COMPOSITIONAL CHARACTERISTICS OF KAMAFUGITES AND CARBONATITES AND THEIR EFFECTS ON PERFORMANCE AS SUPPLEMENTARY CEMENTITIOUS MATERIALS WITH PORTLAND CEMENT IN MORTARS

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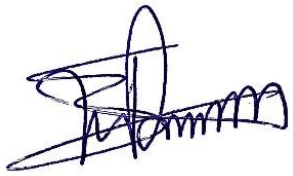
A thesis submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, South Africa, in fulfillment of the requirements for the degree of Doctor of Philosophy.

Johannesburg, 2022

DECLARATION

I declare that this thesis is my own unaided work. It is being submitted to the Degree of Doctor of Philosophy to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other university.



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21st day of September 2022

ABSTRACT

Kamafugites and carbonatites, unlike silica saturated volcanic materials, present a unique set of uncertainties on how compositional differences would affect their performance as supplementary cementitious materials (SCMs) in hydrating Portland cement. Having carbonate minerals as their primary composition, Kamafugites and carbonatites are undersaturated in silica and alumina composition compared to the more commonly studied mafic-felsic materials. The calcite bearing materials have potassic leaning alkalis with some deposits ultra-potassic. They are currently the only feasible source of SCMs in Uganda but no published work on their performance as SCMs existed at the time of this study and reporting.

This thesis presents SCM properties of Kamafugites and carbonatites when blended with Portland cement pastes and mortars. Compositional characteristics of kamafugites and carbonatites and their effects on properties of fresh and hardened cement paste and mortar are reported. TGA, XRD, dilatometry, and Isothermal calorimetry instrumental techniques are applied together with other test procedures in characterizing kamafugites and carbonatites for composition properties, pozzolanic activity, strength development, chemical shrinkage, hydration kinetics and hydration phase assemblage when blended in Portland cement. Showing less pronounced pozzolanic activity, the kamafugites and carbonatites accelerate the hydration reaction of cement phases at early ages mainly due to the filler effect and the presence of calcite minerals and potassic leaning alkalis. The calcite bearing kamafugites and carbonatites have a time-dependent influence on the hydration products of the AFm phases in Portland cement paste with gypsum reactions ending at ettringite and the aluminate phases combining with carbonates to form carboaluminate hydration products. It is also observed that there is a loss of compressive strength of cement with 180 days' strength becoming lower than the 90 days' strength. The loss in strength is attributed to a combined effect of alkalis and carbonates which are observed to participate in the long term hydration reactions. Quantitative expressions based on thermogravimetric analysis results are applied in and proposed for characterisation of the degree of hydration, degree of pozzolanic activity, and the net SCM benefit of supplementary cementitious materials. The quantitative expressions are also applied in development of prediction models for compressive strength and chemical shrinkage of blended cement.

The above findings are important in understanding how Portland cements that are blended with carbonatites and kamafugites are likely to perform in concrete. Considering that the materials are not addressed by existing standards, the experimental works presented in this thesis provide a basis for standardizing application of the kamafugites and carbonatites as SCMs in Portland cement concrete.

List of Publications to emerge from this study

Buregyeya A., Nwaubani S., Schmidt W., Kerali A. G., & Bagampadde U. 2018 “Pozzolanic and hydration properties of kamafugites and carbonatitic lavas as supplementary cementitious materials in portland cement”, African Journal of Science, Technology, Innovation and Development, DOI: 10.1080/20421338.2018.1527539

Buregyeya A., Ballim Y., Nwaubani S., Kerali A.G., Otieno M. 2018 “Effect of Carbonate Minerals and Calcination of Carbonatites and Kamafugites on Their Pozzolanic Performance and Early Age Concrete Properties”. In: Martirena F., Favier A., Scrivener K. (eds) Calcined Clays for Sustainable Concrete. RILEM Bookseries, vol 16. Springer, Dordrecht, DOI: https://doi.org/10.1007/978-94-024-1207-9_15

Buregyeya A., and Nwaubani S. 2022 “Hydration and compressive strength of Portland cement blended with kamafugites and carbonatites: Effect of Physical Properties”. East African Journal of Science, Technology and Innovation, Vol. 3 (2).

Contributions of the author

Field visits and data collection, planning and design of experiments, performing experiments, evaluation of results and writing the manuscripts

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that project pride, and who stay a source of relief when social chaos abounds. To the members of my larger family who, to a great extent, have incited feelings of trust and mistrust in equal measure. Thank you all for you are part of the environment that has established my journey in life to date.

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LIST OF ABBREVIATIONS AND SYMBOLS

General abbreviations

ASTM	American Society for Testing and Materials
BSE	Backscatter Electron
EN	European Standard
TGA	Thermogravimetric Analysis
DTG	Differential Thermogravimetric Analysis
DPA	Degree of Pozzolanic Activity
EDS	Energy-Dispersive X-ray Spectroscopy
FA	Fly Ash
GGBS	Ground Granulated Blast-furnace Slag
PSD	Particle Size Distribution
SCM	Supplementary Cementitious Materials
SE	Secondary Electron
SEM	Scanning Electron Microscopy
SEM-EDS	Scanning Electron Microscopy – Energy-Dispersive X-ray Spectroscopy
SF	Silica Fume
SSA	Specific Surface Area
TAA	Total Admixture Activity
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

Cement notations – Oxides

A	Aluminium oxide; Al_2O_3
Ĉ	Carbon dioxide; CO_2

C	Calcium oxide; CaO
F	Iron oxide; Fe_2O_3
H	Water; H_2O
K	Potassium Oxide; K_2O
M	Magnesium oxide; MgO
N	Sodium oxide; Na_2O
Ŝ	Sulfate; SO_3
S	Silicon dioxide; SiO_2

Cement notations – Anhydrous phases

C_3A	Tricalcium Aluminate (Aluminate); $3CaO \cdot Al_2O_3$
C_4AF	Tetracalcium Aluminoferrite (Ferrite); $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$
C_3S	Tricalcium Silicate (Alite); $3CaO \cdot SiO_2$
C_2S	Dicalcium Silicate (Belite); $2CaO \cdot SiO_2$
$C\hat{S}H_2$	Calcium Sulfate dihydrate (Gypsum); $CaSO_4 \cdot 2H_2O$
$C\hat{C}$	Calcium Carbonate (Calcite); $CaCO_3$ from either incomplete calcination or carbonation of other anhydrous cement phases

Cement notations – Hydrated phases

CH	Calcium Hydroxide (Portlandite); $Ca(OH)_2$
C-A-S-H	Calcium Alumina Silicate Hydrate; $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$
C-S-H	Calcium Silicate Hydrate; $CaO\text{-}SiO_2\text{-}H_2O$
Aft	Ettringite; $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$; $(C_6A\hat{S}_3H_{32}$
AFm	Monosulfoaluminate; $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$
	Monocarboaluminate; $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$
	Hemicarboaluminate; $3CaO \cdot Al_2O_3 \cdot 0.5Ca(OH)_2 \cdot 0.5CaCO_3 \cdot 11H_2O$

CHAPTER 1

INTRODUCTION

1.1 Background

Concrete is a universal construction material. It is a material of choice for almost all modern building and civil engineering infrastructure construction on Earth. Its composites being cement, course and fine aggregates, water, supplementary cementitious materials (SCMs), and mineralogical and chemical admixtures, contemporary concrete is the most consumed construction material on Earth. The advantages of being a relatively high strength, low-cost and low-skill labour requiring material have promoted concrete as a construction material of choice in the modern times (Mehta and Monteiro, 2006; Wight & MacGregor, 2012). Certainly, it is set to be the main construction material for the infrastructure deficient sub-Saharan Africa (Schmidt, Msinjili and Kühne, 2018).

Concrete production world over is still primarily dependent on Portland cement as it's active ingredient for bonding aggregates and strength development (Snellings, Mertens and Elsen, 2012). However, the process of manufacture of Portland cement is energy intensive and presents environmental challenges. According to the International Energy Agency (IEA) and World Business Council for Sustainable Development (WBCSD), Cement Technology Roadmap 2009 (IEA & WBCSD, 2009), the contribution to all global anthropogenic carbon dioxide (CO_2) gas emissions from the Portland cement sector is set to increase by 4% by the year 2050 from the current estimate of 8%. The IEA and WBCSD attribute one-third of this carbon dioxide emissions to fuels and processes in cement production and use, and two-thirds to cement raw materials decomposition. Limestone ($CaCO_3$), a primary raw material in the manufacture of Portland cement, decomposes to lime (CaO) and CO_2 gas at temperatures above 600°C with stoichiometric relationships as shown in Equation 1.1.

$CaCO_{3(s)} + heat \rightleftharpoons CaO_{(s)} + CO_{2(g)}\uparrow$ ……Equation 1.1

100g 56g 44g

To mitigate the environmental challenges associated with cement production and use, the IEA advances four levers for the cement industry premised on process technology improvement, substitution of energy sources, reduction of clinker-to-cement ratio (clinker substitution), and carbon capture and storage (CCS). Of the four levers, clinker substitution dominates in importance as it requires minimal investment in industrial infrastructure and process yet it's the primary intervention for the two-thirds material-based carbon dioxide emissions by the cement industry. Consequently, the cement industry world over adopted partial substitution of clinker with other fine materials that are generally referred to as supplementary cementitious materials (SCMs). Above environmental concerns, adoption of SCMs in clinker substitution has also been motivated by cost and performance benefits (Turanli, Uzal and Bektas, 2004; Kaid et al., 2009; Schneider et al., 2011; Kocak, Tasci and Kaya, 2013), and is seen by researchers as part of the solution to the high housing infrastructure demand in developing countries (Schneider et al., 2011; Schmidt, Msinjili and Kühne, 2018).

For a material to qualify as a suitable SCM, it should have a suitable chemical and mineralogical composition, be easily accessible, of low cost, and advance a benefit of reducing on the environmental impacts of Portland cement use (Snellings, Mertens and Elsen, 2012). SCMs applied in Portland cement concrete are generally grouped as pozzolanic, latent hydraulic (cementitious) and other mineral additions (e.g. limestone, microsilica and nanosilica) (Mehta and Monteiro, 2006; Snellings, Mertens and Elsen, 2012). Pozzolanic materials (or pozzolans) form the largest part of SCMs followed by latent hydraulic materials and limestone. Figure 1.1 presents the different types of SCMs and their relative compositions of the major mineral phases.

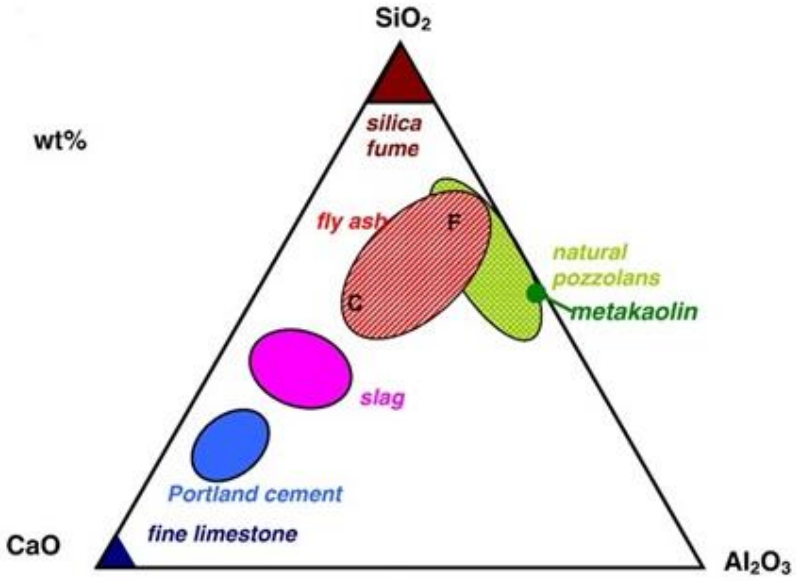

Figure 1.1: A ternary diagram showing relative composition of the major phases in Portland cement SCMs; Natural pozzolans are presented with a light green hatch. (Lothenbach, Scrivener and Hooton, 2011)

Pozzolans are classified as either natural or artificial depending on the source of the materials and whether the materials have been subjected to any processing leading to activation of constituent compounds to achieve pozzolanic reactivity (Mehta and Monteiro, 2006; Snellings, Mertens and Elsen, 2012). Natural pozzolans include volcanic ash and diatomaceous earth while artificial pozzolans include silica fume (SF), calcined clay, fly ash (FA), similar industrial waste materials, and ashes from agricultural waste. Figure 1.2 presents a classification of pozzolanic materials with emphasis on natural pozzolans. Ground granulated blast furnace slag (GGBS) is also a common SCM but it is classified as latent hydraulic (cementitious) because of its ability to independently form hydration products when mixed with water, though at a very slow rate that it needs activation if it is to be applied in construction (Mehta and Monteiro, 2006; Snellings, Mertens and Elsen, 2012). Studies to date have focused more on application of industrial byproducts (mainly GGBS, FA and SF) and little has been published on characterization of natural pozzolans as SCMs (Scrivener et al., 2015).

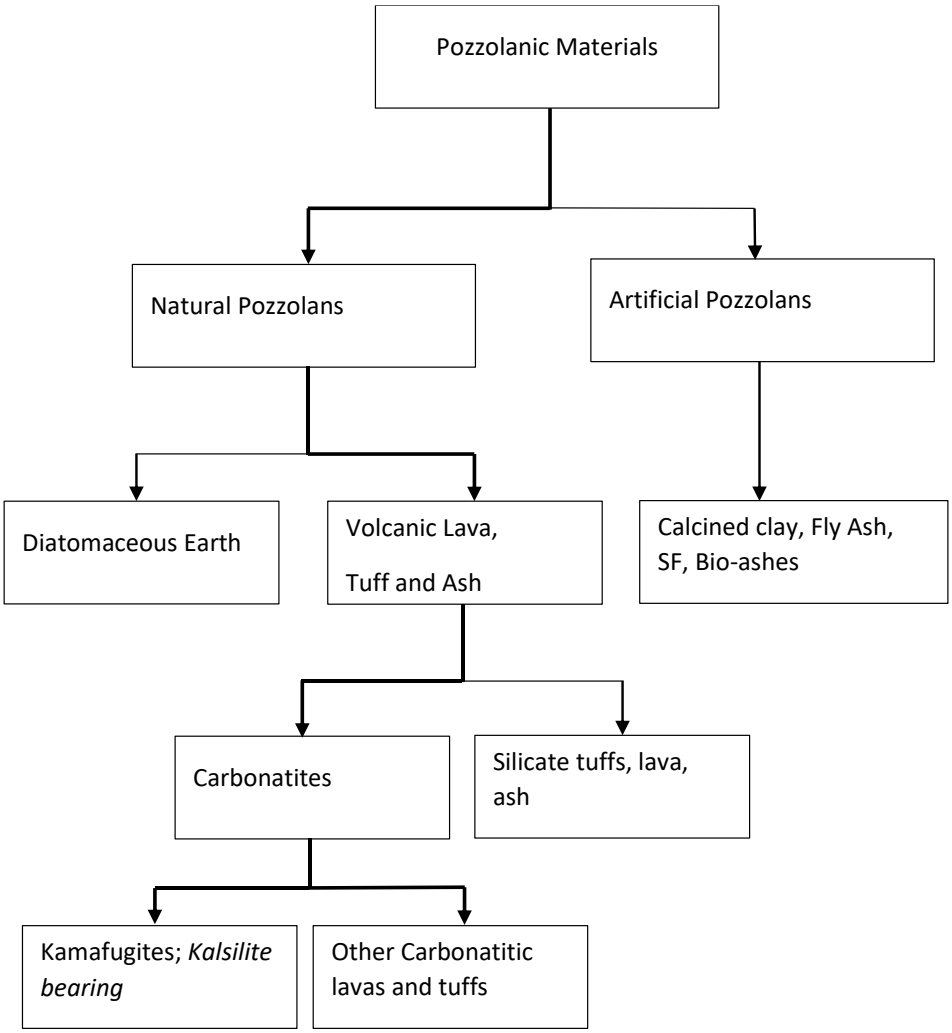

Figure 1.2**:** Classification of natural pozzolans (Carbonatites classification based on Stoppa and Schiazza, 2013)

The problem of high variability of important physico-chemical properties in natural pozzolans of volcanic origin has been partly addressed by the availability of extensively characterized reactive industrial waste such as fly ash, silica fume and blast furnace slag. However, the reduction in industrial waste production due to technological advancement in manufacturing industries and adaptation to more sustainable policies (Damtoft et al., 2008; Schneider et al., 2011) and the growing demand of SCMs, both, increase the importance of characterisation of SCMs of natural origin. Moreover, research on alkali-activation of pozzolanic industrial waste to produce new binder systems (Snellings, Mertens and Elsen, 2012; RILEM TC224

AAM, 2014) forecast a shortage of artificial SCMs as a result of competing applications. Indeed, the IEA tracking report of 2021 shows a global average annual increase of 1.6% in clinker-to-cement ratio for the years 2015-2020 (International Energy Agency, 2021). Also, many less developed regions of the world are deficient of the highly pozzolanic industrial waste yet sufficient in natural pozzolans of volcanic origin that can be used as SCMs (Blanco et al., 2006). Some authors (Schmidt, Msinjili and Kühne, 2018) advance natural pozzolans as the most feasible choice of SCMs for sub-Sahara Africa (SSA).

1.2 Research aim

The focus of this study was the use of ultrapotassic silica-undersaturated carbonatitic natural pozzolans (Kamafugites and carbonatites), sourced from the Toro-Ankore geological deposits of the Western part of the East Africa rift system, as SCMs in Portland cement. The carbonatites and kamafugites are materials of volcanic origin whose composition is predominantly carbonate minerals and potassic leaning alkalis. Consequently, they are relatively low in silica and alumina composition compared to other volcanic materials (Wyllie and Huang, 1978; Stoppa and Schiazza, 2013) that are generally used as natural pozzolans in Portland cement concrete. Considering that the reasonable usage of available SCM resources is a global challenge with more importance for the infrastructure deficient sub-Sahara Africa (SSA), given that SCMs of industrial origin are scarce in SSA due to low industrialization levels, it is very important to develop extensive knowledge that engenders utilization of the accessible resources. Therefore, carbonatites and kamafugites of the Toro-Ankole geological region of the Albertine rift system were studied as SCMs of volcanic origin (natural pozzolans), motivated by their carbonatitic and ultramafic composition.

Although previous research on application of SCMs of volcanic origin in Portland cement concrete and their pozzolanic activity yielded substantial publications, these studies were dominated by the felsic-mafic volcanic materials that are silica saturated. Accordingly, the SCMs easily became responsive to the guiding characterization standards for pozzolanic reactivity (ASTM C618, 2005; BS 3892-1,

1997) that set the sum of oxide composition of silica, alumina and iron in a natural pozzolan at a minimum value of 70% and the reactive silica content at a minimum value of 25%. It appears that these minimum standard composition requirements directed most of the published works on natural pozzolans and would disqualify ultramafic volcanic rocks as possible SCMs. However, studies show benefits from SCMs to go beyond pozzolanic reactions (Escalante-Garcia, 2003; Ballim and Graham, 2009; Berodier and Scrivener, 2014; Scrivener et al., 2015, Nwaubani, 2018) and, for this reason, characterization methods based only on pozzolanic performance are likely to limit usage of SCMs. Pourkhorshidi et al., 2010, while testing reliability of the ASTM C618 method in characterizing pozzolanic performance of four Iranian natural pozzolans, showed pozzolanic performance not to depend solely on the minimum oxide composition requirements. Malhotra and Mehta, 1996, and Walker and Pavı´a, 2011, further stressed the importance of the amorphous state of the minerals and morphological properties of the pozzolanic materials over the chemical composition in determining their performance as SCMs in concrete. These observations advance a need to evaluate the suitability of SCMs more on their holistic performance in concrete than on their chemical composition.

The kamafugites and carbonatites sourced from Toro-Ankole geological region of the East African rift system were tested for their physical and compositional effects on pozzolanic activity, strength development, hydration progression and hydration products characteristics. The natural pozzolans were further calcined/decarbonated to enable assessment of compositional parameters on the different hydration parameters studied. The tools of analysis included isothermal calorimetry, X-ray diffraction, thermogravimetric analysis, and dilatometry instrumental methods. The results were compared to a range of controls that included unblended cement and cements blended with class F fly ash and ground granulated blast furnace slag (ggbs), SCMs that are considered to have already passed the development and testing stages (Snellings, Mertens and Elsen, 2012).

1.3 Objectives of the thesis

The main objective of this thesis was to characterize the compositional properties of kamafugites and carbonatites and their effects on pozzolanic activity, strength development, hydration progression and hydration products characteristics when the kamafugites and carbonatites are used as SCMs in Portland cement mortars.

The specific objectives were as follows.

- To review published works that are fundamental to the understanding and quantification of the influences of compositional properties of SCMs on hydration, strength, and hydration products development of Portland cement paste and mortar systems.
- To evaluate the pozzolanic activity of kamafugites and carbonatites.
- To evaluate the effect of carbonate minerals and calcination of carbonates and kamafugites on cement hydration, strength development and hydration products development.
- To characterize the effect of physical properties of kamafugites and carbonatites on cement hydration, strength development and hydration products assemblage.
- To develop numerical models for estimation and separation of SCM effects on hydration and pozzolanic activity of blended Portland cement systems.

The main research questions addressed in this thesis are as follows.

1. What is the pozzolanic activity and long term strength development characteristics of carbonatites and kamafugites blended portland cements? And, what reaction mechanisms are responsible for the long term loss in strength observed in portland cement samples blended with carbonatites and kamafugites?
2. What compositional effects on strength, chemical shrinkage, hydration and hydration products development are associated with $CaCO_3$ and alkalis?

3. How do physical factors (fineness and replacement level) of kamafugites and carbonatites affect properties of cement paste?

4. Considering that SCMs influence hydrating Portland cement beyond pozzolanic reactions, how can we best approach characterisation of SCMs to address both pozzolanic and non-pozzolanic mechanisms in hydrating blended cements?

1.3 Outline of this thesis

This thesis is presented in 8 chapters covering the scope as follows:

Chapter 2 presents a discussion of the relevant literature covering cement hydration reactions and the effects of supplementary cementitious materials of volcanic origin on both macro and micro characteristics of hydrated Portland cement. The chapter also provides a general perspective of the petrology and geochemistry of volcanic rock deposits in the East African Rift system. Chapter 2 further presents and discusses the different research tools used in the study of Portland cements blended with supplementary cementitious materials. Numerical models for quantification of the degree of hydration of blended cements are also reviewed under Chapter 2. The models inform approaches used in development of numerical models for quantification of the degree of hydration, the degree of pozzolanic activity and the net SCM benefit, single parameters proposed by the current work as a more effective method for characterizing SCMs for Portland cement.

Chapter 3 presents the different materials and their preparation and characterisation methods used in the current work. Results on the physical and compositional properties of kamafugites and carbonatites are also presented and discussed in Chapter 3.

Chapter 4 presents the experimental techniques and results applied in the study of pozzolanic activity and the effect of compositional properties of kamafugites and carbonatites on hydration, strength development, chemical shrinkage and hydration products of Portland cement. The experimental methods range from conventional standardized cement test methods to advanced instrumental techniques that include TGA/DTG, Isothermal calorimetry, dilatometry, XRF and XRD. Experimental results

on pozzolanic activity, long term compressive strength development and the effect of compositional properties of kamafugites and carbonatites on Portland cement pastes and mortars are all presented in Chapter 4. A method for estimation of degree of hydration is proposed based on TGA/DTG results and validated with the strength, chemical shrinkage, and heat of hydration test results.

Chapter 5 presents on the analysis and discussion of results presented in Chapter 4. The long term compressive strength development and the mechanisms behind the loss in strength with time for cements blended with kamafugites and carbonatites are discussed. The role of carbonates and volatile alkalis of kamafugites and carbonatites on Portland cement hydration activity, strength development, and hydration products development is also discussed. Chapter 5 also discusses the importance of fineness and replacement level of kamafugites and carbonatites on the properties of hydrated Portland cement. A method for estimation of degree of hydration presented in Chapter 4 is discussed and validated with the strength, chemical shrinkage, and heat of hydration test results.

Chapter 6 applies results of TGA/DTG, mechanical strength, and chemical shrinkage experiments in Chapter 4 to develop and test numerical models for the estimation of the degree of hydration (α), the degree of pozzolanic activity (β) and the net SCM benefit (λ), parameters that the author considers better placed to characterize SCMs for their benefits that are reported to go beyond pozzolanic activity. The chapter also presents the application of the new models in prediction of mechanical properties of blended cements.

Chapter 7 presents the summary and the main findings of this research.

Chapter 8 advances possible areas for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 General

This chapter reviews published works that are fundamental to the understanding and quantification of the influences of compositional properties of SCMs on hydration, strength, and hydration products development of Portland cement paste systems. The chapter presents the reviewed literature in five parts as follows.

1. A discussion of the composition and hydration reactions of plain Portland cement (CEM I) and how they influence hydration kinetics, microstructure and physical properties of cement pastes and mortars. More factors that drive hydration kinetics and their mechanisms are discussed in the third part of the literature review that addresses blended cements.
2. Classification and perspectives of the use of SCMs. This part presents the different supplementary cementitious materials (SCMs) and the unique properties of natural pozzolans. The distinctiveness of kamafugites and carbonatites is also discussed.
3. The third part of the literature review chapter discusses the different factors that control hydration kinetics, microstructure and physical properties of Portland cement pastes blended with SCMs. Specific attention is given to SCMs classified as natural pozzolans. Compositional parameters and the effect of calcination of natural pozzolans on hydration activity are also discussed.
4. Characterization methods and their philosophies are discussed under part four of the literature review. The use of X-ray diffraction (XRD), dilatometry, and calorimetry and thermal methods (heat of hydration and thermogravimetry) in hydration activity and microstructure studies of blended cements is discussed.
5. Part five of the literature review chapter discusses the different numerical models advanced in estimation of the degree of hydration, a parameter applied in the study of the hydration activity of Portland cement systems.

2.2 Cement composition, hydration, and hydration products development

2.2.1 Formation of clinker phases and cement

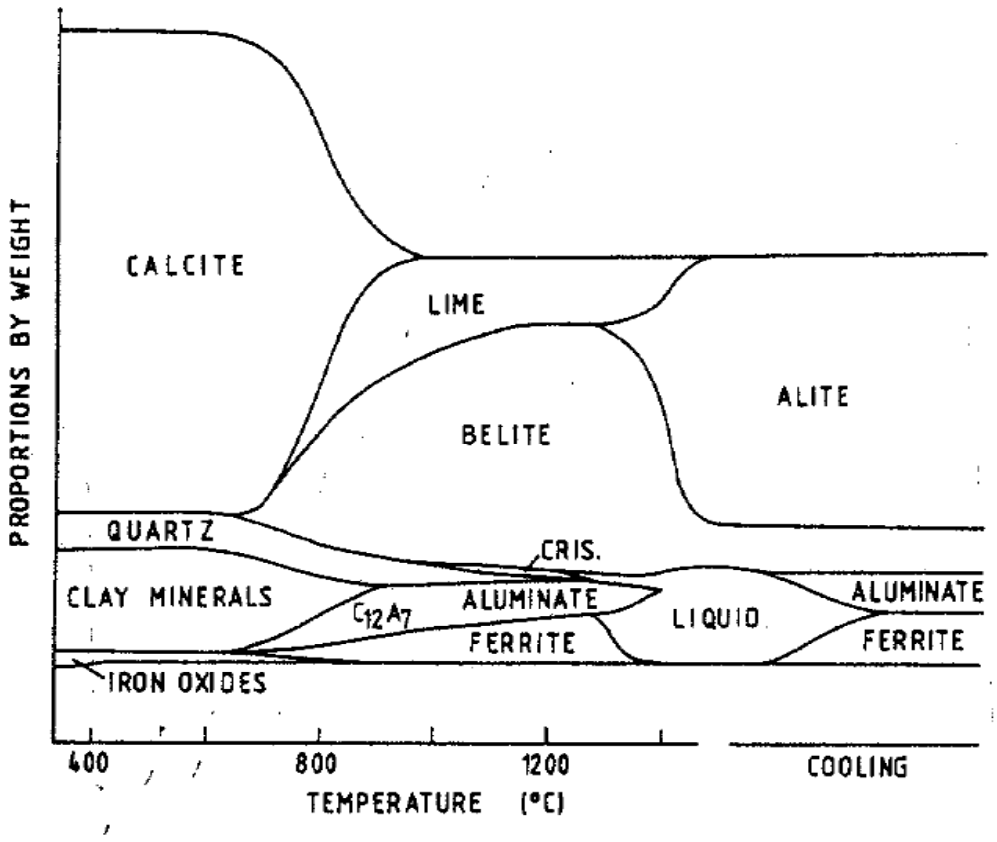

Figure 2.1**:** A simplified illustration of Portland cement clinker formation and phase transformation (Taylor, 1997)

Clinker is a product formed by heating cement raw materials (a blend of materials containing desired composition of calcium, silicon, aluminum, and iron oxides) up to 1450ºC and then subjecting the blend to rapid cooling. The product formed after cooling appears as black balls with dimensions ranging from 3 to 25mm (Neville 2002). The progression of heating and cooling is of high importance in this process because it sets the nature and extent of interaction of the different compounds and the state of chemical equilibrium of the different clinker phases formed (Neville, 2002). Clinker is mainly composed of four phases, C_3S, C_2S, C_3A, C_4AF and a host of other minor compounds which are principally dominated by alkalis. A schematic showing formation of clinker phases from cement raw materials is presented in Figure 2.1. Cement is a product formed through the inter-grinding of clinker with a

small percentage (4-5%) of gypsum into a fine powder (Ramachandran, 2001). It gains in reactivity through the mechanical action of grinding to increase the specific surface of cement powder. The grinding process does not change the chemical composition of the clinker phases. The added gypsum reacts with the aluminate phases and delays the setting of cement to allow successful handling and placing of fresh concrete.

