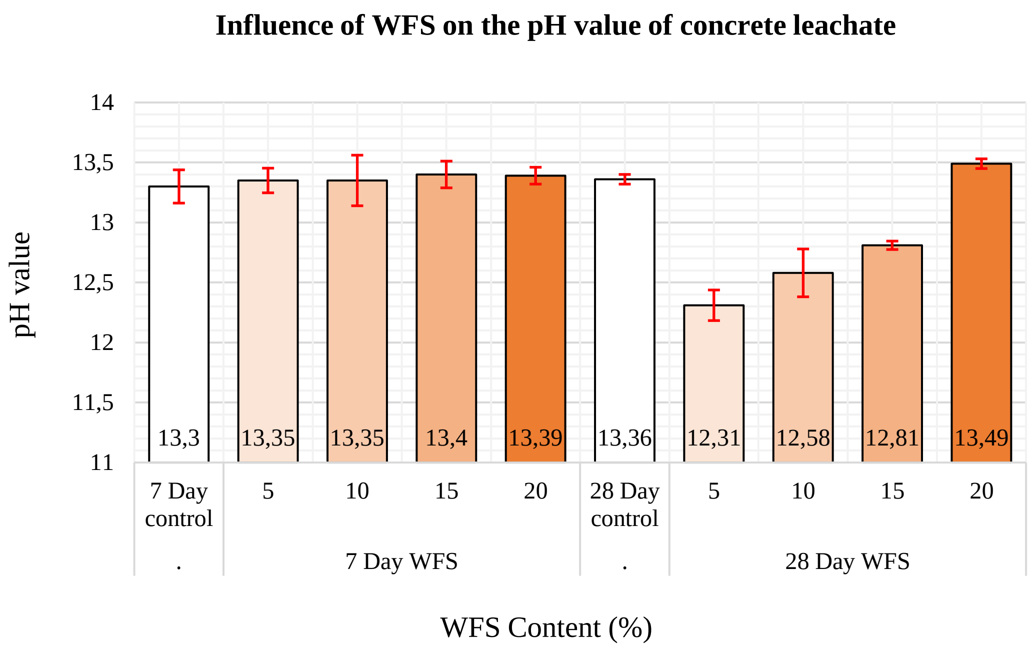


Figure 4.22: *pH of concrete leachate under the influence of incremental additions of WFS*

Table 4.30: *Analysis of pH values for leachate from WFS-concrete*

<u>7-Day statistical analysis</u>			Confidence interval		$t_{(v;a)}$ 2.78		Comparison of means	
Mix ID	**Δ (%)**	**pH value**	**Lower**	**Upper**	t_0	$\bar{x}_i - \bar{x}_c$	**Lower**	**Upper**

Control	-	13.30	12.96	13.64	-	-	-	-
5%WFS	0.38	13.35	13.10	13.61	0.54	0.05	-0.22	0.33
10%WFS	0.38	13.35	12.83	13.88	0.37	0.05	-0.35	0.46
15%WFS	0.75	13.40	13.12	13.68	0.97	0.10	-0.19	0.39
20%WFS	4.51	13.39	13.22	13.57	1.04	0.09	-0.16	0.34
28-Day statistical analysis			**Confidence interval**		**$t_{(v;a)}$ 2.78**		**Comparison of means**	
Mix ID	**Δ (%)**	**pH value**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$**	**Lower**	**Upper**
Control	-	13.36	13.26	13.46	-	-	-	-
5%WFS	-7.86	12.31	12.99	13.62	-0.65	-0.05	-0.26	0.16
10%WFS	-5.84	12.58	12.09	13.07	-6.62	-0.78	-1.10	-0.45
15%WFS	-4.12	12.81	12.72	12.89	-17.79	-0.55	-0.64	-0.46
20%WFS	0.97	13.49	13.39	13.59	4.14	0.14	0.04	0.23

4.13 ION CONDUCTIVITY

The control sample resulted in a leachate that exhibited a 7-day ion conductivity of 6.64 mS/cm whilst at 28-day testing, a 5.56 mS/cm value was observed. The 7-day control displayed a 95 percent confidence interval of 6.25 mS/cm to 7.04 mS/cm, whilst its 28-day counterpart exhibited a range of 5.10 mS/cm to 6.01 mS/cm.

Lower conductivity values indicate that a lower ion presence was leached out. As such, in field conditions, lower conductivity values may indicate a higher resistance to the migration of substances out of the concrete sample and into contacting water. This resistance is often referred to as electrical resistance.

Table 4.31: *Ion conductivity results*

Test material content (%)	**Ion conductivity (mS/cm)**			
	PMBA		**WFS**	
	7 Day	**28 Day**	**7 Day**	**28 Day**
Control	6.64	5.56	6.64	5.56
5	6.41	4.25	4.77	4.20
10	4.87	4.31	4.77	1.50

15	4.92	3.57	5.22	1.89
20	3.58	2.97	4.81	5.38

4.13.1 Influence of PMBA

Figure 4.23 shows a general trend whereby ion conductivity decreases as contents of PMBA increases. This indicates that increasing additions of PMBA results in a higher resistance to ion migration, thereby improving the quality of the resulting leachate. Due to the decreasing trend, the highest ion conductivity was observed at the control samples whilst the lowest was observed at a 20 percent replacement, suggesting that the 20%PMBA concrete performs best in terms of resisting the transportation of contaminants. This indicates that a 20 percent replacement provides a more environmentally-friendly leachate in terms of the decreasing the mobilization of substances out of the concrete. This was the case at both testing ages. As per Table 4.32, in terms of the 7-day results, the 20%PMBA was 46.08 percent less than the control whilst the 28-day counterpart was 46.58 percent lower than the control. Moreover, all 7-day test samples, except the 5%PMBA sample, showed statistical significance when compared to the control. This indicates that a 7-day testing age, incremental additions of PMBA leads to an actual improvement in the quality of the resulting concrete leachate.

In terms of the 28-day statistical analysis, all samples, except the 10%PMBA sample, showed statistical significance when compared to the control. For instance, the 28-day 20%PMBA sample exhibited a test statistic value of -16.56, which exceeded the critical value of -2.78. The 28-day difference in ion conductivity between the control and 20%PMBA samples may further be ascertained by the difference in their respective confidence levels. As stated above, the 28-day control exhibited a 95 percent confidence interval of 5.10 mS/cm to 6.01 mS/cm, whilst the 28-day 10%PMBA sample showed a range of 2.67 mS/cm to 3.27 mS/cm.

As discussed in Section 2.13.4, existing literature informs that there exists a link between the penetrability of concrete (particularly the factors of porosity and WS) and ion conductivity. The results are in contrast with the aforementioned literature, whereby the density of PMBA-concrete was found to peak at a 10 percent replacement and decline thereafter, however, the 10%PMBA sample did not exhibit the lowest ion conductivity. Moreover, ion conductivity still decreased as density increased, suggesting that density (and by extension, porosity), may not have had a major influence. In addition, the WS values of PMBA-concrete also showed no indication of significantly influencing ion conductivity. This analysis stems from the fact that the best WS result shown in the PMBA-concrete samples was obtained via a 10 percent replacement, followed by relatively negative results at 15 and 20 percent replacements. However, ion conductivity was not found to be the lowest in the 10%PMBA and continued decreasing at 15 and 20 percent replacements. These relationships will be further investigated in Section 4.13.2.

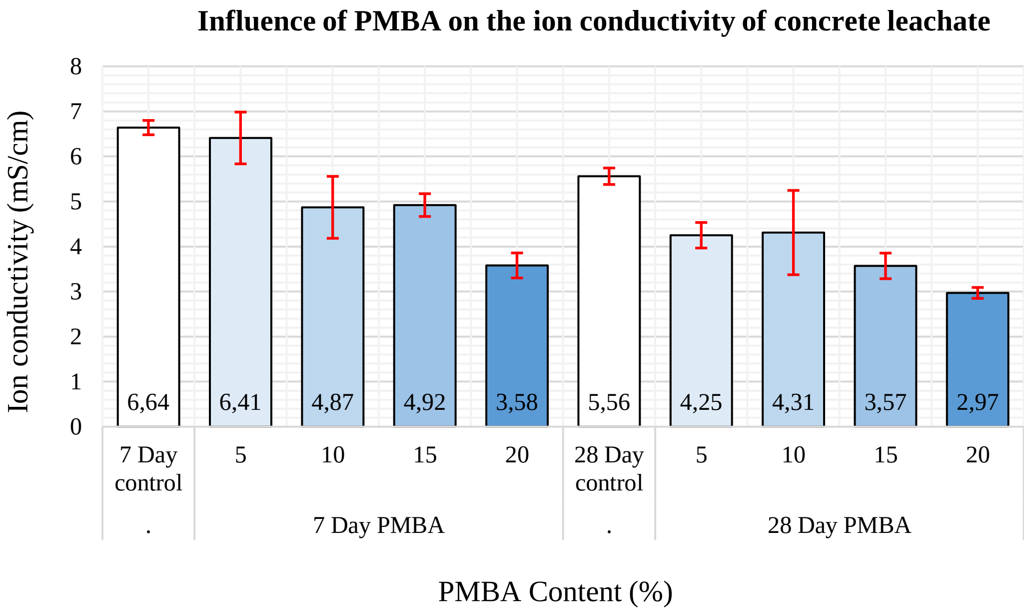


Figure 4.23: *Ion conductivity of concrete leachate under the influence of incremental additions of PMBA*

Table 4.32: *Analysis of ion conductivity values for leachate from PMBA-concrete*

7-Day statistical analysis			**Confidence Interval (mS/cm)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (mS/cm)**	
Mix ID	**Δ (%)**	**Ion conductivity (mS/cm)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (mS/cm)**	**Lower**	**Upper**
Control	-	6.64	6.25	7.04	-	-	-	-
5%PMBA	-3.46	6.41	4.98	7.83	-0.66	-0.24	-1.19	0.72
10%PMBA	-26.66	4.87	3.16	6.58	-4.35	-1.77	-2.90	-0.64
15%PMBA	-25.90	4.92	4.29	5.55	-9.97	-1.72	-2.20	-1.24
20%PMBA	-46.08	3.58	2.89	4.27	-16.56	-3.06	-3.58	-2.55
28-Day statistical analysis			**Confidence Interval (mS/cm)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (mS/cm)**	

Mix ID	Δ (%)	Ion conductivity (mS/cm)	Lower	Upper	t_0	$\bar{x}_i - \bar{x}_c$ (mS/cm)	Lower	Upper
Control	-	5.56	5.10	6.01	-	-	-	-
5%PMBA	-23.56	4.25	3.55	4.95	-6.73	-1.31	-1.85	-0.77
10%PMBA	-22.48	4.31	1.99	6.64	-2.26	-1.25	-2.78	0.29
15%PMBA	-35.79	3.57	2.87	4.28	-10.17	-1.99	-2.53	-1.44
20%PMBA	-46.58	2.97	2.67	3.27	-20.40	-2.59	-2.94	-2.23

4.13.2 Influence of WFS

The results did not show a generalized trend as in the case of PMBA-concrete. However, both the 7 and 28-day results indicate that the best performing sample is the 10%WFS, thereby indicating a higher quality leachate compared to the control and all other WFS samples. The 28-day 10%WFS sample showed a 95 percent confidence level of 0.96 mS/cm to 2.03 mS/cm, whilst the 28-day control ranged from 5.10 mS/cm to 6.01 mS/cm. Accordingly, the difference in ion conductivity between the control and 10%WFS samples were proven to be statistically significant. This is shown in Table 4.33. whereby the test sample exhibited a test statistic value of 24.99, which occurs out of the critical region of -2.78 to 2.78.

It was observed that all conductivity values were less than the control, implying that the integration of WFS in concrete improves the quality of the leachate, in terms of the amount of dissolved substances present. Table 4.33 indicates that all WFS samples showed a reduced ion conductivity as compared to the control. Additionally, all test samples, except the 28-day 20%WFS sample, were shown to exhibit statistical significance when compared to their respective control samples. It must be noted that a significant variation occurs between the 7 and 28-day results at the 10 and 15 percent replacements. Evidently, the aforementioned 7-day values were greater than their 28-day counterparts. In considering that the 28-day control was similar to 7-day values, this suggests that WFS may be more capable in decreasing ion conductivity at later ages.

In terms of the relationship between porosity and ion conductivity, the results suggest that a minor relationship may exist between density and ion conductivity at earlier ages. This was shown whereby decreases in the density of WFS-concrete, corresponded to gradual increases in the 7-day ion conductivity results.

The relationship between WS and 7-day ion conductivity is not entirely clear, however a trend is shown whereby decreasing WS values correspond with decreasing conductivity with a slight discrepancy at a 15 percent replacement. Similarly, this suggests a minor relationship between WS and ion conductivity at earlier ages.

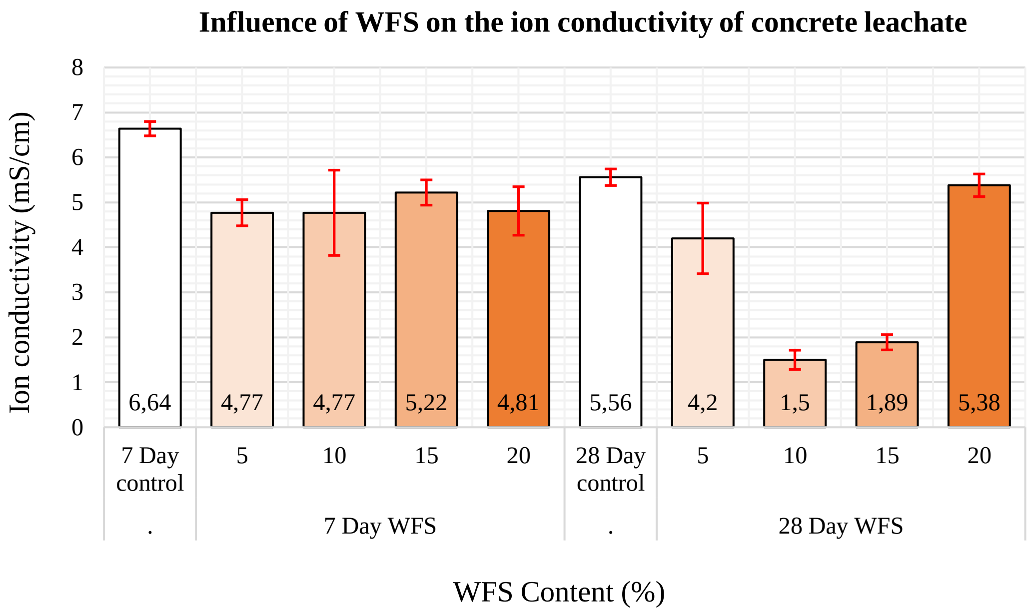


Figure 4.24: *Ion conductivity of concrete leachate under the influence of incremental additions of WFS*

Table 4.33: *Analysis of ion conductivity values for leachate from WFS-concrete*

7-Day statistical analysis			**Confidence Interval (mS/cm)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (mS/cm)**	
Mix ID	**Δ (%)**	**Ion conductivity (mS/cm)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (mS/cm)**	**Lower**	**Upper**
Control	-	6.64	6.25	7.04	-	-	-	-
5%WFS	-28.2	4.77	4.20	5.64	-9.02	-1.72	-2.26	-1.19
10%WFS	-28.2	4.77	2.41	7.12	-3.38	-1.88	-3.42	-0.33
15%WFS	-21.4	5.22	4.52	5.91	-7.65	-1.42	-1.94	-0.91
20%WFS	-27.6	4.81	3.47	6.14	-5.67	-1.84	-2.74	-0.94
28-Day statistical analysis			**Confidence Interval (mS/cm)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (mS/cm)**	

Mix ID	Δ (%)	Ion conductivity (mS/cm)	Lower	Upper	t_0	$\bar{x}_i - \bar{x}_c$ (mS/cm)	Lower	Upper
Control	-	5.56	5.10	6.01	-	-	-	-
5%WFS	-24.5	4.20	2.25	6.15	-2.92	-1.36	-2.66	-0.07
10%WFS	-73.0	1.50	0.96	2.03	-24.99	-4.06	-4.52	-3.61
15%WFS	-66.0	1.89	1.47	2.31	-25.46	-3.67	-4.07	-3.27
20%WFS	-3.2	5.38	4.75	6.01	-1.00	-0.18	-0.68	0.32

4.14 NITRATE CONTENT

Table 4.34 presents the results for the nitrate content test. The 7-day nitrate content in the control leachate was found to be 1.48 mg/L whilst the 28-day counterpart showed a value of 9.73 mg/L. Both results were found to be below the maximum nitrate contaminant level of 45 mg/L, as well as the 11 mg/L maximum for drinking water in SA.