Whereas various authors consider cement to have 4 phases (Neville, 2002; Ramachandran, 2001; Taylor, 1997) the importance of gypsum in influencing fresh properties of concrete as well as durability aspects (delayed ettringite formation) earns it attention as the fifth phase in Portland cement systems. Alkalis too, even in small quantities, can influence the hydration processes of some cement phases leading to modification of the hydration assemblage and other properties of hydrated cement pastes (Jawed and Skalny, 1978; Odler and Wonnemann, 1983).

2.2.2 Cement hydration and the formation of hydration products

Hydration is a term used to describe chemical processes that take place when Portland cement reacts with water leading to formation of a cement paste with binding properties. The mechanisms are both hydration and hydrolysis, but research generally refers to both mechanisms as hydration (Neville 2002). The reactants in this exothermic reaction are the different phases of Portland cement mainly the silicates and aluminates. The products formed are associated with important properties of concrete, both in its fresh and hardened states.

Portland cement is composed of the four major phases that form clinker (C_3S, C_2S, C_3A, C_4AF) which coexist with $C\hat{S}$ (gypsum) and other minor compounds (Taylor, 1997, Ramachandran 2001, Neville 2002). The minor compounds in Portland cement include alkalis (mainly K_2O and Na_2O), MgO, TiO_2, Mn_2O_3 and free CaO (Neville, 2002). Work done by Le Chatelier and others on the practicality of studying the hydration processes and products of cement by studying the individual phase compounds (Neville, 2002) provided significant progress in understanding the hydration of cement but not without limitations (Ramachandran, 2001). These studies revealed that the hydration of the individual cement phases in isolation

progressed in the same manner as when combined but with deviations due to parallel reaction mechanisms and impurities in cement.

The chemical processes in hydration are dependent on time, curing conditions, and the cement properties. Cement paste, at any time, is composed of hydrated cement compounds, anhydrate cement compounds and derivatives of the hydration process such as CH, and pore solution constituents (Taylor, 1997; Ramachandran, 2001; Neville, 2002). The hydration kinetics of the different phases of cement are explained below.

2.2.2.1 Hydration of C_3S and C_2S phases

The silicate phases account for 75-80% of the total Portland cement composition and their hydration reactions are as stated below (Ramachandran, 2001);

C_3S: $2[3CaO{\cdot}SiO_2] + 7H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}4H_2O + 3Ca(OH)_2$ Equation 2.1

C_2S: $2[2CaO{\cdot}SiO_2] + 5H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}4H_2O + Ca(OH)_2$ Equation 2.2

The reaction products nomenclature in equations 2.1 and 2.2 is generally represented as C-S-H and CH for the calcium silicate hydrates and portlandite, respectively.

The influence of C-S-H on paste properties has been reported by Mehta and Monteiro, 2006. C-S-H is the major contributor of strength and durability of concrete. Its characteristic micro-pores influence the shrinkage and creep properties while its environmental stability property enhances durability characteristics of pastes, mortars, and concretes (Mehta and Monteiro, 2006). Reaction mechanisms that affect the C-S-H microstructure phases in hydrated cement, therefore, expressively modify the macro properties of pastes and mortars.

The hydration of the silicate phases also lead to precipitation of CH. CH has no influence on strength for ordinary strength concrete, but studies have showed it to limit strength for high strength concrete (Mehta and Monteiro, 2006). The addition of pozzolanic materials helps in consuming the CH precipitates leading to formation of

extra C-S-H products, a process known as “pozzolanic reaction”. Pozzolanic reaction is discussed in Section 2.4.1 of the current chapter.

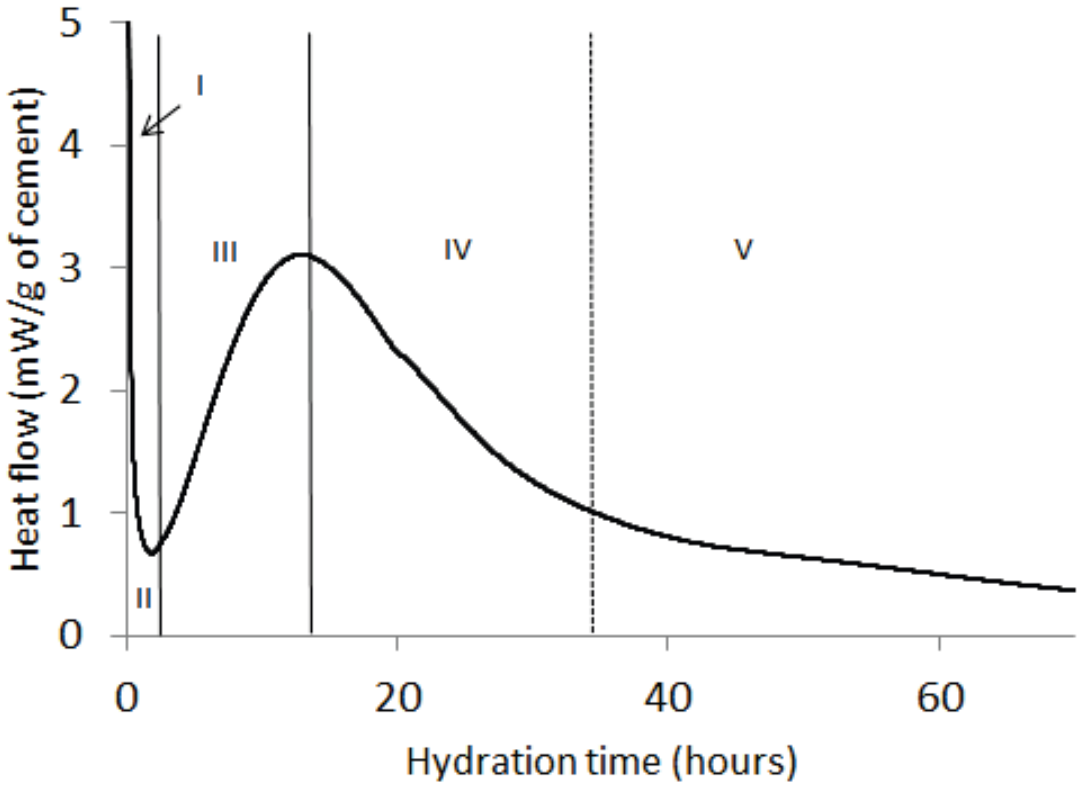

Figure 2.2: A calorimetric graph showing stages in early hydration of cement (Berodier, 2015)

The sequence of hydration of the silicate phases dominates in the study of cement hydration by calorimetric methods. Characteristic result of the isothermal conduction calorimetry presented in Figure 2.2 shows cement and typically the silicate phases to go through five (5) stages of hydration as explained by Taylor, 1997, Ramachandran, 2001, and Neville, 2002. The first stage is termed the pre-induction stage, and it presents a rapid exothermic mechanism that takes place in the first few minutes (15-20 min) after water is introduced into a cement mix. This stage is less important for concreting processes since it is completed before the placement of concrete is normally done. However, the mechanisms that go on in the pre-induction stage influence the microstructure and hydrate assemblage in the early stages of hydration and, subsequently, influence the assemblage of the hydration products at the later ages (Berodier, 2015). Therefore, the preinduction stage is important in

influencing the strength performance of the pastes and mortars. The second stage, termed the dormant stage, is associated with slow reactions (Bullard et al., 2011). The paste remains plastic and little activity in terms of heat emission is recorded. The third stage, the acceleration stage, is the most important for the current study. It is within this stage that both the initial and final setting occur, a condition associated with fast formation of cement hydrates. The dominating hydration mechanism is that of formation of C-S-H and precipitation of CH, the mechanism responsible for strength gain in concrete (Bullard et al., 2011). The fourth and fifth stages represent the deceleration period with a change in rate from fast short-term to slow long-term deceleration respectively. Literature generally refers to the deceleration period to be governed by diffusion mechanisms of hydration, reduction in heat flow rate being a result of confinement of reactants after the cement has set and achieved rigidity. Bullard et al., 2011, however, advances a series of other factors that can easily impact on the characteristic hydration period further making understanding this period complex. These factors include a consideration that the mixing water reduces with time because of chemical shrinkage that leads to a reduction in relative humidity within hydrating paste microstructure; that new hydration products occupy more space shrinking space available for hydration products formed at later stages; and, that finer particles react faster than coarse particles would, which impact the rate of hydration of cement at a later stage.

2.2.2.2 Hydration of C_3A and C_4AF phases

The hydration of the aluminate phases takes place immediately after addition of water and is associated with both flash set and false set (Helmuth, 1994). Both the aluminates and ferrite phases are presented to generate similar hydration products, but the ferrite phase reacts at a slower rate than the aluminate phase (Ramachandran, 2001). Calcium sulfate in the form of gypsum is normally inter-ground with clinker and its purpose is to control the hydration of the aluminate phases to avoid the flash set and false set conditions. The following equations show typical reactions of the two phases with gypsum in cement (Ramachandran, 2001).

C_3A: $C_3A + 3C\hat{S}H_2 + 26H \rightarrow C_3A{\cdot}3C\hat{S}H_{32}$ Equation 2.3

$$C_3A{\cdot}3C\hat{S}H_{32} + 2C_3A + 4H \rightarrow 3[C_3A{\cdot}C\hat{S}H_{12}] \qquad \text{Equation 2.4}$$

Equation 2.4 represents the reaction between the ettringite formed in Equation 2.3 with excess aluminates in cement. Studies on limestone-cement systems have shown to increase ettringite while the excess aluminates reacted with limestone to produce mono- and hemi-carboaluminates (Chowaniec, 2012).

$$C_4AF:\ 3C_4AF + 12C\hat{S}H_2 + 110H \rightarrow 4[C_6(A,F)\,\hat{S}H_{32}] + 2(A,F)H_3 \qquad \text{Equation 2.5}$$

$$3C_4AF + 2[C_6(A,F)\,\hat{S}H_{32}] \rightarrow 6[C_4(A,F)\,\hat{S}H_{12}] + 2(A,F)H_3 \qquad \text{Equation 2.6}$$

Equations 2.5 and 2.6 represent the sequence of formation of sulfo-aluminate phases, Equation 2.6 representing the reaction that is governed by excess C_4AF in the cement paste above what is consumed in Equation 2.5 (Ramachandran, 2001).

The inter-grinding of clinker with gypsum leads to the sulfates being relatively finer than the clinker particles (Helmuth, 1994) enabling it to be readily available to form reaction products with the aluminate phases. Flash set takes place when the aluminates are much higher than what gypsum can absorb (Ramachandran, 2001; Neville, 2002). This leads to a preference of calcium aluminoferrite monosulfate hydrate (AFm) (Equation 2.4) over ettringite (AFt) (Equation 2.3) and subsequent premature stiffening that is generally referred to as flash set. False set, on the other hand, results from having excess of gypsum in the solution that crystalizes into a needle like structure leading to stiffening. If all the other composites are in normal ranges, the occurrence of premature stiffening of cement systems involving admixtures can be used to conclude on suitability of the admixture (Helmuth, 1994).

2.3 Classification and perspectives of SCMs in Portland cement

The original Portland cement as discovered in 1824 by Joseph Aspdin continues to evolve mainly through its partial displacement with other fine materials that are generally referred to as supplementary cementitious materials (SCMs). The adoption of SCMs in concrete technology has been driven by cost, performance, and environmental concerns (Turanli, Uzal and Bektas, 2004; Kaid et al., 2009; Schneider et al., 2011; Kocak, Tasci and Kaya, 2013) and is seen by researchers as

part of the solution to the high housing infrastructure demand in developing countries (Schneider et al., 2011; Schmidt, Msinjili and Kühne, 2018).

2.3.1 The history and importance of SCMs

The realization that finely ground materials of volcanic origin can be blended with calcined lime to form a hydraulic binder is associated with the Greek civilization. The Akrotiri settlement archeological site on Santorin Island in Greece is advanced as the oldest record of evidence of integration of volcanic ash in lime mortars (Snellings, Mertens and Elsen, 2012). The Romans later adopted the technology and applied it in construction on a larger scale (Delatte, 2001; Lancaster, 2005; Saddall, 2000; Snellings, Mertens and Elsen, 2012). The Pantheon is a typical example revealing that integration of volcanic materials in binder systems in construction had reached a credible level of sophistication. The lime and siliceous volcanic ash binder system presented good strength and excellent durability performance (Delatte, 2001; Lancaster, 2005; Saddall, 2000; Snellings, Mertens and Elsen, 2012), though not to levels exhibited in modern applications. The discovery of Portland cement in 1824 by Joseph Aspdin and its later modifications presented new possibilities of application of volcanic and other siliceous materials in cement binder systems as supplementary cementitious materials (SCMs). Later, the inclusion of SCMs in Portland cement systems created a new need to understand how the SCMs would affect the properties of hydrating Portland cement.

Portland cement came as a second-generation cement after lime cements. It offered an advantage of higher early strength and better performance properties than lime cements and quickly replaced lime cements in concrete production. Portland cements are principally produced by further burning of lime in a blend of aluminosilicates and iron bearing minerals at high temperatures to form unstable anhydrous cement compounds. This process is energy intensive and ecologically unsustainable. Partial replacement of Portland cement with supplementary cementitious materials (SCMs) is considered a plausible measure towards making Portland cement concrete a sustainable construction material. This realization presented new possibilities of application of volcanic and other siliceous materials in

cement binder systems as SCMs. The last part of last century saw a growing interest in partial replacement of cement with SCMs (Burris and Juenger, 2016; Shannag and Yeginobali, 1995; Martinez-Ramirez et al., 2006; Caputo, Liguori and Colella, 2008; Pourkhorshidi et al., 2010; Uzal et al., 2010; Luke, 2007; Mertens et al., 2009; Turanli, Uzal and Bektas, 2004; Snellings et al., 2010, Snellings, Mertens and Elsen, 2012 and others). SCMs are inorganic materials that are added to Portland cement with a goal of making cements cheaper, more sustainable, more durable and, ultimately, stronger (Taylor, 1997; Turanli, Uzal and Bektas, 2004; Blanco et al., 2006; Mehta and Monteiro, 2006; Kaid, Julien and Khelafi, 2009, Schneider et al., 2011, Kocak, Tasci and Kaya, 2013). They are considered as either latent hydraulic or pozzolan, but limestone and inert fillers also fall into this category. Pozzolans dominate in the group of SCMs in Portland cement.

The names pozzolan and pozzolana mean the same and come from the association with the original importance of the volcanic deposits at Pozzuoli, in current Italy, where much of the volcanic materials used in Greco-Roman concrete were sourced (Snellings, Mertens and Elsen, 2012). Pozzolans are defined under ASTM C618, 2005, as materials of aluminosilicate composition that independently have little or no cementitious value but can react chemically with portlandite (or lime ($Ca(OH)_2$)) in the presence of water and at ordinary temperature to form hydration products with characteristics similar to those formed by hydrated Portland cement. Pozzolans must have, in their composition, reactive silica and alumina that consume $Ca(OH)_2$ to undergo a chemical reaction (pozzolanic reaction) that leads to formation of products with binding properties. As a result, pozzolans are tested on their ability to contribute to strength and increase on the desired hydration products of blended cement paste. Various works (Taylor, 1997; Mehta and Monteiro, 2006) present the reactivity of a pozzolan to primarily depend on the amorphous/glassy content of a pozzolanic material. This criterion is emphasized under ASTM C618, 2005, standard with a requirement for a minimum amorphous content of 25% which is represented by the reactive silica content in a test pozzolan.

2.3.2 Classification of SCMs

Pozzolans, being the primary class of SCMs, are generally characterized as natural or artificial (Figure 1.2) considering the source of the materials and whether the materials require pozzolanic activation beyond milling and blending with cement (Snellings, Mertens and Elsen, 2012; Taylor, 1997). Natural pozzolans include volcanic ashes, volcanic tuffs, and diatomaceous earth while artificial pozzolans include silica fume (SF), calcined clay, fly ash (FA), and other industrial waste materials. FA takes the largest share of pozzolans used globally in Portland cement and is a byproduct of burnt coal produced in thermal power plants. The action of burning coal and rapid cooling of the ash produced is what activates the pozzolanic properties of FA. SF is a waste byproduct of silicon alloys producing industries (Mehta and Gjørvb, 1982). It is also referred to as microsilica or condensed silica fume. Calcined clays as implied by their reference are processed for pozzolanic activation through burning of natural clay (kaolinite and other impure clays) at high temperatures (about 600°C) (Scrivener and Favier, 2015). The high temperatures dehydrate the clay mineral structure and forms new aluminosilicate mineral structures that can combine portlandite in hydrated cement paste to form extra hydration products that have binding properties. The process of calcining clay makes new mineral structures and, accordingly, new products hence calcined clay is considered an artificial pozzolan. Ground granulated blast furnace slag (GGBS), also an industrial byproduct from steel processing, is considered latent hydraulic, a term that refers to SCMs that harden under water but at a rate that is slow and impractical for application in concrete production. Latent hydraulic materials are therefore activated by alkali media which hydrating cement provides through the precipitated portlandite. Studies to date have focused more on application of industrial byproducts (mainly GGBS, FA and SF) and little has been published on characterization of natural pozzolans as SCMs (Scrivener et al., 2015).

2.3.3 Performance of volcanic rocks as SCMs

Volcanic rocks are primarily characterized as igneous rocks and result from magma flows through volcano vents to the earth's surface. The ejected molten lava that is

deposited at the surface of earth cools fast leaving little time for crystallization to take place. The resulting glassy (amorphous) silica mineral structures are known to enhance pozzolanic reaction of the volcanic materials (Snellings, Mertens and Elsen, 2012). Pozzolanic activity, a measure of the presence and time rate of a reaction between a pozzolan and lime or portlandite when water/moisture is added, is used to characterize reactivities of different pozzolans, and, certainly, volcanic rocks as SCMs. Volcanic rocks are generally classified as natural pozzolans.

Works on natural pozzolans of volcanic origin show their performance to be generally driven by composition, fineness, and replacement levels (Burris and Juenger 2016; Shannag and Yeginobali 1995). The influence of fineness level of pozzolans is not linear as Burris and Juenger, 2016, in their work on a natural zeolite, established a peak fineness level beyond which no significant benefit to pozzolanic performance is realized. This is an important observation given that, from the energy economy perspectives in cement production, the amount of processing involved in milling pozzolans reflects on the cost of the cement product and on the relief gained in improving the sustainability functions of Portland cement concrete.

The natural pozzolans are observed to slow down hydration, prolong setting time and delay strength development (Shannag and Yeginobali, 1995) although these limitations can be mitigated. Their reactivity is generally observed to increase with increase in fineness (Burris and Juenger, 2016) while increase in replacement level initially leads to higher strength up to an optimum level of cement replacement beyond which the long-term strength begins to drop as observed in Mehta, 1981. High volume replacement of Portland cement with natural pozzolans is reported successful in Celik et al., 2014. Most natural pozzolans studied are, however, silica saturated and potentially felsic igneous rocks (Burris and Juenger, 2016; Shannag and Yeginobali, 1995; Martinez-Ramirez et al., 2006; Caputo et al., 2008; Pourkhorshidi et al., 2010; Uzal et al., 2010; Luke, 2007; Mertens et al., 2009; Turanli, Uzal and Bektas, 2004; Snellings et al., 2010, Snellings, Mertens and Elsen, 2012 and others), unlike kamafugites and carbonatites. Kamafugites and carbonatites are ultramafic to mafic rocks that are largely ultrapotassic and relatively high in carbonate minerals. They are silica undersaturated as a result of carbonates

enrichment (Stoppa and Schiazza, 2013). Little is known about their performance as mineral admixtures in Portland cement concrete.

2.3.4 Petrology of the East African (E.A) volcanic rocks

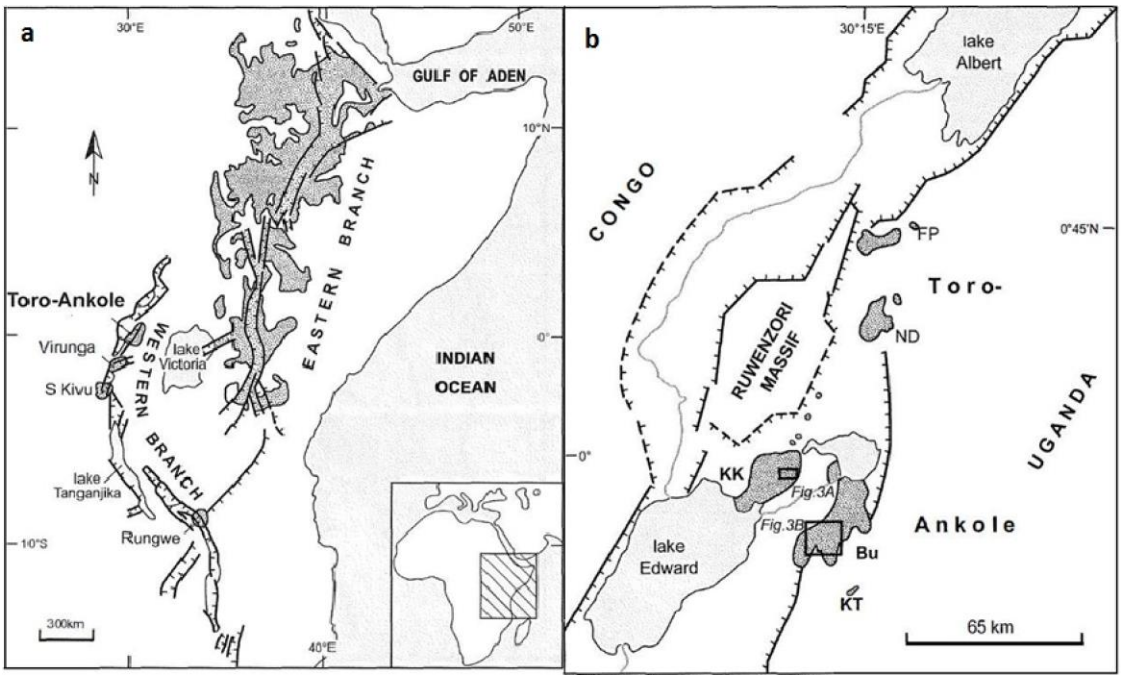

Figure 2.3: (a) A sketch map of eastern Africa showing the rift system and occurrence of lava deposits. The Albertine rift or the western branch is composed of Toro-Ankore, Birunga and South Kivu series. The hairy lines represent the main rift faults. (Map adapted from Tappe, Foley and Pearson, 2003) (b) Location of volcanic tuff deposits in the Toro-Ankore series (after Tappe et al., 2003).

The petrology and geochemistry of volcanic deposits in the different volcanic zones of the East African rift system has been extensively studied (Barker and Nixon, 1989; Holmes, 1942; Jones, Genge and Carmody, 2013; Kampunzu, and Mohr, 1991; Morley, 1999; Rosenthal et al., 2009; Tappe, Foley and Pearson, 2003; Williams, 1972; Wyllie and Huang, 1976). The deposits are predominantly carbonatites and alkali volcanic rocks. The Western arm (figure 2.3b) shows a variation in the chemistry of volcanic deposits from basaltic volcanic deposits that are weak in alkalinity to strongly silica undersaturated high potassium carbonate-rich carbonatites and kamafugites. The Eastern arm of the rift system is dominated by sodium-rich dolomite and calcite deposits of carbonatite complexes with carbonatite, nephelinite, nephelinesyenite, ijolite and phonolite rock series. The Western rift is

dominated by katungite, mafurite, ugandite, basanite, leucitite, nephelinite, and melilitite rock series. The occurrence and location of these deposits is mainly associated with the rift system (Jones, Genge and Carmody, 2013). The deposits are distinctly different from each other following their individual points of volcanic eruption. The variability is attributed to the composition of the parent magma and the conditions it was exposed to at the time of deposition (Bell and Doyle, 1971). The estimated volume of volcanic deposits in the western branch of the East African rift system is approximately 100,000 cubic kilometers (Kampunzu and Mohr, 1991) while that for the eastern branch ranges from 220,000 to over 900,000 cubic kilometers (Morley, 1999; Williams, 1972).

2.3.5 Petrology of Volcanic deposits of the western branch of the E. A rift

The west branch of the rift system is divided into three volcanic deposit series, the South Kivu, Virunga and Toro-Ankore geological series (Tappe, Foley and Pearson, 2003). These deposits are different in physicochemical properties from the carbonatites in the eastern branch of the rift system. The western rift is mostly potassic while the eastern branch is sodic (Rosenthal et al., 2009). The Toro-Ankole series are potassic to ultrapotassic, silica undersaturated and carbonatitic deposits (Holmes, 1942; Tappe, Foley and Pearson, 2003) while the South Kivu and Virunga series are basanite and subalkaline tholeiitic magmas (Rosenthal et al., 2009). Pouclet et al., 1981, (cited in Rosenthal et al., 2009) observed a progressive decrease in concentrations of potassium and carbon dioxide and an increase in silica content as one moves from the propagating tip of the western branch (Toro-Ankore series) to South Kivu series. The carbonatites are mainly located in the northern deposits of Fort Portal (FP) and Ndale (ND) (Tappe, Foley and Pearson, 2003) while Kamafugites occupy Katwe_Kikorongo (KK), Bunyaruguru (Bu) and Katunga (KT) deposits.

2.3.6 Petrology of Kamafugites and carbonates of Toro-Ankole series

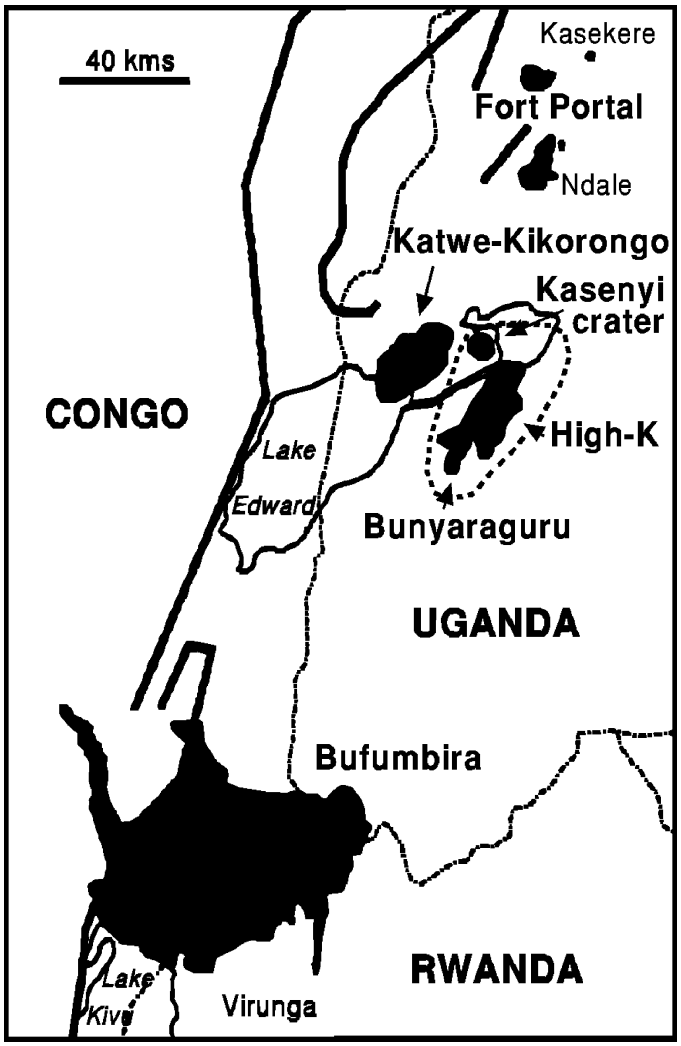

Figure 2.4: A sketch map showing two of the magma deposit series, Virunga and Toro-Ankole, of the western part of Eastern Africa rift system. (Map adapted from Eby et al., 2003).

The classification “kamafugite” comes from a combination of the katungite, mafurite and ugandite rock mineral series (Sahama, 1974). They are ultrapotassic zeolitised volcanic tuffs containing feldspathoidal minerals. They appear as either ultramafic or mafic rocks and are defined by the presence of kalsilite, a mineral in the form of $KAlSiO_4$ (Holmes, 1942). They fall within the family of carbonatitic lavas because of their relatively high composition of CO_2 appearing mainly in the form of calcite and dolomite. Their characteristic silica and alumina undersaturation is a result of carbonates and potassium alkalis enrichment (Wyllie and Huange, 1976). They were first reported by Arthur Holmes and Henry Francis Harwood (Holmes and Harwood,

1932) in the Toro-Ankore geological region of the East Africa Rift system (Figure 2.1). Kamafugites deposits dominate the southern parts of the Toro-Ankole geological series while the carbonatites are located mainly in the Fort Portal region (Figure 2.4).