Table 4.34: *Nitrate content results*

Test material content (%)	Nitrate content (mg/L)			
	PMBA		WFS	
	7 Day	28 Day	7 Day	28 Day
Control	1.48	9.73	1.48	9.73
5	2.22	8.41	6.51	8.76
10	3.83	8.10	18.44	2.21
15	1.97	5.89	20.12	4.81
20	5.37	4.13	25.86	7.11

4.14.1 Influence of PMBA

As per Figure 4.25 below, the 7-day results indicate a general increase in nitrate content as PMBA content increases. However, all nitrate contents were well below both the maximum contaminant level and drinking water requirement in SA. The lowest 7-day nitrate content was shown in the leachate of the 15%PMBA sample and was found to be 33.11 percent greater than the control. Table 4.35 shows that the 7-day difference between the 15%PMBA and control samples is not considered statistically significant. Moreover, the 95 percent confidence interval for this test sample was found to be 1.19 mg/L to 2.74 mg/L.

The 28-day results drastically differed from those of the 7-day, whereby nearly all mixes showed an increase in nitrate content. More importantly, a new trend was observed whereby nitrate content was found to decrease as PMBA content increased. The role of PMBA in influencing the increase in 28-day nitrate content may not be commented on as the 28-day control experienced a similar increase in nitrate content. The 20%PMBA sample displayed the lowest 28-day nitrate content. Moreover, the 20%PMBA sample displayed a 95 percent confidence interval of 3.11 mg/L to 5.14 mg/L, whilst the 28-day control ranged from 6.10 mg/L to 13.35 mg/L. Accordingly, the 20%PMBA sample produced a result that was shown to be statistically significant when compared to the 28-day control sample

All PMBA leachates displayed nitrate contents that were below the 45 mg/L contaminant level and the 11 mg/L drinking water requirement. Incidentally, the 28-day control sample exhibited the highest nitrate content of 9.73 mg/L.

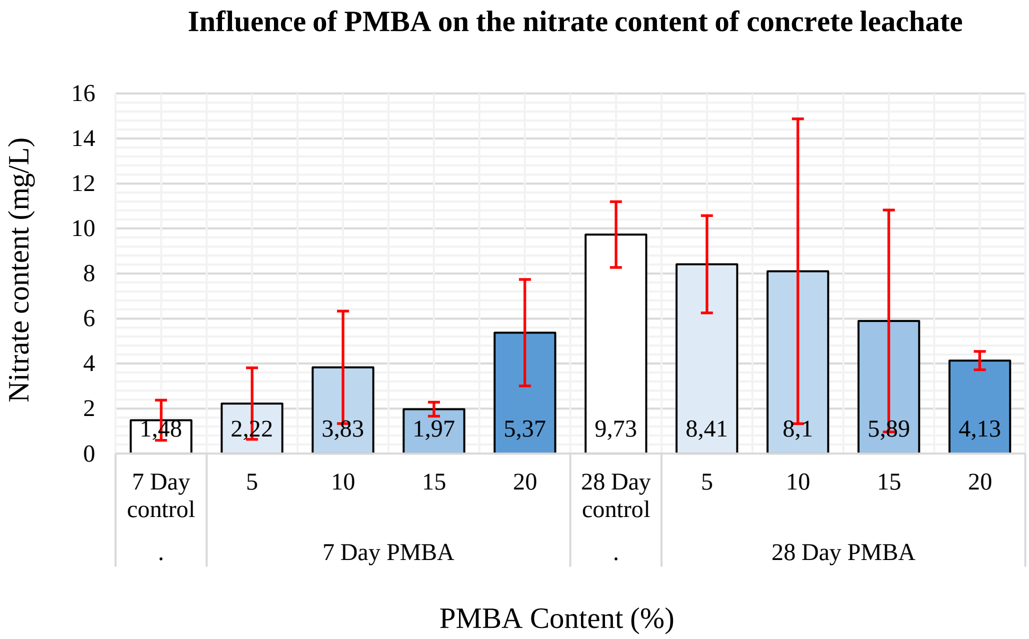


Figure 4.25: *Nitrate content of concrete leachate under the influence of incremental additions of PMBA*

__Table 4.35:__ Analysis of the nitrate content present in the leachate from PMBA-concrete

7-Day statistical analysis			**Confidence Interval (mg/L)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (mg/L)**	
Mix ID	**Δ (%)**	**Nitrate content (mg/L)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (mg/L)**	**Lower**	**Upper**
Control	-	1.48	-0.74	3.69	-	-	-	-
5%PMBA	50.00	2.22	-1.73	6.16	0.71	0.75	-2.18	3.67
10%PMBA	158.78	3.83	-2.37	10.03	1.54	2.36	-1.90	6.62
15%PMBA	33.11	1.97	1.19	2.74	0.91	0.50	-1.02	2.01
20%PMBA	262.84	5.37	-0.50	11.25	2.67	3.90	-0.16	7.96
28-Day statistical analysis			**Confidence Interval (mg/L)**		**$t_{(v;a)}$ 2.78**		**Comparison of means (mg/L)**	
Mix ID	**Δ (%)**	**Nitrate content (mg/L)**	**Lower**	**Upper**	**t_0**	**$\bar{x}_i - \bar{x}_c$ (mg/L)**	**Lower**	**Upper**
Control	-	9.73	6.10	13.35	-	-	-	-
5%PMBA	-13.57	8.41	3.05	13.78	-0.87	-1.31	-5.50	2.88
10%PMBA	-16.75	8.10	-8.72	24.92	-0.41	-1.62	-12.75	9.50
15%PMBA	-39.47	5.89	-6.35	18.13	-1.29	-3.84	-12.10	4.42
20%PMBA	-57.55	4.13	3.11	5.14	-6.39	-5.60	-8.04	-3.16

4.14.2 Influence of WFS

As per Figure 4.26 below, the 7-day results show drastic increases in nitrate content as quantities of WFS increases. The only 7-day WFS-sample that conformed to the drinking water and maximum contaminant standards was the 5%WFS leachate. The greatest nitrate content observed at 7-day testing was the 20%WFS leachate.

The 28-day results show a significant deviation to those of the 7-day, particularly at the 10, 15 and 20 percent replacements. Accordingly, the 28-day nitrate content, at replacements of 10 and 15, decreased drastically. The 28-day 10%PMBA performed best by displaying the lowest nitrate content of 2.21 mg/L, which was 77. 29 percent lower than the control. However, Table 4.36 indicates that the difference in nitrate content between the 28-day 10%PMBA and 28-day control samples, is not considered statistically significant. In comparing the nitrate content results for all

WFS samples, statistical significance was associated solely with the 28-day 20%WFS sample. The nitrate content of this sample was 26.93 percent lower than the 28-day control. Moreover, this sample exhibited a 95 percent confidence interval of 3.11 mg/L to 5.14 mg/L, whilst the 28-day control ranged from 6.10 mg/L to 13.35 mg/L. Finally, the nitrate contents for all 28-day WFS samples complied with both the requirements for drinking water and the permissible contaminant level.

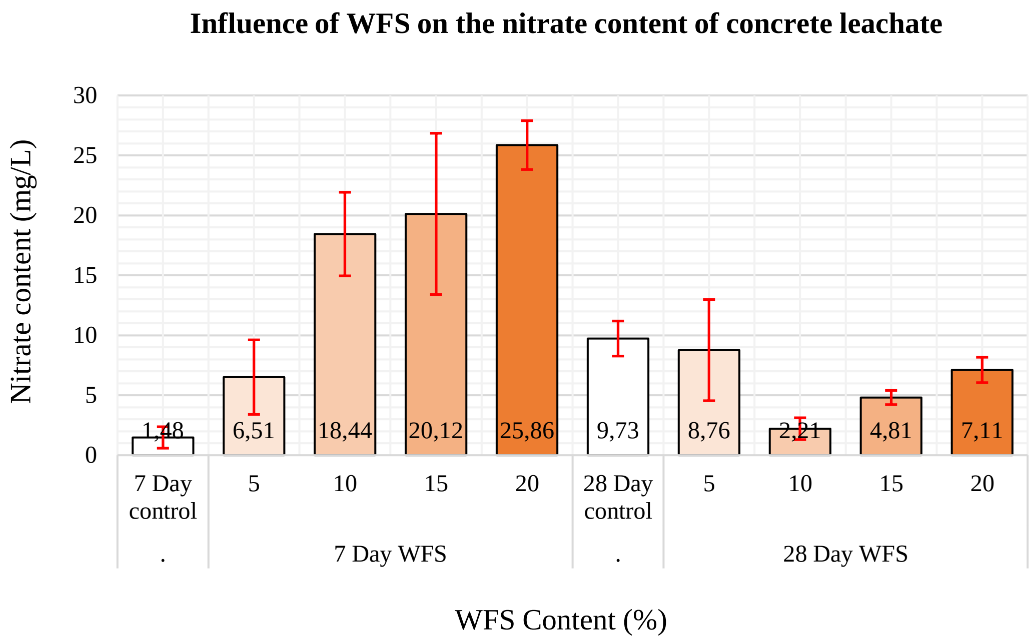


Figure 4.26: *Nitrate content of concrete leachate under the influence of incremental additions of WFS*

Table 4.36: *Analysis of the nitrate content present in the leachate from WFS-concrete*

7-Day statistical analysis			**Confidence Interval (mg/L)**		$\mathbf{t_{(v;a)}}$ **2.78**		**Comparison of means (mg/L)**	
Mix ID	**Δ (%)**	**Nitrate content (mg/L)**	**Lower**	**Upper**	$\mathbf{t_0}$	$\bar{x}_i - \bar{x}_c$ **(mg/L)**	**Lower**	**Upper**
Control	-	1.48	-0.74	3.69	-	-	-	-
5%WFS	339.86	6.51	-1.73	6.16	0.71	-0.75	-2.18	3.67
10%WFS	1145.95	18.44	-2.37	10.03	1.54	2.36	-1.90	6.62
15%WFS	1259.46	20.12	1.19	2.74	0.91	0.50	-1.02	2.01
20%WFS	1647.30	25.86	-0.50	11.25	2.67	3.90	-0.16	7.96

28-Day statistical analysis			Confidence Interval (mg/L)		$t_{(v;a)}$ 2.78		Comparison of means (mg/L)	
Mix ID	Δ (%)	Nitrate content (mg/L)	Lower	Upper	t_0	$\bar{x}_i - \bar{x}_c$ (mg/L)	Lower	Upper
Control	-	9.73	6.10	13.35	-	-	-	-
5%WFS	-9.97	8.76	3.05	13.78	-0.87	-1.31	-5.50	2.88
10%WFS	-77.29	2.21	-8.72	24.92	-0.41	-1.62	-12.75	9.50
15%WFS	-50.57	4.81	-6.35	18.13	-1.29	-3.84	-12.09	4.42
20%WFS	-26.93	7.11	3.11	5.14	-6.39	-5.60	-8.04	-3.16

4.15 CHAPTER SUMMARY

This chapter presented the results from the experimentation programme in graphical form. In addition, the result from each test sample was compared to the control and the percentage differences were tabulated. The following summary relate to the key findings in the experimentation programme.

Sieve analysis showed that WFS was finer than Umgeni river sand. The former had a FM of 3.3 whilst the latter showed a FM of 3.4. The characteristic particle distribution curve for both WFS and Umgeni river sand did not lie within the proposed grading limits stipulated by SANS 1083 and C & CI. The greatest deviation was observed at the finer particles, whereby 5 to 25 percent of the sample did not pass the 150 μm sieve. However, such sands may be adequate for concrete works if the mix is designed well (Owens, 2013). Soil classification showed that WFS exhibited a more uniform grading as compared to Umgeni river sand.

Workability, through slump, was observed to continuously increase as PMBA ranged from 5 to 20 percent. The 5%PMBA sample showed a slump of 75 mm, which was 25 percent higher than the control. The 20%PMBA sample showed a slump of 140 mm, which was 133 percent higher than the control. The 5 and 10 percent samples showed a 'medium' degree of workability; validating their applicability for use in normal concrete applications. The 15 and 20 percent samples showed 'high' degrees of workability, indicating that their potential for use in thin or congested sections, trench-filled foundations and situations that require concrete to flow a great distance. The reasons for increasing slumps were attributed to the spherical, glassy particles and the hydrophilic nature of PMBA. An analysis of linear correlation revealed that the Pearson's coefficient of correlation produced a value of 1, thereby indicating a perfect direct correlation between incremental additions of PMBA and increases in slump. Workability was found to continuously and dramatically increase as WFS content increased. The 5%WFS sample had a slump of 130 mm, which was 117 percent higher than the control. The 20%WFS sample showed a slump of 230 mm, which was 283 percent higher than the control. All WFS samples produced slumps that were classified as having a 'high' degree of workability. All mixes except the 5%WFS mix showed slumps exceeding 150 mm and so, may experience aggregate segregation in the fresh state. The high increases in slumps were due to the fact that WFS absorbs less water than Umgeni river sand, coupled with the cubical, sub-rounded and rounded particles of waste sand. Pearson's coefficient of correlation was determined to be 0.98, which suggested a fair direct correlation.

Density was increased by the integration of PMBA. All PMBA samples exhibited higher densities than the control. The 10%PMBA sample showed the highest density in the study, which was 2 percent higher than the control. The decline in density observed after the 10 percent replacement was attributed to the lower density of PMBA compared to that of cement. It was reasoned that the difference in densities become more influential in affecting concrete density as the content of PMBA exceeds 10 percent. When compared to the control, the only PMBA samples that were associated with statistical significance were the 10%PMBA and 15%PMBA samples. The integration of WFS in concrete showed that the only improvement in density occurred in the 5%WFS sample, which was 0.3 percent greater than the control. The reason for the 10, 15 and 20 percent samples exhibiting densities that were lower than the control was the poor grading of the WFS. None of the WFS samples showed statistical significance when compared to the control.

Compressive strength was shown to increase due to the integration of PMBA. All 28-day strengths were greater than the control, however the 10%PMBA sample showed the peak strength, which was 8.6 percent greater than the control. The increase in strength was attributed to the prevalence of amorphous phases (particularly SiO_2) present in PMBA, the consumption of CH and the fine-filler effect. A declining strength trend was noticed after a 10 percent replacement, which continued until the 20%PMBA sample. The strength reduction was possibly due to the higher values of LOI and SO_3 displayed by PMBA when compared to cement. It was noted that all 28-day strengths of PMBA were typical of structural concrete. When compared to the control, none of the 28-day PMBA samples suggested statistical significance. All WFS samples showed reduced compressive strength compared to the control and strength decreased as WFS increased. The highest test strength was observed in the 5%WFS concrete. The poor gradation of WFS was labelled as the reason for the decrease. Gradation becomes more influential at greater replacements of WFS. Statistical significance was observed in all WFS samples in relation to the control.

Flexural strength was found to decrease with PMBA content, however the strength peaked in the 10%PMBA sample, which was 12.8 percent greater than the control. Strength continued declining after a 10 percent replacement. All PMBA samples exhibited strengths that meet the requirement for minor roads. None of the 28-day PMBA samples exhibited statistical significance in relation to the 28-day control. All WFS-concrete samples were found to exhibit strengths that were lower than the control. In addition, increasing contents of WFS resulted in a general decrease in strength. The 5%WFS sample showed the highest test strength, which was 5.8 percent lower than the control. The poor grading of WFS was put forth as the reason for strength decrease. It was only the 5%WFS and 10%WFS samples that were shown to be acceptable for minor roads. When compared to the 28-day control, only the 15%WFS and 20%WFS samples showed statistical significance.

Tensile-splitting strength, at 7 and 28-day testing, was found to peak in both the control and the 10%PMBA sample and decrease at the 5, 15 and 20 percent samples. These results correlated to investigations involving fly ash as a partial cement replacement, such as in the work of Yerramala et al. (2012) and Barbuta et al. (2017). None of the 28-day PMBA samples showed statistical significance relative to the control. WFS was shown to result in strengths that are lower than the control, with the exception occurring in the 20%WFS sample. When compared to the 28-day control, none of the WFS samples displayed statistical significance.

OPI was found to decrease with the inclusion of PMBA, except for the 5%PMBA sample. This sample was classified as having an 'excellent' degree of durability and showed the highest OPI, which was 0.1 percent greater than the control. The fine-filler effect was attributed as the reason for this. By being less permeable, the 5%PMBA sample may exhibit the greatest resistance to carbonation. Whilst PMBA resulted in decreased OPI in the 10, 15 and 20 percent samples, the 15 and 20 percent samples had 'excellent' degrees of durability against permeability whilst the 10 percent sample had a 'good' degree of durability. It was noted that despite the 10%PMBA sample showing the highest density, the sample showed the lowest OPI. WFS resulted in samples with OPI less than the control, the exception to this occurred in the 5 percent sample. This sample showed the highest OPI, which was 0.4 percent higher than the control and was classified as having an 'excellent' degree of durability. In relation to the control, only the 10%PMBA sample showed statistical significance. It was observed that at a 5 percent replacement, WFS may exhibit its own filler effect. In terms of OPI, the worst performing WFS samples were still classified having a 'good' degree of durability. Both the 10%WFS and 15%WFS samples exhibited statistical significance when compared to the control.

WS was reduced in all PMBA samples and were all classified as showing an 'excellent' degree of durability against sorptivity. The greatest reduction occurred in the 10%PMBA sample, which was 11.1 percent lower than the control. This improvement in resisting sorptivity was attributed to the fine-filler effect. Additionally, the MC of the 10%PMBA did not correlate with the reduction in WS. WS was observed to show increases as the content of PMBA exceeded 10 percent. None of the PMBA samples showed statistical significance when compared to the control. All WFS samples showed decreased WS compared to the control and were all classified as exhibiting ‘excellent’ degrees of durability against WS. The greatest WS result came from a 5 percent replacement, which was 20.9 percent lower than the control and was the best WS result observed in this study. This sample showed statistical significance when compared to the control. The fine-filler effect was noted as the reason for the improvement in resisting WS. These results contradict the results obtained by Bhardwaj & Kumar (2018), who observed that sorptivity showed a continued decrease as WFS increased. Additionally, it may also be possible that the relatively high MC of the 5%WFS concrete may have reduced capillary absorption, thereby decreasing WS. This supports the understanding that MC and WS are related.

CC varied with different percentages of PMBA. The 15%PMBA sample was the only sample greater than the control. The 10%PMBA performed best by exhibiting the lowest CC, which was 7.7 percent lower than the control. This indicated that this sample may display a greater ability to resist the reinforcement of corrosion. Due to the sensitivity of CC to porosity, the fine-filler effect was attributed to the improved resistance at the 10 percent replacement. Evidence to suggest this was that the 10%PMBA sample exhibited the highest density, indicating the least porous sample. This analysis is in line with statements made by Mackechnie (1996) and Shekhovtsova et al. (2014), who informed of the importance of pore structure as an influence of CC. None of the PMBA samples showed statistical significance when compared to the control. The integration of WFS showed that, compared to the control, WS decreases at lower replacements and increases at higher replacements. All WFS samples were classified as having ‘excellent’ degrees of durability against WS. The 10%WFS showed the lowest WS, which was 15.4 percent lower than the control. This was the only sample to show statistical significance in relation to the control. It is unclear as to whether the filler effect contributed to the improvement in WS as the 10%WFS was less dense than the 5%WFS sample, but the former showed superior performance in resisting sorptivity.

pH assessments showed a general trend whereby the pH value of concrete decreases with increasing contents of PMBA. This was attributed to the consumption of CH during pozzolanic reactions. The results suggest that more CH is consumed at higher replacements. In accordance with claims made by Mehta & Monteiro (2006), despite the decrease in CH, and consequent decrease in pH, all PMBA samples still displayed an adequate pH value that was higher than required for steel protection. In terms of leachate quality, the 28-day samples indicate that the addition of greater amounts of PMBA may produce a more environmentally-friendly leachate by reducing alkalinity. When compared to the 28-day control, only the 15%PMBA and 20%PMBA samples showed statistical significance. The integration of WFS showed a general increase in pH value as WFS content increased. The 7 and 28-day results show a marked difference whereby 28-day pH values were drastically lower compared to their 7-day counterparts; however, the 28-day control resembled the 7-day results. This suggests that WFS may show more influence in reducing concrete and leachate pH values at later ages. All 7 and 28-day pH values were sufficient for preserving the passivation layer. The results further suggest that less basic leachates occur at lower replacements of WFS. When compared to the 28-day control, the 10%WFS, 15%WFS and 20%WFS samples were shown to be statistically significant.

Ion conductivity was shown to decrease with increasing contents of PMBA. Accordingly, all samples performed better than the control. The lowest ion conductivity was displayed by the leachate of the 20%PMBA sample. This sample showed an enhanced ability to prevent the mobilization of contaminants out of concrete due to contacting water. The 28-day statistical analysis indicates that, when compared to the control, the 5%PMBA, 15%PMBA and 20%PMBA samples showed statistical significance. The use of WFS showed that all WFS samples exhibited lower ion conductivity. In addition, smaller additions of WFS produced lower conductivity than higher additions. The 7-day WFS results were greater than their 28-day counterparts whilst the 28-day control resembled the 7-day control; suggesting that WFS may exert more influence in affecting ion conductivity at later ages. The lowest ion conductivity was observed in the 28-day 10%WFS leachate, which was 73 percent lower than the control. This indicates that a 10 percent replacement may result in a more environmentally-friendly leachate. The 28-day statistical analysis showed that, relative to the control, the 5%WFS, 10%WFS, and 15%WFS samples showed statistical significance.

Nitrate content, through the integration of increasing quantities of PMBA, was found to increase during 7-day testing and decrease at 28-day testing, however the 28-day results indicated greater quantities of nitrate. All PMBA leachates displayed nitrate contents that were below the 45 mg/L contaminant level and the 11 mg/L drinking water requirement. In terms of the 28-day results, only the 20%PMBA sample showed statistical significance when compared to the control. Regarding WFS, the 7-day results show drastic increases in nitrate content as quantities of WFS increases. The only 7-day WFS-sample that conformed to the drinking water and maximum contaminant standards was the 5%WFS leachate. Compared to all other 7-day WFS samples, the 5%WFS leachate contained the lowest amount of nitrate, which was 339.86 percent greater than the control. Compared to the 7-day results, the 28-day results showed an extreme reduction in the nitrate contents of 10%WFS and 15%WFS samples. The 28-day 10%WFS sample performed best by displaying the lowest nitrate content, which was 77. 29 percent lower than the control. When compared to the 28-day control, the 10%WFS, 15%WFS and 20%WFS samples showed statistical significance.

The next chapter concludes the study by validating the aims and objectives and providing an answer to the research questions. In addition, the recommendations of the study are listed. This is followed by future scope.

5. CHAPTER FIVE: CONCLUSIONS & RECOMMENDATIONS

5.1 INTRODUCTION

This study seeks to investigate the effects of PMBA, in the role of a partial cement replacement, and WFS, in the role of a partial fine aggregate replacement, on the resulting two sets of 'green' concrete properties. In order to accomplish this, the contents of each test material varied and the resulting concrete was subjected to a variety of testing to assess the properties as they relate to workability, mechanical strengths, durability and the basic properties of the resulting leachate. This chapter is dedicated to concluding the research by providing all key findings, responding to the research questions, making recommendations and discussing future scope.

5.2 CONCLUSIONS & RECOMMENDATIONS – PMBA CONCRETE

Four separate samples of PMBA-concrete were investigated. These mixes were designed by replacing cement by 5, 10, 15 and 20 percent, by mass, with PMBA. These mixes were denoted as 5%PMBA, 10%PMBA, 15%PMBA and 20%PMBA, respectively.

5.2.1 Workability

- A 5 percent replacement showed greater workability than the control sample. In addition, workability continued to increase as the PMBA content increased.
- The 5 and 10 percent replacements gave a 'medium' degree of workability whilst the 15 and 20 percent replacements resulted in a 'high' degree of workability. This indicates that the water requirement for a given mix will be reduced with additions of PMBA.
- Despite PMBA being finer than cement, improvements in slump were still observed, even at higher contents of PMBA.

- The improvements in workability were attributed to the hydrophilic nature of the PMBA, coupled with its spherical, glassy particles. This suggests that the influence of these properties is more dominant in influencing slump than that of PMBA fineness.
- The high LOI and SO_3 value of PMBA, as compared to cement, did not show a noticeable effect in reducing workability.
- PMBA behaves more like fly ash as opposed to PMS ash. This is suggested by the increase in workability, which is widely reported as a result of fly ash, whilst it is generally reported that the fineness of PMS ash reduces workability.

5.2.2 Saturated Hardened Density

- Integrating low levels of PMBA (5 to 20 percent) showed that the 28-day density of all PMBA samples increased as compared to the control sample. These increases were not uniform, and occurred such that a 5 percent replacement showed improved density over the control. The 10 percent replacement then showed a peak density value, followed by continued decreases as replacements exceeded 10 percent.
- Accordingly, the 10%PMBA was denser than all samples investigated in this study. It was observed that, despite exhibiting a lower RD value than cement, PMBA still improved density.
- Decreases in density was attributed to the lower RD of PMBA when compared to cement.
- All samples were categorised as normal-weight concrete.

5.2.3 Compressive Strength

- Integrating a PMBA range of 5 to 20 percent showed that the 28-day strengths of all samples increased in relation to the control. Moreover, all 28-day strengths arising from PMBA were typical of structural concrete.
- The 10%PMBA sample displayed the highest 7 and 28-day strengths compared to all samples tested in the study. This indicates that a 10 percent replacement may be optimum for enhancing compressive strength. This sample exhibited a strength of 38 MPa, which was 8.6 percent higher than the control. This is significant as the integration of 10 percent PMBA produces concrete that may be regarded as having a higher quality than conventional concrete.

- The 7-day 15%PMBA and 20%PMBA samples showed decreased strength relative to the control. This indicates that the delay in pozzolanic reactions at early ages is more prevalent at greater quantities of PMBA. This further supports the notion that PMBA behaves more like fly ash than PMS ash.
- Improvements in strength gain may be attributed to the largely amorphous constitution, particularly reactive SiO_2 of PMBA, the consumption of CH to produce C-S-H, the high specific surface compared to cement, and the fine-filler effect
- It was shown that the 10%PMBA showed the highest density and strength, suggesting that the fine-filler effect refined the concrete pore structure. However, OPI tests indicate that the 10%PMBA sample was more permeable than all other PMBA samples. Hence, it is possible that the fine-filler effect may not be as influential in strength development as are the amorphousness of PMBA and the consumption of CH.
- The high carbon content of PMBA, as indicated by its high LOI content, may be responsible for the reductions in compressive strength that occur when PMBA content exceeds 10 percent.
- The 7 and 28-day compressive strengths showed similar strength fluctuations, suggesting that PMBA-concrete behaves consistently under compressive loads.

5.2.4 Flexural Strength

- A 5 percent replacement exhibits 7 and 28-day strengths that are lower than the control. Accordingly, PMBA should not be integrated at 5 percent in applications where flexural strength is the ruling criteria, such as in rigid pavements. An exception to this condition may occur when strength requirements are low enough, such as the requirement for minor roads.
- Replacing cement with 10 percent of PMBA resulted in the highest 7 and 28-day flexural strengths as compared to all samples tested in this study. Thus, a 10 percent replacement may be the optimum content for enhancing flexural strength. This sample showed a 28-day strength of 4.85 MPa, which was 12.8 percent higher than the control.
- The aforementioned strength development may have been as a result of the characteristics of PMBA (fine-filler effect, amorphousness and consumption of CH).
- In terms of application, all 28-day flexural strengths were greater than 4 MPa, indicating the satisfaction of the 4 MPa strength requirement associated with minor roads. However, none of the 28-day strengths resembled that of typical structural concrete (6 MPa).

- Both the 7 and 28-day results displayed similar trends in strength fluctuation, indicating the consistent behaviour of PMBA-concrete under the action of bending loads.

5.2.5 Tensile-splitting Strength

- Strength fluctuations demonstrates that both the 7 and 28-day strengths decrease at a 5 percent replacement, increases at a 10 percent replacement and decreases thereafter. This indicates that PMBA-concrete exhibits similar behaviour at 7 and 28-days when exposed to tensile loading.
- In comparison to all PMBA samples, the results suggest that 10%PMBA is able to match the tensile-splitting strength of the control. Both samples exhibited the highest tensile-splitting strength of 2.7 MPa. This indicates that a 10 percent replacement compares well with conventional concrete in terms of resisting tensile forces.
- All samples displayed tensile-splitting strengths that are not reminiscent of the typical 3 MPa strength of structural concrete.

5.2.6 Durability

The results from the OPI tests indicate the following:

- The 5%PMBA sample showed the highest reduction in permeability, and by extension, the greatest resistance to carbonation than all other samples in the study. The sample was classified as having an ‘excellent’ degree of durability in terms of OPI. This indicates that the fine-filler effect may still be influential at smaller contents of PMBA.
- The 10%PMBA sample was found to be the most permeable concrete compared to all PMBA samples. The sample was still classified as having a ‘good’ degree of durability with respect to OPI.
- Replacements exceeding 10 percent were found to improve OPI to an extent that the resulting 15%PMBA and 20%PMBA samples were classified as having an ‘excellent’ degree of durability.

The results from the WS tests show the following:

- The integration of 5 to 20 percent PMBA, results in samples that exhibit improved WS when compared to the control sample. WS showed continuous improvements at 5 and 10 percent replacements, followed by a decline at replacements exceeding 10 percent.
- Accordingly, the 10%PMBA sample showed the greatest improvement in WS and displayed an ‘excellent’ degree of durability against sorptivity. This analysis suggests that a 10 percent replacement is ideal in reducing capillary absorption.
- It is unlikely that the moisture content of the 10%PMBA sample contributed to the improved WS as it exhibited a lower moisture state than other WFS samples. A more likely reason for the improvements in WS is the fine-filler effect of PMBA, which may have played a role in refining the pore structure of the 10%PMBA sample, resulting in poorly connected pores, thereby weakening the capillary absorption mechanism.
- The results indicate that replacements exceeding 10 percent produce concrete samples that show unfavourable increases in WS. However, the 15%PMBA and 20%PMBA were still classified as having ‘excellent’ durability in terms of WS.

The results from the CC tests show the following:

- From all PMBA samples, the 10%PMBA was the only sample to experience an improvement in CC when compared to the control (7.7 percent lower than the control). This was followed by disadvantageous increases in CC values at higher replacements. This may indicate that a 10 percent replacement is ideal for reducing the transportation of chloride. By extension, this sample may experience enhanced capacity to prevent steel corrosion.
- Due to CC showing extreme sensitivities to pore structure and porosity, it is reasonable to suggest that the fine-filler effect is responsible for refining the pore structure, thereby reducing the diffusion of chloride ions.
- A replacement of 15 percent resulted in the worst CC value observed in the experimentation programme, however the sample was still classified as exhibiting an ‘excellent’ resistance against chloride diffusion.

5.2.7 Leaching Tests

The assessment of pH values indicated the following:

- The 28-day results showed that increasing quantities of PMBA result in decreasing pH values. This indicates that the highly alkaline leachate becomes less basic, however the ability of concrete to maintain the passivation layer is not compromised as pH values were greater than 11. This suggests that, when ranging from 5 to 20 percent, PMBA may only consume a certain portion of CH, such that sufficient amounts are left to maintain concrete pH.
- The decreasing pH trend is likely due to the consumption of CH during pozzolanic reactions. Additionally, greater amounts of CH are consumed as PMBA content increases.
- The 7-day results contradict the 28-day results as the decreasing pH trend was not continuous at 7-day testing. Accordingly, the continuous decreasing trend observed at 28-day testing may indicate that the later age pH values are continuously reduced as the content of PMBA increases. This may occur as a result of the consumption of CH at later ages.