The Toro-Ankole deposit is indicated to include Bunyaruguru (presently referred to as Kataara-Rubirizi), Katwe-Kikorongo, Fort Portal, Ndale and other deposits. The third series (South Kivu deposits) are located south of Virunga and are not shown on the sketch map.

2.3.7 Kamafugites and Carbonatites as SCMs

A study of the phase compositions in kamafugites and carbonatites that influence their performance as SCMs in Portland cement concrete is partly petrological and partly engineering. Understanding the physicochemical characteristics from the petrological perspective and then projecting the observed characteristics to performance of the SCMs in Portland cement concrete presents an opportunity for prognosis in application of the volcanic materials as SCMs. Several studies on petrology and geochemistry of volcanic material in the rift valley regions of East Africa (Bell and Doyle, 1971, Tappe et al., 2003; Rosenthal et al., 2009; Barker and Nixon, 1989) reveal an abundance of highly variable deposits. The variability is attributed to the composition of the parent magma and the conditions it was exposed to at the time of deposition. Studies conducted by Bell and Doyle, 1971, reveal highly alkaline magmatism with sodic carbonatites dominating in the Eastern and potassic carbonatites dominating the western branches of the East African rift system. Reported in this thesis is the Toro-Ankole geological series in the western branch (the Albertine rift system) of the East African rift system. Potassic feldspathoids that are highly alkaline and with low silica activity (kamafugites) and carbonatites dominate in the Toro-Ankore series. Studies conducted by Tappe et al., 2003, and Rosenthal et al., 2009, reveal a uniquely low silica composition for continental magmatism. The studies established SiO_2 in the range of 31.8-41.8% by weight while CaO and K_2O reached percentage weight compositions of up to 16.6% and 7% respectively. The samples had a MgO-rich composition ranging from 6% to 22.5%.

The Al_2O_3 was characteristically low with a maximum composition of 8% although Tappe et al., 2003, found composition of 11.0% in a sample taken from one of the deposits (Katwe-Kikorongo). The mineral abundance is potassic olivine melilitite, olivine-pyroxene kalsilitite, olivine_kalsilite leucitite and potassic nephelinite (Rosenthal et al., 2009, Bell and Doyle, 1971; Holmes, 1942). This characteristic composition is unique to the Toro-Ankore series. The complete deficiency of plagioclase (silicate minerals that form 90% of the earth crust) distinguishes the kamafugites of Toro-Ankore series from other carbonatitic lavas (Rosenthal et al., 2009). Other known kamafugite sites are in the Umbria-Latium region of Italy (central Italy) (Stoppa et al., 2004), the Parana Basin region of Brazil and Paraguay (Sgarbi et al., 2000) and the west Quniling region of China (Guo et al., 2014). Classification research conducted by Tappe S. et al., 2003, and Guo et al., 2014, to compare these different Kamafugites reveal that the Toro-Ankore kamafugites are closer to the silica-undersaturated kamafugites of Brazil and China than those of Italy. The Italian Kamafugites are characteristically high in the oxide contents of Si, Al and K. To the best of my knowledge no published work on the performance of kamafugites and carbonatites as SCMs existed at the time of this study and reporting.

2.4 Cements blended with SCMs

2.4.1 Microstructure development in SCM blended Portland cement

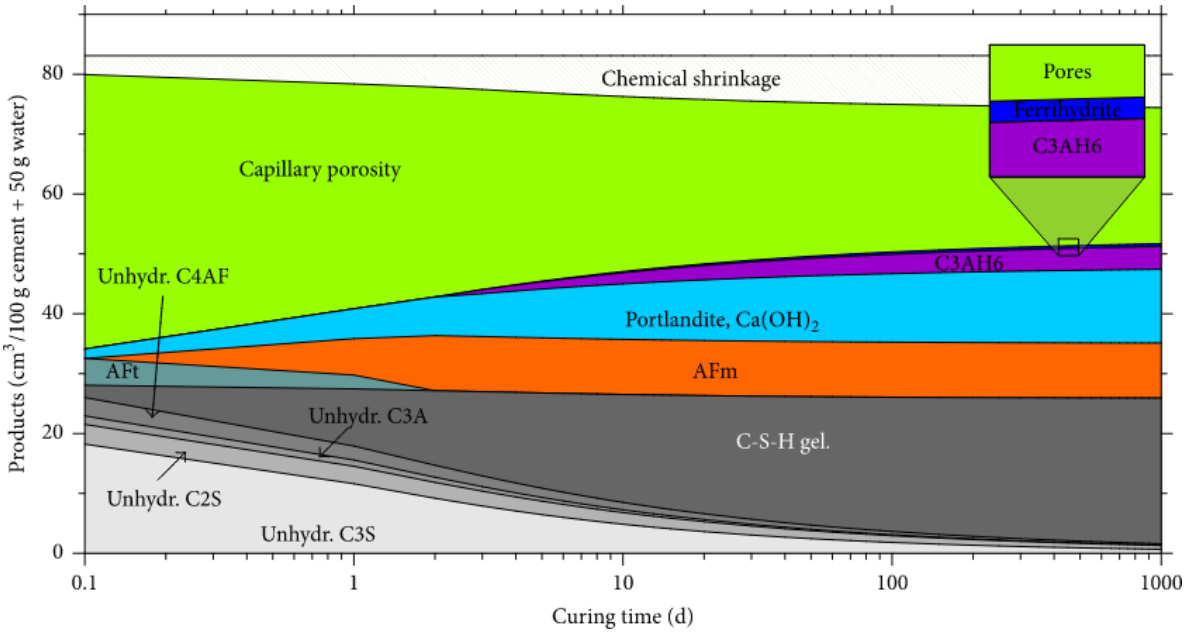

Figure 2.5: Cement hydration products evolution with curing time (Lui et al., 2017)

Hydration products, pore structure, pore solution and unreacted cement particles form the microstructure of cement systems. These features are what is considered as cement gel. When conditions facilitate reactions of cement phases, as it usually is the case, the microstructure features are sustained in a transient state, hydration products increasing as reactants reduce (Figure 2.5). As explained in section 2.4.2, of this thesis, SCMs may act as catalysts in the hydration reactions and chemically through pozzolanic reactions and other reactions with cement phases and their hydrates. Moreover, when zeolites are used as SCMs, the associated pozzolanic reaction plays a significant role in modifying the microstructure of cement gel. The rate of pozzolanic reaction largely depends on the supply of CH crystal products from the reaction of the C_3S phase of cement. The source of the CH precipitate is the hydration reaction between the silicate phases in the clinked component of the cement mix (Equation 2.7) (Kocaba, Gallucci and Scrivener, 2012).

OPC + Water → C-S-H + CH + other hydrates Equation 2.7

The C-S-H solid precipitate is the hydrate responsible for the aggregates binding and paste impermeability properties of concrete. These two properties consequently influence the strength and durability performance of cement pastes. The rate of deposition of C-S-H is dependent on availability of water to facilitate the hydration reaction (avoid self-desiccation) and on availability of space and nucleation sites within the paste matrix environment. SCMs are associated with the dilution effect and provision of nucleation sites facilitating fast deposition of C-S-H and growth of the hydrates at early stages of hydration (Scrivener et al, 2015). This phenomenon is not limited to pozzolanic SCMs as limestone powder achieves the same benefit (Berodier, 2015).

A pozzolanic reaction follows the precipitation of the CH according to Equation 2.8.

Pozzolan + CH + water → C-S-H + other hydrates Equation 2.8

The extra C-S-H precipitates are associated with extra strength since the displaced CH crystals do not contribute to strength.

2.4.2 Hydration kinetics of SCM blended cements

Work done by Le Chatelier and others showed that cement compounds can be isolated and tested for hydration progression in conditions modeled to be similar to the actual conditions of cement hydration (Neville, 2002). The hydration progression of the individual cement phases follows a defined sequence and is similar to that observed when in cement but with minor interference (Neville, 2002). As a result, it is possible to study the role of each of the four phases in cement and how they interact with SCMs and other additions. Applying various instrumental techniques that include isothermal calorimetry, SEM-EDX, X-ray powder diffraction, shrinkage measurement and other characterisation methods, the various studies on natural pozzolan SCMs are reported in Snellings et al., 2010, Lothenbach, Scrivener and Hooton, 2011, Scrivener et al., 2015 and others to show hydration kinetics, strength and microstructure development to be driven by the filler effect, dilution effect, and pozzolanic reaction, three factors that are discussed below.

Of all the methods applied in the characterization of hydration kinetics of cement and its phases, isothermal calorimetry seems to be the most common (Taylor, 1997; Nevile, 2002; Berodier, 2015). The evolution of a cement hydration as a function of heat released over time for both pure cement and cement blended with natural pozzolana materials has been presented in Figure 2.2. Cement when mixed with water undergoes 5 active stages of reaction, the pre-induction, induction (dormant stage), acceleration and the deceleration stages. The fifth stage is characteristically slow in hydration and takes a long time to reach completion (1 year) (Neville, 2002). Each of these stages relates to the reaction progression of each of the four phases of cement and define the hydration kinetics and microstructure development processes ongoing during cement hydration. By observing how the isotherms change when cement is blended with SCMs, researchers have been able to make conclusions about the role of SCMs on hydration kinetics and microstructure of blended Portland cement systems (Berodier, 2015). Still, studies on microstructure and hydration kinetics of cement systems with natural pozzolan SCMs have mainly utilized high silica and alumina zeolitic tuffs and basaltic ashes (Snellings et al., 2010; Perraki et al., 2010; Celik et al., 2014) and tend to not give importance to non-pozzolanic reactions between SCMs and hydrating Portland cement. SCM effects on hydration kinetics of hydrating cement paste is reported driven by both their physical and compositional properties (Mehta and Monteiro, 2006; Kocak, Tasci and Kaya, 2013). Therefore, the role of exchangeable alkali cations in kamafugites and carbonatites on hydration kinetics is a knowledge gap the current thesis attempted to address. And, though literature on the role of $CaCO_3$ on hydration kinetics is not common in the domain of pozzolanic SCMs research, it has been included here for the interest of reference to kamafugites and carbonatitic lavas which are enriched with carbonate minerals.

The common modes of interaction between cement and supplementary cementitious materials have been grouped by various researchers (Kastis et al, 2006; Berodier, 2015; Scrivener et al., 2015 and many others) as filler effect, dilution effect, pozzolanic reaction and hydration reactions. It can therefore be advanced that SCMs interact beyond pozzolanic reactions in Portland cement systems. The four modes of interaction are explained below.

2.4.2.1 The filler effect:

Topical works show the presence of SCMs in a cement paste to affect the rate of hydration of clinker phases and, consequently, lead to an accelerated gain in mortar strength at an early age. This effect is what is known as the filler effect. The filler effect is driven by the particle size of the SCMs in relation to cement (Tangpagasit et al., 2005), the chemical nature of the SCMs (Kadri et al., 2010) and the replacement levels of cement with a test SCM (Scrivener, Juilland and Monteiro, 2015). A recent review by Scrivener, Juilland and Monteiro, 2015, advance two mechanisms namely, clinker bulk density reduction effect and a dispensation of extra sites for precipitation and growth of hydration products.

The clinker bulk density reduction effect as a result of partial replacement of Portland cement with an SCM leads to availability of more space for clinker hydration products to form unconfined (Scrivener, Juilland and Monteiro, 2015). Space is one of the parameters that control the rate of hydration of clinker phases (Berodier, 2015). The hydrates are known to cause an increase in volume in relation to the cement anhydrous phases and, therefore, require extra space for the hydration reaction to take place. Berodier, 2015, refers to this filler effect mechanism as the dilution effect, however, the current discussion chose to limit the term ‘dilution effect’ to only apply in relation to mixing water.

The precipitation and growth of hydrates has been observed to be heterogeneous (grows on surfaces of both cement and SCM grains in the paste) with some SCM types providing more sites than others, an observation Kadri et al., 2010, attributed to the chemical nature of SCMs. A study by Kadri et al., 2010, showed limestone to provide more sites for precipitation than quartz (used in the tests as an inert material) and ground granulated blast furnace slag (ggbs).

The filler effect as observed in literature is significant at early ages (up to 3 days) and therefore it only affects early age strength tests

2.4.2.2 The dilution effect:

The dilution effect of an SCM is characteristic of reduced clinker content in a binder material unit which reflects on the total reactants available in a cement system and the paste properties, both at early and later stages of hydration. Cement substitution with SCMs leaves less clinker content that is responsible for production of the primary hydration products and, subsequently, CH that is necessary for pozzolanic reaction. This effect is emphasized in Khan et al., 2017, where increase in replacement levels above 10% unbalances the benefits associated with the filler effect. Therefore, the dilution effect results in reduced strength associated with the reduction of cement content and increase in water-to-cement ratio.

For an optimum replacement level, the loss in strength due to the dilution effect is balanced by the pozzolanic reaction. Even then, studies show that mortar strength at early stages of hydration (1-3 days) are principally governed by only the hydration of clinker phases (Scrivener et al., 2015; Berodier, 2015) and pozzolanic reaction grows in significance after three days and continues for a long time. The dilution effect is therefore important at early stages of hydration when strength contribution from the pozzolanic reaction is still negligible.

For SCMs that increase water demand of blended Portland cements, the assumption that the water-to-clinker ratio increases with increase in replacement levels can be misleading. It is highly likely that the morphological properties that lead to increase in water demand can significantly reduce the available water to participate in clinker hydration for fixed amount of mixing water. Trial mixes conducted in the current study showed that increasing water content of blended Portland cements to achieve a flow within the range of 10% of the control sample as is a requirement of the test standards leads to a reduction in compressive strength of mortar samples at all ages up to 90 days compared to mixes where water content was fixed. The presence of an SCM can therefore play a strength enhancing or reducing role depending on its effect on the water budget in the paste. For fixed mixing water, the dilution effect is therefore more important as far as the clinker factor in a paste is concerned. More so, studies that focus on time dependent changes in strength of a test sample due to pozzolanic reaction are less dependent on mixing water if the initial amount was

enough to facilitate casting of the sample. Studies on the effect of mixing water on compressive strength (Donatello, Tyrer and Cheeseman, 2010) recommend an amendment of both the BS 3982-1, 1997, and ASTM C618, 2005, test procedures to adopt a fixed amount of mixing water in order to minimize on the variables in the experimental design. The current study used a fixed water to cementitious materials ratio of 0.5 for all the mortar mixes and considers time dependent changes in strength to be governed by mechanisms other than the quantity of mixing water.

2.4.2.3Pozzolanic reaction:

Pozzolans are insoluble materials possessing relatively high contents of amorphous alumino/silicate minerals that, when pulverized, will react with lime ($Ca(OH)_2$) in the presence of water and at normal temperatures leading to formation of cementitious products (ASTM C618, 2005). The sequence of a pozzolanic reaction is that of reactive silica in a pozzolanic material bonding with the $Ca(OH)_2$ product to form new C-S-H hydration products with bonding properties similar to those of cement hydration products (Mehta and Monteiro, 2006).

$$3Ca(OH)_2 + 2SiO_2 \rightarrow 3CaO.2SiO_2.3H_2O \qquad \text{Equation 2.9}$$

Equation 2.9 is generally written in a short format as follows

$$CH + S \rightarrow C\text{-}S\text{-}H \qquad \text{Equation 2.10}$$

Alumina substitution of silica is common in cement reactions with natural pozzolanic materials that have a substantial quantity of alumina composition (Ramachandran 2001) leading to formation of hydrates that take on a nomenclature of C-A-S-H. However, the pozzolanic reaction that presents a more significant cementitious value is that of CH and silica, hence pozzolanic reactions are mainly defined by Equation 2.9.

The available CH for the pozzolanic reaction is supplied by the cement C_3S and C_2S hydration reactions (Equations 2.1 and 2.2). The proportions of C_3S and C_2S and their rates of hydration vary with different Portland cement types. This variability affects the rate of supply of the CH hence the rate of pozzolanic reaction. The extent of displacement of Portland cement with pozzolanic materials also determines the

amount of CH available in a hydration reaction. Higher cement replacement leads to less CH formation since the total quantity of C_3S and C_2S will have been reduced.

The reactivity of a pozzolanic material (i.e its level of reaction with CH or lime to form hydration products similar to C-S-H) is related to its importance in enhancing the strength and durability properties of concrete. A pozzolanic material that is highly reactive is considered to form more hydration and strength enhancing products under favourable circumstances. Pozzolanic reaction is, however, a slow reaction that follows the hydration of the calcium silicate phases in cement. As indicated above, the hydration of the silicate phases leads to formation of calcium silicate hydrates (C-S-H) and calcium hydroxide (CH). The precipitated CH crystals react with amorphous silica in pozzolanic SCMs to form extra C-S-H leading to improved strength and permeability (through pore refinement) properties of hardened concrete (Mehta and Monteiro, 2006). Moreover, the pozzolanic reaction follows the hydration reaction and its effects are observed to start after 3-4 days from the start of hydration (Berodier, 2015). Portland cements that are blended with pozzolanic materials are therefore expected to have higher normalized strengths (normalized strength is a rating of strength for a unit quantity of cement in a binder material) at later stages of hydration ≥ 7 days.

2.4.2.4Hydration reactions and other reactions that are not pozzolanic:

A pozzolanic material may also present other reactants that are able to combine with hydrating cement phases and their products or simply act as catalysts to the hydration reactions. Gabrovšek, Vuk and Kaučič, 2006, report hydration products that include magnesium, carbonates, and alkalis. The alkalis and carbonates in the kamafugites and carbonatites are candidate examples in influencing cement hydration reactions and hydration products. Celik et al., 2014, used a back-scattered image in scanning electron microscopy to study the pozzolanic reaction of the basaltic glass component of blended cement systems. The natural pozzolan was sourced from Saudi Arabia. The study found a yellow-brown gel-palagonite as the predominant pozzolanic reactive component of the natural pozzolan. Elemental composition studies of the interfacial zones of gel-palagonite features gave Ca/(Al +

Si) ratios in the range of 0.4-0.6 while those for Na + Mg + K + Ti + Fe/(Al + Si) were 0.6-0.7, showing a reduction in Ca while an increase in the alkali content in relation to hydrating cement particles. The study also found the Ca/(Al + Si) ratio of C-A-S-H hydrate composition to vary between 0.7 and 1.9 leading to hypothesizing association of the C-A-S-H hydration products to the gel-palagonite and generally natural pozzolan phases in the binder mix.

2.4.3 Calcination of SCMs: Effects of calcite in hydrating cement

Calcite in SCMs react with the aluminate and sulfate phases in cement to form carboaluminates and AFm respectively (Ipavec et al, 2011; Mohamed, Elsalamawy, and Ragab, 2015). As a result, this leads to acceleration of the early hydration reactions of C_3S (Matschei, Lothenbach, and Glasser, 2007). More so, studies on SCM systems that include limestone/calcite present them to react with the aluminate phases of cement (C_3A) forming both monocarboaluminate and hemicarboaluminate microstructure phases (Berodier and Scrivener, 2014; Kakali et al., 2000; Lothenbach et al., 2008; Matschei, Lothenbach and Glasser, 2007; Ipavec et al., 2011; Mohamed, Elsalamawy and Ragab, 2015). Due to low solubility of $CaCO_3$, the reaction between limestone and C_3A leading to formation of the carboaluminates is said to take place after gypsum has completely reacted to form ettringite. Monosulfate phase, a product of a reaction between ettringite and excess aluminates, is absent in cement-limestone systems but there is an increase in the volume of hydration products leading to a denser microstructure, a condition that gains the durability property of the cementitious material. Work done by Klieger and Hooton, 1990, reveal a small percentage of limestone (1 to 1.5%) involved in the hydration process. This percentage is much lower than what is thermodynamically predicted to form the carboaluminates but also shows that small quantities of limestone can have a significant influence on the hydration of Portland cement. The carbonate phases present in kamafugites and carbonatitic lavas present volumes that are sufficient to cause the reaction with aluminate phases.

2.4.4 Effects of alkalis in hydrating cement

Alkalis are generally reported to accelerate hydration of cement phases (Neville, 2002), but Jawed and Skalny, 1978, and Odler and Wonnemann, 1983, report sodic alkalis to have a different effect on hydration from potassic alkalis. Jawed and Skalny, 1978, and Odler and Wonnemann, 1983, report potassic alkalis to accelerate hydration of the aluminate phases while sodic alkalis retard the early hydration processes. Later studies by Turanli, Uzal and Bektas, 2005, on ultrapotassic volcanic tuffs from Turkey established an accelerating effect supporting the conclusions of Jawed and Skalny, 1978, and Odler and Wonnemann, 1983.

Zeolites modified to a high soluble alkali cation content altered the chemical composition of the pore solution, shortened the induction period and accelerated C_3S hydration rate, CH precipitation and hydration of the aluminate phases forming AFt (Snellings et al., 2010). The CH precipitation follows the consumption of C_3S reaching its peak concentration in 2 to 3 days before the pozzolanic reaction. The work supported studies (Özen et al., 2016) that found zeolites with exchangeable alkali cations (K^+ and Na^+) to have a higher rate of pozzolanic reaction than the Ca^{2+} based zeolites. The high C_3S hydration rate is however attributed to adsorption of the Ca^{2+} in the pozzolanic reaction. C_3S hydration controls the setting property and dominates the strength development property of cement

2.4.5 Factors affecting pozzolanic activity of SCMs

Different works on pozzolanic activity of volcanic tuffs, ashes and lavas (Pourkhorshidi et al., 2010; Massazza, 1974; Liebig and Althaus, 1998; Snellings, Mertens and Elsen, 2012; Mertens et al., 2009; etc.) identified four parameters to influence the pozzolanic reactivity of the natural pozzolans. These parameters are discussed below in relation to their influence on reaction mechanisms between test pozzolans and lime or portlandite in a cement paste.

2.4.5.1 Chemical composition requirement

The sum of the major oxides content (i.e SiO_2, Al_2O_3 and Fe_2O_3), also referred to as the acidic oxide content, is presented in ASTM C618, 2005, and BS 3892-1, 1997, to be a minimum of 70% for a material to be considered sufficiently pozzolanic for both class F fly ash and natural pozzolans. Several topical works have found this requirement not to contribute to the pozzolanic performance of natural pozzolans as far as strength development is concerned.

Pourkhorshidi et al., 2010, tested the reliability of the ASTM C618, 2005, method in assessing pozzolanic activity of natural pozzolans. The researchers used four (4) Iranian natural pozzolans and generated findings that showed inconsistencies with the minimum composition requirements of the sum of the major acidic oxides.

Malhotra and Mehta, 1996, however stress the importance of the amorphous state of the minerals and morphological properties of the pozzolanic materials over the chemical composition in determining their performance as SCMs in concrete.

ASTM C618, 2005, puts a limit of 10% of volatile elements content which are classified as loss on ignition (LOI). Different researchers have found a correlation between LOI and water demand of mortars and pastes, a condition they associate to the carbon content of test pozzolanic materials. Where the reason for a high LOI is not because of organic content but carbonates, the effect of LOI values may have negligible influence on strength. Carbonates are known to react with aluminate phases forming mono- and hemicarboaluminates, a reaction that was observed by (Ipavec et al., 2010; Lothenbach and Wieland, 2006; Kakali et al., 2000) to limit the reduction of ettringite to monosulfates in portland cement systems with more aluminates than the sulfates can fix in the first stage of their reaction.

2.4.5.2 The amorphous content in the structure of a test pozzolan

The amorphous content is also referred to as reactive silica content or glass content. Because of rapid cooling of lava on the surface of earth, some minerals do not get sufficient time to crystalize and form stable compounds (Mehta and Monteiro, 2006). This results in a volcanic deposition with highly unstable silicious compounds that

easily combine with CH precipitates in hydrating cement and, as a result, a pozzolanic reaction. The amorphousness of test pozzolans is measured using quantitative XRD method and optical microscopy (Ramachandran, 2001).

2.4.5.3 Particle fineness of the test pozzolan

Fineness is presented as a physical requirement in standards for assessment of pozzolanic activity of different SCMs (ASTM C618, 2005; BS 3892-1, 1997). Natural pozzolans to be applied in a pozzolanic activity test are required to have at most 34% of the particles retained on a 45 μm sieve.

Studies on the role of fineness on pozzolanic activity of natural pozzolans present results that are largely similar for early stages of hydration and differing over the long-term performance.

Day and Shi (1994) observed a general increase in pozzolanic performance with fineness that was sustained throughout a test period of 90 days. The study reported dependence on fineness to be higher at early stages of hydration. The materials used to study fineness were lime-pozzolan mortars and not Portland cement-pozzolan mortars, a factor that can affect the nature of results given that lime hardens in a slow carbonation reaction while Portland cement hydration is a relatively very fast reaction.

Burris and Juenger, 2016, however found fineness to show importance at early stages of hydration but lost significance over time. Both groups of authors used natural pozzolans that passed the minimum fineness requirement provided in the standards. The current experimental work used a single fineness level for each test pozzolan to address the associated variabilities.

2.4.6 Effect of compositional parameters of kamafugites and carbonatites

Whereas no previous works that focused on carbonatites and kamafugites as SCMs could be established, a literature search revealed some works on natural pozzolans that either had a high content of calcite or high alkali content or both. Turkmenoglu and Tankut, 2002, studied volcanic tuffs from central Turkey that are enriched with K+ and Na+ alkalis and calcite. The study reported a reduction in mechanical

strength with increase in K+ and Na+ alkali content. The study also presents a presence of kaolinite and calcite minerals among others to have a negative effect on mechanical strength. Calcite and kaolinite are secondary minerals generated as a consequence of alteration of volcanic glass (Habert et al., 2008). A different study by Kastis et al., 2006, presents the SCM properties of calcareous diatomite. The diatomite contained a high content of reactive/amorphous silica (31.68%/37.58%) and calcite (37.58%) and satisfied the composition requirements for natural pozzolans stated in ASTM C618, 2005, and EN 197-1, 2000. The study focused on pozzolanic aspects of the reactive silica, and no attention was given to the influence of calcite in the hydration reactions and the pozzolanic activity. The diatomite also had no K^+ and Na^+ alkalis indicating its reaction mechanisms with cement and resulting hydration products can only be different from carbonatites. Jawed and Skalny, 1978, reported on the effect soluble alkalis have on hydration and strength development of cement. The assertion that soluble alkalis in cement pastes accelerate its hydration and, also, influence the morphological properties of the hydration products is made in this work. The alkalis were also reported to reduce final compressive strength. Odler and Wonnemann, 1983, found Na^+ based alkalis to have a prolonging effect on setting time while those that are K^+ based shortened the setting time of cement. This was rationalized by the delayed hydration of the aluminate phase in cement that was associated with the Na^+ alkalis. The effect of alkalis is also supported in Ogawa, Uchikawa and Takemoto, 1980. Ogawa, Uchikawa and Takemoto, 1980, explains the hydration acceleratory effect of alkalis (Na+, K+ etc) as a deductive consequence of the water-soluble alkalis that accelerate the dissociation of water molecules, which in turn accelerate the dissolution of silica and alumina ions in the system, and the precipitation of hydration products that follows. This same reaction mechanism carries the explanation for early depletion of pozzolanic reactants in the kamafugites and carbonatites. Ogawa, Uchikawa and Takemoto, 1980, observed that alkali enriched pozzolans lost the hydration products precipitate from their particle surfaces, a phenomenon the authors attributed to weak adhesion that gives way to osmotic pressure buildup due to differences in ionic concentrations between the inner and outer layers of the surrounding precipitate. As a consequence, the hydrates layer slips off the surface

of the pozzolan particles giving more exposure and leading to more dissolution of alkalis into the system and the resulting dissociation of water molecules and resulting protonic attacks sustaining the acceleration of hydration and pozzolanic reactions.

Studies on the effect of calcite on Portland cement hydration (Berodier and Scrivener, 2014; Kakali et al., 2000; Lothenbach et al., 2008; Matschei, Lothenbach and Glasser, 2007; Ipavec et al., 2011; Mohamed, Elsalamawy and Ragab, 2015) indicate a set accelerating effect and a modification of paste microstructure specifically of the aluminates and sulphate phases. The accelerating phenomena is attributed to the "filler effect", which Berodier and Scrivener, 2014, explain to be driven by the interparticle distance contrary to previous belief that mineral admixtures provide extra surfaces for nucleation sites of hydrates (Mohamed, Elsalamawy and Ragab, 2015). Consequently, limestone or calcite gives a higher filler effect compared to other SCMs (Berodier and Scrivener, 2014). The filler effect is the concern of the first few hours of hydration (up to the final setting of cement paste) but it is reported to influence the type and distribution of paste microstructure (Berodier, 2015) hence impacting on later strength of blended cements.

Kaolinite, a secondary mineral formed through alteration of the primary rock minerals (Habert et al., 2008), is a common mineral in pozzolanic materials of natural origin. When thermally destabilized, kaolinite, a clay mineral, is known to have pozzolanic properties. Habert et al., 2008, presents a higher strength with thermal destabilization of kaolinite enriched volcanic materials. Extensive work on pozzolanic nature of kaolinite and how it influences Portland cement properties is presented in the RILEM book series on Calcined Clays for Sustainable Concrete (Scrivener and Favier, 2015).