The ion conductivity values of concrete leachate indicate the following:

- Increasing contents of PMBA decreases ion conductivity; resulting in a higher resistance to ion migration. By extension, this may indicate the presence of lower concentrations of dissolved solids in the leachate of PMBA-concrete. Due to the continuous decreasing trend observed, it may be possible that as PMBA increases in the range of 5 to 20 percent, the resulting leachate may contain lower contents of dissolved solids. This was the observation at both testing ages.
- The relationships observed between ion conductivity and penetrability did not correlate with existing knowledge. The results found that porosity does not influence ion conductivity as the 10%PMBA sample exhibited the greatest density but did not exhibit the lowest ion conductivity value. In addition, the WS values of PMBA-concrete also showed no indication of significantly influencing ion conductivity. This deduction stems from the 10%PMBA sample showing the best performance in terms of WS, however the sample did not exhibit the lowest ion conductivity value.

The tests involving the nitrate content of concrete leachate indicate the following:

- The 7-day results contradict the 28-day results. The former shows a general increase in nitrate content as PMBA content increases, whilst the latter shows that nitrate content drastically decreased as PMBA content increased

- The lowest 7-day nitrate content was shown in the leachate of the 15%PMBA sample and was found to be 33.11 percent greater than the control. The 28-day counterpart occurred at a 20 percent replacement and was found to be 57.55 percent lower than the control.
- At both testing ages, all leachates arising from PMBA-concrete displayed nitrate contents that were below the 45 mg/L contaminant level and the 11 mg/L drinking water requirement.

5.3 CONCLUSIONS & RECOMMENDATIONS: WFS CONCRETE

Four separate samples of WFS-concrete were investigated. These mixes were designed by replacing fine aggregate by 5, 10, 15 and 20 percent, by mass, with WFS. These mixes were denoted as 5%WFS, 10%WFS, 15%WFS and 20%WFS, respectively.

5.3.1 Workability

- A 5 percent replacement resulted in a drastic, 117 percent increase in workability as compared to the control sample. It was shown that increasing contents of WFS continued increasing workability by great margins.
- The 10 ,15 and 20 percent mixes resulted in a slump exceeding 150 mm. These samples may be prone to aggregate segregation and will require the application of additives to be used as structural concrete. This indicates that WFS should be limited a maximum of 5 percent if additives are not to be used.
- All WFS samples produced concrete exhibiting ‘high’ degrees of workability. This indicates that the water requirement for a given mix will be significantly reduced with additions of WFS. Accordingly, WFS may be useful in producing high-slump concrete for specialised applications of concrete such as tremie mixes for underwater concreting.
- The high slumps may have resulted from the reduced capacity of WFS to absorb water and the occurrence of cubical, sub-rounded and rounded particles.

5.3.2 Saturated Hardened Density

Results from the 28-day density testing indicate the following:

- The only improvement in density was observed as arising from a 5 percent replacement. This density was 0.3 percent higher than the control. When WFS content exceeds 5 percent, density showed a continuous decrease as the WFS content increased.
- A possible reason for the improvement of density in the 5%WFS sample is the greater density of WFS compared to Umgeni river sand.
- The decreases in density that occur after the 5 percent replacement may be due to the poorly graded WFS which leads to voids. In addition, the continuous decreasing trend indicates that the poor gradation of WFS may become more influential in affecting density at greater waste contents.

5.3.3 Compressive Strength

- Replacing Umgeni river sand with WFS results in reduced compressive strengths at all levels of replacement.
- The reductions observed were gradual and continuous in the range of 5 to 20 percent WFS. As such, the 5%WFS sample showed the highest strength from all WFS samples. This is may be due to the reduced presence of voids and the possible fine-filler effect of WFS.
- Poor grading may be a possible reason for the reduction in strength as the content of WFS increases. These results further support the observation that the grading of WFS becomes more influential with higher additions of waste. Moreover, the density results show a correlation to the strength results. This supports the notion that reductions in strength occur due to increased voids arising from poor gradation.
- These results suggest that WFS should not be used at contents exceeding a 5 percent replacement.
- In terms of reacting to loadings, it was observed that the 7 and 28-day strengths fluctuated in similar patterns, indicating that WFS-concrete behaves consistently under compressive loads.

5.3.4 Flexural Strength

- The integration of WFS results in flexural strengths that are all lower than the control. Moreover, these strengths show continuous decreases with increasing contents of waste.

- Accordingly, the greatest strength from all WFS samples occurred at a 5 percent replacement. These results once again correlate with the notion that voids, as resulting from the poor gradation of WFS, may be responsible for strength loss.
- It was observed that the 7 and 28-day strengths showed similar fluctuations, indicating that WFS-concrete may behave in a consistent manner under bending loads.

5.3.5 Tensile-splitting Strength

- The highest 7-day strength was the control whilst the highest 28-day strength was the 20 %WFS sample, which was 1.9 percent greater than the control.
- Both the 7 and 28-day tensile-splitting strength decreased at a 5 percent replacement and increased at a 20 percent replacement.
- The variations in strength between the 7- and 28-days suggests that WFS-concrete under, tensile loading, may behave differently at certain ages.

5.3.6 Durability

The results from the OPI tests indicate the following:

- The 5%WFS sample resulted in the least permeable concrete, which incidentally was the only sample that was less permeable than the control. Accordingly, this sample may experience the greatest resistance to carbonation than the control and all other WFS samples. The sample was classified as having an 'excellent' degree of durability in terms of OPI.
- The filler effect becomes more evident in the OPI test, considering that the control was more permeable than the 5%WFS sample. This indicates that the combined action of the filler effect and the reduced voids may be responsible for the reduced permeability at a 5 percent replacement.
- Concrete becomes more permeable when WFS contents exceed 5 percent, indicating that 5 percent WFS is the optimum content for reducing permeability. In addition, this supports the statement made in Section 5.3.2 which suggested that at higher replacements, grading exerts an increasing influence on the properties of WFS-concrete.

The results from the WS tests show the following:

- All WFS samples showed reduced WS values compared to the control. Accordingly, these samples were classified as having ‘excellent’ durability against sorptivity.
- The 5%WFS sample showed the lowest WS value than all samples in the study, indicating that it performs best in resisting capillary absorption.
- Similar to PMBA, the filler effect may be a possible reason for the reduction in WS. This is supported by the fact that the 5%WFS sample showed the greatest density as compared to all WFS samples.
- The 5%WFS concrete exhibited the highest moisture content from all WFS samples. In accordance with the relationship between moisture content and WS, the high moisture state may have reduced capillary absorption, thereby decreasing WS.

The results from the CC tests show the following:

- The 5%WFS sample exhibited a reduced CC of 0.23 mS/cm. which was 11.5 percent lower than the control.
- From all samples tested in this study, the lowest CC was displayed by the 10%WFS sample. This may indicate that a 10 percent replacement is ideal for reducing the diffusion of chloride, indicating that the sample may experience a greater resistance to chloride attack than all samples in the study.
- All WFS samples showed ‘excellent’ degrees of durability against chloride diffusion, thereby indicating their ability to resist corrosion of reinforcements.

5.3.7 Leaching Tests

The assessment of pH values indicated the following:

- As the content of WFS increases, a general increase in pH value is observed, indicating an increasing ability to maintain the passivation layer.
- The 7 and 28-day results share the same trend; however, the 28-day pH values are significantly lower as compared to their 7-day counterparts. This suggests that WFS may be more capable in reducing pH at later ages.
- The quality of leachate, in terms of reductions in alkalinity, improves with lower replacements of WFS.

The ion conductivity values of concrete leachate indicate the following:

- All WFS leachate samples exhibited a lower ion conductivity when compared to the control, indicating that WFS leads to a higher quality leachate with reduced contents of dissolved solids.
- Both the 7 and 28-day results indicate that the best performing sample is the 10%WFS leachate. This suggests that a 10 percent replacement is ideal for improving the quality of leachate.
- At the 10 and 15 percent replacements, the 7-day values were greater than the 28-day values whilst the 28-day control resembled 7-day values. This suggests that WFS may be more influential in reducing ion conductivity at later ages.
- A minor relationship was observed between density and ion conductivity at earlier ages. This was supported by the correlation between the decreasing density of WFS-concrete and the gradual increases in the 7-day ion conductivity results. This may indicate that denser WFS-concrete results in leachates with reduced ion conductivity. By extension, this suggests that the filler effect and the denser waste sand may have been responsible for the WFS leachate samples showing a reduced ion conductivity compared to the control.
- Similarly, a minor relationship was observed between WS and ion conductivity. This was supported by the correlation between the decreasing WS values and the decreasing ion conductivity. This indicates that WFS-concrete with higher resistances to sorptivity may result in leachates with lower ion conductivity.

The tests involving the nitrate content of concrete leachate indicate the following:

- The 7-day results show drastic increases in nitrate content as quantities of WFS increases. The only 7-day WFS leachate that conformed to the drinking water and maximum contaminant standards was the 5%WFS leachate sample. The greatest nitrate content observed at 7-day testing was in the 20%WFS leachate.
- The 28-day results show a significant contradiction to those of the 7-day. The 10%PMBA sample performed best by displaying the lowest nitrate content, which was 77. 29 percent lower than the control. Additionally, the nitrate contents of all 28-day WFS samples complied with both the requirements for drinking water and the permissible contaminant level.

5.4 COMPLETION OF OBJECTIVES

The objectives, as stated in Section 1.5, were met as follows:

(A). “As part of a comprehensive literature review, document the relevant properties of cement, fine aggregate, PMBA and WFS and identify potential factors that may influence concrete”.

The literature review as presented in Chapter 2 details the properties of cement (Section 2.4.3), fine aggregate (Section 2.6.2), PMBA (Section 2.5.5) and WFS (Section 2.7.5) and the ways in which these properties influence concrete (Sections 2.9.2, 2.10.2, 2.11.4, 2.12.5 and 2.13.5). Past studies have shown that for cement and PMBA, it is the particle fineness, particle shape, non-crystalline phases, and the characteristics of reactions that are key properties that influence concrete. In terms of the sand materials, it is the particle shape, absorptive capabilities, quality of grading and fineness that are key.

(B). “Investigate the effect of various contents of each test material (5%, 10%, 15% and 20%) on concrete workability, density, compressive strength, flexural strength, tensile-splitting strength, durability and the pH value, ion conductivity and nitrate content of the resulting leachate”.

In order to conduct the investigation, the methodology in Chapter 3 was adhered to. The results in Sections 4.4 to 4.14 indicate that the properties of PMBA-concrete showed a general improvement in relation to the control, whereby a 10 percent replacement showed the most overall improvement. The properties of WFS-concrete show a general decline as WFS content exceeds 5 percent. Accordingly, the WFS sample that performed best resulted from a 5 percent replacement. The 10, 15 and 20 percent WFS samples exhibited a reduced overall performance compared to the control sample. The effects of varying proportions of waste material on each concrete property are detailed in Sections 4.4 to 4.14 and summarised in Section 4.15.

(C). “Use knowledge gained from the literature review to explain the effect of the incremental additions of each test material on concrete and assess how the properties of PMBA and WFS achieves this effect”.

It was observed that the effects of PMBA on concrete properties are governed by the properties of the waste ash itself, particularly the following:

- The hydrophilic nature improves rheological properties by facilitating wetting. This effect becomes more prevalent as PMBA content increases.

- The high specific surface of PMBA improves pozzolanic reactivity by providing a greater surface for the reaction to take place, thereby enhancing strength development.
- Glassy particle texture and spherical particles improve rheological properties by decreasing water requirement through reducing the area that requires wetting. In addition, spherical particles behave as miniature ball bearings which applies a lubricating effect to fresh concrete. The influences of particle characteristics become more influential as PMBA content increases.
- The largely amorphous constitution (particularly amorphous SiO_2) and high fineness of PMBA enhances pozzolanic reactivity, thereby improving strength development.
- The characteristic consumption of CH during pozzolanic reactions improves strength by replacing the weak CH with the primary strength-giving C-S-H. In addition, greater contents of PMBA lead to lesser contents of CH, which reduces leachate alkalinity. The reduced CH content did not impair the ability of concrete to maintain the passivation layer.
- The fine-filler effect was observed to aid in reducing porosity by refining the pore structure, thereby contributing in the improvement of compressive strength, flexural strength, tensile-splitting strength, OPI, WS and CC. The fine-filler effect appeared to peak at a 10 percent addition of PMBA.
- The high LOI content may decrease strength with greater additions of PMBA.

Key properties of WFS that influences concrete properties are as follows:

- The particle shapes of WFS largely occur as cubical, sub-rounded and rounded. These shapes reduce the surface requiring wetting, thereby reducing the water requirement. Additionally, the sub-rounded and rounded particles are able to easily roll over each other, reducing particle friction, which leads to a more workable mix. Compared to conventional fine aggregate, WFS is reported as having a reduced capacity to absorb water, potentially leading to a reduced water requirement. The influence of particle shapes in improving workability becomes more evident as WFS content increases.
- The poor gradation of WFS led to inefficient packing of the concrete microstructure, leading to the increase of voids as WFS increased. At additions of WFS exceeding 5 percent, this high void content had more influence than the beneficial filler effect, thus reducing density, strength and durability.

5.5 RESPONSE TO RESEARCH QUESTIONS

- By replacing cement, by mass, with 5, 10, 15 and 20 percent PMBA, the resulting concrete exhibits an overall improvement when compared to the control. The results indicate that the optimum effect is achieved at a 10 percent addition of PMBA. When compared to the control and other PMBA samples in the study, the 10%PMBA sample showed various improvements, specifically a degree of workability suitable for normal concrete applications, the highest density/compressive strength/flexural strength/tensile-splitting strength, 'good' degree of durability against permeability, the highest degree of durability against water sorptivity and chloride conductivity, a pH value that allows for steel protection whilst providing an environmentally-friendly leachate, fourth lowest ion conductivity value, and third lowest nitrate content (which adhered to the minimum quality requirements in SA).
- By replacing fine aggregate, by mass, with 5, 10, 15 and 20 percent WFS, the resulting concrete exhibits a reduced overall performance compared to the control, except for the concrete arising from a 5 percent addition of WFS. When compared to the control and other WFS samples in the study, the 5%WFS samples exhibited a substantial improvement in workability, the highest density, second highest compressive and flexural strengths, fourth highest tensile-splitting strength, the highest degree of durability against permeability, the highest degree of durability against water sorptivity, the second highest degree of durability against chloride conductivity, a pH value that allows for steel protection whilst providing an environmentally-friendly leachate, third lowest ion conductivity, and fourth lowest nitrate content (which adhered to the minimum quality requirements in SA).

By displaying improved overall performance compared to the control, the optimum mixes show promise for application in industry. Additionally, with further testing, such as their effects under a wider range of testing variables and their respective economic and environmental performances, these mixes may be proven to be superior than ordinary concrete in more ways than just the common concrete properties. The potential implication may be the adoption of 10%PMBA concrete and 5%WFS-concrete in the South African construction industry. From an environmental viewpoint, these adoptions may significantly reduce the quantities of waste being landfilled, may provide higher leachate quality, may reduce the high reliance on cement and fine aggregate, along with the associated concerns with greenhouse gas generation, energy consumption, and raw material preservation in SA. A framework exists for the integration of fly ash in cement in SA. Accordingly, it can be reasoned that a similar framework be used for the potential adoption of PMBA in the cement industry.

As indicated in Figures 2.18 and 2.26 in Sections 2.5.3 and 2.7.3 respectively, the majority of pulp/paper mills and foundries in SA are situated in the Gauteng, KZN, and Western Cape. In the year 2016, Gauteng, KZN, and the Western Cape occupied titles, respectively, of the first, second and third highest economic contributors to the country (DEA, 2018). These provinces, respectively, contributed 35, 16, and 14 percent to the national GDP in 2016 (DEA, 2018), whilst contributing 40, 21, and 15 percent to the manufacturing industry in 2010 (SEDA, 2016). These provinces experience higher urbanisation and manufacturing rates as compared to their counterparts, thus experiencing the correlating elevated rates of concrete usage and test material production required to effectuate the waste-reuse initiative. Moreover, Figure 2.2 in Section 2.2.1 shows that the major metropolitan municipalities in SA, namely City of Johannesburg, City of eThekwini, and City of Cape Town, will experience complications in the landfill situation, particularly the consumption of landfill airspace, thereby adding more incentive to effectuate the waste-reuse initiative.

5.6 RECOMMENDATIONS

In relation to the results of the study, the following is a summary of recommendations based on the usage of PMBA and WFS:

- PMBA should not be integrated at 5 percent in applications where flexural strength is the ruling criteria, such as in rigid pavements. An exception to this condition may occur when strength requirements are low enough, such as the requirement for minor roads.
- As per the discussion in Section 5.5, the optimum content of PMBA is 10 percent by mass of cement. However, consideration must be given to selecting an appropriate concrete cover depth, which should accommodate the reduction in OPI that arises from the 10 percent replacement.
- The content of WFS should not exceed 5 percent. This is required to impart durability, preserve strength and reduce aggregate segregation in fresh concrete.

5.7 FUTURE SCOPE

The following related topics may warrant potential avenues of research:

- An investigation into long-term relationships between high-volume PMBA concrete and the resulting consumption of CH via pozzolanic reactions.

- An investigation into the influence of increasing quantities of PMBA and the reductions in strength due to LOI.
- An investigation into the influence of WFS in affecting the pH of the resulting leachate at a range of testing ages.
- An investigation into the relationship between greater testing ages and the nitrate content of the leachates from PMBA-concrete and WFS-concrete.
- An investigation into the relationship between greater testing ages and ion conductivity of the leachates from PMBA-concrete and WFS-concrete.
- An investigation into the separate effects of the fine-filler effect on OPI.
- An investigation into the influence of W/B ratio on the properties of PMBA-concrete and WFS-concrete.
- An investigation into the influence of varying cement types on the properties of PMBA-concrete.
- An investigation into the influence of furan resin binder of the density of WFS-concrete.
- An investigation into the relationship between water sorptivity and porosity of both PMBA-concrete and WFS-concrete.
- The development of a sustainability model which must include a life-cycle assessment and an economic analysis.
- The development of SANS-approved specifications to allow PMBA-concrete and WFS-concrete to be used in industry. This must integrate the characteristics of each material to develop a mix design method, similar to the C & CI method, whereby strength may be designed based on the characteristics of the PMBA and WFS and their respective interactions in concrete.

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7. APPENDICES

Appendix A: General Cement Conformity Criteria

<table>
<tr><th rowspan="3">Strength class</th><th colspan="4">Compressive strength (MPa)</th><th rowspan="2">Initial setting time</th><th rowspan="2">Soundness (Expansion)</th></tr>
<tr><th colspan="2">Early strength</th><th colspan="2">Standard strength</th></tr>
<tr><th>2 Days</th><th>7 Days</th><th colspan="2">28 Days</th><th>min</th><th>mm</th></tr>
<tr><td>**32.5 L**</td><td>-</td><td>≥ 12.0</td><td rowspan="3">≥ 32.5</td><td rowspan="3">≤ 52.5</td><td rowspan="3">≥ 75</td><td rowspan="9">≤ 10</td></tr>
<tr><td>**32.5 N**</td><td>-</td><td>≥ 16.0</td></tr>
<tr><td>**32.5 R**</td><td>≥ 10.0</td><td>-</td></tr>
<tr><td>**42.5 L**</td><td>-</td><td>≥ 16.0</td><td rowspan="3">≥ 42.5</td><td rowspan="3">≤ 62.5</td><td rowspan="3">≥ 60</td></tr>
<tr><td>**42.5 N**</td><td>≥ 10.0</td><td>-</td></tr>
<tr><td>**42.5 R**</td><td>≥ 20.0</td><td>-</td></tr>
<tr><td>**52.5 L**</td><td>≥ 10.0</td><td>-</td><td rowspan="3">≥ 52.5</td><td rowspan="3">-</td><td rowspan="3">≥ 45</td></tr>
<tr><td>**52.5 N**</td><td>≥ 20.0</td><td>-</td></tr>
<tr><td>**52.5 R**</td><td>≥ 30.0</td><td>-</td></tr>
</table>

<table>
<tr><th>Property</th><th>Test reference</th><th>Cement type</th><th>Strength class</th><th>Requirement</th></tr>
<tr><td>**Loss on ignition**</td><td rowspan="6">EN 196-2</td><td>CEM I
CEM III</td><td>All</td><td>≤ 5.0%</td></tr>
<tr><td>**Insoluble residue**</td><td>CEM I
CEM III</td><td>All</td><td>≤ 5.0 %</td></tr>
<tr><td rowspan="3">**Sulphate content (as SO_3)**</td><td rowspan="2">CEM I
CEM II
CEM IV
CEM V</td><td>32.5 N
32.5 R
42.5 N</td><td>≤ 3.5 %</td></tr>
<tr><td>42.5 R
52.5 N
52.5 R</td><td rowspan="2">≤ 4.0%</td></tr>
<tr><td>CEM III</td><td>All</td></tr>
<tr><td>**Chloride content**</td><td>All</td><td>All</td><td>≤ 0.10 %</td></tr>
<tr><td>**Pozzolanicity**</td><td>EN 196-5</td><td>CEM IV</td><td>All</td><td>Satisfies the test</td></tr>
</table>

Appendix B: General Fine Aggregate Conformity Criteria

Property	Fine aggregate derived from the natural disintegration of rock and any mixture (blend) of this class and fine aggregate derived from the mechanical crushing or milling of rock	Fine aggregate derived from the mechanical crushing or milling of rock
Grading, mass percentage that passes sieves that have square apertures of nominal size:		
5000 µm	92 – 100	
4750 µm	90 – 100	
150 µm	5 – 25	
Dust content, material passing a 75 µm sieve, mass percentage, max.	5	10
Methylene blue adsorption value, max.	0.7	
Clay content, material of particle size smaller than 5 µm, mass percentage, max.	2.0	
Fineness modulus	1.2 – 3.5	
Chloride content, expressed as Cl^-, mass percentage, max	Fine aggregate for – Concrete for prestressing: 0.01 - Normal reinforced concrete: 0.03 - Non-reinforced concrete: 0.03	
Organic impurities	The colour of the liquid above the fine aggregate shall not be darker than the colour of the reference solution, except that this requirement shall not be applicable if the fine aggregate complies with the requirement for soluble deleterious impurities	-
Presence of sugar	Free from sugar unless the fine aggregate complies with the requirement for soluble deleterious impurities	-
Soluble deleterious impurities	The strength of specimens made with fine aggregate shall be at least 85 % of that of the specimens made with the same fine aggregate after it has been washed, except that this requirement shall not be applicable if the fine aggregate complies with the requirements both for organic impurities and for the presence of sugar	-

Appendix C: Data from sieve analysis

Material: Umgeni river sand			**Sample mass:** 500 g	
Sieve Size (microns)	**Mass retained (g)**	**Mass retained (%)**	**Cumulative mass retained (%)**	**Cumulative mass passing (%)**
4750	7	1.4	1.4	98.6
2360	20	4.0	5.4	94.6
1180	58	11.6	17.0	83.0
600	108	21.6	38.6	61.4
300	189	37.8	76.4	23.6
150	103	20.6	97.0	3.0
Pan	14	2.8	99.8	0.2
		FM = 3.4		
Material: WFS			**Sample mass:** 500 g	
Sieve Size (microns)	**Mass retained (g)**	**Mass retained (%)**	**Cumulative mass retained (%)**	**Cumulative mass passing (%)**
4750	2	0.4	0.4	99.6
2360	9	1.8	2.2	97.8
1180	20	4.0	6.2	93.8
600	151	30.2	36.4	63.6
300	235	47	83.4	16.6
150	72	14.4	97.8	2.2
Pan	11	2.2	100	0.6
		FM = 3.3		

Appendix D: Control Concrete Mix Design

C & CI: CONCRETE MIX DESIGN

CLIENT:	STUDENT No	214550060		PROJECT	MSc. Eng			
REQUIREMENTS:	STRENGTH:	35	MPa	SLUMP:	60	mm	W/C:	0,53

MATERIAL	TYPE AND SOURCE	SIZE [mm]	RD:	LBD [kg/m^3]	CBD [kg/m^3}	FM	K VALUES STONE	HAND COMP	MOD VIBR	HEAVY VIBR
CEMENT	NPC CEMIIB-S 42.5N		3,1				9,5	0,75	0,8	1
FA/SLAG							13,2	0,84	0,9	1,05
STONE 1	TILLITE STONE	19	2,65	1360	1446		19,0	0,94	1	1,05
STONE 2							26,5	1	1,06	1,1
SAND 1	UMGENI RIVER SAND		2,65	1320	1400	3,40		FOR CBD [kg/m^3}		1446
SAND 2								STONE		19
TEST MATERIAL			Dosage:	0	% mass			SELECTED K		1
1 m^3 (1000 l)		NOTE: kg/RD = litres						STONE REQD [kg]		954,36

STONE REQUIRED [from chart using stone size and FM of sand] 954,36 kg

	MIX 1		MIX 2		MIX 3		MIX 4	
MATERIAL	kg	litre	kg	litre	kg	litre	kg	litre
WATER	240	240	230	230	220	220	210	210
CEMENT	453	146	434	140	415	134	396	128
FA/SLAG	0	0	0	0	0	0	0	0
STONE 1	954	360	954	360	954	360	954	360
STONE 2	0	0	0	0	0	0	0	0
SAND 1	673	254	715	270	758	286	800	302
SAND 2	0	0	0	0	0	0	0	0
ADMIXTURE	0	ml	0		0		0	
TOTAL	2320	1000	2333	1000	2347	1000	2361	1000
FACTOR	mix size/1000 x (water mix 1)/(water mix X)							
0,0944	0,0944		0,0985		0,1029		0,1078	

LAB MIX

	MIX 1			MIX 2			MIX 3			MIX 4	
MATERIAL	kg	Litre	Add kg	kg	Litre	Add kg	kg	Litre	Add kg	kg	Litre
WATER	22,6	22,6	0,0	22,6	22,6	0,0	22,6	22,6	0,0	22,6	22,6
CEMENT	42,7	13,8	0,0	42,7	13,8	0,0	42,7	13,8	0,0	42,7	13,8
FA/SLAG											
STONE 1	90,1	34,0	3,9	94,0	35,5	4,3	98,2	37,1	4,7	102,9	38,8
STONE 2											
SAND 1	63,5	23,9	7,0	70,4	26,6	7,6	78,0	29,4	8,3	86,3	32,6
SAND 2											
ADMIXTURE	0,0			0,0			0,0			0,0	
Total	218,9	94,4		229,8	98,5		241,6	102,9		254,6	107,85

	MIX 1		MIX 2		MIX 3		MIX 4	
SLUMP		mm		mm		mm	60	mm

Appendix E: Data from slump tests

Mix ID	Slump (mm)
Control	60
5%PMBA	75
10%PMBA	95
15%PMBA	120
20%PMBA	140
5%WFS	130
10%WFS	170
15%WFS	190
20%WFS	230

Appendix F: Data from SHD tests

Mix ID	Mass (kg)			Density (kg/m^3)			$Density_{ave}$
	1	2	3	1	2	3	(kg/m^3)
Control	11.79	11.68	11.85	2358.6	2335	2369	2354
5%PMBA	11.72	11.88	11.88	2344	2375.8	2375.8	2365
10%PMBA	11.95	12.02	12.03	2389.2	2404.6	2406.6	2400
15%PMBA	11.91	11.92	11.97	2382.8	2384.8	2394.8	2387
20%PMBA	11.74	11.98	12.02	2347.4	2395.2	2404.8	2382
5%WFS	11.71	11.80	11.90	2341.8	2360.8	2380.6	2361
10%WFS	11.59	11.79	11.72	2318.6	2357.4	2344.6	2340
15%WFS	11.39	11.51	11.80	2278.8	2302.2	2359.6	2314
20%WFS	11.3	11.67	11.27	2264.6	2334	2253.2	2284

Appendix G: Data from mechanical strength tests

Mix ID	Sample No.	Compressive strength				Flexural strength				Tensile-splitting strength			
		7-Day		28-Day		7-Day		28-Day		7-Day		28-Day	
		Load (kN)	Strength (MPa)	Load (kN)	Strength (MPa)	Load (kN)	Strength (MPa)	Load (kN)	Strength (MPa)	Load (kN)	Strength (MPa)	Load (kN)	Strength (MPa)
Control	1	535.20	23.79	774.70	34.43	7.54	2.26	15.36	4.61	141.50	2.00	196.30	2.78
	2	483.30	21.48	809.50	35.98	8.10	2.43	13.75	4.13	165.0	2.33	187.80	2.66
	3	535.60	23.80	785.70	34.92	8.25	2.48	13.70	4.11	157.50	2.23	185.20	2.62
Strength$_{AVE}$ (MPa)		23.0		35.0		2.45		4.3		2.20		2.70	
15% Average		3.45		5.25		0.37		0.65		0.33		0.41	
Strength difference		2.32		1.55		0.21		0.50		0.33		0.16	
5%PMBA	1	549.00	24.40	798.10	35.47	8.44	2.53	13.45	4.04	128.60	1.82	186.90	2.64
	2	529.80	23.55	802.70	35.68	8.33	2.50	15.37	4.61	110.60	1.56	172.90	2.45
	3	537.30	23.88	809.20	35.96	7.54	2.26	13.40	4.02	118.00	1.77	183.00	2.59
Strength$_{AVE}$ (MPa)		24.0		35.5		2.4		4.2		1.70		2.55	
15% Average		3.60		5.33		0.36		0.63		0.26		0.38	
Strength difference		0.85		0.49		0.27		0.59		0.25		0.20	
10%PMBA	1	584.30	25.97	896.30	39.84	8.94	2.68	15.25	4.58	150.70	2.13	187.60	2.65
	2	537.50	23.89	797.30	35.44	8.58	2.57	15.58	4.67	150.10	2.12	205.20	2.90
	3	582.70	25.90	885.40	39.35	8.75	2.68	17.48	5.24	162.10	2.29	183.10	2.59
Strength$_{AVE}$ (MPa)		25.5		38.0		2.65		4.85		2.20		2.70	
15% Average		3.83		5.70		0.38		0.73		0.33		0.41	
Strength difference		2.08		4.40		0.11		0.67		0.17		0.31	
15%PMBA	1	492.50	21.89	873.30	38.81	7.91	2.37	14.41	4.32	164.20	2.32	205.40	2.91
	2	515.30	22.90	807.30	35.88	8.41	2.52	13.37	4.01	147.40	2.09	179.90	2.55
	3	513.80	22.84	881.00	39.16	8.55	2.57	14.40	4.32	145.40	2.06	185.50	2.62
Strength$_{AVE}$ (MPa)		22.5		38		2.5		4.2		2.15		2.70	
15% Average		3.38		5.70		0.38		0.63		0.33		0.41	
Strength difference		1.01		3.28		0.19		0.31		0.27		0.36	

Mix ID	Sample No.	Compressive strength				Flexural strength				Tensile-splitting strength			
		7-Day		28-Day		7-Day		28-Day		7-Day		28-Day	
		Load (kN)	Strength (MPa)	Load (kN)	Strength (MPa)	Load (kN)	Strength (MPa)	Load (kN)	Strength (MPa)	Load (kN)	Strength (MPa)	Load (kN)	Strength (MPa)
20%PMBA	1	458.60	20.38	805.80	35.81	8.57	2.57	15.41	4.62	119.60	1.70	178.10	2.52
	2	450.90	20.04	776.50	34.51	8.31	2.49	14.39	4.32	130.00	1.84	191.70	2.71
	3	449.40	19.97	865.60	38.47	7.79	2.34	14.87	4.46	136.30	1.93	170.20	2.41
Strength$_{AVE}$ (MPa)		20.0		36.5		2.45		4.45		1.80		2.55	
15% Average		2.45		5.48		0.37		0.67		0.27		0.38	
Strength difference		0.41		3.96		0.23		0.31		0.24		0.30	
5%WFS	1	495.00	22.00	738.50	32.82	7.39	2.22	14.21	4.26	164.40	2.33	168.40	2.38
	2	495.60	22.03	734.10	32.63	7.91	2.37	13.13	3.94	145.60	2.06	184.60	2.61
	3	480.70	21.36	706.10	31.38	7.52	2.26	13.36	4.00	150.10	2.12	165.00	2.33
Strength$_{AVE}$ (MPa)		22.0		32.5		2.3		4.05		2.15		2.45	
15% Average		3.30		4.88		0.35		0.61		0.32		0.37	
Strength difference		0.66		1.44		0.156		0.32		0.27		0.28	
10%WFS	1	409.30	18.19	698.20	31.03	7.37	2.21	14.23	4.27	115.30	1.63	163.90	2.32
	2	390.60	17.36	654.80	29.10	6.97	2.09	12.94	3.88	118.90	1.68	190.10	2.69
	3	427.10	18.98	704.90	31.33	7.11	2.13	13.22	3.97	119.80	1.69	187.20	2.65
Strength$_{AVE}$ (MPa)		18.0		30.5		2.15		4.05		1.65		2.55	
15% Average		2.70		4.58		0.32		0.61		0.25		0.38	
Strength difference		1.62		2.23		0.12		0.39		0.06		0.37	
15%WFS	1	426.60	18.96	636.90	28.31	6.25	1.88	11.75	3.53	102.70	1.45	163.70	2.32
	2	438.20	19.48	680.90	30.26	6.64	2.00	10.88	3.26	105.50	1.49	185.30	2.62
	3	430.30	19.12	704.30	31.30	6.77	2.03	10.75	3.23	101.90	1.44	160.10	2.27
Strength$_{AVE}$ (MPa)		19.0		30.0		1.95		3.35		1.45		2.40	
15% Average		2.85		4.50		0.29		0.50		0.22		0.36	
Strength difference		0.52		3.00		0.16		0.30		0.05		0.35	
20%WFS	1	434.50	19.31	713.50	31.71	6.21	1.86	10.67	3.20	123.10	1.74	194.00	2.74
	2	421.2	18.72	626.60	27.85	6.57	1.97	10.94	3.28	121.90	1.72	193.80	2.74
	3	427.2	18.99	692.30	30.77	6.21	1.86	12.06	3.62	109.30	1.55	198.30	2.81
Strength$_{AVE}$ (MPa)		19.0		30.0		1.9		3.35		1.65		2.75	
15% Average		2.85		4.50		0.29		0.50		0.25		0.41	
Strength difference		0.59		3.86		0.11		0.42		0.20		0.06	