2.5 Experimental techniques for characterization of SCMs

2.5.1 Objectives of characterization of SCMs

The scientific principles, procedures, and their adaptation to the characterisation applications of different Portland cement concrete constituents are explored in this section. Modern concrete technologies continue to stretch concrete composition to

include various forms of granulated materials, chemical and mineralogical additions, and inert materials, all with the aim of making concrete greener while enhancing its performance and addressing its global demand increase. The presence of SCMs in Portland cement concrete is known to influence concrete properties both in fresh and hardened state. Effects of SCMs on fresh concrete properties have been documented by various authors (Berodier, 2015; Neville, 2002; Ramachandran, 2001) to include mainly workability, hydration, mix stability and setting properties. The effects on hardened concrete properties are associated with reduction in early strength gain, increased strength at a later age with some SCMs, and improved durability. The cost of cementitious materials is another benefit associated with the use of most SCMs. The importance of SCMs in partially substituting clinker in cement systems is however presented in literature as universal because of its CO_2 emission reduction per unit of concrete produced (Bianchi, 2014). Characterisation methods for SCMs like other concrete constituents are largely premised on three aims (adapted from Alexander and Mindess, 2005, for aggregate characterisation).

1. To enable testing for conformity to minimum performance requirements. This is achieved through testing protocols that follow standard tests.

2. To enable comparative study of performance of different cementitious materials. This is achieved through standardized experimental protocols.

3. To evaluate how the specific quantifiable properties of the study materials influence the properties of concrete in both fresh and hardened states.

Emphasis is put on the third premise for the consideration of works presented in this thesis.

2.5.2 Test methods for cement hydration and pozzolanic activity

Test methods for pozzolanic activity mainly assess the progress of reaction between reactive components of the pozzolanic material and $Ca(OH)_2$ crystal precipitate from the hydration of cement for a set time period. The test methods have been characterized by Scrivener et al., 2015, and Donatello, Tyrer and Cheeseman, 2010,

as either direct or indirect. Direct methods rely on actual measurement of unreacted SCMs in composite cement at a given time while the indirect methods rely on proxy indicators such as strength activity index and heat of hydration to deduce the degree of reaction of a specific SCM (Scrivener et al., 2015). This section of literature review discusses the different test methods used in characterisation of blended cements and their scientific basis. Most studies that focus on understanding cement interaction with admixtures are limited to pastes and mortar samples and eliminate coarse aggregates in sample preparation. The exclusion of course aggregates in the mix advances the benefit of more homogeneous samples as reported by Scrivener et al., 2015, and by Alexander and Mindess, 2005, in their review of studies done by Richard and Cheyrezy, 1994, on reactive powder concretes.

The accuracy of these methods depends on the accuracy of models adopted to explain the hydration process (Scrivener et al., 2015) and the assumption that the composition of an SCM does not influence the hydration kinetics in ways other than through the pozzolanic reaction. Mechanisms such as the filler effect or dilution effect (discussed in Section 2.4.2 of the current chapter) introduce errors in results and require correction to minimize these errors. Scrivener et al., 2015, discusses different methods used to characterize reactivities of different SCMs and stresses the anomalies in determining pozzolanicity of different types of test materials. The author acknowledges the importance of the strength activity index as a more reliable indicator of performance of a pozzolanic material in Portland cement concrete. Moreover, Donatello, Tyrer and Cheeseman, 2010, compared three standard methods used to test pozzolanic activity, the saturated lime test, the Frattini test (EN 196-5) and the strength activity index test (ASTM C618, BS 3892). This study found the Frattini test to correlate with the strength activity index test and not with the saturated lime test.

Lothenbach and Winnefeld, 2006, Berodier, 2015, and others applied thermodynamic modelling to different cement systems based on hydration observations. These studies applied X-ray diffraction (XRD), scanning electron microscopy (SEM-EDX) and thermogravimetric analysis alongside isothermal conduction calorimetry to study clinker phase changes as hydration progressed.

Most of the experimental techniques require complementary tests if conclusive analyses about microstructure changes and hydration kinetics are to be made. The reaction kinetics observed by the different researchers and their conclusions are presented in Section 2.4 of the current chapter and have informed the analysis and discussion of experimental results generated in this work.

The different properties of cement constituents determine its overall performance. Whereas there is no single test method that can capture all the important properties of cement, different experimental procedures that test properties of cement constituents, pastes, mortars, and concretes as products exist. The following is a presentation and discussion of the different test methods that are of interest to the general scope of this study.

2.5.2.1 The strength activity index test method

Following the standard procedures for testing FA blended cements as described in ASTM C618, 2005, BS3892-1, 1997, and as discussed in Donatello, Tyrer and Cheeseman, 2010, the strength activity index offers a quantitative relationship between cement content and compressive strength at a specific period of curing. The strength activity index is calculated as a percentage ratio of the test sample (sample that has partially been replaced by test pozzolan) and the control sample. The calculated result is compared against the percentage replacement of the test sample for quantification of gain, assuming that an inert sample would produce a linear correlation with cement content in a sample. Evidence of non pozzolanic reaction mechanisms that influence cement hydration demand additional tests to make a conclusive judgment on the pozzolanic property of test pozzolans.

2.5.2.2 The Frattini Test method

The frattini test is a wet chemistry test method used to estimate the concentration of Ca^{2+} and OH^{-} ions present in a solution containing Portland cement and a test pozzolan cured for a specific period. The calculated concentration is analysed in relation to Ca^{2+} ionic concentration expected to saturate a solution of a similar PH (EN 196-5). It is expected that a pozzolanic reaction leads to Ca^{2+} ionic concentration

less than the saturation value for a hydrating cement system at a specific alkalinity (PH 12.5) for a standard curing period. Curing is done in an oven at a controlled temperature of 40ºC and for 8 or 15 days. The Frattini test method is based on the assumption that the Ca^{2+} ions are only contributed by the hydrating cement component of the test solution (Donatello, Tyrer and Cheeseman, 2010).

2.5.2.3Heat of hydration studies

The hydration of cement is discussed in section 2.1 of the current chapter. One of the two common approaches to hydration studies is based on measurements of rate and amount of heat generated by the hydration reaction. The reaction between cement constituents and water leads to a release of heat which is monitored as a proxy indicator in characterizing performance of a cementitious material. The main functional reason for heat of hydration studies is for quality control of concrete. Concrete is a composite material with constituents whose coefficients of thermal expansion are different. The extent of variability in the coefficient of thermal expansion of concrete constituents increases the possibility of high internal stresses and cracks that are associated with thermal stresses due to heat of hydration (Struble and Hawkins, 1994). This technique of calorimetry can also be used for comparative studies and to assess the effect of admixtures on hydration of cement. The key approaches to the study of hydration of Portland cements are mainly the chemical (ASTM C186), the instrumental techniques and chemical shrinkage measurement approaches.

The chemical method for heat of hydration estimation: The chemical method relies on subjecting a dry sample and a sample that has undergone hydration for a specific period of hydration (normally 7 and 28 days of hydration) to dissolution in either nitric acid or hydrofluoric acid (ASTM C186). The difference in the heats of solution between the unhydrated sample and a sample hydrated for a specific period is considered as the heat of hydration. The ASTM C186 presents the presence of some insoluble cement compounds as a possible source of error in estimation of the heats of hydration of cements when the chemical method is used.

Calorimetric methods for heat of hydration measurement: The instrumental techniques are based on calorimeters which are produced to different scales in capacity and sensitivity and differ in measurement techniques. The measurement techniques are either based on isothermal conduction calorimetry, semi-adiabatic or adiabatic calorimetry technique.

Isothermal conduction calorimetry is a constant temperature measurement where the heat released by a hydrating cement sample is removed from the sample and the sample is kept at a constant temperature. The heat released from the sample is compared against a reference sample, normally deionized water of matching heat capacity as the test sample (Berodier, 2015). Berodier Elise, in her PhD thesis, presents the relationship used to calculate the quantity of deionized water for the reference sample as follows.

$$M_{water-ref} = \frac{C_{p-paste}\ X\ M_{paste}}{C_{p-water}} \qquad \text{Equation 2.11}$$

Where: $M_{water-ref}$ is the mass of deionized water for reference sample

M_{paste} is the mass of paste

$C_{p-paste}$ is the specific heat capacity of the paste

$C_{p-water}$ is the specific heat capacity of water = 4.18 $J.g^{-1}.K^{-1}$

Thermogravimetric analysis (DTA/TGA) in heat of hydration measurement: The other approach relies on the different thermal analysis methods where changes in mass of hydrating cement is observed against time and controlled temperature increase through dehydration of gypsum, dehydroxylation of CH and decomposition of $CaCO_3$. The change in estimated hydration products with curing period is used to characterize reactivity of the cementitious materials, the hydration progression and hydration products.

2.5.2.4Chemical shrinkage as a method for cement hydration studies

The process of hydration involves consumption of the mixing water by the reactants leading to a progressive change in total volume of the mix as hydration goes on. The resulting hydrates are less in volume compared to the volume of reactants (cement phases, SCMs and water) (Helmuth, 1994). This is because the specific volume of water is reduced when it transitions from a liquid state and is bound with the cement compounds to form hydration products (Kocaba, Gallucci and Scrivener, 2012). A dilatometer that measures the change in specific volume of water as a result of conversion of reactants (water and cementitious materials) to hydrates is explained in Berodier, 2015, and Kocaba, Gallucci and Scrivener, 2012. The method is more adaptable to long term measurement in hydration studies than the calorimetry methods because the change in heat rate is too small to accurately be measured at later days of hydration (after 28 days). The experimental setup utilizes basic apparatus that is achievable in most laboratory conditions. Berodier, 2015, carried out a chemical shrinkage experiment using 5 grams of paste and an apparatus that included a 2cm diameter by 5cm height plastic container, ultrasonic bath, rubber stopper fitted with a 10ml pipette tube, syringe, and water bath. The ultrasonic bath was used in freeing bubbles from the sample. A rubber stopper fitted with a 10 ml pipette tube was fitted on the sample bottle to create an air and water-tight seal and to fill water to the graduation marks in the pipette tube. A syringe was used to introduce coloured oil on top of the water level in the pipette tube for easy observation of changes in the water level. The oil on top of the water level also served to stop water evaporation from the setup. The whole setup was placed in a water bath at a controlled temperature of 20 ºC. The experiment was run in triplicate for each sample for a period of six months.

Theoretical background

The hydration process between cement and water results into hydration products that are less in volume than the absolute volumes of the reactants. This change phenomenon is referred to as chemical shrinkage (Geiker and Knudsen, 1982; Wild, Khatib and Roose, 1998; Tazawa, Miyazawa and Kasai, 1995). Tazawa, Miyazawa

and Kasai, 1995, distinguishes chemical shrinkage also referred to as hardening shrinkage from autogenous shrinkage. While chemical shrinkage addresses stoichiometric changes due to reaction of cement phases with water, autogenous shrinkage is defined as a macroscopic change in cement paste or concrete dimensions at a fixed temperature and in closed boundary conditions where moisture is not exchanged through the boundary into or out of the concrete or paste (Tazawa, Miyazawa and Kasai, 1995). Both chemical shrinkage and autogenous shrinkage are important properties in cement hydration and exhibit similar trends and amounts up to the point when cement attains structural rigidity (Wild, Khatib and Roose, 1998). The modes of measurement of the two forms of shrinkage in pastes are different hence the two are studied differently.

Chemical shrinkage was first reported by Le Chatelier in 1901 (Geiker and Knudsen, 1982) and in his honor is also referred to in some literature as the Le Chatelier contraction (Mehta and Monteiro, 2006). Le Chatelier is reported to have observed a reduction in volume of cement paste placed under water in a glass beaker that had a glass tube connected to it to aid measurement (Geiker and Knudsen, 1982).

The chemical shrinkage phenomenon has been explained through stoichiometric quantification of volume parameters of reactants and hydration products in a cement-water system (Tazawa, Miyazawa, and Kasai, 1995; Mehta and Monteiro, 2006), the assumption being that the reduction in volume due to the consumption of water is the only cause of chemical shrinkage. Tazawa, Miyazawa, and Kasai, 1995, presents eight possible reaction paths (hydration equations) for a typical portland cement at ordinary temperature emphasizing the complexity in trying to model chemical shrinkage on the basis of stoichiometry for a constantly changing degree of hydration. It was observed in Tazawa, Miyazawa, and Kasai, 1995, that accurate predictions of chemical shrinkage can be made through stoichiometric calculations only if one has established the right hydration equations for the cement paste or concrete being investigated.

Whereas the chemical shrinkage phenomenon in cement hydration is associated with the consumption of free water, the pozzolanic reaction (Equation 2.12) does not involve free water.

$$3Ca(OH)_2 + 2SiO_2 \rightarrow 3CaO.2SiO_2.3H_2O \qquad \text{Equation 2.12}$$

The pozzolanic reaction (Equation 2.12) is a process of interaction between the calcium hydroxide (CH) precipitates from hydration of cement and the reactive silica component of a pozzolan. The pozzolanic reaction is therefore not considered to contribute to chemical shrinkage for long term observation in ideal conditions. Different studies have however revealed the presence of pozzolanic materials in cement paste to influence early hydration rate (Shannag and Yeginobali, 1995; Ballim and Graham, 2009; Kaid et al., 2010; Berodier and Scrivener, 2014; Berodier, 2015), self-desiccation (Wild, Khatib and Roose, 1998) and microstructure of hydration products (Mehta and Monteiro, 2006; Berodier, 2015), all factors that influence shrinkage measurement. Moreover, the presence of pozzolanic materials also influence the composition of the hydration products through non-pozzolanic reaction mechanisms that form high density reaction products (e.g., the reaction between aluminate phases and carbonates leading to formation of carboaluminates hydrates with higher density than the reactants) (Bouasker et al., 2008). Therefore, it is hypothesized that these influences should be detected through chemical shrinkage measurements.

2.5.2.5 Thermogravimetric analysis: Quantification of pozzolanic activity and degree of hydration

By heating a hydrating cement sample in a controlled environment and monitoring the change of mass with increase in temperature, one can have a fair estimation of composition of a sample. Thermogravimetric analysis (TGA) is an instrumental technique that applies temperature driven mass loss of a material to characterize the material properties by comparing the observed trends with thermal data of pure minerals that are considered present in the material. Certainly, following TGA procedures, it is possible to establish the changing composition of hydrating cement. When compared against reference samples, the reaction mechanisms in blended

cements are assessed, especially through stoiciometrically quantifying hydration products using chemically bound water as a proxy variable since the reactions are predominantly hydration reactions, but also by monitoring changes in the mineral phases of the test pozzolans from natural sources. The observed changes with test variables help in understanding the actual mechanisms of interaction between the test pozzolans and Portland cement and, as a result, quantification of the degree of hydration (α) and pozzolanic reaction (β).

Existing models used in prediction of the degree of hydration (α) of Portland cements are advanced by Bhatty (Bhatty, 1986) (Equation 2.13) and Pane and Hansen, 2005, (Equation 2.14) for the three TGA phase parameters, dehydration (Ldh), dihydroxylation (Ldx) and decarbonation (Ldc). Research has since focused on improvement of these models for applications in characterization of artificial pozzolans (Fly ash and GGBS) (Mounanga, 2011; Deboucha et al, 2017) and no applications could be established for natural pozzolans. The present work focused on testing the existing models on their responsiveness to the TGA data generated in the works of this thesis. Modified models that characterize the stoichiometric interactions of test pozzolans in hydrating cement systems are advanced. The new models are tested against chemical shrinkage, heat of hydration and strength data for validation.

Bhatty, 1985: $W_B = Ldh + Ldx + 0.41(Ldc)$, $\alpha = \frac{W_B}{0.24}$ Equation 2.13

Where 0.41 is a correction factor addressing water lost in the carbonation reaction of CH in the hydrating cement paste system while 0.24 represents the theoretical chemically bound water at infinite time of hydration.

Pane and Hansen, 2005:

$W_B = Ldh + Ldx + (Ldc - Ldc_a), \quad \alpha = \frac{W_B}{W_{B\infty}}$ Equation 2.14

Where, Ldc_a is the mass loss due to decarbonation and $W_{B\infty}$ is weight loss at infinite time of curing.

It is expected that the $Ca(OH)_2$ content in pastes blended with pozzolanic materials will reduce with time while that of the control sample increases. This is due to the pozzolanic reaction that consumes the $Ca(OH)_2$ precipitate from the hydration of silicate phases in Portland cement.

2.5.2.6X-ray diffraction

X-ray diffraction (XRD) is a common instrumental technique applied in identification of crystalline mineral phases of inorganic compounds. The XRD generates skins with pattern characteristics that are specific to crystalline phases following Bragg's law (Equation 2.15) (Ramachandran, 2001).

$$n\lambda = 2dSin\theta \qquad \text{Equation 2.15}$$

Where n represents a positive integer, λ wavelength of the incident wave, d is the characteristic distance between the crystallographic planes, and θ the angle of incidence of the X-rays. By comparing XRD patterns with databases of known crystalline phases as compiled in the Inorganic Crystal Structure Database (ICSD), complemented by preliminary knowledge of test material and instrument parameters, test samples are characterized for their mineralogical composition. XRD technique was applied in characterisation of the mineralogy of carbonatites and kamafugites and in the identification of hydration phases and reactive mineral phases of anhydrous cement systems.

2.6 The degree of hydration of blended cement

Results of this study and published literature (Escalante-Garcia, 2003; Ballim and Graham, 2009; Berodier and Scrivener, 2014; Scrivener et al., 2015), both, show SCMs to influence Portland cement paste hydration in ways beyond what can be characterized as pozzolanic reactions. SCMs must therefore be characterized for their combined influence and not necessarily for the pozzolanic performance. One such method of characterizing blended cement is by tracking the influence of SCMs on the rate of formation and deposition of characteristic hydration products in blended cement paste systems (Bhatty and Reid, 1985; Bhatty, 1986; Pane and Hansen, 2005; Kocaba, Gallucci and Scrivener, 2012; Monteagudo et al., 2014;

Deboucha et al., 2017). The degree of hydration, a parameter that characterizes the content of a cement paste system that has undergone hydration at a specific time from the start of hydration (Pang et al., 2013), engenders comparative analysis of SCM blended Portland cement systems (Kocaba, Gallucci and Scrivener, 2012; Monteagudo et al., 2014; Deboucha et al., 2017).

Different tools are applied in quantification of degree of hydration and pozzolanic performance, all exhibiting varying levels of reliability (Ramachandran, 1979; Taylor, 1997; Kocaba, Gallucci and Scrivener, 2012). These include scanning electron microscopy (SEM-BSE)-image analysis, chemical shrinkage, calorimetry, chemical extraction, conductometric titration, X-Ray diffraction, strength activity index (SAI) and thermogravimetric/differential thermal analysis (TGA/DTG). As presented in Neville, 1996, the methods are established in measurement of cement paste properties that include heat of hydration, quantity of calcium hydroxide precipitate, non-evaporable water in hydrating cement paste, anhydrous cement in the paste matrix, compressive strength, specific gravity of hydration paste and the volume of hydration products etc. The degree of hydration (α) is a quantitative expression in a form of a percentage ratio of a quantifiable cement paste property at a given time to the cement property at complete hydration (infinite time), as shown in Equation 2.16 (Bhatty, 1986).

$$\alpha = \frac{\mathrm{H_t}}{\mathrm{H_\infty}} \qquad \text{Equation 2.16}$$

Where, H_t and H_∞ represent the measured paste property at a specified time and at complete hydration (infinite time) respectively.

Reviews of the performance of cement paste characterisation methods provided in Ramachandran, 1979, in Ramachandran, 2002, in Kocaba, Gallucci and Scrivener, 2012, in Pang et al., 2013 and later in Deboucha et al., 2017, advance the TGA/DTG as a favorable method for its ease of use, high value results output and short time of experiment. Moreover, TGA/DTG is a well developed and tested tool for estimation of cement hydration products, characterisation of hydration kinetics and determination of hydrates composition of cement paste systems (EI-Jazairi and lllston, 1977; Fordham and Smalley, 1985; Ramachandran, 2002; Lothenbach and

Wieland, 2006; Monteagudo et al., 2014; Deboucha et al., 2017). The method aids estimation of chemically bound water in hydrating cement systems which is then used in stoichiometric quantification of the assumed hydration products or as a relative value to characterize the extent of consumption of reactants in a hydration reaction.

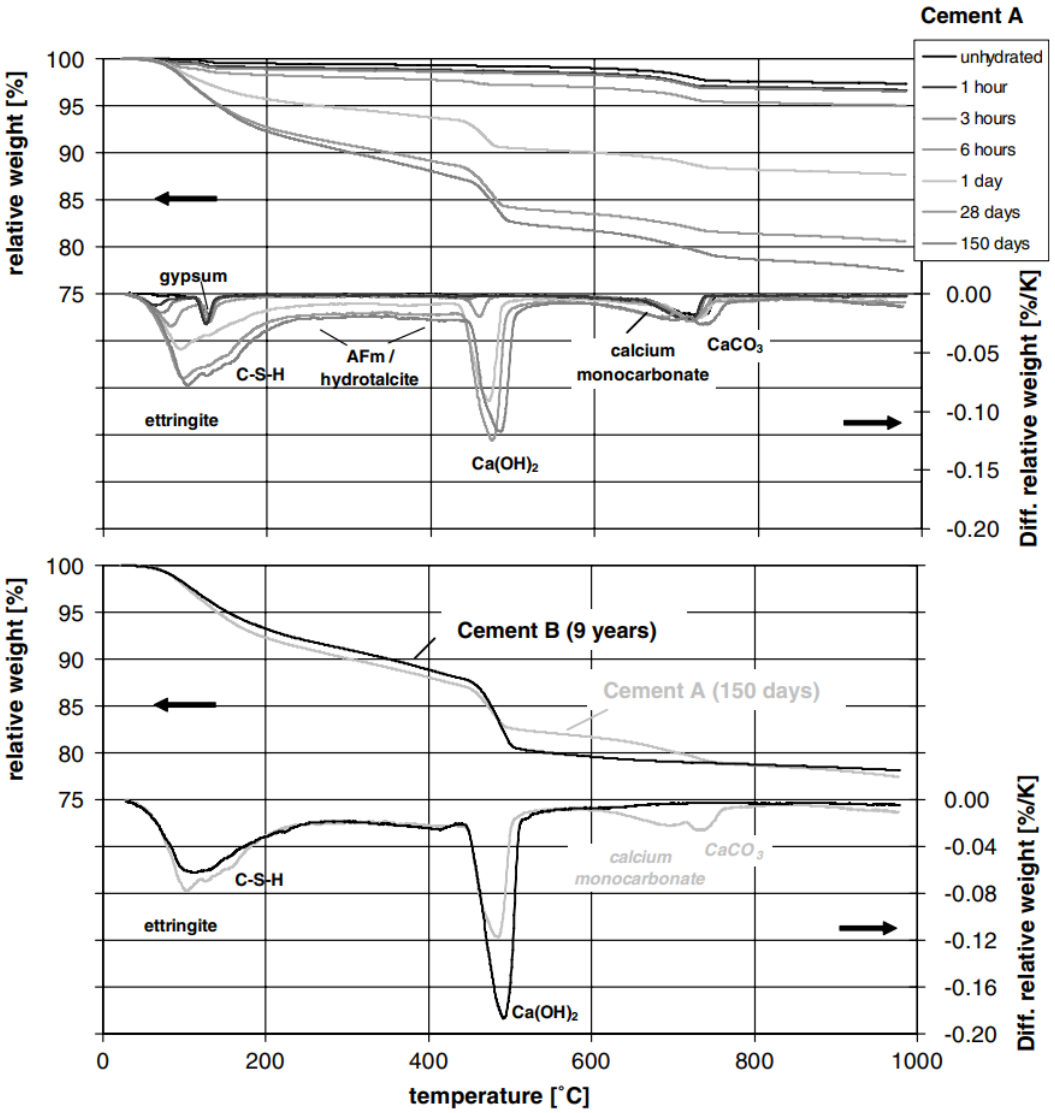

Figure 2.6: TGA/DTG of a hydrating cement showing changes in hydration products with time up to 150 days (Lothenbach and Wieland, 2006).

Typical results of TGA are presented in a form of a mass loss vs temperature graph, and its first derivative as the DTG graph as shown in Figure 2.6. The graph shows three endothermic peak zones representing dehydration (Ldh), dehydroxylation

(Ldx) and decarbonation (Ldc) phases at temperature ranges of 105°C-400°C, 400°C-600°C, and 600°C-850°C respectively (Monteagudo et al., 2014; Deboucha et al., 2017). Through observation of the changes in the 1st derivative curves (DTG) with varying parameters of cement paste, consideration can be made for the type of hydration products present and how these products are changing with time, replacement level, composition, fineness and other properties. The 1st derivative curves are therefore applied in estimation of CH consumption, characterisation of hydration products and changes in the carbonate phases against the parameters studied. Works by Taylor, 1997, Ramachandran et al., 2002, Hewlett, 2004, Gabrovšek, Vuk and Kaučič ,2006, Lothenbach et al., 2008, and others show decomposition temperatures of different cement phases in the following ranges.

100-130°C	Loss of adsorbed water
115-125°C	Decomposition of C-S-H phases
120-130°C	Decomposition of ettringite phases
130-250C	Decomposition of monocarbonate, monosulfate
180-200°C	Decomposition of AFm/Hydrotalcite phases
400-600°C	Decomposition of CH
600-800°C	Calcination (decomposition of carbonates)

Lothenbach and Wieland, 2006, further characterize the calcination phase of cement paste to indicate presence of a monocarbonate phase as a broad peak appearing between 550°C and 680°C with calcite decomposition reaching 800°C. More so, Mehta and Monteiro, 2001 put an estimate of 50-60% of hydrated cement paste microstructure to C-S-H, 20-25% to CH, and 15-20% to the hydrated aluminate phases, a small percentage remaining to cover voids and anhydrous cement particles. It is therefore considered that the important hydrates in the dehydration (Ldh) zone are C-S-H and the aluminate phases. It is also considered that the dehydroxylation (Ldx) and the decarbonation (Ldc) phases of cement samples are

distinct and do not overlap. The TGA can therefore be applied in hydration products characterisation and quantification of the degree of hydration of Portland cements.

2.6.1 Numerical models in determination of the degree of hydration

A substantial amount of work has been done in modeling degree of hydration of mineral admixed Portland cement using TGA/DTG as a tool (El-Jazairi and Illston, 1977; Bhatty, 1986; Marsh and Day, 1987; Mounanga, 2004; Pane and Hansen, 2005; Gabrovšek, Vuk and Kaučič, 2006; Monteagudo et al., 2014; Deboucha et al., 2017). The models focus on cumulative addition of the chemically bound water in the dehydration (Ldh), dehydroxylation (Ldx) and decarbonation (Ldc) phases of the TGA decomposition profiles as an indicator of hydration progression. The reviewed models are discussed below.

2.6.1.1Bhatty-El-Jazairi-Illston model.

A significant contribution to numerical characterization of degree of hydration of portland cement using TGA/DTG data was first published by El-Jazairi and Illston, 1977. Bhatty, 1985, applied the El-Jazairi-Illston quantitative expressions of chemically bound water in a hydrating cement paste to study cements made with mine tailings, though, some published works (Monteagudo et al., 2014; Deboucha et al., 2017) wrongly associate the initial works to Bhatty, 1985. To calculate the non-evaporable water in hydrating cement paste, El-Jazairi and Illston proposed a quantitative expression stated in Equation 2.17. Bhatty applied El-Jazairi-Illston equation and proposed Equation 2.18 to calculate the degree of hydration as follows;

$$\mathrm{W_B} = \mathrm{Ldh} + \mathrm{Ldx} + 0.41(\mathrm{Ldc}) \qquad \text{Equation 2.17}$$

$$\alpha = \frac{\mathrm{W_B}}{0.24} \qquad \text{Equation 2.18}$$

Where, W_B represents the mass loss due to decomposition of chemically bound water in a hydrating cement paste at a given stage of hydration. Ldh, Ldx, and Ldc are respectively the mass losses due to the dehydration, dehydroxylation and decarbonation phases of decomposition. The value 0.24 is considered as the amount of chemically bound water required for complete hydration of cement

following Bogue's formula. α represents the degree of hydration. The value 0.41 in Equation 2.17 is a stoichiometric coefficient that accounts for the water lost by the CH phase in the carbonation reaction (Equation 2.19) calculated from the CH-Carbonate stoichiometric relationship.

$$\mathrm{Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O} \qquad \text{Equation 2.19}$$

$$\mathrm{CaCO_3 \rightarrow CaO + CO_2} \qquad \text{Equation 2.20}$$

$$\mathrm{W_{Carbonation\ H_2O}} = \frac{\mathrm{M_{H_2O}}}{\mathrm{M_{CO_2}}} = 0.41 \qquad \text{Equation 2.21}$$

Where, M_{H_2O} and M_{CO_2} are the molar masses of water and carbon dioxide respectively.

El-Jazairi and lllston, 1977, used the residual weight after ignition to 1007 °C as their base weight in their percentage calculations which would give an inflated value than actual measurable proportions.

Though they used the more sensitive semi-isothermal thermogravimetric technique, other authors have used dynamic thermogravimetry with differential thermal analysis to advance plausible results (Fordham and Smalley, 1985).

The Bhatty-El-Jazairi-Illston model assumes a zero carbonate content at anhydrous state. All detected carbonates are assumed to be as a result of carbonation of the CH in the hydrating cement paste (Pane and Hansen, 2005).

The model also assumes that all the hydrates in a cement paste contribute to its properties in a linear and cumulative manner and respond identically to external factors and secondary influences on reaction rates (e.g. carbonation rates and the use of admixtures).

2.6.1.2Pane and Hansen model.

Pane and Hansen, 2005, proposed modifications to the El-Jazairi and Illston, 1977, and Bhatty, 1985, quantitative expressions as follows.

$$\mathrm{W_B = Ldh + Ldx + Ldc - Ldc_a} \qquad \text{Equation 2.22}$$

$$\alpha = \frac{W_B}{W_{B\infty}}$$ Equation 2.23

Where, Ldc_a is the mass loss due to decarbonation at anhydrous state and $W_{B\infty}$ is the chemically bound water at infinite time (at complete hydration of cement). Pane and Hansen, 2005, recognized a need to offset the carbonates at anhydrous state of a cement. The work also recognized that the chemically bound water at complete hydration changes with cement type and the quantity of mineral admixtures.

Pane and Hansen, 2005, however, did not consider the stoichiometric conversion coefficient that converts the weight loss due to decarbonation to the equivalent CH bound water, though their model further reinforces the assumptions made by the Bhatty-El-Jazairi-Illston model.

2.6.1.3Monteagudo model

Monteagudo et al., 2014, built on the works by El-Jazairi and Illston, 1977, Bhatty, 1985, and Pane and Hansen, 2005, with the following modifications to the quantification of the degree of hydration of blended Portland cement.

$$W_B = Ldh + Ldx + 0.41(Ldc - Ldc_a),$$ Equation 2.24

$$W_B = \frac{W_{B\infty} \times t}{t+k}$$ Equation 2.25

Monteagudo modified the Pane and Hansen's equation to include the 0.41 stoichiometric coefficient for correction of decarbonation weight to equivalent water lost in the CH carbonation reaction. The works further proposed a method for estimation of chemically bound water at complete hydration of cement (Equation 2.25) based on the Michaelis and Menten equation. Michaelis and Menten kinetic theory of enzyme action guides on reaction velocity on the basis of reactants concentration and a constant enzyme substrate. The parameter t represents curing time for cement hydration in hours and k is a constant.

Monteagudo's experimental study had an inconsistent setup. The TGA results of the control sample (Figure 2.7) at anhydrous state showed a substantial mass loss to decarbonation which informs that the ordinary Portland cement (OPC) control

sample used was not a CEM I 42.5N as reported in the results. The results analysis does not show any correction for the high carbonates content at anhydrous state which has a consequence of overestimation of the chemically bound water in the hydrating cement paste. Indeed, Monteagudo et al., 2014, report degree of hydration results for paste samples at 90 days of curing in excess of 100%.

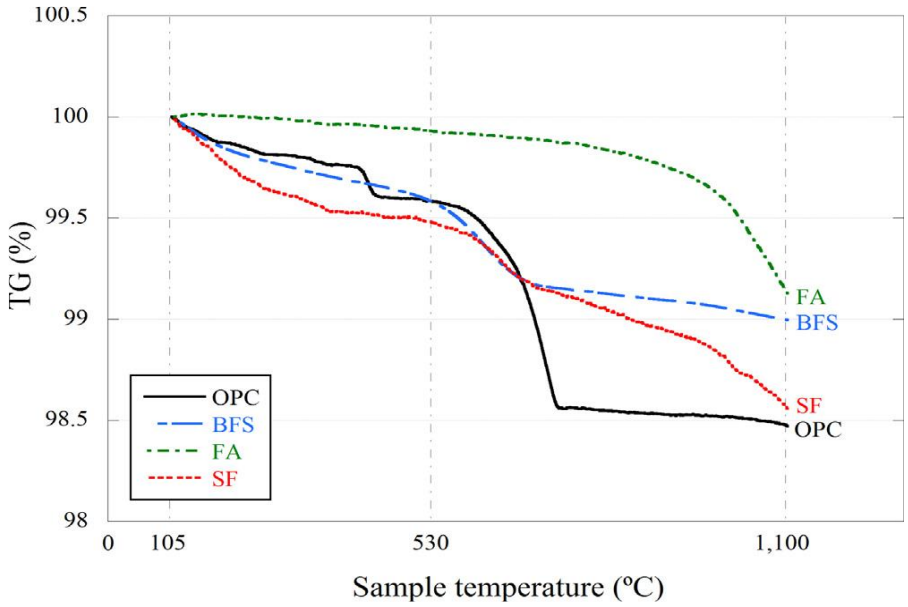

Figure 2.7: TGA curves of anhydrous samples used in Monteagudo et al., 2014.

The model also reinforces the assumptions made by Bhatty-El-Jazairi-Illston model.

2.6.1.4Mounanga- Deboucha model

Deboucha et al., 2017 reviewed previous models and promoted the Mounanga model (Mounanga, 2004) to offer a more reliable approach in quantification of the degree of hydration. The model is also established on the fundamental principles of the El-Jazairi and Illston, 1977, and Bhatty, 1985, models with modifications in quantifications as follows.

$$W_B = Ldt - Ldc + m_d - m_c \times LOI_c \qquad \text{Equation 2.26}$$

$$\propto = \frac{W_B}{W_{B\infty} \times m_c} \qquad \text{Equation 2.27}$$

Where Ldt is the mass loss between 140°C and 1100°C, Ldc is the mass loss due to decarbonation phase, m_d represents a measurement recorded when the TGA is

run with no sample loaded in the sample holder, the device drift, m_c the mass of anhydrous cement in the test sample, and LOI_c the loss on ignition of the anhydrous cement contained in the sample.

Deboucha et al., 2017, used non-normalized data that could not have enabled them to perform a comparative analysis of results.

The model also reinforces the assumptions made by El-Jazairi and Illston, 1977, and Bhatty, 1985.

The works on TGA/DTG characterisation of blended cements above all advance the degree of hydration (α) as a simplified parameter in tracking compositional, physical and exposure factors that control reaction kinetics and cement paste microstructure development. The works are established in TGA studies on cement pastes done by EI-Jazairi and lllston, 1977, and Fordham and Smalley, 1985, and reviews by Ramachandran, 2002. The models however present some non-universal assumptions and exhibit some gaps in knowledge that are discussed below.

a) The previous models relied on other important properties of concrete such as strength, heat of hydration and chemical shrinkage to correlate for validation, but this is misleading as not all hydration mechanisms in cement contribute cumulatively and in equal proportion to the development of the important concrete properties. For example, the silicate phases are reported to represent 50-60% of the total hydration products and to dominate the strength budget of cement paste while the CH precipitate has negligible effects on paste strength (Papadakis, 1999; Mehta and Monteiro, 2001). Considering CH as a cumulative contributor to the degree of hydration wrongly assumes the different phases to have a linear trend with equal influence on the hydrating cement paste properties.

b) The CH consumption by the pozzolanic, aluminate and sulphate phases in cement (Popovic, 1998; Toropovs et al., 2014; Kim and Olek, 2012), and carbonation reactions (Kim and Olek, 2012) is not clearly quantified by the previous models that treat the CH phase as a cumulative contributor to the degree of hydration. The models, therefore, are not able to quantify pozzolanic and other admixture benefits that are important for characterisation of SCMs.

c) As observed in published works, research has since focused on modifying the El-Jazairi and Illston, 1977, and the Bhatty, 1985, models for applications in characterisation of artificial pozzolans (Fly ash and GGBS) (Mounanga, 2004; Monteagudo et al., 2014; Deboucha et al., 2017) and no studies on its application in natural pozzolans characterisation could be established.

The degree of hydration is affected by a number of factors that include physical properties of the materials (fineness, shape and surface characteristics, mix proportions, water cement ratio etc) (Merzouki et al, 2013), chemical properties (amorphous content, soluble elements etc) (Ramachandran, 2002), exposure factors (curing temperature, age etc) (Escalante-Garcia, 2003) and experimental variables (sample preparation, testing and results interpretation) (Kim and Olek, 2012). The current study reviewed changes associated with kamafugites and carbonatites as SCMs in Portland cement on the basis of these variables.

Kamafugites and carbonatitic tuffs, though not common natural pozzolans, are the main option for supplementary cementitious materials in regions surrounding the Western part of the East African Rift valley system. The tuffs are silica undersaturated, carbonatitic and largely ultrapotassic. Milled in two fineness levels, the test pozzolans are characterized for composition of reactive compounds and process effects. It is considered that the test pozzolans present multiple effects on hydrating Portland cement in equal importance to the most common pozzolanic reactions. The current study prefers the degree of hydration (α), the degree of pozzolanic performance (β) and the net SCM benefit (λ) as three parameters that integrate all effects of mineral admixtures in Portland cement paste systems. The present work, therefore, applied TGA/DTG data in developing quantitative expressions that can be applied to characterize the three parameters above.

2.7 Summary and gaps in literature

Relevant literature on compositional characteristics of SCMs and how they’re likely to affect hydration activity, hydration products development and strength development of Portland cement concrete has been reviewed. The literature review gave importance to SCMs of natural origin, specifically natural pozzolans.

Regardless of all the gaps in literature about their behavior in concrete and mortars, their historic role as SCMs in hydraulic mortars still present natural pozzolans as viable SCM materials especially in regions that lack sufficient supply of more reactive industrial waste. Moreover, the absence of highly pozzolanic industrial waste in the study area limits the options to only kamafugites and carbonatites. This thesis addresses the role of compositional properties of kamafugites and carbonatites on pozzolanic activity, effect on hydration activity, strength development and hydration products development of blended Portland cements. The role of carbonates and alkalis in the kamafugites and carbonatites on hydration activity, hydration products development, strength development and chemical shrinkage has been studied. There was no published literature on the application of these materials as SCMs in Portland cement concrete. While SCMs in Portland cement paste advance modifications that go beyond pozzolanic reactions, existing characterisation methods do not separate their pozzolanic contribution from other mechanisms in blended cement that are non-pozzolanic. Reviewed numerical models were found inadequate in characterizing SCM effects in Portland cement systems. New theoretical models have been developed and experimental results applied in testing these models that are considered best placed to characterise the effects of SCMs on hydrating blended Portland cements that go beyond just the pozzolanic activity.

CHAPTER 3

MATERIALS USED AND THEIR CHARACTERISATION

3.1 General

This chapter presents the materials used in this study and their characteristics. It presents results on and discusses the compositional and physical properties of kamafugites and carbonatites that are important for their characterisation as SCMs in Portland cement concrete. The physical properties relate to the physical occurrence of the SCMs, their particle morphology, and particle size distribution. The compositional parameters relate to the mineralogy and elemental and chemical oxide composition of the kamafugites and carbonatites. The compositional properties of kamafugites and carbonatites were studied following the experimental plan summaried in Figure 3.1 and further presented in detail in the current chapter.

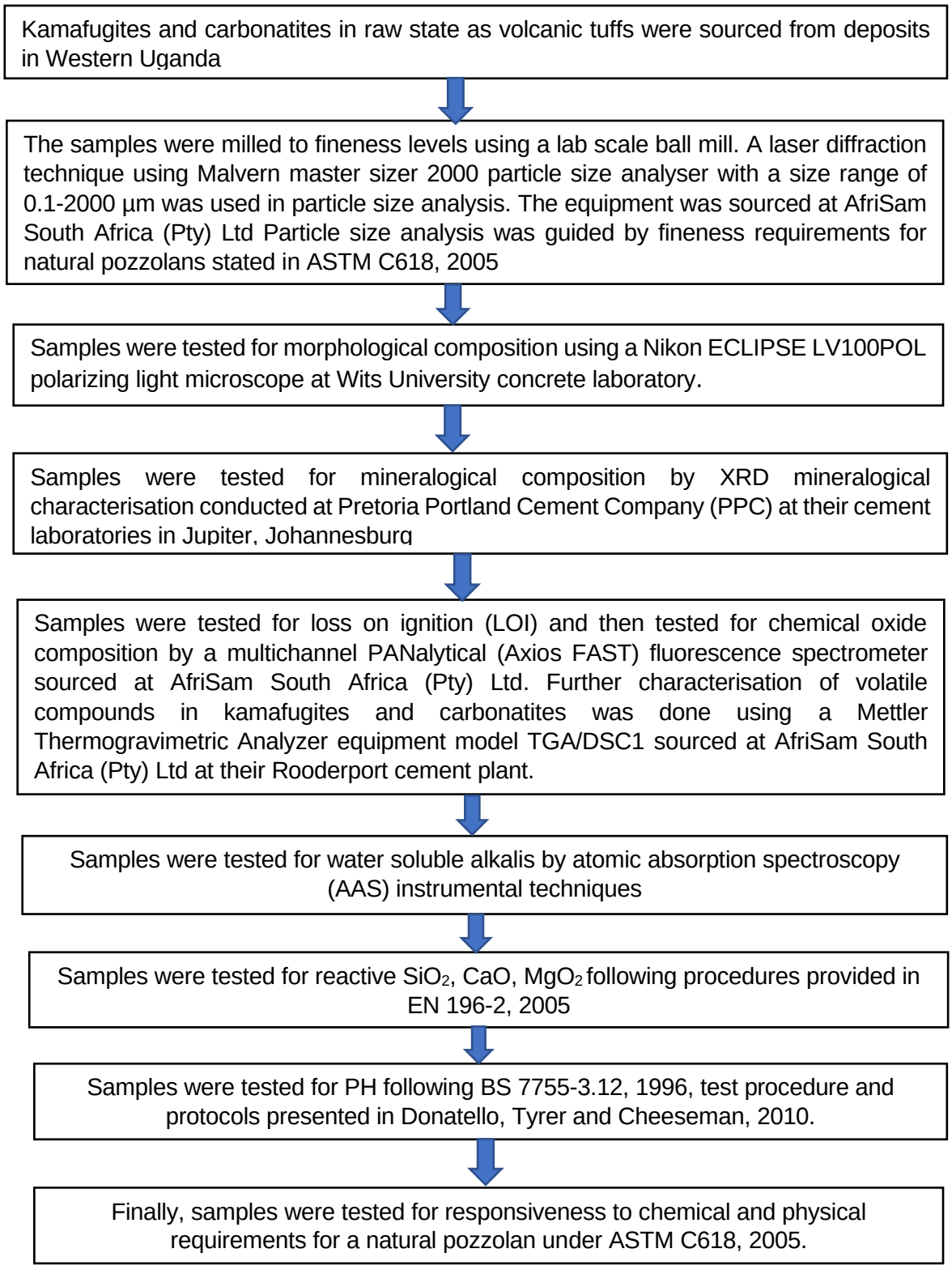

Figure 3.1: A flow diagram showing the experimental processes followed in characterizing the composition of kamafugites and carbonatites

3.2 Materials used

3.2.1 Kamafugites and carbonatites

Three samples of volcanic rocks were sourced from deposits in Toro-Ankole geological region of the East African rift system. Sample 1 (Poz-1), a carbonatite, was sourced from Fort Portal while Samples 2 and 3 (Poz-2 and Poz-3 respectively), both kamafugites, were sourced from Katwe-Kikorongo and Kataara-Rubirizi deposits respectively. The samples appear as layered tuffs (Figures 3.2, 3.3 and 3.4), due to fractional crystallization (Guo, Niu, and Yu, 2014) and multiple lava flow events.

Collection of the kamafugite and carbonatite samples from their deposits: Field work to the three major deposits, Fort Portal, Katwe-Kikorongo, and Kataara-Rubirizi, in Toro-Ankole geological series was conducted in August 2014. At the time of the field work, the deposits were all active with mining processes for a cement plant in the region. Samples, each approximately 30 kilograms, were taken from the lots already reduced in size and stockpiled waiting for transportation to a cement plant.

Carbonatites (Poz-1): The Fort Portal deposits are scattered over a wide area and are characteristically shallow. A sample was picked at a quarry located about GPS coordinates 0º41’36”N 30º16’52”E in the north of the Toro-Ankole series (Figure 2.3(b) on page 2-12 and Figure 2.4 on page 2-14 of Chapter 2). The deposits are exclusively composed of extrusive calcio-carbonatites. These deposits were studied by Baker and Nixon, 1989, and are found to have about 50 eruption points, a distinctive lava deposit from one eruption point in the west covering an area of about 0.3 km^2 and varying thicknesses from one meter to five meters. The tuffs generally have five distinct layers, some of which are vesicular indicating rapid cooling of lava with entrapped air (Figure 3.2(a)). The layers, also, indicate that the volcanic events that led to the deposition occurred over different times. The layers are locally referred to as Baheka-1, Baheka-2, Kinyaburo, Karambi and Ekisenyu according to the occurrence of the tuff layers from the surface up to the bottom of the tuff. Ekisenyu refers to a sandy medium as the last layer settles on a coarse sand material. The mineralogy is predominantly calcite, spurite, gehlenite, reinhardbraunsite, rosenhahnite, olivine, monticellite, phlogopite, clinopyroxene, periclase, perovskite, and hydrous calcium silicates (Baker and Nixon,

1989). The alkali content of the carbonatites is very low, a condition Baker and Nixon, 1989, attribute to calcite enrichment. These tuffs are also silica undersaturated because of calcite enrichment (Wyllie and Huange, 1976). The tuffs are covered by vegetable/black soil of an average depth of 1 meter.

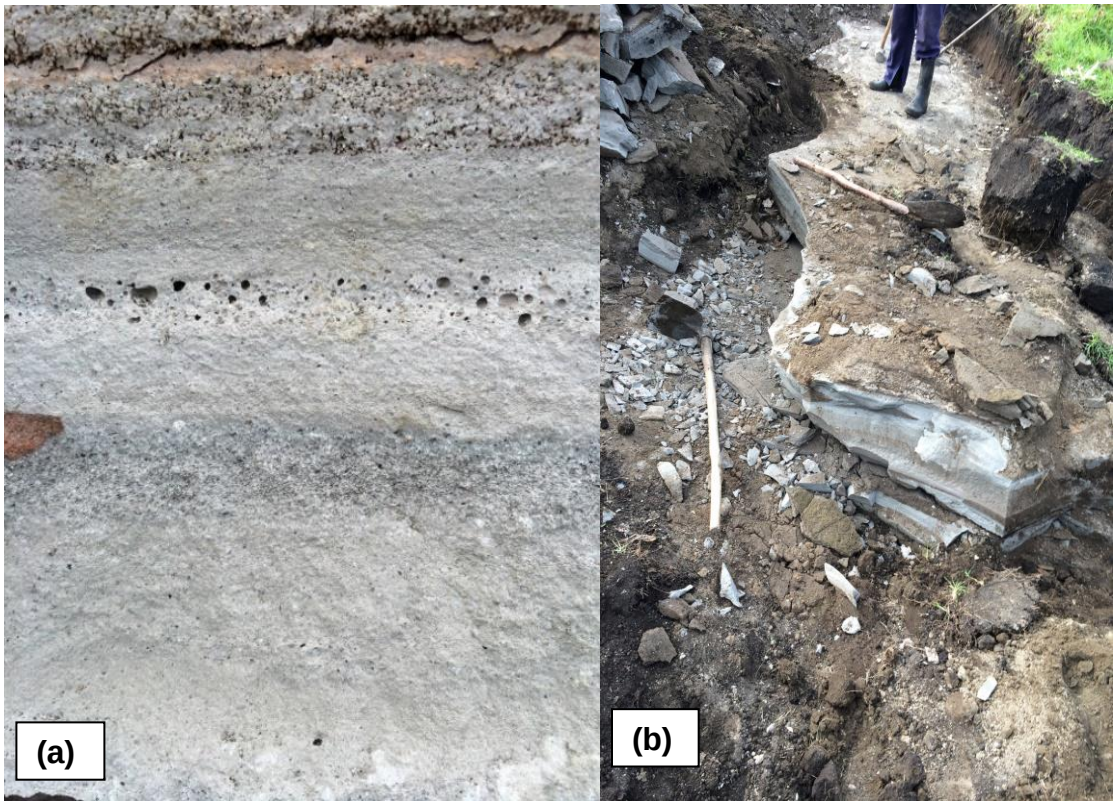

Figure 3.2: Photographs showing the occurrence of the Fort Portal tuff; (a) is an enlarged part of the vertical section (approx. 600mm high) showing the tuff to be layered, one of the layers is vesicular indicating a magmatic flow that had entrapped gasses as it cooled rapidly; (b) shows the location of a deposit in the ground.

Katwe-Kikorongo kamafugites (Poz-2): The volcanic materials of Katwe-Kikorongo (Figure 3.3) are classified Kamafugites. Located around GPS coordinates 0º0'50"S 29º53'46"E, 80 km in the south of Fort Portal deposits (Figure 2.4 on page 2-14 of Chapter 2), the materials appear both as tuffs and ashes. The deposits of Katwe-Kikorongo are in a game reserve, Queen Elizabeth National Park. The materials are relatively high in carbonatite composition, the carbonates being calcite and, to a less extent, dolomite (Stoppa et al., 2000). The materials are potassium enriched, silica undersaturated and with slightly lower carbonate content than that of Fort Portal deposits. Tappe, Foley, and Pearson, 2003, present olivine, pyroxene, and leucite as

primary minerals while Stoppa et al., 2000, established depositions of lapilli that are predominantly carbonatitic. These deposits are parked in layers with deposits averaging about 3 meters in depth. A review of literature (Lloyd et al., 1991) shows the volume combination of the deposits in katwe-Kikorongo with the Kataara-Rubirizi (described in the next section) deposits sum up to about 63 km^3.

Figure 3.3: Photographs showing the occurrence of the Katwe-Kikorongo deposits.

Kataara-Rubirizi Kamafugites (Poz-3); Kataara-Rubirizi lava deposits (Figure 3.4) are located approximately 0º14’35”S 30º4’54”E and are to the east of the Katwe-Kikorongo deposits (Figure 2.4 on page 2-14 of Chapter 2). The deposits are relatively higher in silica content and are ultrapotassic. Because of their high silica content, their carbonate content is much lower compared to that of Katwe-Kikorongo and Fort Portal deposits. They are part of the kamafugite family and are polymineralic containing olivine, pyroxene and kalsilite as primary minerals (Tappe, Foley, and Pearson, 2003). The materials are layered clearly showing the identity of different volcanic events that led to depositions. The lava deposits are bomb deposits that were ejected from craters that are out of proximity.

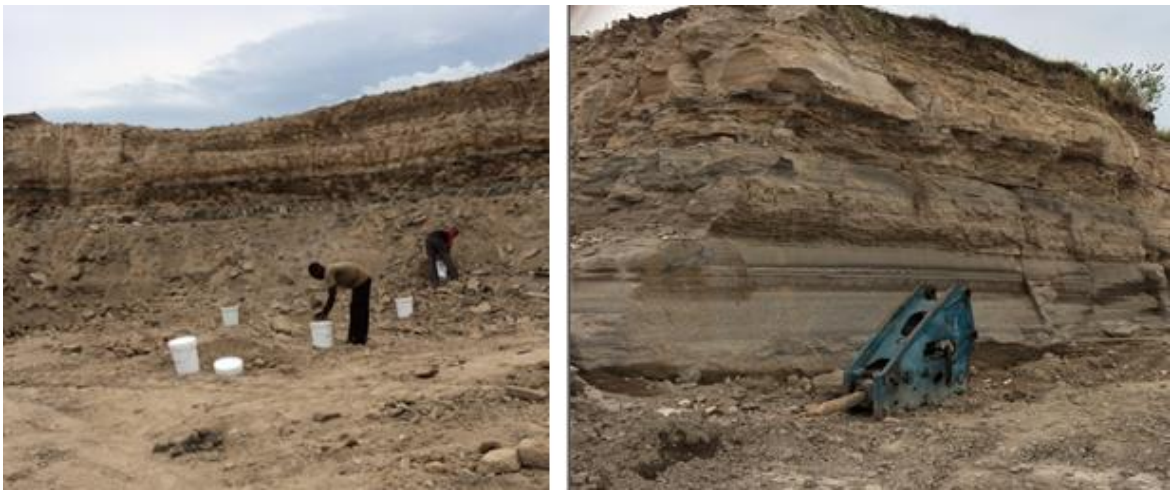

Figure 3.4: Photographs showing the occurrence of the Kataara-Rubirizi deposit.

Different studies on kamafugites and carbonatites are established in geological literature domain. These studies do not characterize the materials as SCMs for application in Portland cement. The materials are reported polymineralic and with deposit specific composition. The silica undersaturated carbonatitic nature of the Fort Portal and Katwe-Kikorong deposits and the ultrapotassic nature of kataara-Rubirizi and Katwe-Kikorongo deposits are unique compositional features of these volcanic materials that create interest in the study of their performance as SCMs in Portland cement production.

3.2.2 Portland cement

For preparation of control samples, activation of pozzolanic reactions and evaluation of the natural pozzolans’ influence on the physical, chemical, and mechanical properties

of Portland cement systems, plain Portland cement, CEM I 52.5 R was used. A single bulk sample of 50 kgs was taken alongside the normal daily mill clinker sampling routine at Afrisam (South Africa)(Pty) Ltd Rooderport cement factory. The mill clinker had been blended with gypsum at the time of milling and it met EN 197-1 standards for CEM I 52.5R. The sample was stored in an airtight plastic container that was carefully handled to avoid contamination or deterioration.

3.2.3 Slagcem

The choice of slagcem was considered after noticing that the kamafugites and carbonatites had their calcium and silica percentage oxide compositions in the ranges similarity to those of ground granulated blast furnace slag (GGBS). Slagcem is a blend of mill clinker and GGBS. The GGBS comes from milling iron slag. The rapid cooling of molten slag, a nonmetallic byproduct in the formation of pig iron leads to formation of a highly glassy material that can react with water to form cementitious products. Because of its ability to react with water, this material is considered as a latent hydraulic material since its reaction rate is very slow compared to cement. Addition of cement to the slag activates the reaction rate and the slag is therefore used as a blend with Portland cement in varying proportions. For reference purposes in the study of heat of hydration progression of the kamafugites and carbonatites blended Portland cement, slagcem was used as a second control in isothermal conduction calorimetry studies. The cementitious material was a blend of 35% slag and 65% CEM I 52.5 R.

3.2.4 Fly Ash (FA)

Fly ash is a known pozzolan that is a by-product of coal combustion mainly in coalfired power plants. It has a historical record of significantly mitigating technical and environmental concerns associated with Portland cement when used as a low-cost cement partial replacement material. ASTM C311, 2002, presents a pozzolanic activity test method that groups class F fly ash together with natural pozzolans and, because of this association, class F fly ash sourced from Ash resources (Pty) Ltd in Johannesburg, South Africa, and conforming to SABS 1491: Part 2, 1989, was used as a second control in strength activity index (SAI) and chemical shrinkage characterisation experiments.

3.2.5 Sand

Standard sand according to EN 196-1, 2005, was used in preparation of mortar prisms. The standard sand provided at Afrisam (South Africa) (Pty) Ltd cement laboratories at Rooderport was imported from France and came pre-weighed and prepackaged in plastic bags, each weighing 1,350 ±5 grams. The sand was stored under dry conditions and no moisture was introduced in the sand until the time of its use in mortar preparation.

Andesite sand stocked at Wits University concrete laboratories was used in the chemical shrinkage experiments.

3.2.6 Water

Distilled water was used in preparation of samples for setting time, Chemical shrinkage, XRD, and TGA. Distilled and de-ionized water was used in the Frattini test for pozzolanicity (EN 196-5, 2005) and heat of hydration tests. Potable water from a tap was used in mortar mixes for the strength activity index (SAI) studies. The potable water tap installed in the curing room at Afrisam (South Africa) (Pty) Ltd cement laboratories at Rooderport is set up to maintain the water temperature to that of the curing room (20 ±1 ^{o}C) hence eliminating possible variations in samples due to differences in water temperatures.

3.3 Physical and morphological properties of kamafugites and carbonatites

3.3.1 Particle size distribution of kamafugites and carbonatites

1. Preparation of kamafugites and carbonatites

The kamafugites and carbonatites studied in the current work appear in their natural geological state as layered tuffs, some due to fractional crystallization (Guo, Niu, and Yu 2014) or multiple lava flow events. Therefore, there was a requirement to mill them to levels of fineness to facilitate reactivity with cement hydrates. The samples were subjected to jaw crushing at the Entebbe Geological Surveys mineral dressing laboratory in Uganda and then packed for shipping from Uganda to the Witwatersrand University Civil Engineering laboratory in Johannesburg, South Africa. 15 kilograms of

each of the three samples were separated and milled to desired finesses using a lab scale ball mill provided by Afrisam (South Africa)(Pty) Ltd at their Vanderbijlpark cement plant.