Appendix H: Data from durability tests

Mix ID	Sample No.	OPI (log value)	WS (mm/$\sqrt{hr}$)	CC (mS/cm)
Control	1	10.38	7.01	0.25
	2	10.30	5.30	0.24
	3	10.49	6.06	0.27
	4	10.07	6.74	0.26
Average:		**10.31**	**6.28**	**0.25**
Coefficient of variation:		**44.28**	**12.18**	**6.2**
5%PMBA	1	10.23	5.78	0.25
	2	10.52	5.93	0.27
	3	10.35	5.36	0.27
	4	10.19	5.58	0.25
Average:		**10.32**	**5.66**	**0.26**
Coefficient of variation:		**30.65**	**4.36**	**3.9**
10%PMBA	1	9.68	5.08	0.23
	2	10.08	5.79	0.25
	3	9.80	5.75	0.27
	4	9.80	5.68	0.24
Average:		**9.84**	**5.58**	**0.25**
Coefficient of variation:		**33.93**	**5.97**	**6.5**
15%PMBA	1	9.88	5.89	0.27
	2	10.56	5.99	0.25
	3	10.12	5.82	0.27
	4	10.36	5.71	0.28
Average:		**10.23**	**5.85**	**0.27**
Coefficient of variation:		**66.57**	**2.02**	**3.70**
20%PMBA	1	10.30	5.64	0.25
	2	9.86	5.74	0.26
	3	10.39	5.88	0.28
	4	9.88	6.09	0.25
Average:		**10.11**	**5.83**	**0.26**
Coefficient of variation:		**57.40**	**3.30**	**6.10**
5%WFS	1	10.32	5.71	0.26
	2	10.36	4.32	0.24
	3	10.32	4.35	0.20
	4	10.27	5.49	0.22
Average:		**10.32**	**4.97**	**0.23**
Coefficient of variation:		**8.45**	**14.82**	**11.00**
10%WFS	1	10.02	5.54	0.23
	2	9.80	5.54	0.20
	3	9.68	6.18	0.25
	4	10.15	6.40	0.20
Average:		**9.87**	**5.92**	**0.22**
Coefficient of variation:		**47.47**	**7.43**	**10.60**
15%WFS	1	10.00	6.26	0.27
	2	9.73	5.38	0.25
	3	9.95	5.65	0.25
	4	9.89	5.18	0.22
Average:		**9.88**	**5.62**	**0.25**
Coefficient of variation:		**28.68**	**8.31**	**7.6**
20%WFS	1	10.29	5.98	0.27
	2	9.86	5.47	0.26
	3	10.40	5.74	0.26
	4	9.88	6.02	0.25
Average:		**10.05**	**5.80**	**0.26**
Coefficient of variation:		**57.23**	**4.40**	**3.7**

Appendix I: Data from leaching tests

Appendix I-1: Data for determining content of deionized water

Mix ID	$M_{crucible}$ (g)		$M_{crucible+wet\ sample}$ (g)		$M_{crucible+dry\ sample}$ (g)		$M_{wet\ sample}$ (g)		$M_{dry\ sample}$ (g)		Total Solids (%)		Total Solids$_{AVE}$ (%)		Moisture Content (%)	
	Testing age (day)															
	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day	7 Day	28 Day
Control	42.680	54.437	51.747	59.004	50.951	58.481	9.067	4.567	8.270	4.043	91.217	88.529	91.401	89.909	8.599	10.091
	49.540	63.546	58.484	63.546	57.706	62.823	8.944	7.324	8.166	6.601	91.304	90.132				
	48.013	63.467	56.194	63.467	55.514	62.623	8.181	9.450	7.501	8.606	91.682	91.067				
5%PMBA	49.545	48.762	59.447	51.819	58.294	51.390	9.902	3.056	8.749	2.627	88.359	85.951	89.597	87.341	10.403	12.659
	54.145	44.812	65.941	47.858	64.752	47.483	11.796	3.036	10.607	2.661	89.920	87.648				
	48.014	44.904	57.720	48.338	56.800	47.941	9.706	3.434	8.785	3.036	90.513	88.424				
10%PMBA	47.263	54.433	52.915	58.602	52.633	58.341	5.651	4.169	5.369	3.907	95.017	93.737	94.995	93.966	5.005	6.034
	40.519	54.013	45.896	59.254	45.640	58.951	5.377	5.240	5.121	4.937	95.233	94.218				
	48.546	56.225	53.429	60.192	53.172	59.952	4.883	3.967	4.626	3.726	94.735	93.942				
15%PMBA	47.253	44.907	51.493	47.155	51.120	47.033	4.240	2.248	3.867	2.126	91.210	94.578	91.179	94.890	8.821	5.110
	40.516	48.761	43.697	51.212	43.417	51.090	3.180	2.451	2.900	2.329	91.196	95.018				
	48.540	44.822	51.214	49.086	50.976	48.876	2.673	4.263	2.436	4.053	91.131	95.074				
20%PMBA	47.262	42.893	49.982	48.923	49.832	48.575	2.719	6.029	2.569	5.681	94.473	94.228	94.463	94.108	5.537	5.892
	48.545	49.517	50.704	57.614	50.858	57.127	2.159	8.097	2.039	7.610	94.478	93.985				
	40.519	56.214	42.757	61.377	42.633	61.073	2.238	5.163	2.113	4.859	94.437	94.112				
5%WFS	48.735	54.099	53.844	60.407	53.376	60.069	5.108	6.308	4.640	5.970	90.844	94.645	91.141	94.310	8.859	5.690
	52.516	48.714	59.596	59.078	58.968	58.354	7.080	10.364	6.451	9.640	91.128	93.012				
	52.973	48.537	61.273	57.505	60.563	57.081	8.300	8.967	7.590	8.543	91.451	95.272				
10%WFS	52.167	48.506	55.932	52.961	55.538	52.840	3.764	4.455	3.370	4.33	89.542	97.264	89.597	97.272	10.403	2.728
	53.985	42.693	58.828	46.434	58.372	46.332	4.843	3.740	4.387	3.638	90.587	97.267				
	54.415	45.927	57.919	50.470	57.522	50.347	3.504	4.543	3.107	4.419	88.663	97.286				
15%WFS	54.425	53.327	58.110	57.331	57.997	57.236	3.684	4.004	3.572	3.909	96.949	97.627	97.008	97.625	2.992	2.375
	54.005	54.189	57.174	57.202	57.064	57.129	3.169	3.013	3.059	2.940	96.522	97.564				
	52.529	40.808	59.660	45.249	59.485	45.146	7.130	4.441	6.956	4.338	97.554	97.685				
20%WFS	54.028	40.800	56.824	43.353	56.670	43.352	2.795	2.553	2.642	2.552	94.502	99.960	94.561	95.489	5.439	4.511
	54.448	56.689	57.992	58.215	57.789	58.051	3.544	1.525	3.341	1.361	94.286	89.274				
	52.560	45.031	56.506	47.691	56.305	47.617	3.945	2.659	3.744	2.586	94.895	97.232				

Appendix I-2: Readings of pH values, ion conductivity and nitrate content

Mix ID	7-Day readings									28-Day readings								
	pH value			Ion conductivity (mm/$\sqrt{hr}$)			Nitrate content (mS/cm)			pH value			Ion conductivity (mm/$\sqrt{hr}$)			Nitrate content (mS/cm)		
	Testing intervals (Hour)																	
	24	**36**	**72**	**24**	**36**	**72**	**24**	**36**	**72**	**24**	**36**	**72**	**24**	**36**	**72**	**24**	**36**	**72**
Control	13.14	13.38	13.38	6.550	6.826	6.550	2.467	0.745	1.200	13.38	13.31	13.38	5.699	5.352	5.627	11.40	8.72	9.05
Average		**13.30**			**6.642**			**1.471**			**13.36**			**5.559**			**9.72**	
5%PMBA	13.27	13.33	13.40	5.937	6.234	7.047	1.980	0.761	3.913	13.23	13.14	13.37	4.125	4.051	4.574	10.89	6.91	7.44
Average		**13.33**			**6.406**			**2.218**			**13.25**			**4.25**			**8.414**	
10%PMBA	13.08	13.17	13.30	4.137	4.973	5.500	6.660	2.900	1.930	13.13	13.24	13.34	3.332	4.414	5.196	15.90	4.70	3.70
Average		**13.18**			**4.87**			**3.830**			**13.24**			**4.314**			**8.100**	
15%PMBA	13.24	13.23	13.27	4.763	4.788	5.213	1.857	2.320	1.727	13.07	13.12	13.19	3.330	3.506	3.886	11.58	3.08	3.00
Average		**13.25**			**4.921**			**1.968**			**13.13**			**3.574**			**5.891**	
20%PMBA	13.09	13.20	13.21	3.288	3.841	3.610	2.653	6.513	6.953	13.06	13.10	13.02	2.837	3.072	3.007	4.28	4.43	3.66
Average		**13.17**			**3.580**			**5.373**			**13.06**			**2.972**			**4.128**	
5%WFS	13.24	13.44	13.38	4.729	4.773	5.252	3.590	9.777	6.173	13.16	13.37	13.39	3.352	4.341	4.904	3.91	10.6	11.7
Average		**13.35**			**4.768**			**6.513**			**13.31**			**4.199**			**8.760**	
10%WFS	13.11	13.47	13.48	3.758	4.904	5.639	14.60	19.33	21.40	12.35	12.69	12.70	1.271	1.519	1.697	1.28	2.24	3.10
Average		**13.35**			**4.767**			**18.444**			**12.58**			**1.496**			**2.21**	
15%WFS	13.28	13.50	13.42	4.931	5.491	5.230	19.43	27.16	13.76	12.81	12.77	12.84	1.874	1.725	2.064	4.40	5.48	4.53
Average		**13.40**			**5.217**			**20.122**			**12.81**			**1.888**			**4.808**	
20%WFS	13.32	13.40	13.46	4.242	4.858	5.315	28.10	25.33	24.13	13.54	13.47	13.47	5.658	5.167	5.313	7.72	5.88	7.71
Average		**13.39**			**4.805**			**25.855**			**13.49**			**5.379**			**7.107**	

Appendix J: Data from statistical analysis

Appendix J-1: Data for Pearson's coefficient of correlation for slump results

	PMBA content, X (%)	Slump, Y (mm)	X - $\bar{X}$	Y - $\bar{Y}$	X^2	Y^2	XY
	0	60	-10	-38	100	1444	380
	5	75	-5	-23	25	529	115
	10	95	0	-3	0	9	0
	15	120	5	22	25	484	110
	20	140	10	42	100	1764	420
Sum	**50**	**490**			**250**	**4230**	**1025**
Mean	**$\bar{x}$ = 10**	**$\bar{Y}$ = 98**					

	WFS content, X (%)	Slump, Y (mm)	X - $\bar{X}$	Y - $\bar{Y}$	X^2	Y^2	XY
	0	60	-10	-96	100	9216	960
	5	130	-5	-26	25	676	130
	10	170	0	14	0	196	0
	15	190	5	34	25	1156	170
	20	230	10	74	100	5476	740
Sum	**50**	**780**			**250**	**16720**	**2000**
Mean	**$\bar{x}$ = 10**	**156**					

Appendix J-2: Data for determining 95 percent confidence intervals

Property: SHD		**Confidence level: 95%**	**Significance level: 0.05**	**Sample size, n: 3**	**$t_{(v;a)}$: 4.3**
Mix ID	**Mean, $\bar{x}$ (kg/m^3)**	**Standard deviation, s (kg/m^3)**	**$\frac{s}{\sqrt{n}}$**	**Confidence Interval (kg/m^3)**	
				Lower	**Upper**
Control	2354.20	17.42	10.06	2310.95	2397.45
5%PMBA	2365.20	18.36	10.60	2319.62	2410.78
10%PMBA	2400.13	9.52	5.50	2376.50	2423.77
15%PMBA	2387.47	6.43	3.71	2371.51	2403.43
20%PMBA	2382.47	30.75	17.75	2306.14	2458.80
5%WFS	2361.07	19.40	11.20	2312.90	2409.23
10%WFS	2340.20	19.77	11.41	2291.12	2389.28
15%WFS	2313.53	41.58	24.00	2210.32	2416.75
20%WFS	2283.93	43.73	25.25	2175.36	2392.50

Property: 7-Day Compressive strength		Confidence level: 95%	Significance level: 0.05	Sample size, n: 3	$t_{(v;a)}$: 4.3
Mix ID	Mean, $\bar{x}$ (MPa)	Standard deviation, s (MPa)	$\frac{s}{\sqrt{n}}$	Confidence Interval (MPa)	
				Lower	Upper
Control	23.02	1.34	0.77	19.71	26.34
5%PMBA	23.94	0.43	0.25	22.88	25.00
10%PMBA	25.25	1.18	0.68	22.32	28.19
15%PMBA	22.54	0.57	0.33	21.14	23.95
20%PMBA	20.13	0.22	0.13	19.59	20.67
5%WFS	21.80	0.38	0.22	20.86	22.74
10%WFS	18.18	0.81	0.47	16.17	20.19
15%WFS	19.19	0.27	0.15	18.53	19.85
20%WFS	19.01	0.30	0.17	18.27	19.74

Property: 28-Day Compressive strength		Confidence level: 95%	Significance level: 0.05	Sample size, n: 3	$t_{(v;a)}$: 4.3
Mix ID	Mean, $\bar{x}$ (MPa)	Standard deviation, s (MPa)	$\frac{s}{\sqrt{n}}$	Confidence Interval (MPa)	
				Lower	Upper
Control	35.11	0.79	0.46	33.14	37.08
5%PMBA	35.70	0.25	0.14	35.09	36.31
10%PMBA	38.28	2.46	1.42	32.17	44.39
15%PMBA	37.95	1.80	1.04	33.48	42.42
20%PMBA	36.26	2.02	1.17	31.25	41.27
5%WFS	32.28	0.78	0.45	30.33	34.22
10%WFS	30.49	1.21	0.70	27.48	33.49
15%WFS	29.96	1.52	0.88	26.19	33.73
20%WFS	30.11	2.01	1.16	25.11	35.11

Property: 7-Day Flexural Strength		Confidence level: 95%	Significance level: 0.05	Sample size, n: 3	$t_{(v;a)}$: 4.3
Mix ID	Mean, $\bar{x}$ (MPa)	Standard deviation, s (MPa)	$\frac{s}{\sqrt{n}}$	Confidence Interval (MPa)	
				Lower	Upper
Control	2.39	0.12	0.07	2.10	2.68
5%PMBA	2.43	0.15	0.09	2.06	2.80
10%PMBA	2.64	0.06	0.04	2.49	2.80
15%PMBA	2.49	0.10	0.06	2.23	2.75
20%PMBA	2.47	0.12	0.07	2.18	2.76
5%WFS	2.83	0.08	0.04	2.09	2.48
10%WFS	2.14	0.06	0.04	1.99	2.30
15%WFS	1.97	0.08	0.05	1.77	2.17
20%WFS	1.90	0.06	0.04	1.74	2.05