2. Measurement of particle size distribution

A laser diffraction technique using Malvern master sizer 2000 particle size analyzer with a size range of 0.1-2000 µm was employed in particle size analysis. The particle size analyzer used in this study had its optical constants (refractive index real and imaginary components) preset and locked for general quality control of cement at the Afrisam (South Africa) (Pty)Ltd Rooderport cement plant. The preset conditions that were standardized for composite refractive index of cement applied for all the fine powders used in this study. This assumption, of course, presents deviations in the particles that lie in the d_{10} region for the natural pozzolana materials (Loizeau et al., 1994), the particle size range that dominate in specific surface characteristics of a powder. The deviations were assumed less significant to limit comparative studies. Also due to the nature of natural pozzolans and milling process, the produced powders appear as mixed mineral phases that have visible inclusions and a rough texture. The milling process produces irregular particles that are largely angular and cannot fall within the assumed spherical shape in laser diffraction analysis. Therefore, the angular particles lead to errors that affects actual absolute measurement of PSD. The errors were considered less relevant in comparative studies since the kamafugites and carbonatites presented similar morphological features.

The three accessible parts of the Malvern master sizer 2000 equipment, the sample holder, strainer, and suction tube were all removed and cleaned using compressed air for each new sample. Approximately 15 grams of a sample was loaded into the sample chamber and locked. The machine is self-loading and uses aerosol mechanism to disperse the particles as they interact with the laser beam in particle size measurement. Three test runs were conducted per sample to check reproducibility before unloading and cleaning all the accessible parts for a new sample.

3. Particle size results

The samples were milled to three finesses levels, F1, F2 and F3 using a lab scale ball mill provided by Afrisam (South Africa) (Pty) Ltd at their Vanderbijlpark cement plant. The pulverized materials used in the current tests had their mean particle diameters as provided in Table 3.1. Figure 3.5 presents a comparison of the particle size distribution for the test pozzolans and CEM I 52.5R for the F3 grading characterisation, the highest for each of the three samples. Notably, the fineness requirement for pozzolanic test under ASTM C618, 2005, limits the parameter to a maximum of 34% retained on sieve No. 325 (45-micron aperture) following wet sieving procedures. All samples tested met this requirement.

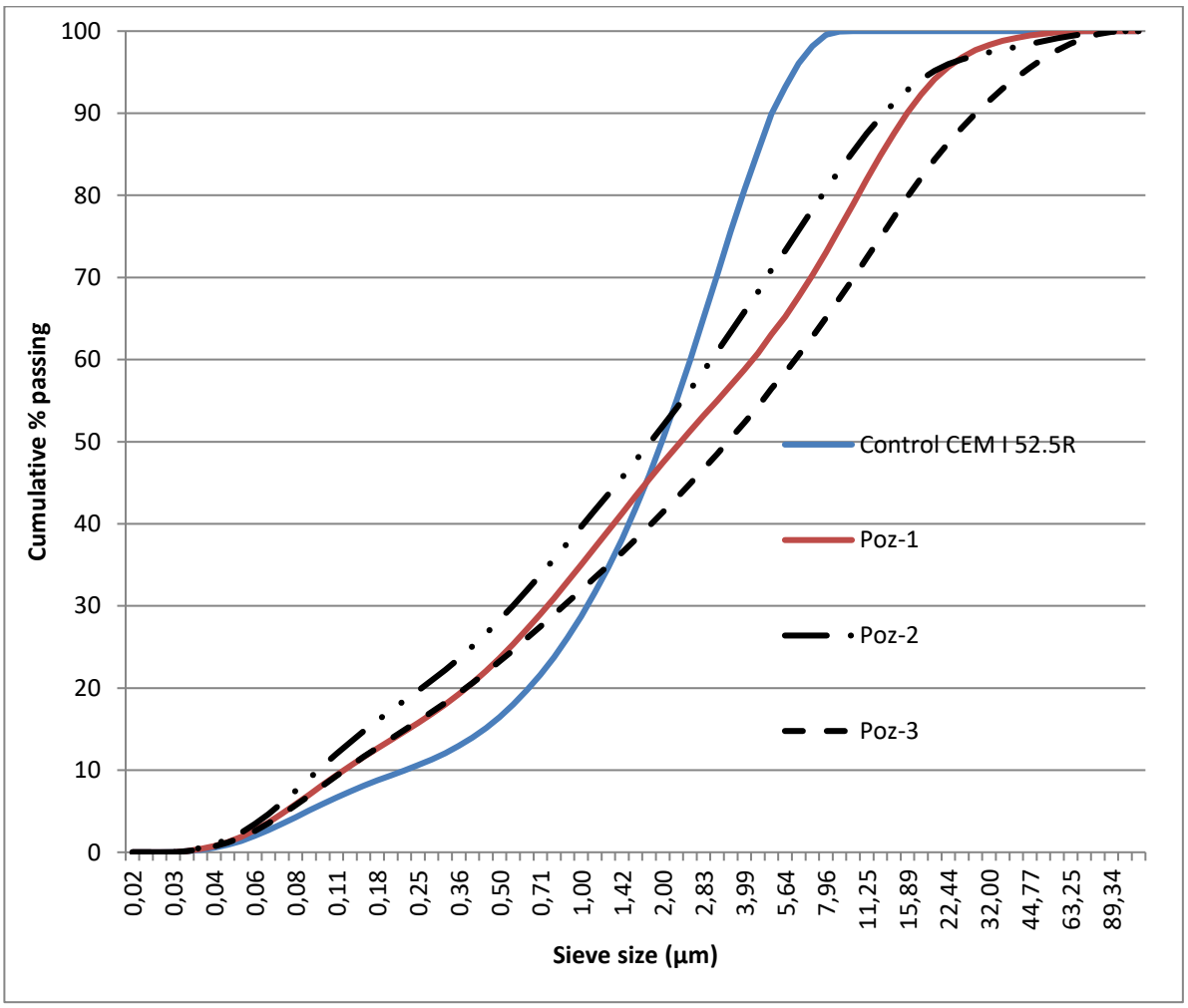

Figure 3.5**:** Particle size distribution of the different SCMs milled to F3 grading characterisation and CEM I (52.5R) control sample by laser diffraction technique.

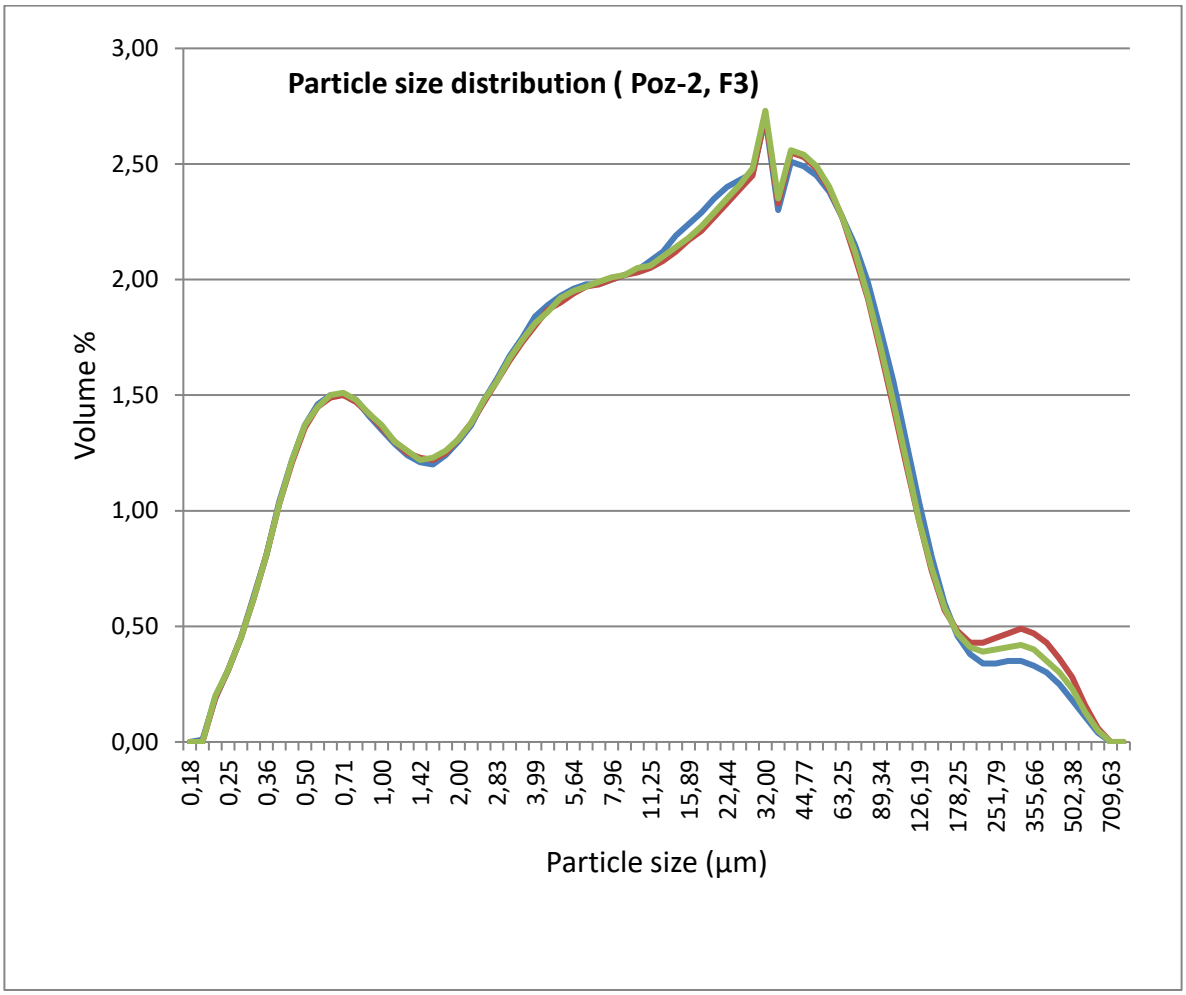

Figure 3.6**:** Reproducibility of particle size analysis results for Poz-2, F3, using Malvern master sizer 2000 particle size analyser. The different colours represent repeat tests with the same material.

The typical multimodal particle size distribution shown in Figure 3.6, the curves in Figure 3.6 and data in Table 3.1 reveal existence of different mineral phases with highly varying hardness levels for each milling operation. The data reveals a noticeable difference in grindability of the different samples, both within the minerals that form each sample and between the different samples. The samples had a wide particle size distribution compared to the control sample of Portland cement (CEM I 52.5R). It is expected that mineral components are broken down preferentially in the milling process according to their level of hardness. Calcite scales low (value three (3)) on Mohs' relative hardness scale, a condition that segregates it to the finer part (d_{10}) of the bulk sample on milling hence giving it a more influential role based on its specific surface in relation to the other minerals in the bulk. This skewed distribution of particle size for

calcite giving it a more pronounced influence in the polymineralic test SCMs. The variability in particle size for all the samples tend to increase after d_{10} particle size (Table 3.1) indicating similarities in the mineral phases only for the very fine components of the particle size distribution.

Table 3.1**:** Laser diffraction particle size results and percentage retained on a 45µm sieve in wet sieving

Sample name	Fineness Class	Specific surface area (m2/g)	Retained on 45 µm sieve (%)	d(0.1) (µm)	d(0.5) (µm)	d(0.9) (µm)
Control (CEM I 52.5R)	**Control**	1.75	2.0	1.422	12.533	32.070
Poz-1	**F1**	1.22	30.6	2.380	48.320	158.386
	F2	1.63	21.9	1.374	22.467	115.496
	F3	2.18	17.5	0.848	14.695	99.808
Poz-2	**F1**	1.67	25.5	1.241	24.685	107.460
	F2	2.28	18.1	0.795	14.611	86.885
	F3	2.64	15.6	0.683	11.391	82.190
Poz-3	**F1**	1.46	31.0	1.484	39.712	188.151
	F2	1.79	26.5	1.077	26.155	186.670
	F3	2.10	23.9	0.852	21.898	178.719

The specific surface area of the control sample (1.75 m^2/g) was significantly lower than for all the test pozzolans samples used in the pozzolanicity test. The higher specific surface area is probably due to a much lower d10% value of the test pozzolans in relation to the control sample fineness. The results for the control sample compare well with those published by Nwaubani and Parsons, 2021, where the specific surface of their control sample was recorded at 1.934 m^2/g. Nwaubani and Parsons, 2021, defined the importance of this high fineness of the cement to high strength and rapid hardening characteristics of the control sample. Therefore, the high fineness of kamafugites and carbonatites used in the study is hypothesised to support charcaterisation of their SCMs properties.

3.3.2 Morphorogical properties of kamafugites and carbonatites

Morphology of the particles, which is a parameter that characterizes the shape, phase composition and surface texture of different particles, was studied using a Nikon ECLIPSE LV100POL polarizing light microscope at Wits University concrete laboratory. To differentiate amorphous phases from crystalline phases, images were observed in both plane-polarized and cross-polarized light. Figure 3.7 presents the morphological images of milled particles of Poz-3, a kamafugite, observed in both plane polar and cross polar phases. The figure shows the existence of both crystalline and amorphous phases in the test pozzolan. The particles are irregular, angular and with rough textures that reveal inclusions of amorphous phases in crystalline particles.

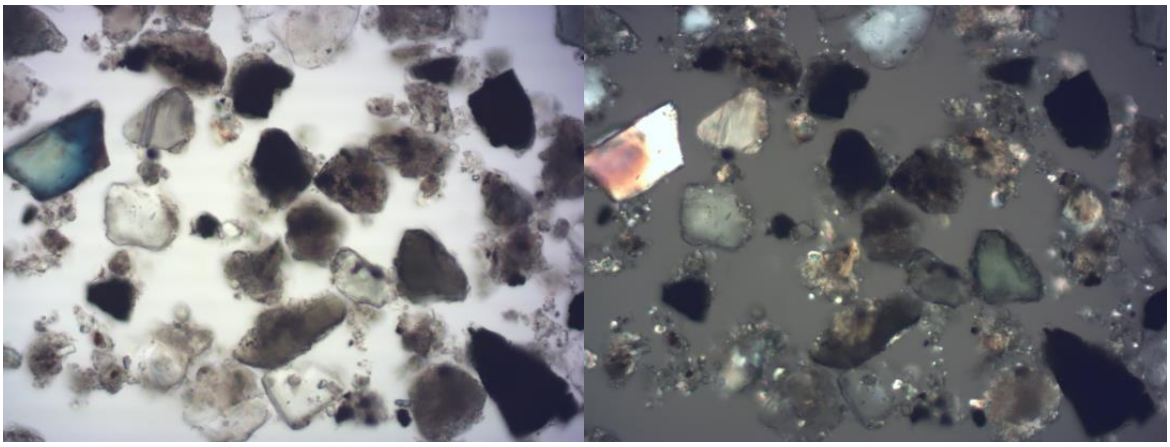

Figure 3.7***:*** Plane-polarized (a) and cross-polarised (b) light microscopy images of Poz-3, a kamafugite sample passing 45µm sieve size (Largest particles = 44µm in size).

The shape and surface texture of different particles in a mortar mix influence water demand of the mix (Alexander and Mindess, 2005). Porous textural surfaces can absorb mixing water reducing the amount of water available for lubrication, hence producing a harsh mix. Dented surface textures act as water pockets and, together with a high angularity of the SCMs milled particles, lead to increase in water demand for mixes involving blends of SCMs. Angular particles are known to produce higher internal friction hence will require more water to achieve good workability (Neville, 2002). Because the specific surface area of the fines in mortar or concrete mixes is relatively much higher than that of coarse aggregates, fines tend to have a greater influence on the water demand and workability of mixes compared to coarse aggregates. Oja and

Tuunila, 2000, report the shape features to be determined by the milling action and to vary with change in the milling equipment.

3.4 Mineralogical and chemical properties of kamafugites and carbonatites

3.4.1 Mineralogical composition of kamafugites and carbonatites

To characterize mineralogical composition of kamafugites and carbonatites, X-ray diffraction (XRD) instrumental techniques were applied on milled natural pozzolans. The XRD mineralogical characterisation was conducted at Pretoria Portland Cement Company (PPC) at their cement laboratories in Jupiter, Johannesburg. For each test, a sample powder was placed in a plastic XRD sample holder and straight edge was used to press the sample into the holder, trim its surfaces and finish it flat to the brim of the sample holder to create a specimen face in the focusing angle of the diffractometer. XRD patterns generated were compared with reference XRD patterns to identify the different mineral compositions.

Table 3.2: Mineralogical composition of test pozzolans

Minerals present	Poz-1	Poz-2	Poz-3	Chemical Formula
Calcite	√	√	√	$(Mg_{0.03}Ca_{0.97})(CO_3)$
Pigeonite	√	√	√	$(Ca,Mg,Fe)(Mg,Fe)Si_2O_6$
Quartz	√	√	√	SiO_2
Muscovite	√	√	√	$KAl_2(AlSi_3O_{10})(F,OH)_2$
Olivine	√	√	√	$Na_2(SiO_4)$
Apatite	√	√	√	$Ca_{10}(PO_4)_6(OH)_2$
Augite	x	√	x	$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$
Epidote	x	√	√	$Ca_2Al_{2.4}Fe_{0.6}(SiO_4)_3(OH)$
Kaolinite	x	x	√	$Al_4(OH)_8(Si_4O_{10})$

√- Mineral detected; x- Mineral not detected

Results: The mineralogy of the test kamafugites and carbonatites detected by XRD instrumental techniques is presented in Table 3.2. The minerals are predominantly calcite, pigeonite, quartz, muscovite, olivine and apatite. Kaolinite, a secondary

(authigenic) mineral was observed in Poz-3. Formed as a result of alteration of volcanic glass (Habert et al. 2008), kaolinite has a detrimental effect on strength performance (Turkmenoglu and Tankut 2002). This is because kaolinite is not pozzolanic in its raw state and requires calcination for its pozzolanic properties to be activated.

3.4.2 Chemical composition of kamafugites and carbonatites

For loss on ignition (LOI), 5 grams was weighed in an aluminium crucible for each of the oven dried samples and placed in a furnace at 1050ºC for 30 minutes. The resulting change in mass was calculated as the LOI.

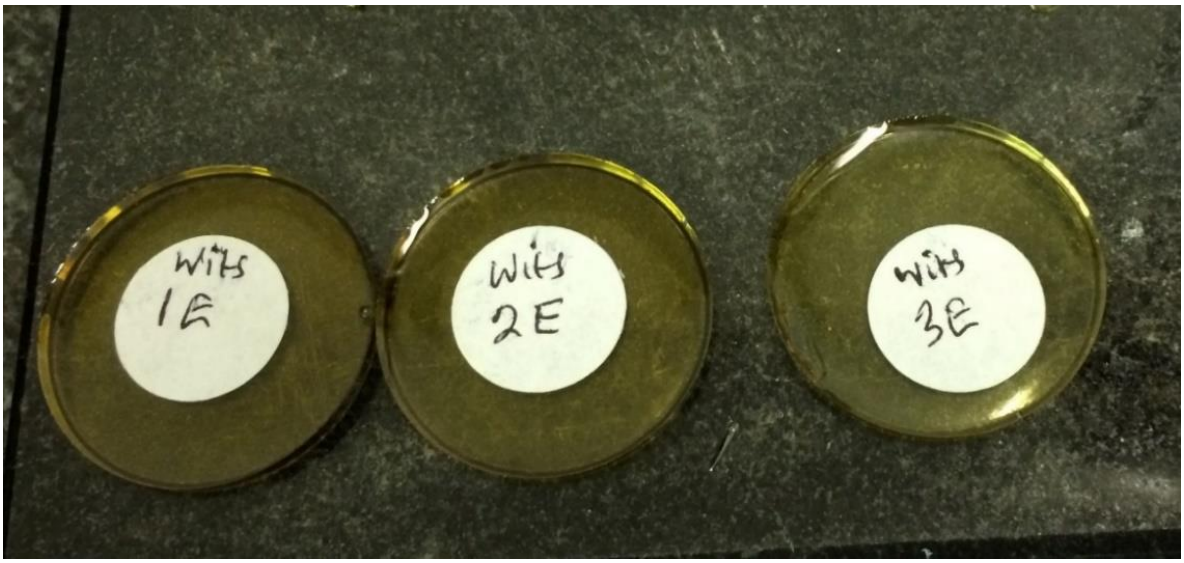

Figure 3.8: Samples processed for XRF oxide composition characterization; Wits 1E for Poz-1, 2E for Poz-2 and 3E for Poz-3.

The samples from LOI measurement were further pulverized using a mortar and pestle and the fine materials were used in estimation of oxide composition using X-ray fluorescence (XRF) analysis. XRF instrumental technique is currently a primary mode of assessment for elemental and chemical composition of inorganic materials in cement and concrete industry. The method is based on quantification of characteristic X-rays (efflorescent x-rays) emitted after an inorganic material has been bombarded with gamma rays (high energy X-rays) (Ramachandran, 2001). XRF experiments were conducted using a multichannel PANalytical (Axios FAST) fluorescence spectrometer sourced at AfriSam South Africa (Pty) Ltd. Figure 3.8 shows processed samples for the spectrometer. Further validation studies for oxide composition and reactive

components of SiO_2 and CaO were conducted at a different cement laboratory (PPC cement laboratories at Jupiter - Johannesburg).

Table 3.3 presents the percentage oxide compositions and LOI. The main oxides in the carbonatites and kamafugites are CaO, SiO_2, Al_2O_3 and MgO. The silica content in the test pozzolans is dependent on the CaO content, increase in the later leading to a reduction in the former. All the test pozzolans exceed the ASTM C618, 2005, 10% minimum LOI requirement.

Table 3.3: Chemical oxide composition, reactive SiO_2, reactive CaO, watersoluble alkalis, PH and relative density of kamafugites and carbonatites

Chemical composition	**Poz-1**	**Poz-2**	**Poz-3**	**Fly Ash**	**GGBS**	**CEM I (52.5R)**
(%)						
SiO_2	35.88	41.7	57.5	55.7	39.97	20.33
Al_2O_3	9.41	8.92	8.83	31.44	15.02	4.41
Fe_2O_3	14.09	12.3	8.13	3.41	0.64	2.53
CaO	25	19.71	8.47	4.44	30.79	65.19
MgO	5.49	6.42	7.05	1.15	8.65	1.8
K_2O	1.09	2.82	4.77	0.68	1.07	0.48
Na_2O	1.71	1.1	0.32	0.26	0.28	0.09
P_2O_5	2.84	1.95	1.07	0.54	0.01	0.08
TiO_2	2.39	3.29	2.75	1.63	0.66	0.41
Mn_2O_3	0.44	0.27	0.16	0.03	1.21	0.1
Cr_2O_3	0.02	0.03	0.03	0.05	0.01	0.01
V_2O_5	0.05	0.06	0.05	0.03	0.02	0.01
LOI	13.57	16.55	10.43	1.19	0.69	0.09
XRF Total	98.4	98.57	99.15	100.55	99.02	95.42
Sum of acidic oxides	59.38	62.92	74.46			

3.4.3 PH of kamafugites and carbonatites

The samples were tested for PH following BS 7755-3.12, 1996, test procedure and protocols presented in Donatello, Tyrer and Cheeseman, 2010. The procedure adapted involved mixing 20 grams of sample material in 100 grams of deionized water for each Poz-1, Poz-2 and Poz-3. The mixture was shaken for 5 minutes and then left to settle for 3 hours to attain a state of equilibrium before testing for PH. The procedure was repeated three times for each of the three samples and a mean PH reading was taken.

The PH results are presented in Table 3.4. The PH of all the kamafugites and carbonatites ranges between 9 and 10.

3.4.4 Reactive SiO_2, reactive CaO and water soluble alkalis in the kamafugites and carbonatites

The analysis for reactive silica and calcium oxide was done following procedures provided in EN 196-2, 2005. The reactive silica content is the percentage of the total volume of the silicates that is readily available to participate in a pozzolanic reaction. The minimum requirement stated in ASTM C 618 is 25% for a material to be considered suitable for SCM applications in concrete. Atomic absorption spectroscopy (AAS) instrumental technique was applied in determination of water-soluble alkalis of the test carbonatites and kamafugites using samples prepared following European Standard EN 196-2, 2005. Results presented in Table 3.4 show Poz-1 and Poz-2 to have reactive silica below the minimum requirement of 25% while Poz-3 is sufficient with 26.6% of reactive silica. All the test natural pozzolans have significant quantities of reactive calcite minerals. Indeed, Klieger and Hooton, 1990, reports SCM calcite quantities as low as 1 to 1.5% to influence cement hydration. Alkali cations are also known to influence hydration kinetics, paste microstructure and ultimate strength of concrete (Jawed and Skalny, 1978; Odler and Wonnemann, 1983). Details on the effect of alkalies in cement paste are covered under the discussion of specific paste properties in Chapter 5 of this thesis

Table 3.4: Reactive SiO_2, reactive CaO, water soluble alkalis, PH and relative density of kamafugites and carbonatites

Parameter	**Poz-1**	**Poz-2**	**Poz-3**	**CEM I (52.5R)**
Reactive SiO_2 (%)	18.8	23.3	26.6	
Reactive CaO (%)	8.4	1.81	5	
Soluble K+ (ppm)	48	125	105	
Soluble Na+ (ppm)	6	23	8	
Soluble Mg+ (ppm)	737	775	875	
PH	9.09	9.25	9.15	
Relative density	2.75	2.63	2.38	3.14

3.4.5 Volatile compounds in kamafugites and carbonatites

Thermogravimetric analysis (TGA) was applied on the kamafugites and carbonatites as a sequel to the standard LOI test to characterize the volatile elements that led to a high LOI value. Powder samples of carbonatites (Poz-1) and kamafugites (Poz-2 and Poz-3) weighing between 50 and 70 grams were placed in aluminium crucibles as sample container in a furnace cell of a Mettler Thermogravimetric Analyzer equipment model TGA/DSC1 (Figure 3.9). The TGA equipment was accessed at Afrisam South Africa (PTY) Ltd at their Center for Products Excellence, Rooderport. The samples were then heated and their thermal decomposition features observed from 100°C to 950°C at a heating rate of 20°C/min while the chamber gas used was air flowing at 200ml/min. TGA temperature was raised from 105°C to 950 °C while monitoring changes in sample mass. TGA results presented in Figures 3.10, 3.11 and 3.12. The results show endothermic peaks that appear in the 600ºC -850ºC temperature range, a characteristic of $CaCO_3$ decomposition to CaO and the escape of CO_2 gas into the atmosphere (Lothenbach and Wieland, 2006; Ramachandran, 2001). The samples attain stable mass after 850ºC indicating the end of thermal destabilization of the carbonates.

Figure 3.9: Thermogravimetric analysis (TGA) instrument used in characterisation of volatile compounds in kamafugites and carbonatites

Not all carbonatitic deposits are ultrapotassic. The ultrapotassic deposits are only in the south of the Toro-Ankore geological region of Rubirizi (Poz-3). These deposits are also silica saturated opposing what has been reported in literature in geological domain (Baker and Nixon, 1989). The silica undersaturated samples are located towards the northern parts of the study area (Katwe-Kikorongo and Fort Portal deposits). The silica undersaturated deposits are relatively higher in CaO composition compared to those that are silica saturated. Results on reactive CaO (Table 3.4) showed most of the CaO in Poz-2 (Katwe-Kikorongo deposit) to be non-reactive, a condition hypothesized to contribute to the distinctiveness in reaction kinetics of Poz-2 compared to Poz-1 and Poz-3.

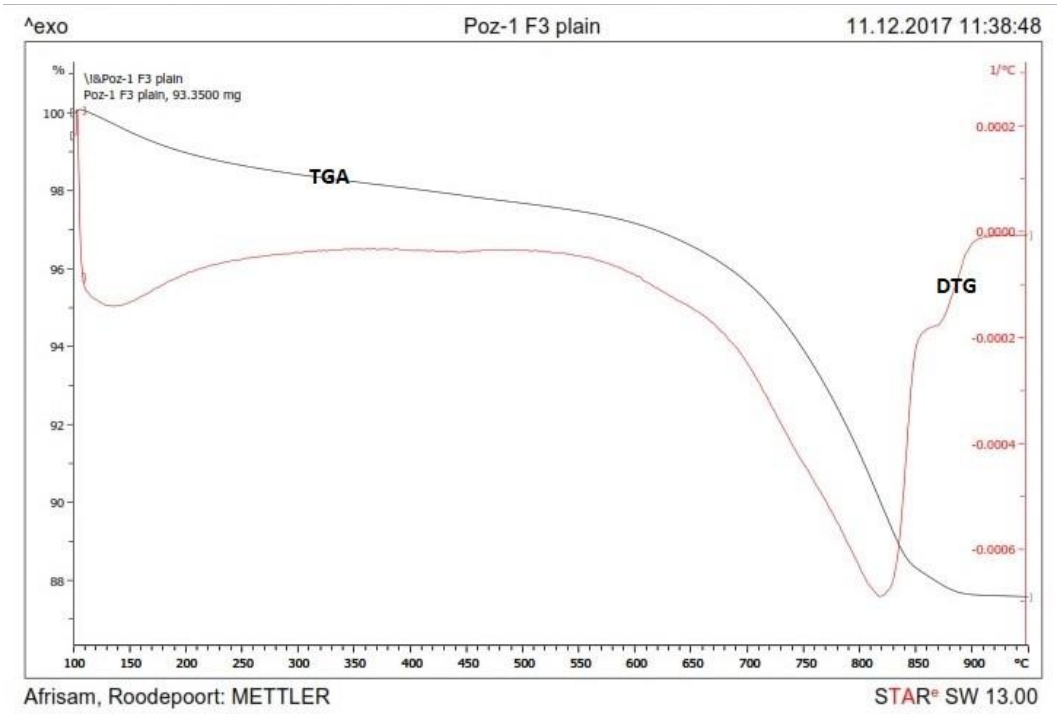

Figure 3.10**:** TGA/DTG curve of Poz-1 (a carbonatite) showing decomposition of calcite in the range 600-850°C as a dominating reason for the high LOI value

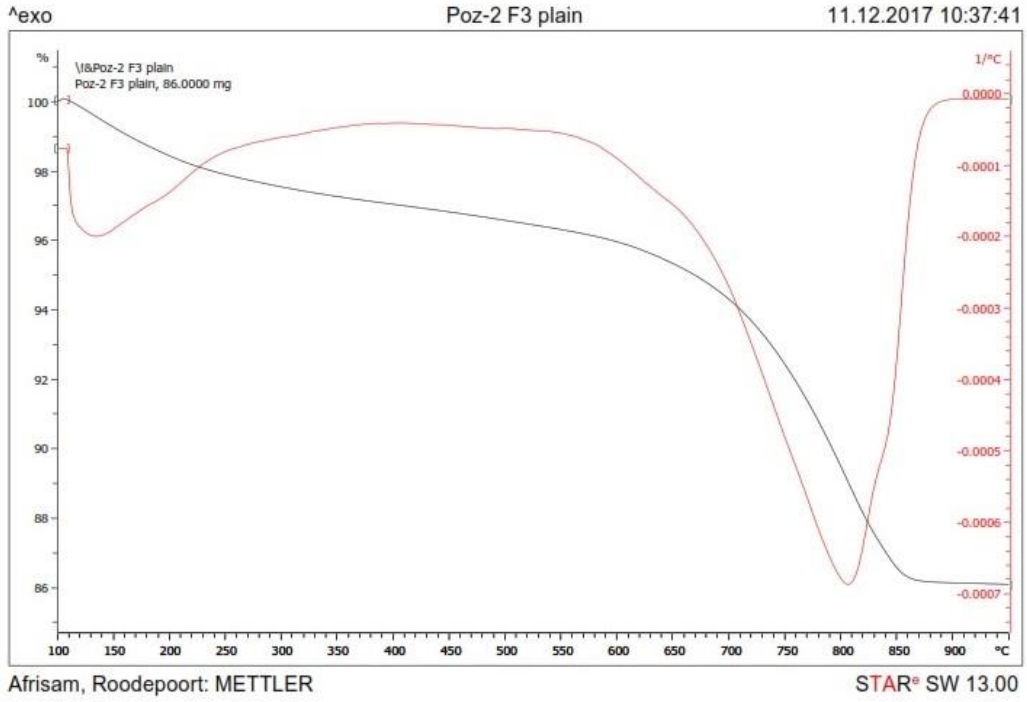

Figure 3.11**:** TGA/DTG curve of Poz-2 (a kamafugite) showing decomposition of calcite in the range 600-850°C as a dominating reason for the high LOI value

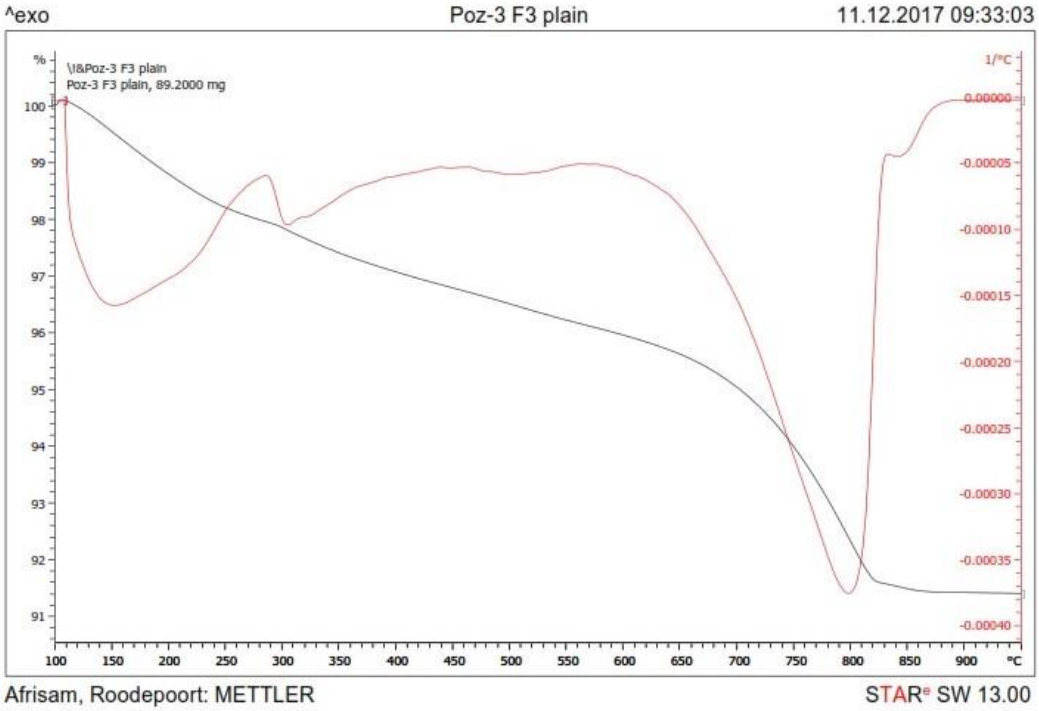

Figure 3.12*:* TGA/DTG curve of Poz-3 (a kamafugite) showing decomposition of calcite in the range 600-850°C as a dominating reason for the high LOI value

3.4.6 Pozzolanic characteristics of kamafugites and carbonatites

The European standard EN 197-1, 2000, requires the reactive silica content of natural pozzolans to be at least 25% while the sum of oxide composition of silica, alumina and iron to be at least 70%. Similar minimum requirements are presented in ASTM C618 (2005). The summary assessment of these requirements for the three test pozzolans has been presented in Table 3.5. Table 3.5 also presents an extract of processed results on the strength activity index (SAI), an evaluation of the pozzolanic activity of pozzolanic SCMs discussed in detail under Chapter 5 of this thesis. It is observed that the test pozzolans Poz-1 and Poz-2 do not meet the 70% minimum chemical composition requirement for the sum of the acidic oxides and the 25% requirement for reactive silica. However, the SAI results reveal the kamafugites and carbonatites as beneficial SCMs since they lead to a gain in compressive strength.

Table 3.5: Summary of physical properties and pozzolanic activity of the different pozzolana materials following EN 197, 2000, and ASTM C618, 2005, standards

Parameter	Minimum equirements	Test Pozzolan		
		Poz-1	Poz-2	Poz-3
Chemical composition	Sum (SiO_2, Al_2O_3, Fe_2O_3) % ≥ 70%	59.38	62.92	74.46
	SO_3% ≤ 4%	0.07	0.01	0.01
	LOI, % ≤ 10%	13.57	16.55	10.43
	Reactive SiO_2 ≥ 25%	18.8	23.3	26.6
Physical properties	% retained on a 45μ sieve ≤ 34%	17.5	15.6	23.9
	7 days SAI, % ≥ 80%	84	92	84
	28 days SAI, % ≥ 80%	90	92	100
Conclusion		Fail	Fail	Fail

The ASTM C618, 2005, method for testing pozzolanicity of natural pozzolans required the maximum LOI value to be below 10%. This requirement is established in the need to limit organic matter based volatile elements as these negatively impact on hydration and strength development of Portland cements. However, where the LOI is not caused by a high organic content but carbonates, its effect on cement strength has negligible

importance. Characterisation of volatile elements in carbonatites and kamafugites (Section 3.3.5 above) shows them to be dominated by carbonate phases.

3.5 Chapter summary

In the current chapter, kamafugites and carbonatites are studied for their physical and compositional properties. The following conclusions are drawn based on results from the current experimental study.

1. The kamafugites and carbonatites are nonresponsive to the minimum chemical composition, volatile compounds (LOI) and reactive silica content required for natural pozzolans under ASTM C618 and EN 197-1. Their main oxides are CaO, SiO_2, Al_2O_3 and MgO. The silica content is dependent on the CaO content, increase in the later leading to a reduction in the former. The LOI is dominated by the carbonate minerals in the natural pozzolans. There is no standard that addresses the parallel reaction mechanisms of calcite-aluminosilicate-alkalis reactions, yet all these mechanisms are reported independently to influence cement performance.
2. The silica undersaturated carbonatitic nature of the Fort Portal and Katwe-Kikorong deposits and the ultrapotassic nature of kataara-Rubirizi and Katwe-Kikorongo deposits are unique compositional features of these volcanic materials that create interest in the study of their performance as SCMs in Portland cement production.
3. The kamafugites and carbonatites present significant quantities of reactive CaO and water-soluble alkalis which are considered to influence hydration products assemblage and paste microstructure of hydrating Portland cement. The PH of the natural materials range between 9 and 10. The alkalis are predominantly potassic.
4. The kamafugites and carbonatites are polymineralic. The minerals present highly varying levels of hardness, a condition that led to particle size driven segregation of minerals. Calcite, a mineral that ranks low on the Mohs' relative hardness scale, dominated the finer part (d_{10}) of the bulk sample on milling, a consideration that would consequently give it a dominant role in influencing reactivity of the natural pozzolans.

5. Both crystalline and amorphous phases exist in the test kamafugites and carbonatites. The particles are irregular, angular and with rough textures that reveal inclusions of amorphous phases in crystalline particles.

CHAPTER 4

EXPERIMENTAL DETAILS AND RESULTS

4.1 General

This chapter presents experimental procedures followed in the study of the effects of compositional properties of kamafugites and carbonatites on Portland cement pastes and mortars when these materials are used as supplementary cementitious materials (SCMs) in Portland cement. The materials used in this study and their compositional and physical characteristics are presented in Chapter 3 of this thesis. The current chapter focused on evaluating the effects of the compositional parameters of kamafugites and carbonatites as SCMs on pozzolanic activity, long-term compressive strength development, influence on hydration kinetics, chemical shrinkage, and hydration products assemblage. The experimental techniques applied in this study included compressive strength testing, strength activity index (SAI), Thermogravimetric analysis (TGA), X-Ray diffraction (XRD), dilatometry, and Isothermal calorimetry and other standard test procedures established in EN 196, 2005, and ASTM C618, 2005. The study followed an experimental plan shown in Table 4.1. The results generated from the experimental processes are also presented in the current chapter.

Table 4.1: Summary experimental procedures followed in characterisation of kamafugites and carbonatites as SCMs in Portland cement.

SN	Tests carried out	Parameters	Properties tested
1	Characterisation of pozzolanic activity and other SCM properties of kamafugites and carbonatites	Tests for pozzolanic activity and SCM effects on cement conducted at a fixed replacement level of 20% test pozzolans in their natural state (uncalcined)	**Fresh properties of blended cement** • Paste consistency/water demand • Setting time • Soundness **Pozzolanicity of kamafugites and carbonatites** • Indirect test: Compressive strength and strength activity index (SAI)-ASTM C618, 2005 • Direct test: Frattini test (EN 196-5, 2005) for tracking consumption of Ca^{2+} ions **Hydration kinetics of blended cements** • Isothermal calorimetry in heat of hydration studies • Dilatometry in chemical shrinkage studies **Hydration products development** • Thermogravimetric analysis (TGA) in hydration products development, pozzolanic activity and estimation of degree of hydration • XRD in identification of CH consumption in blended samples and, also, in evaluating the effects of calcination on mineralogical composition of kamafugites and carbonatites
2	Effect of fineness of test pozzolans	Three fineness levels considered for each of the three test pozzolans (Table 3.1). Tests conducted at a fixed replacement level for blended pastes and mortars	
3	Effect of replacement level of test pozzolans	Replacement level of 5%, 10%, 20% and 35% considered for the three test pozzolans	
4	Effect of calcination of kamafugites and carbonatites	Kamafugites and carbonatites were decomposed to break calcite to CaO and CO_2. The process also removed water-soluble alkalis. Material characterisation tests applied in testing the effect of calcination followed procedures already discussed in Chapter 3	

4.2 Pozzolanic and other SCM properties of kamafugites and carbonatites

The results presented in the current section are grouped in seven parts that report on the influence of kamafugites and carbonatites on fresh properties, the pozzolanic activity, strength development of cements blended, hydration kinetics and hydration products assemblage. In order to report coherently following the objectives set for this research, results that follow the experimental plans that test compositional effects and the role of physical properties of kamafugites and carbonatite minerals are presented

in Sections 4.3 and 4.4 of the current thesis chapter. Accordingly, the results presented in Section 4.2 are mainly those conducted at a fixed replacement level of 20% for the test SCMs using CEM I 52.5R as a control sample. A fixed replacement level is important for comparative analysis of results of the different test SCMs. Also, considering that the results in the current chapter are applied in development of numerical models for characterizing the degree of hydration (α), the degree of pozzolanic activity (β) and the net SCM benefit (λ) of the kamafugites and carbonatites, the test methods applied in pozzolanic activity characterisation are evaluated and discussed for their reliability in characterizing the pozzolanic property of kamafugites and carbonatites.

4.2.1 Fresh properties of kamafugites and carbonatites as SCMs

This section presents the effect of kamafugites and carbonatites on the properties of fresh Portland cement pastes and mortars. The fresh cement paste properties presented at this stage include setting time, water demand, slump flow and soundness. Characterisation of fresh properties of blended cements was guided by the test requirements for pozzolans as stated in the standards (ASTM C618, 2005). The standards consider the tests on fresh properties of Portland cement as prerequisites for pozzolanic activity characterisation.

4.2.1.1 Cement paste consistency

Consistency is a rheological parameter of fresh cement pastes that is dependent on water/cement ratio, cement fineness, flocculation, rate of hydration of cement (Struble and Hawkins, 1994) and morphological features of cement particles. A vicat apparatus with a 10mm diameter plunger is used in the study of consistency property of different cements. A term standard consistency is used to mean a state of flow of a cement paste that achieves a penetration depth of 33-35 mm from the surface of the paste (5-7mm reading on vicat apparatus). The variable in standard consistency measurement is the water-to-cement ratio required to achieve the set penetration (33-35 mm) for the test cement. The standard consistency is important in setting time, paste strength and soundness studies. The test for cement consistency followed procedure provided in EN 196, 2005, standard.

1. **Sample preparation and testing**

The test procedure applied for consistency and setting time measurement is based on EN 196-3, 2005, standard. 500 grams of a sample to be tested (500 grams of CEM I for the control sample and a 20% and 35% displacement of the CEM I with test pozzolan) was weighed and mixed in a standard mixer following the procedure as provided in EN 196-3, 2005. A vicat apparatus fitted with the 10 mm diameter plunger for consistency measurement was used. The plunger was gently lowered to touch the surface of the paste in a standard frustum cone shaped mould and then released to penetrate the paste. The procedure was repeated for all trial mixes by varying mix water content until a penetration reading in the range of 5-7 mm was observed with vacant measurement.

4.2.1.2 Flow table tests

Workability is a property of fresh concrete that depends on the quantity of mixing water, chemical and physical properties of cement, the proportioning of solid constituents, and physical properties of the different aggregate types in a mix. Optimisation of concrete mixing equipment and the use of water reducing and plastcising admixtures also improve the workability of a concrete mix. Whereas a number of tests are available to evaluation workability of concrete mixes (sump test, flow table test, slump-flow test, V-funnel test, etc), workability test for mortar mixes prepared in laboratory conditions are more adapted to the flow table test (EN 196-1, 2005).

Sample preparation and testing

A standard flow table with three circular marks of different diameters grooved around the center of the circular table (Figure 4.1) was used for works in this thesis. The circular markings guide in placement of the standard mould. The standard mould is a frustum cone shaped steel mould with a smooth internal finishing. The mould was held firmly on top of the flow table and filled in two layers with mortar mix prepared according to EN 196-1, 2005. Each mortar layer was tamped ten times with a standard wooden piece. Excess mortar after filling and compacting the mould was cut off using a trowel to a flat surface that flashed with the rim of the frustum cone shaped mould. The mould was carefully lifted off the table and the table was jolted 15 times. Three diameter

readings were taken from the mortar spread and a mean of the three readings was calculated and taken as the flow of the mortar (Figure 4.1). The test procedure was conducted on mortars made using the control sample and the three natural pozzolana samples that are a subject of this study.

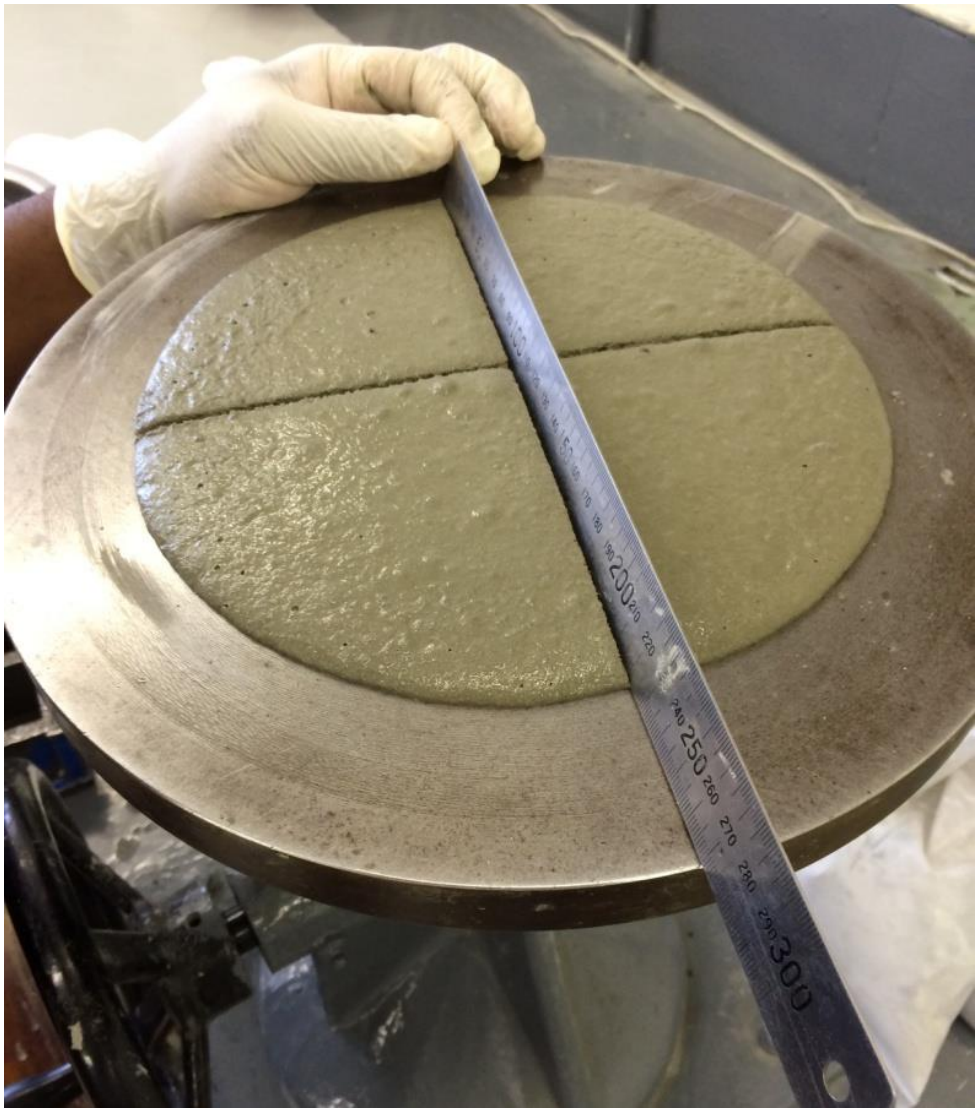

Figure 4.1: Flow table test

4.2.1.3Setting time

Setting time is a parameter used to characterize the time dependent stiffening property of a cementitious material. It is presented as initial and final setting times referring to the times from when water is added to a cementitious material to the time when the cement paste loses workability and hardening begins respectively. The initial setting

time is associated with a significant loss in slump (Ramachandran, 2001). Addition of admixtures (mineral or chemical), cement fillers and SCMs affects the setting times (Ramachandran, 2001; Berodier, 2015). Both the European standards (EN 197-1, 2000) and the American standards (ASTM C150, 2009) provide for the minimum time for initial setting for different Portland cement types ranging from 45 to 60 minutes.

1. Sample preparation and testing

The sample that passed the consistency test was used for the initial and final setting time measurements. An automatic vicat apparatus was used in measurement of both initial and final setting times. The paste sample was placed to fill the test mould and was leveled flat on top. The sample was then placed in a water bath in the automatic vicat apparatus setup (Figure 4.2). This guaranteed a 100% relative humidity throughout the time of experiment. The temperature was maintained at 20±2ºC.

Figure 4.2: An automatic vicat apparatus used in measurement of both initial and final setting times

4.2.1.4 Soundness

This is the property that characterizes the change in volume of a hardened cement paste. Volume change is attributed to delayed hydration of free lime (CaO), MgO (in form of periclase) and gypsum (calcium sulfate) in a cement paste that has achieved some form of rigidity and restraint to volume change movements (Neville, 2002). EN 196-3, 2005, provides the procedure for testing cement for soundness property using the Le Chatelier's mould (Figure 4.3). A paste of standard consistency that has been cast in the Le Chatelier's mould and kept under 100% relative humidity for 24 hours is immersed in boiling water for 1 hour to thermally activate any expansive reaction in the paste. Cement is considered sound if its expansion observed using a Le Chatelier's mould does not exceed 10 mm.

1. Sample preparation and testing

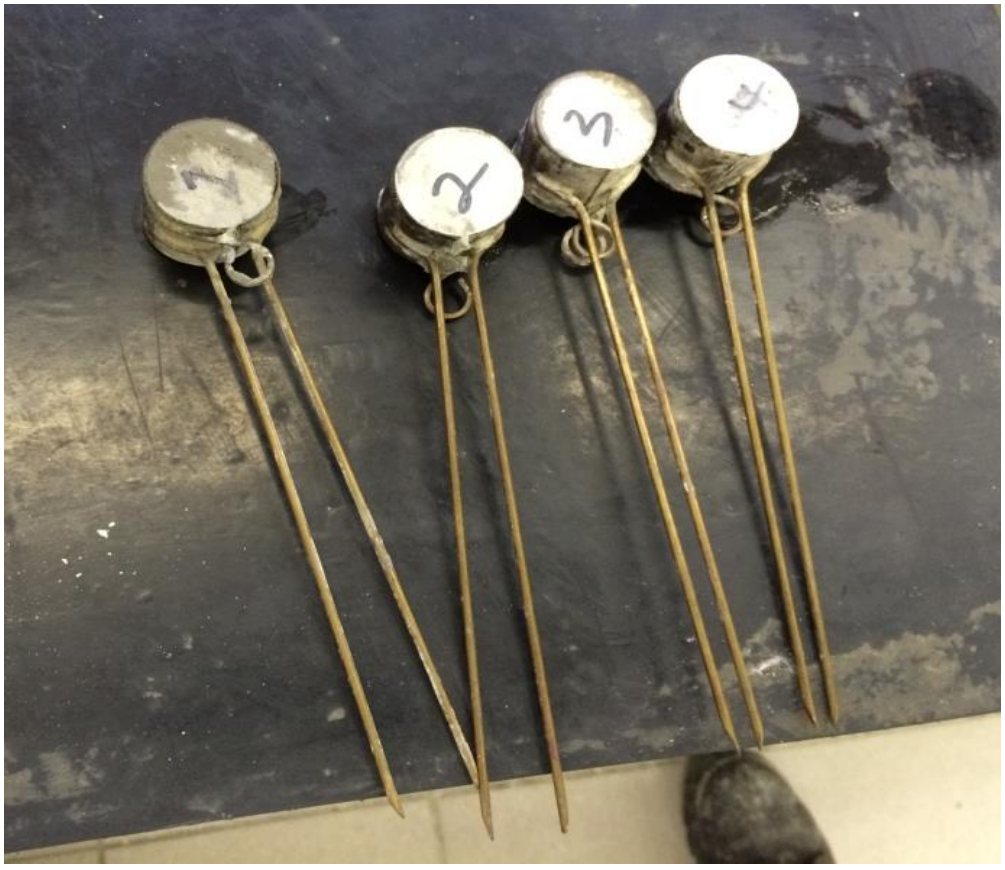

Figure 4.3: Blended cement paste sample in Le Chatelier's mould after being under boiling water for 3 hours

A paste of standard consistency was gently placed to fill a clean Le Chatelier's mould that had a release agent applied to its internal walls. The paste was placed in the mould with care not to apply pressure in the mould to open the split. The openings on the sides of the mould were covered with glass pieces and a light weight was placed on the glass to stop the whole assembly from tipping. The whole assembly was placed in a water bath at 20±2ºC for 24 hours. The samples were then removed from the water bath, the glass covers removed and then the samples were labeled using a water-resistant marker. The distance between the indicator points was then taken and recorded as the initial reading, I. The samples were placed in boiling water for three (3) hours and then removed and allowed to cool. The distance between the indicator points of the mould was taken again and recorded as the final reading, F.

The expansion of a paste is calculated as the difference (F-I) and must not exceed 10 mm for a cement paste to pass the soundness test.

The experimental procedure was conducted on cement blends at both 20% and 35% replacement of CEM I with the kamafugites and carbonatites.

4.2.1.5 Results

Table 4.2**:** Setting times, water demand and soundness properties for natural pozzolana blended cements

Parameters	**Poz-1**	**Poz-2**	**Poz-3**	**CEM I 52.5R Control**
Initial Setting time (min) 80:20 ratio	200	200	190	215
Final Setting time (min) 80:20 ratio	245	255	246	286
Initial Setting time (min) 65:35 ratio	180	180	170	201
Final setting time (min) 65:35 ratio	245	250	225	281
Water demand (%) (80:20 ratio)	30.70	32.30	33.10	29.20
Water demand (%) (65:35 ratio)	30.75	32.30	34.40	29.30
Slump flow (%) (80:20 ratio)	95.3	92.1	87.9	100
Soundness (mm)	0.0	0.0	0.0	0.0

The kamafugites and carbonatites generally reduced the setting time of the cement system (Table 4.2). Factors such as the temperature and relative humidity that influence setting time (Neville, 2002) and the amount of pozzolanic admixture were controlled and monitored through the experimental process. This left the setting time to be influenced by the interaction between the test SCM materials and cement phases and water.

The water-binder (w/c) ratio for standard consistency increased with addition of natural pozzolans. The trend of variability in both the slump flow data and water demand data is similar for the different natural pozzolana blended cements showing a direct relationship between workability and water demand.

The kamafugites and carbonatites blended cements registered no volume change for the soundness property.

4.2.2 Compressive strength development studies

4.2.2.1Preparation of samples

Mortar prisms of 40x40x160mm standard size were cast according to EN 196-1, 2005, using a standard mould and mix proportions presented in Table 4.3. The experimental design focused on characterizing the effects of fineness, replacement level, and calcination of kamafugites and carbonatites on compressive strength development. EN 196-1, 2005, standard presents a combination weight ratio of 1:3 for cement to sand and a water binder ratio of 0.5. Standard sand according to EN 196-1, 2005, was used. Water amounting to 225 mls was placed in the mixing bowl and then the cement blend was added in the water. Minor premixing was done on natural pozzolana-CEM I mix before introducing the mix into water. Mixing at low speed was started immediately on addition of the cement mix and sand was added after 30 seconds without stopping the mixing. Mixing at low speed lasted up to 60 seconds and then high-speed mixing was initiated to run for 30 seconds. The mixer was stopped and mortar stuck on the sides of the bowl was scrapped off within the first 15 seconds of the 90 seconds rest period. Mixing was resumed at high speed and run for 60 seconds. A flow table test was conducted immediately at the end of mixing. The test mortar from the flow table test was returned into the mixing bowl and remixed with a trowel before casting.

Table 4.3: Mix proportioning for compressive strength tests: Effect of fineness and replacement level for each of test kamafugites and carbonatites

%age replacement level, F3	Fineness Level (F1, F2, F3)	Remarks	CEM I 52.5R (g)	Test Pozzolan (g)	Standard sand (g)	Water (g)
0%	-	Control sample	450.00	0.00	1350	225
5%	F3	Test SCM	427.50	22.50	1350	225
10%	F3	Test SCM	405.00	45.00	1350	225
20%	F1, F2, F3	Test SCM	360.00	90.00	1350	225
35%	F3	Test SCM	292.50	157.50	1350	225

To minimize environmental influences on results, proportioning and mixing was done to completion for all the five batches of one sample before starting on a different sample.

4.2.2.2 Mortar placement and compaction

The procedure for placement and compaction followed the EN 196-1, 2005, standard. The standard mould fixed on a standard vibrating table was filled in two cycles within the first 45 seconds after the start of vibration. Vibration lasted for two minutes. The experiments were conducted in laboratory conditions at Afrisam (South Africa)(Pty) Ltd cement laboratory and both temperature and humidity were monitored every after three hours.