Property: 28-Day Flexural Strength		Confidence level: 95%	Significance level: 0.05	Sample size, n: 3	$t_{(v;a)}$: 4.3
Mix ID	Mean, $\bar{x}$ (MPa)	Standard deviation, s (MPa)	$\frac{s}{\sqrt{n}}$	Confidence Interval (MPa)	
				Lower	Upper
Control	4.28	0.28	0.16	3.58	4.99
5%PMBA	4.22	0.34	0.19	3.39	5.06
10%PMBA	4.83	0.36	0.21	3.94	5.72
15%PMBA	4.22	0.18	0.10	3.77	4.66
20%PMBA	4.47	0.15	0.09	4.09	4.84
5%WFS	4.07	0.17	0.10	3.64	4.49
10%WFS	4.04	0.20	0.12	3.53	4.55
15%WFS	3.34	0.17	0.10	2.93	3.75
20%WFS	3.37	0.22	0.13	2.81	3.92

Property: 7-Day Tensile-splitting Strength		Confidence level: 95%	Significance level: 0.05	Sample size, n: 3	$t_{(v;a)}$: 4.3
Mix ID	**Mean, $\bar{x}$ (MPa)**	**Standard deviation, s (MPa)**	$\frac{s}{\sqrt{n}}$	**Confidence Interval (MPa)**	
				Lower	**Upper**
Control	2.19	0.17	0.10	1.77	2.61
5%PMBA	1.72	0.14	0.08	1.37	2.06
10%PMBA	2.18	0.10	0.06	1.94	2.42
15%PMBA	2.16	0.14	0.08	1.80	2.51
20%PMBA	1.82	0.12	0.07	1.54	2.11
5%WFS	2.17	0.14	0.08	1.82	2.52
10%WFS	1.67	0.03	0.02	1.59	1.75
15%WFS	1.46	0.26	0.02	1.39	1.53
20%WFS	1.67	0.10	0.06	1.41	1.93
Property: 28-Day Tensile-splitting Strength		**Confidence level: 95%**	**Significance level: 0.05**	**Sample size, n: 3**	$t_{(v;a)}$: **4.3**
Mix ID	**Mean, $\bar{x}$ (MPa)**	**Standard deviation, s (MPa)**	$\frac{s}{\sqrt{n}}$	**Confidence Interval (MPa)**	
				Lower	**Upper**
Control	2.69	0.08	0.05	2.48	2.89
5%PMBA	2.56	0.10	0.06	2.32	2.80
10%PMBA	2.71	0.16	0.09	2.31	3.12
15%PMBA	2.69	0.19	0.11	2.22	3.17
20%PMBA	2.55	0.15	0.09	2.17	2.92
5%WFS	2.44	0.15	0.09	2.07	2.81
10%WFS	2.55	0.20	0.12	2.05	3.06
15%WFS	2.40	0.19	0.11	1.93	2.87
20%WFS	2.76	0.04	0.02	2.66	2.86
Property: OPI		**Confidence level: 95%**	**Significance level: 0.05**	**Sample size, n: 4**	$t_{(v;a)}$: **3.18**
Mix ID	**Mean, $\bar{x}$ (log value)**	**Standard deviation, s (log value)**	$\frac{s}{\sqrt{n}}$	**Confidence Interval (log value)**	
				Lower	**Upper**
Control	10.31	0.18	0.09	10.03	10.59
5%PMBA	10.32	0.15	0.07	10.09	10.56
10%PMBA	9.84	0.17	0.08	9.57	10.11
15%PMBA	10.23	0.29	0.15	9.76	10.70
20%PMBA	10.11	0.28	0.14	9.67	10.55
5%WFS	10.32	0.04	0.02	10.26	10.38
10%WFS	9.91	0.21	0.11	9.58	10.25
15%WFS	9.89	0.12	0.06	9.71	10.08
20%WFS	10.11	0.28	0.14	9.67	10.55
Property: WS		**Confidence level: 95%**	**Significance level: 0.05**	**Sample size, n: 4**	$t_{(v;a)}$: **3.18**
Mix ID	**Mean, $\bar{x}$ (mm/√h)**	**Standard deviation, s (mm/√h)**	$\frac{s}{\sqrt{n}}$	**Confidence Interval (mm/√h)**	
				Lower	**Upper**
Control	6.28	0.76	0.38	5.06	7.49
5%PMBA	5.66	0.25	0.12	5.27	6.06
10%PMBA	5.58	0.33	0.17	5.05	6.10
15%PMBA	5.85	0.12	0.06	5.67	6.04
20%PMBA	5.84	0.20	0.10	5.53	6.15
5%WFS	4.97	0.74	0.37	3.80	6.14
10%WFS	5.92	0.44	0.22	5.21	6.62
15%WFS	5.62	0.47	0.23	4.87	6.36
20%WFS	5.80	0.25	0.13	5.40	6.21

Property: CC		Confidence level: 95%	Significance level: 0.05	Sample size, n: 4	$t_{(v;a)}$: 3.18
Mix ID	**Mean, $\bar{x}$ (mS/cm)**	**Standard deviation, s (mS/cm)**	$\frac{s}{\sqrt{n}}$	**Confidence Interval (mS/cm)**	
				Lower	**Upper**
Control	0.26	0.01	0.006	0.23	0.28
5%PMBA	0.26	0.01	0.006	0.24	0.28
10%PMBA	0.25	0.02	0.008	0.22	0.28
15%PMBA	0.27	0.01	0.006	0.25	0.29
20%PMBA	0.26	0.01	0.007	0.24	0.28
5%WFS	0.23	0.03	0.013	0.19	0.27
10%WFS	0.22	0.02	0.012	0.18	0.26
15%WFS	0.25	0.02	0.010	0.21	0.28
20%WFS	0.26	0.01	0.004	0.25	0.27
Property: 7-Day pH Value		**Confidence level: 95%**	**Significance level: 0.05**	**Sample size, n: 3**	$t_{(v;a)}$: **4.3**
Mix ID	**Mean, $\bar{x}$**	**Standard deviation, s**	$\frac{s}{\sqrt{n}}$	**Confidence Interval**	
				Lower	**Upper**
Control	13.30	0.14	0.08	12.96	13.64
5%PMBA	13.33	0.07	0.04	13.17	13.49
10%PMBA	13.18	0.11	0.06	12.91	13.46
15%PMBA	13.25	0.02	0.01	13.19	13.30
20%PMBA	13.17	0.07	0.02	13.00	13.33
5%WFS	13.35	0.10	0.06	13.10	13.61
10%WFS	13.35	0.21	0.12	12.83	13.88
15%WFS	13.40	0.11	0.06	13.12	13.68
20%WFS	13.39	0.07	0.04	13.21	13.57
Property: 28-Day pH Value		**Confidence level: 95%**	**Significance level: 0.05**	**Sample size, n: 3**	$t_{(v;a)}$: **4.3**
Mix ID	**Mean, $\bar{x}$**	**Standard deviation, s**	$\frac{s}{\sqrt{n}}$	**Confidence Interval**	
				Lower	**Upper**
Control	13.36	0.04	0.02	13.26	13.46
5%PMBA	13.25	0.12	0.07	12.96	13.53
10%PMBA	13.24	0.11	0.06	12.98	13.50
15%PMBA	13.13	0.06	0.03	12.98	13.28
20%PMBA	13.06	0.04	0.02	12.96	13.16
5%WFS	13.31	0.13	0.07	12.99	13.62
10%WFS	12.58	0.20	0.12	12.09	13.07
15%WFS	12.81	0.04	0.02	12.72	12.89
20%WFS	13.49	0.04	0.02	13.39	13.59
Property: 7-Day Ion Conductivity Value		**Confidence level: 95%**	**Significance level: 0.05**	**Sample size, n: 3**	$t_{(v;a)}$: **4.3**
Mix ID	**Mean, $\bar{x}$ (mS/cm)**	**Standard deviation, s (mS/cm)**	$\frac{s}{\sqrt{n}}$	**Confidence Interval (mS/cm)**	
				Lower	**Upper**
Control	6.64	0.16	0.09	6.25	7.04
5%PMBA	6.41	0.57	0.33	4.98	7.83
10%PMBA	4.87	0.69	0.40	3.16	6.57
15%PMBA	4.92	0.25	0.15	4.29	5.55
20%PMBA	3.58	0.28	0.16	2.89	4.27
5%WFS	4.92	0.29	0.17	4.20	5.64
10%WFS	4.77	0.95	0.55	2.41	7.12
15%WFS	5.22	0.28	0.16	4.52	5.91
20%WFS	4.81	0.54	0.31	3.47	6.14
Property: 28-Day Ion Conductivity Value		**Confidence level: 95%**	**Significance level: 0.05**	**Sample size, n: 3**	$t_{(v;a)}$: **4.3**

Mix ID	Mean, $\bar{x}$ (mS/cm)	Standard deviation, s (mS/cm)	$\frac{s}{\sqrt{n}}$	Confidence Interval (mS/cm)	
				Lower	Upper
Control	5.56	0.18	0.11	5.10	6.01
5%PMBA	4.25	0.28	0.16	3.55	4.95
10%PMBA	4.31	0.94	0.54	1.99	6.64
15%PMBA	3.57	0.28	0.16	2.87	4.28
20%PMBA	2.97	0.12	0.07	2.67	3.27
5%WFS	4.20	0.79	0.45	2.25	6.15
10%WFS	1.50	0.21	0.12	0.96	2.03
15%WFS	1.89	0.17	0.10	1.47	2.31
20%WFS	5.38	0.25	0.15	4.75	6.00
Property: 7-Day Nitrate Content		**Confidence level: 95%**	**Significance level: 0.05**	**Sample size, n: 3**	$t_{(v;a)}$: **4.3**
Mix ID	**Mean, $\bar{x}$ (mg/L)**	**Standard deviation, s (mg/L)**	$\frac{s}{\sqrt{n}}$	**Confidence Interval (mg/L)**	
				Lower	**Upper**
Control	1.47	0.89	0.52	-0.74	3.69
5%PMBA	2.22	1.59	0.92	-1.73	6.16
10%PMBA	3.83	2.50	1.44	-2.37	10.03
15%PMBA	1.97	0.31	0.18	1.19	2.74
20%PMBA	5.37	2.37	1.37	-0.50	11.25
5%WFS	6.51	3.11	1.79	-1.20	14.23
10%WFS	18.44	3.49	2.01	9.79	27.10
15%WFS	20.12	6.73	3.88	3.42	36.82
20%WFS	25.85	2.04	1.18	20.80	30.91
Property: 28-Day Nitrate Content		**Confidence level: 95%**	**Significance level: 0.05**	**Sample size, n: 3**	$t_{(v;a)}$: **4.3**
Mix ID	**Mean, $\bar{x}$ (mg/L)**	**Standard deviation, s (mg/L)**	$\frac{s}{\sqrt{n}}$	**Confidence Interval (mg/L)**	
				Lower	**Upper**
Control	9.72	1.46	0.84	6.10	13.35
5%PMBA	8.41	2.16	1.25	3.05	13.78
10%PMBA	8.10	6.77	3.91	-8.72	24.92
15%PMBA	5.89	4.93	2.85	-6.35	18.13
20%PMBA	4.12	0.41	0.24	3.11	5.14
5%WFS	8.74	4.22	2.43	-1.73	19.20
10%WFS	2.21	0.91	0.53	-0.05	4.47
15%WFS	4.80	0.59	0.34	3.34	6.27
20%WFS	7.10	1.06	0.62	4.47	9.73

Appendix J-3: Data for determining statistical significance and comparison of means

SHD – PMBA	Control	5%	10%	15%	20%
$\bar{x}$	2354,2	236520%	2400,13333	2387,466667	2382,4667
Standard deviation	17,42182539	18,3597386	9,52120441	6,429100507	30,745623
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	17,8969271	14,0387559	13,13113349	24,988131
Critical value	-	2.78	2.78	2.78	2.78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	1100%	45,9333333	33,26666667	28,266667

Test statistic	-	0,75276574	4,00723646	3,102792263	1,385436

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-29,62352783 51,62352783	14,06731596 77,7993507	3,460825509 63,07250782	-28,45290363 84,98623697

SHD – WFS	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	2354,2	236107%	2340,2	2313,533333	2283,9333
Standard deviation	17,4218253 9	19,4013745	19,7706854	41,57515284	43,732063
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	18,438185	18,6333035	31,87485948	33,286734
Critical value	-	2.78	2.78	2.78	2.78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	687%	-14	-40,6666667	-70,26667
Test statistic	-	0,45611403	-0,9202033	-1,56255721	-2,585376

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-34,9854411 48,71877443	-56,29499955 28,29499955	-113,018151 31,68481764	-145,8229094 5,289576061

7-Day compressive strength - PMBA	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	23,02333333	2394%	25,2533333	22,54333333	20,13
Standard deviation	1,336575225	0,4285246	1,18119995	0,566598035	0,2193171
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,99248846	1,26128242	1,02651514	0,9577404
Critical value	-	2.78	2.78	2.78	2.78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	92%	2,23	-0,48	-2,893333
Test statistic	-	1,13529309	2,16540009	-0,57269252	-3,699954

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-1,33281033 3,172810336	-0,632935129 5,092935129	-2,810046165 1,850046165	-5,067270423 -0,719396243

28-Day compressive strength - PMBA	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	35,11	3570%	38,2766667	37,95	36,263333
Standard deviation	0,792275205	0,24583192	2,46090092	1,801194048	2,0185473
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,58657196	1,82807731	1,39140217	1,5333351
Critical value	-	2.78	2.78	2.78	2.78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	59%	3,16666667	2,84	1,1533333
Test statistic	-	1,23886241	2,12155073	2,499834705	0,9212201

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-0,738103191 1,924769857	-0,982813811 7,316147144	-0,318288819 5,998288819	-2,327123538 4,633790204

7-Day compressive strength - WFS	Control	5%	10%	15%	20%
$\overline{x}$	23,02333333	2180%	18,1766667	19,18666667	19,006667
Standard deviation	1,336575225	0,3784618	0,8100823	0,266333125	0,2953529
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,9822593	1,10513951	0,963682174	0,9679015
Critical value	-	2,78	2,78	2,78	2,78
$\overline{x}_{Test}$ - $\overline{x}_{Control}$	0	-123%	-4,8466667	-3,83666667	-4,016667
Test statistic	-	-1,5294879	-5,3712044	-4,87602443	-5,082534

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-3,456258249 1,002924915	-7,355179179 -2,338154155	-6,024090764 -1,649242569	-6,213668068 -1,819665266

28-Day compressive strength - WFS	Control	5%	10%	15%	20%
$\overline{x}$	35,11	3228%	30,4866667	29,95666667	30,11
Standard deviation	0,792275205	0,78232559	1,21022037	1,517904257	2,0128587
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,78731612	1,02282289	1,210729807	1,5295914
Critical value	-	2,78	2,78	2,78	2,78
$\overline{x}_{Test}$ - $\overline{x}_{Control}$	0	-283%	-4,6233333	-5,15333333	-5
Test statistic	-	-4,4075187	-5,536055	-5,21298685	-4,003503

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-4,620431082 -1,046235584	-6,944998607 -2,301668059	-7,901521093 -2,405145573	-8,471959203 -1,528040797

7-Day flexural strength - PMBA	Control	5%	10%	15%	20%
$\overline{x}$	2,39	243%	2,64333333	2,486666667	2,4666667
Standard deviation	0,115325626	0,14798649	0,06350853	0,1040833	0,1167619
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,13266499	0,09309493	0,10984838	0,116046
Critical value	-	2,78	2,78	2,78	2,78
$\overline{x}_{Test}$ - $\overline{x}_{Control}$	0	4%	0,25333333	0,096666667	0,0766667
Test statistic	-	0,36927447	3,33282047	1,077776512	0,8091372
Comparison of means: 95% Confidence Interval					

5%	10%	15%	20%
-0,261131024 0,341131024	0,042020821 0,464645845	-0,152673832 0,346007166	-0,186741491 0,340074825

28-Day flexural strength - PMBA	Control	5%	10%	15%	20%
$\bar{x}$	4,283333333	422%	4,83	4,216666667	4,4666667
Standard deviation	0,283078317	0,33501244	0,3579106	0,178978583	0,1501111
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,31013438	0,32267114	0,2368192	0,2265686
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-6%	0,54666667	-0,06666667	0,1833333
Test statistic	-	-0,2369447	2,07495219	-0,34477635	0,9910312

Comparison of means: 95% Confidence Interval

5%	10%	15%	20%
-0,763961776 0,643961776	-0,185751814 1,279085148	-0,604213212 0,470879879	-0,330945795 0,697612462

7-Day flexural strength - WFS	Control	5%	10%	15%	20%
$\bar{x}$	2,39	228%	2,14333333	1,97	1,8966667
Standard deviation	0,115325626	0,07767453	0,06110101	0,079372539	0,0635085
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,09831921	0,09228579	0,098994949	0,0930949
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-11%	-0,2466667	-0,42	-0,493333
Test statistic	-	-1,3287277	-3,2735673	-5,19615242	-6,490229

Comparison of means: 95% Confidence Interval

5%	10%	15%	20%
-0,329837553 0,11650422	-0,456142531 -0,037190802	-0,644704725 -0,195295275	-0,704645845 -0,282020821

28-Day flexural strength - WFS	Control	5%	10%	15%	20%
$\bar{x}$	4,283333333	407%	4,04	3,34	3,3666667
Standard deviation	0,283078317	0,17009801	0,20420578	0,165227116	0,2230097
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,23352373	0,24681302	0,231768563	0,2548202
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-22%	-0,2433333	-0,94333333	-0,916667
Test statistic	-	-1,1363359	-1,2074778	-4,98489807	-4,405784

Comparison of means: 95% Confidence Interval

5%	10%	15%	20%

-0,74673296 0,313399627	-0,803564456 0,31689779	-1,469415638 -0,417251029	-1,495072968 -0,338260366

7-Day tensile-splitting strength - PMBA	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	2,186666667	172%	2,18	2,156666667	1,8233333
Standard deviation	0,169213869	0,13796135	0,09539392	0,142243922	0,1159023
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,15438048	0,13735599	0,156311655	0,1450287
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-47%	-0,0066667	-0,03	-0,363333
Test statistic	-	-3,7286455	-0,0594438	-0,23505826	-3,068293

Comparison of means: 95% Confidence Interval

5%	**10%**	**15%**	**20%**
-0,820422158 -0,119577842	-0,318445591 0,305112258	-0,384805649 0,324805649	-0,692528325 -0,034138342

28-Day tensile-splitting strength - PMBA	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	2,686666667	256%	2,71333333	2,693333333	2,5466667
Standard deviation	0,08326664	0,09848858	0,16441817	0,190875177	0,1517674
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,09119576	0,13032012	0,147252617	0,1224064
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-13%	0,02666667	0,006666667	-0,14
Test statistic	-	-1,7011136	0,2506126	0,055448697	-1,400778

Comparison of means: 95% Confidence Interval

5%	**10%**	**15%**	**20%**
-0,33366832 0,080334987	-0,269141822 0,322475156	-0,327576232 0,340909566	-0,417845513 0,137845513

7-Day tensile-splitting strength - WFS	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	2,186666667	217%	1,66666667	1,46	1,67
Standard deviation	0,169213869	0,14177447	0,0321455	0,026457513	0,1044031
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,15609826	0,12179217	0,121106014	0,140594
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-2%	-0,52	-0,72666667	-0,516667
Test statistic	-	-0,1307664	-5,2291319	-7,3487785	-4,500796

Comparison of means: 95% Confidence Interval

5%	**10%**	**15%**	**20%**
-0,37098794 0,337654606	-0,796451241 -0,243548759	-1,001560424 -0,451772909	-0,835795383 -0,19753795

28-Day tensile-splitting strength - WFS	Control	5%	10%	15%	20%
$\bar{x}$	2,686666667	244%	2,55333333	2,403333333	2,7633333
Standard deviation	0,08326664	0,14933185	0,20305993	0,189296945	0,0404145
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,12089941	0,15518806	0,146230412	0,0654472
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-25%	-0,1333333	-0,28333333	0,0766667
Test statistic	-	-2,4988024	-1,0522673	-2,37304294	1,4347006
Comparison of means: 95% Confidence Interval					
5%	**10%**	**15%**	**20%**		
-0,521091455 0,027758122	-0,485588575 0,218921909	-0,615255968 0,048589302	-0,071889301 0,225222634		

7-Day pH value - PMBA	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	13,3	1333%	13,1833333	13,24666667	13,166667
Standard deviation	0,138564065	0,06506407	0,1106044	0,02081666	0,0665833
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,10824355	0,12536613	0,099079093	0,1087045
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	3%	-0,1166667	-0,05333333	-0,133333
Test statistic	-	0,37715714	-1,1397568	-0,65926851	-1,502232
Comparison of means: 95% Confidence Interval					
5%	**10%**	**15%**	**20%**		
-0,21236443 0,279031097	-0,401230294 0,16789696	-0,278229052 0,171562386	-0,380077366 0,1134107		

28-Day pH value - PMBA	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	13,35666667	1325%	13,2366667	13,12666667	13,06
Standard deviation	0,040414519	0,11590226	0,10503968	0,060277138	0,04
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,08679478	0,07958224	0,051316014	0,0402078
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-11%	-0,12	-0,23	-0,296667
Test statistic	-	-1,5521894	-1,846761	-5,48934526	-9,036581
Comparison of means: 95% Confidence Interval					
5%	**10%**	**15%**	**20%**		
-0,307012036 0,087012036	-0,300640589 0,060640589	-0,346480194 -0,113519806	-0,387932749 -0,205400584		

7-Day pH Value - WFS	**Control**	**5%**	**10%**	**15%**	**20%**

$\bar{x}$	13,3	1335%	13,3533333	13,4	13,393333
Standard deviation	0,138564065	0,10263203	0,21079216	0,111355287	0,0702377
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,12192894	0,17837227	0,125698051	0,1098484
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	5%	0,05333333	0,1	0,0933333
Test statistic	-	0,53571962	0,36619889	0,974354704	1,0406118

Comparison of means: 95% Confidence Interval

5%	10%	15%	20%
-0,223428353 0,33009502	-0,351546835 0,458213502	-0,18531704 0,38531704	-0,156007166 0,342673832

28-Day pH Value - WFS	Control	5%	10%	15%	20%
$\bar{x}$	13,35666667	1331%	12,58	12,80666667	13,493333
Standard deviation	0,040414519	0,1274101	0,19924859	0,035118846	0,0404145
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,09451631	0,14375906	0,037859389	0,0404145
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-5%	-0,7766667	-0,55	0,1366667
Test statistic	-	-0,6479013	-6,6167554	-17,7924076	4,1416254

Comparison of means: 95% Confidence Interval

5%	10%	15%	20%
-0,264538844 0,164538844	-1,102979673 -0,450353661	-0,635935531 -0,464064469	0,044931347 0,228401986

7-Day Ion Conductivity - PMBA	Control	5%	10%	15%	20%
$\bar{x}$	6,642	641%	4,87	4,921333333	3,5796667
Standard deviation	0,159348674	0,57464163	0,68731288	0,252899848	0,2777451
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,42166634	0,49889428	0,211365008	0,2264225
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-24%	-1,772	-1,72066667	-3,062333
Test statistic	-	-0,6854704	-4,3501159	-9,97032429	-16,5645

Comparison of means: 95% Confidence Interval

5%	10%	15%	20%
-1,193123761 0,721123761	-2,904420411 -0,639579589	-2,200435749 -1,240897585	-3,576280912 -2,548385754

28-Day Ion Conductivity - PMBA	Control	5%	10%	15%	20%
$\bar{x}$	5,559333333	425%	4,314	3,574	2,972

Standard deviation	0,18312928	0,2830212	0,93601496	0,284168964	0,1213466
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,23836666	0,67441098	0,239048461	0,1553405
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-131%	-1,2453333	-1,98533333	-2,587333
Test statistic	-	-6,7274478	-2,2615522	-10,1716899	-20,39921

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-1,850392408	-2,776152169	-2,527939991	-2,939934566
-0,768274259	0,285485502	-1,442726676	-2,2347321

7-Day Ion Conductivity - WFS	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	6,642	492%	4,767	5,217333333	4,805
Standard deviation	0,159348674	0,29008792	0,94795411	0,280214799	0,5384598
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,23403312	0,67970913	0,227938954	0,3970712
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-172%	-1,875	-1,42466667	-1,837
Test statistic	-	-9,0220571	-3,378499	-7,65491446	-5,666129

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-2,255222528	-3,4178449	-1,942056293	-2,738296122
-1,192777472	-0,3321551	-0,90727704	-0,935703878

28-Day Ion Conductivity - WFS	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	5,559333333	420%	1,49566667	1,887666667	5,3793333
Standard deviation	0,18312928	0,78568378	0,21395638	0,169912723	0,2521316
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	0,57045391	0,19914024	0,176644653	0,2203482
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-136%	-4,0636667	-3,67166667	-0,18
Test statistic	-	-2,9205887	-24,992212	-25,4570679	-1,00048

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-2,655184134	-4,51568722	-4,072625386	-0,680159695
-0,065482532	-3,611646113	-3,270707948	0,320159695

7-Day Nitrate content - PMBA	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	1,470666667	222%	3,83	1,968	5,373
Standard deviation	0,892337567	1,58942096	2,49837947	0,31169376	2,3658402

Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	1,28889979	1,87592195	0,668363424	1,787941
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	75%	2,35933333	0,497333333	3,9023333
Test statistic	-	0,71013486	1,54035268	0,911340189	2,6731098

Comparison of means: 95% Confidence Interval

5%	**10%**	**15%**	**20%**
-2,17828938 3,672956047	-1,898747795 6,617414462	-1,019758399 2,014425066	-0,156043403 7,96071007

28-Day Nitrate content - PMBA	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	9,723333333	841%	8,1	5,886666667	4,1233333
Standard deviation	1,461380626	2,16116481	6,77347769	4,930733549	0,4082075
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	1,84475834	4,89977721	3,636465775	1,0729088
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-131%	-1,6233333	-3,83666667	-5,6
Test statistic	-	-0,869716	-0,4057673	-1,29217161	-6,392502

Comparison of means: 95% Confidence Interval

5%	**10%**	**15%**	**20%**
-5,497344079 2,877344079	-12,74514405 9,49847738	-12,09093667 4,417603338	-8,035353342 -3,164646658

7-Day Nitrate content - WFS	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	1,470666667	651%	18,4433333	20,11666667	25,853333
Standard deviation	0,892337567	3,10750902	3,48563242	6,726338776	2,0360828
Number of samples	3	3	3	3	3
Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	2,28614071	2,54419925	4,797910986	1,5719255
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	504%	16,9726667	18,646	24,382667
Test statistic	-	2,70148732	8,17042393	4,759694987	18,997431

Comparison of means: 95% Confidence Interval

5%	**10%**	**15%**	**20%**
-0,146553811 10,23188714	11,19768929 22,74764404	7,755411394 29,53658861	20,81461503 27,9507183

28-Day Nitrate content - WFS	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	9,723333333	874%	2,20666667	4,803333333	7,1033333
Standard deviation	1,461380626	4,21604475	0,91045776	0,589604387	1,0594495
Number of samples	3	3	3	3	3

Degree of freedom	4	4	4	4	4
Standard deviation$_{test}$	-	3,15520734	1,21749059	1,11428602	1,2763359
Critical value	-	2,78	2,78	2,78	2,78
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-99%	-7,5166667	-4,92	-2,62
Test statistic	-	-0,3829907	-7,5614539	-5,40771818	-2,514096

Comparison of means: 95% Confidence Interval

5%	10%	15%	20%
-8,148547152 6,175213819	-10,28020046 -4,753132877	-7,449273816 -2,390726184	-5,517104441 0,277104441

OPI - PMBA	Control	5%	10%	15%	20%
$\bar{x}$	10,31	1032%	9,84	10,23	10,1075
Standard deviation	0,177951304	0,14818344	0,16970563	0,294618397	0,276812211
Number of samples	4	4	4	4	4
Degree of freedom	6	6	6	6	6
Standard deviation$_{test}$	-	0,16374523	0,17387735	0,243378991	0,232692573
Critical value	-	2,45	2,45	2,45	2,45
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	1%	-0,47	-0,08	-0,2025
Test statistic	-	0,10795838	-3,8226967	-0,4648597	-1,23071503

Comparison of means: 95% Confidence Interval

5%	10%	15%	20%
-0,271174136 0,296174136	-0,771227143 -0,168772857	-0,501632591 0,341632591	-0,605619315 0,200619315

OPI - WFS	Control	5%	10%	15%	20%
$\bar{x}$	10,31	1032%	9,9125	9,8925	10,1075
Standard deviation	0,177951304	0,03685557	0,21187654	0,117295922	0,278013789
Number of samples	4	4	4	4	4
Degree of freedom	6	6	6	6	6
Standard deviation$_{test}$	-	0,12850097	0,19565062	0,150706669	0,233407726
Critical value	-	2,45	2,45	2,45	2,45
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	1%	-0,3975	-0,4175	-0,2025
Test statistic	-	0,08254102	-2,8732333	-3,91777064	-1,22694416

Comparison of means: 95% Confidence Interval

5%	10%	15%	20%
-0,215116578 0,230116578	-0,736447413 -0,058552587	-0,678585983 -0,156414017	-0,606858256 0,201858256

WS - PMBA	Control	5%	10%	15%	20%
$\bar{x}$	6,2775	566%	5,575	5,8525	5,8375
Standard deviation	0,764476945	0,24743686	0,3331166	0,117862915	0,195
Number of samples	4	4	4	4	4

Degree of freedom	6	6	6	6	6
Standard deviation$_{test}$	-	0,56817691	0,58965739	0,546953685	0,557875434
Critical value	-	2,45	2,45	2,45	2,45
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-62%	-0,7025	-0,425	-0,44
Test statistic	-	-1,530758	-1,6848513	-1,09888786	-1,11539948

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-1,599316276 0,369316276	-1,724029304 0,319029304	-1,372548916 0,522548916	-1,406469881 0,526469881

WS - WFS	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	6,2775	497%	5,915	5,6175	5,8025
Standard deviation	0,764476945	0,73595176	0,4422292	0,469636384	0,253820803
Number of samples	4	4	4	4	4
Degree of freedom	6	6	6	6	6
Standard deviation$_{test}$	-	0,75034992	0,62449646	0,634422309	0,569583181
Critical value	-	2,45	2,45	2,45	2,45
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-131%	-0,3625	-0,66	-0,475
Test statistic	-	-2,4690078	-0,8209052	-1,47122971	-1,17937373

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-2,609914913 -0,010085087	-1,444384927 0,719384927	-1,759080577 0,439080577	-1,461752518 0,511752518

CC - PMBA	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	0,255	26%	0,25	0,2675	0,26
Standard deviation	0,012909944	0,01154701	0,01632993	0,012583057	0,014142136
Number of samples	4	4	4	4	4
Degree of freedom	6	6	6	6	6
Standard deviation$_{test}$	-	0,01224745	0,0147196	0,012747549	0,013540064
Critical value	-	2,45	2,45	2,45	2,45
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	1%	-0,005	0,0125	0,005
Test statistic	-	0,57735027	-0,4803845	1,386750491	0,522232968

Comparison of means: 95% Confidence Interval			
5%	**10%**	**15%**	**20%**
-0,016217622 0,026217622	-0,030500408 0,020500408	-0,009584002 0,034584002	-0,018456964 0,028456964

CC - WFS	**Control**	**5%**	**10%**	**15%**	**20%**
$\bar{x}$	0,255	23%	0,22	0,2475	0,26

Standard deviation	0,012909944	0,02581989	0,0244949	0,020615528	0,008164966
Number of samples	4	4	4	4	4
Degree of freedom	6	6	6	6	6
Standard deviation$_{test}$	-	0,02041241	0,0195789	0,017199806	0,010801234
Critical value	-	2,45	2,45	2,45	2,45
$\bar{x}_{Test}$ - $\bar{x}_{Control}$	0	-3%	-0,035	-0,0075	0,005
Test statistic	-	-1,7320508	-2,5281029	-0,61666984	0,654653671

Comparison of means: 95% Confidence Interval

5%	**10%**	**15%**	**20%**
-0,060362704 0,010362704	-0,068918714 -0,001081286	-0,037297144 0,022297144	-0,013712184 0,023712184