Figure 4.4: Mortar prism samples placed in a curing room and covered with glass for 24 hrs before demoulding.

4.2.2.3Sample number and storage

Five batches of each sample blend for the kamafugites, carbonatites and reference materials were made for 7, 28, 56, 90 and 180 days compressive strength tests. This gave a total of 25 batches that were cast in two days. Samples cast in 40x40x160mm standard moulds were covered with glass sheets after casting and stored in a humid room at Afrisam (South Africa)(Pty) Ltd cement laboratory for 24 hours (Figure 4.4). The temperature and relative humidity were kept at 20 ºC± 1 and >90% respectively. Samples were demoulded after 24(+2) hours starting with the first sample to be cast and were marked to show the sample name, number and date of testing using a water-resistant marker (Figure 4.5). Samples were then placed under water in a curing tank for a period up to the time of testing.

Figure 4.5: Samples marking showing sample 2 (Poz-2) to be tested on 3rd of August 2015 for 90 days of curing.

4.2.2.4 Curing of mortar prisms

Mortar prisms, immediately after demoulding and marking, were placed submerged under water in a curing chamber maintained at (20±1) ºC. The mortar prisms were placed in a metal grating allowing sufficient space for water to freely circulate to all the sides of the prisms (Figure 4.6).

Figure 4.6: Curing of mortar prisms

4.2.2.5 Strength activity index (SAI) test for pozzolanic activity

To study the effect of the different test pozzolans on hydration and strength development of concrete, the strength activity index method was used. The Strength Activity Index (SAI) was based on the standard procedure for fly ash (BS 3892, 1997) as adopted by Donatello, Tyrer and Cheeseman, 2010, but fixing the water content following recommendations in published work by Pourkhorshidi et al., 2010. The ASTM C311 standard sets a cement displacement of 20% CEM 1 with a test pozzolan for

pozzolanic activity test. The same test procedure was followed for all the tests at varying replacement levels. Equation 4.1 provides a mathematical relationship for calculation of the SAI.

$$\boldsymbol{SAI} = \frac{\boldsymbol{P_{test\ sample}\ (MPa)}}{\boldsymbol{P_{control\ sample}(MPa)}} \times \mathbf{100}\% \qquad \text{Equation 4.1}$$

Where $P_{test\ sample}$ represents the mean compressive strength of test sample and $P_{control\ sample}$ is the mean compressive strength of the control sample at the same curing period.

The SAI value is compared against the percentage replacement level of the blended cement and the compressive strength value of the control sample. A test pozzolan causing an SAI value more than the cement content is considered to positively participate in cement reactions. The modes of this interaction are discussed in detail in chapter 2 of this thesis and standards consider the strength benefit as a proxy indicator of pozzolanic reaction between the test pozzolan and cement hydration products.

To stress the importance of test pozzolans, some results are presented as normalized strength (Equation 4.2) which is the calculated effective strength contribution for the cement content in a test sample.

$$\boldsymbol{P_{Normalised}(MPa)} = \frac{\boldsymbol{P_{test}\ (MPa)}}{\boldsymbol{cement\ content\ in\ test\ sample}\ (\%)} \qquad \text{Equation 4.2}$$

4.2.2.6 Measurement and analysis

Samples due for testing were removed from water and tested for compressive strength within 10 minutes after removal from water. The samples were broken into halves and the sides in contact with the testing equipment cleaned with a brush before commencing the testing process. The testing equipment was preset to load at a rate of 2500 N/s. The results were recorded by a computer connected to the compressive strength testing equipment (Figure 4.7).

Six test results were collected per sample and tested for variance. The mean of the six test results was taken as the compressive strength of the test sample.

Figure 4.7: Compressive strength testing for mortar prisms

The strength activity index (SAI) was calculated according to the formula stated in Equation 4.1. The sample is considered to have passed the pozzolanicity test if its SAI is equal to or greater than 80% (i.e if the strength of the sample is at least 80% the strength of the control sample).

The common variables that influence compressive strength of pozzolanic cements, the filler effect and the pozzolanic reaction, are time defined and their effect can be separated. The influence of the filler effect is only at the initial stages of strength

development while the pozzolanic reaction is a continuous process that shows strength gain over a long period.

4.2.2.7 Results

Table 4.4**:** Mortar compressive strength and strength activity index (SAI) values for 7, 28, 56, 90 and 180 days curing period.

a) Mortar prisms compressive strength (MPa)

Curing period (Days)	Control 1 CEM 1 (52.5R)	Control 2 Class F Fly Ash	Test Poz-1	Test Poz-2	Test Poz-3
7	49.2	40	41.5	45.4	41.2
28	57	54.2	51.1	52.3	56.8
56	61.9	64.3	52.4	54.9	57.1
90	63.4	69.7	53.2	56.1	57.4
180	65.3	72.1	53.1	58.1	56.6

b) Strength Activity Index (SAI) (%)

Curing period (Days)	Control 1 CEM 1 (52.5R)	Control 2 Class F Fly Ash	Test Poz-1	Test Poz-2	Test Poz-3
7	100	81	84	92	84
28	100	95	90	92	100
56	100	104	85	89	92
90	100	110	84	89	91
180	100	110	81	89	87

The compressive strength and strength activity index (SAI) values for samples blended with test pozzolans at 20% replacement level are presented in Table 4.4. Each mean compressive strength value is calculated from six compressive strength results tested according to EN 196-1, 2005, procedures for each of the kamafugite and carbonatite samples and the controls at the same curing period. The details of individual test results and relevant validation statistical checks are provided in Appendix 2. The samples were found to be within the normal limits of variability and the results were considered to be reliable. As observed, the measured compressive strengths for all samples blended with the test natural pozzolans are lower than those of the control values (CEM I 52.5R) for all test periods.

4.2.3 Frattini test (EN 196-5)

The frattini test is a wet chemistry test method used to estimate the concentration of Ca^{2+} and OH^{-} ions present in a solution containing Portland cement and a test pozzolan cured for a specific period. The calculated concentration is analysed in relation to Ca^{2+} ionic concentration expected to saturate a solution of a similar PH (EN 196-5). It is expected that a pozzolanic reaction leads to Ca^{2+} ionic concentration less than the saturation value for a hydrating cement system at a specific alkalinity (PH 12.5) for a standard curing period. Curing is done in an oven at a controlled temperature of 40ºC and for 8 or 15 days. The Frattini test method is based on the assumption that the Ca^{2+} ions are only contributed by the hydrating cement component of the test solution (Donatello et al 2010)

4.2.3.1 Sample preparation and testing

Figure 4.8: Samples removed from oven before filtration

The sample preparation and testing process followed the procedure provided in SANS 50196-5 (2014) which is an EN 196-5 equivalent test standard. The process of sample preparation started with placing in a glass bottle 100 ml of distilled deionized water that had been freshly boiled and left to cool at room temperature. Six (6) glass bottles

were used in this experiment, two (2) bottles for each of the three natural pozzolan samples. The bottles containing 100mls of distilled deionized water each were placed in an oven preset at 40ºC and left for one (1) hour to equilibrate. Blending of the test samples with CEM I (52.5R) to a ratio of 1:4 for natural pozzolans to CEM I (Table 4.5) was done using cement supplied by Afrisam (South Africa) (Pty) Ltd Rooderport cement plant, the same cement sample batch used in other experiments presented in the current chapter. Twenty grams (20g) of the materials for the three blended samples in this study were each placed in a glass bottle, sealed immediately and labeled accordingly (Figure 4.8). The samples were then shaken together for homogeneity and placed in an oven preset at 40ºC. The samples were kept in the oven for 8 days.

Table 4.5: Mix proportioning for the Frattini test

Experiment	Remarks	CEM I (g)	Test Material (g)	Water (g)
EN 196-5 (Frattini)	CEM I/S1	16	4	100
EN 196-5 (Frattini)	CEM I/S2	16	4	100
EN 196-5 (Frattini)	CEM I/S3	16	4	100
EN 196-5 (Frattini)	CEM I/S4	16	4	100

At the end of the curing period, samples were removed from the oven and then vacuum filtered through a 2.7 µm nominal size filter paper fitted in a Buchner funnel. The filtrate was sealed and allowed to cool at room temperature. 50 mls of the filtrate was measured using a pipette and placed in a conical flask. Five drops of methyl orange indicator was added to the conical flask and titration against 0.1 molar HCL solution to estimate the hydroxyl (OH^-) ion concentration in the filtrate. The filtrate was then adjusted to a PH of 12.5 by adding sodium hydroxide solution. About 0.1 grams of murexide indicator was added into the titrate solution and titration against a 0.03 molar EDTA solution was done in estimation of Ca^{2+} ions. Both the 0.1 molar HCL and 0.03 molar EDTA were standardized and their factors f_2 and f_1 calculated according to procedures stated in section 8 of SANS 50196-5, 2014, which is similar to EN 196-5, 2005.

The EN 196-5 test method gives the equation below (Equation 4.3) as the relationship governing saturation concentration of the calcium and hydroxyl ions.

$$[\mathbf{CaO}] = \frac{\mathbf{350}}{[\mathbf{OH}]-\mathbf{15.0}} \qquad \text{Equation 4.3}$$

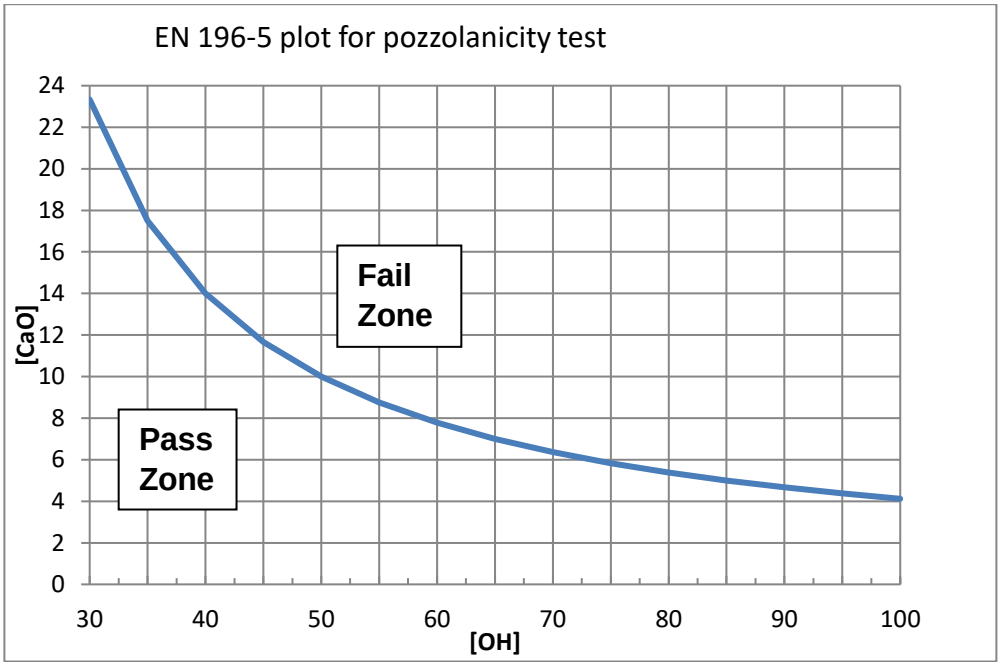

Figure 4.9: Calcium and hydroxyl ions saturation graph for testing pozzolanicity of pozzolanic cements.

The relationship plotted on a graph paper gives a curve that acts as a boundary for decision on whether the values of the calcium and hydroxyl ions estimated from a test sample qualifies to pass for pozzolanicity test. A test sample with calcium and hydroxyl values that places it's plot above the saturation concentration curve is considered to have failed the pozzolanicity test. Test samples whose values are below the saturation curve are considered positive for the pozzolanicity test (Figure 4.9).

4.2.3.2 Frattini test results

Titrimetry results and the deduced values of CaO and OH are presented in Table 4.6

Table 4.6: Titrimetry results and calculated CaO and OH values (EN 196-5)

Sample No.	V3-1	V3-2	V3	V4-1	V4-2	V4	CaO	OH
	f1	0.8618		f2	1.054			
Poz-1	26.2	25.2	25.7	37.0	36.0	36.5	18.9	54.2
Poz-2	26.7	28.0	27.4	29.5	28.9	29.2	15.1	57.7
	f1	0.8312		f2	1.053			
Poz-3	22.9	22.5	22.7	27.2	27.7	27.5	13.7	47.8

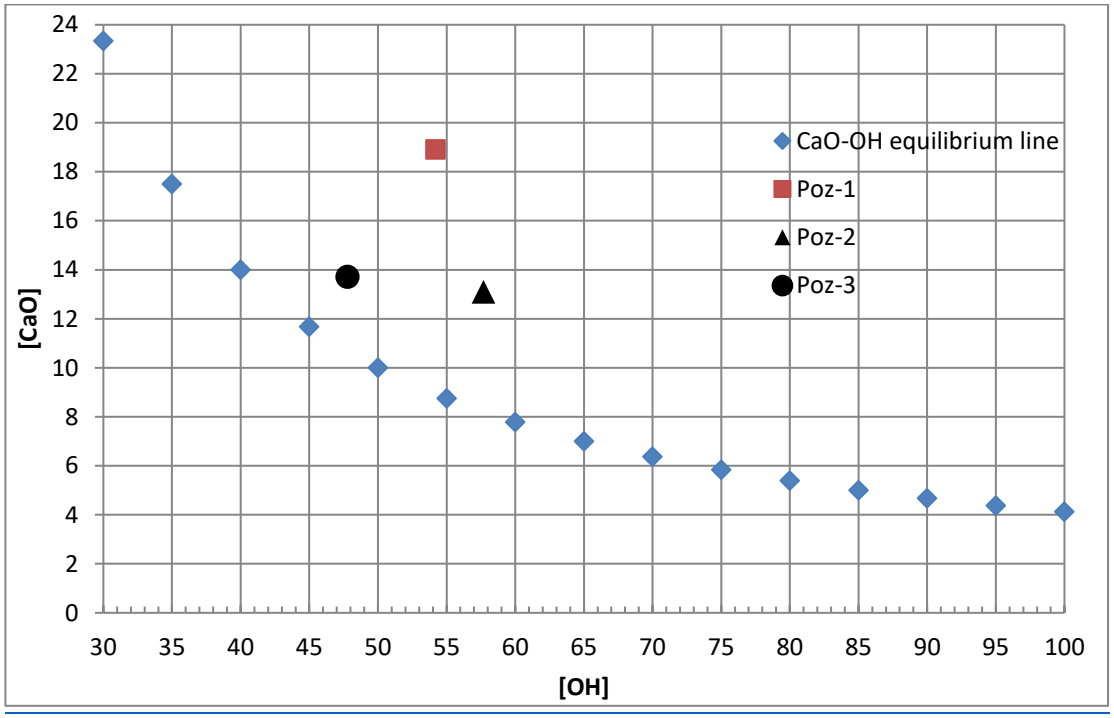

Figure 4.10: Plot of pozzolanicity test results for the Frattini test (EN 196-5)

4.2.4 Heat of hydration studies

Isothermal conduction calorimetry (TAM Air, TA Instruments) (Figure 4.11) was used to study the influence of carbonatites and kamafugites on hydration progression using heat of hydration as a proxy indicator. Both heat rates and total heat generated during hydration processes were recorded and normalized. The carbonatites and kamafugites were compared against two controls, CEM I 52.5 R and a GGBS blended cement samples following the experimental design in Table 4.7. Six (6) samples for each of the test kamafugites and carbonatites were prepared and loaded in an eight channel isothermal calorimeter to run for 92 hours for the samples that studied the effect of calcination and 162 hours for the samples that were used in the study of the effect of fineness and replacement levels of kamafugites and cerbonatites in Portland cement.

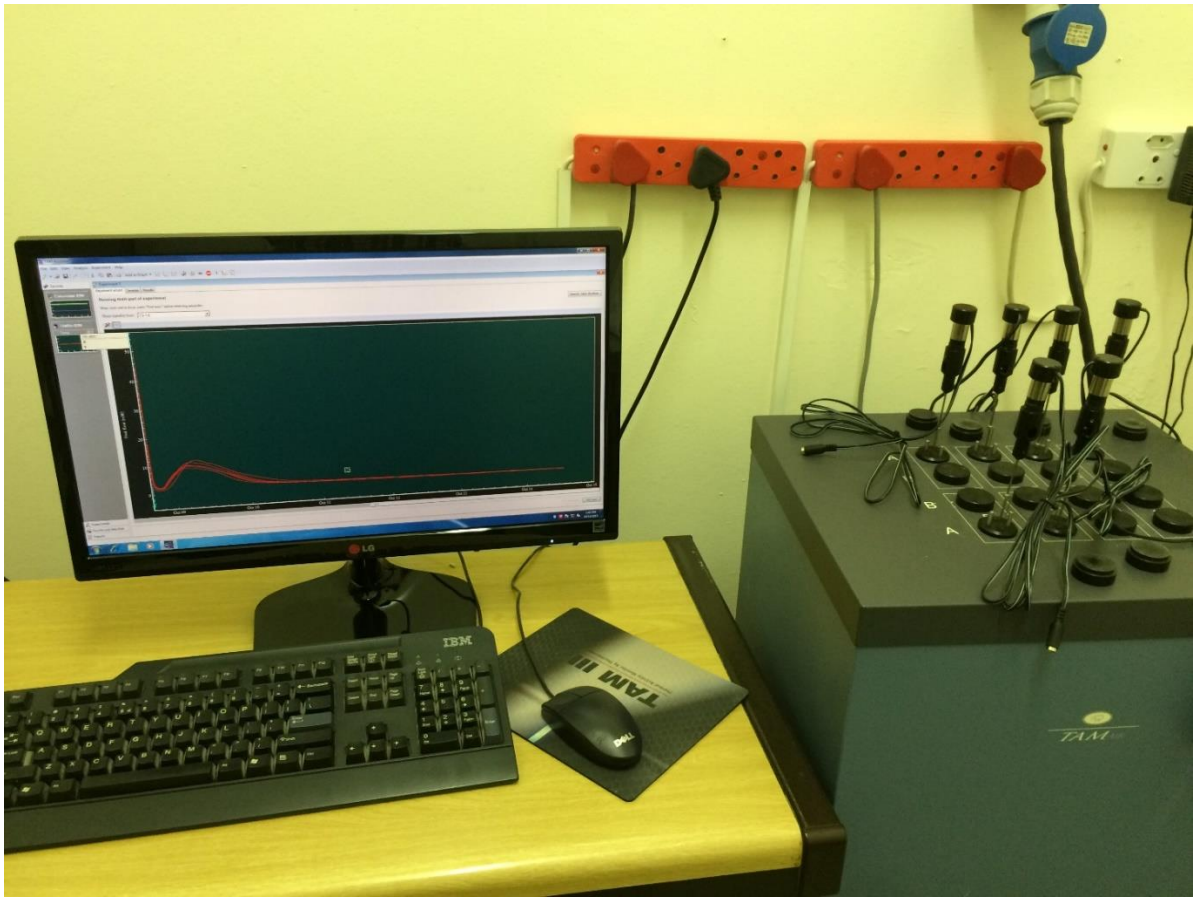

Figure 4.11: Equipment used in the heat of hydration studies

Table 4.7 provides mix proportioning details followed in characterizing the effects of fineness and replacement level of kamafugites and carbonatites on Portland cement hydration kinetics.

Table 4.7: Mix proportions for heat of hydration studies on the effect of fineness and replacement levels of test kamafugites and carbonatites.

Sample Name		**Poz-1 (g)**			**Poz-3 (g)**			**CEM 1 (g)**	**Total weight per sample (g)**
Fineness		**F1**	**F2**	**F3**	**F1**	**F2**	**F3**	Control	Blend
Percentage replacement level (weight in grams) of the total test sample weight of 4.0 grams	**10%**			0.4g			0.4g	3.6 g	4.0 g
	20%	0.8g	0.8g	0.8g	0.8g	0.8g	0.8g	3.2 g	4.0 g
	30%			1.2g			1.2g	2.8 g	4.0 g
Control sample CEM1(52.5R)		4.0 grams			4.0 grams			0 g	4.0 g

The mix proportioning for the characterisation of pozzolanic reactions followed the arrangement presented in Table 4.8. The experiment involved integration of slagcem as a second control and CEM I 52.5R type cement replaced at 20% level with test pozzolan.

Table 4.8: Mix proportioning for heat of hydration studies at 20% replacement level

Experiment	**Remarks**	**CEM I (g)**	**Test Material (g)**	**Water (g)**
Heat of Hydration	Control 1 (CEM I)	4	0	2
Heat of Hydration	Control 2 (65:35 CEMI: Slag)	4	0	2
Heat of Hydration	CEM I/Poz-1	3.2	0.8	2
Heat of Hydration	CEM I/Poz-2	3.2	0.8	2
Heat of Hydration	CEM I/Poz-3	3.2	0.8	2

4.2.4.1 Preparation of samples

The evolution of heat of hydration at early ages (0-96 hours) was recorded using an 8 channel isothermal conduction calorimeter (TAM Air) (Figure 4.11). The experiment protocol obtaining for isothermal conduction calorimetry experiments at Afrisam (South

Africa) (Pty) Ltd Rooderport cement laboratories was adapted for the current work and hence the reference samples in the calorimeter was not changed. The experimental set up required 4 grams of a test sample and therefore 4 grams of each of the different test samples blended following the experimental design (Tables 4.7 and 4.8) and control samples were prepared and placed in ampules. Two milliliters of distilled and deionised water was used in all the experiments for a water-to-binder ratio of 0.5. The water was dispensed into the samples by special syringes that are inbuilt in the rubber ampule tops together with an electric mixer. The setup of this experiment (Figure allows observation of the evolution of heat of hydration through all the five (5) characteristic stages, namely the preinduction stage (initial hydrolysis), the dormant period (induction stage), the hydration acceleration, the hydration deceleration, and the long-term steady state.

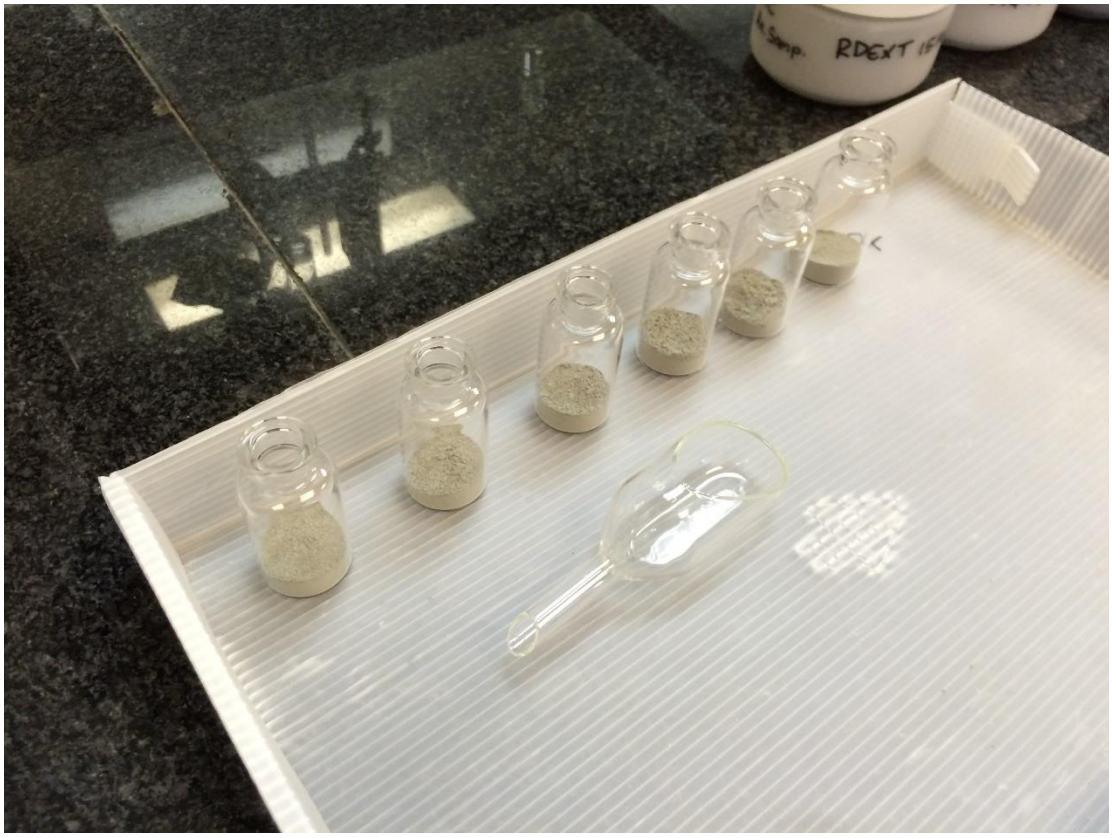

Figure 4.12: Samples placed in ampules ready to be covered and loaded in the isothermal calorimeter for equilibriation before water is added and mixing done inside the testing equipment.

4.2.4.2 Measurement of heat of hydration (HoH)

The ampules containing the reactants and covered with rubber stoppers that are supporting the syringes and the electric mixer are inserted in the different compartments of the calorimeter. The setup is left for about 45 minutes to equilibrate so that the temperature of the sample and the mixing water are brought to the test temperature. The heat of hydration measurements for the current experiments were taken at a constant temperature of 20ºC. When the system had equilibrated, water was injected into the reactants and mixing was achieved with the electric mixer. The mixer was switched on for one minute for each of the ampules at the time water was being introduced. Care was taken to achieve the mixing consistency for all the samples since mixing conditions have been found to affect hydration kinetics (Juilland et al., 2012). The experiment ran for 96 hours. The collected data was normalized to get heat rate over unit mass (in grams) of the different reactants before data analysis begun.

4.2.4.3 Results

Table 4.9**:** Total heat (J/g) normalized by cement content

Sample ID	Total heat (J/g) normalized to cement content vs time of hydration (hrs)						
	1 hrs	2 hrs	3 hrs	7 hrs	24 hrs	48 hrs	92 hrs
Poz-1	0.95	10.07	13.75	29.45	201.66	268.53	329.82
Poz-2	0.09	10.93	14.99	29.6	206.66	272.29	336.44
Poz-3	0.16	10.14	14.45	30.4	200.37	267.2	325.27
Control CEM 1 (52.5R)	0.14	6.52	9.55	23.37	193.99	265.7	322.26
Control-GGBS	0.09	9.85	12.35	26.2	227.4	310.41	390.6

The results from the heat of hydration experiments for 92 hours testing period are presented summarised in Table 4.9. More results have been saved under folder name “Heat of Hydration” on the DVD drive submitted together with this thesis. The results show samples blended with kamafugites and carbonatites and GGBS to have a higher heat release per unit cement content compared to the control sample (CEM I

52.5R). Various research (Malhotra and Mehta, 1996; Schöler et al., 2017) reveal the pozzolanic reaction to be more evident in concrete mixes after 28 days. The intention for characterisation of the early age heat of hydration of OPC blended with test pozzolans was therefore to review their effect on the important hydration processes that are responsible for the transition of concrete through setting, hardening and strength development stages. Moreover, highly pozzolanic SCMs may contribute to strength gain at an earlier age. Riding et al., 2012, stresses the importance of early hydration in influencing the micro-characteristics of concrete that are responsible for its strength, vulnerability to delayed ettringite formation and development of internal residual stresses that would compromise concrete durability.

4.2.5 Chemical shrinkage tests

Chemical shrinkage measurement came as a sequel to characterisation of the kamafugites and carbonatites as pozzolans in Portland cement after inconsistencies appeared in the previous results from two test methods. Two standard test methods for pozzolanicity, one direct, the Frattini test, (EN 196-5) and one indirect, the strength activity index (SAI), (BS 3982), used to characterize pozzolanicity of kamafugites and carbonatites yielded contradicting results. The direct method which relies on estimation of free Ca^{2+} ions in a test solution resulted in a higher concentration of the ions indicating a lack of pozzolanic reaction of the kamafugites and carbonatites while the indirect method, the strength activity index, showed the kamafugites and carbonatites to be pozzolanic with strength gain against the control sample up to 28 and 90 days of curing. It was hypothesized that the presence of free Ca^{2+} ions in the kamafugites and carbonatites limited the application of the direct test method (EN 196-5, 2005). The EN 196-5, 2005, standard method assumes that test pozzolans, which are mostly silicic, do not significantly contribute to Ca^{2+} ions concentration in the test solution (BS EN 196-5, 2005; Donatello, Tyrer and Cheeseman, 2010). Carbonatites are primarily composed of calcite and minor quantities of dolomite minerals (Stoppa and Schiazza, 2013) that can be a source of extra Ca^{2+} ions above these supplied by the hydrating cement leading to circulation levels beyond the maximum expected for a pozzolanic cement and therefore causing the EN 196-5, 2005, standard method to fail to detect pozzolanic properties.

To strengthen the basis for testing the hypothesis above, a third pozzolanicity test method, the chemical shrinkage measurement, was proposed to characterize the pozzolanic nature of carbonatites. The chemical shrinkage method presents the advantage of indirectly assessing chemical processes in a water-cement mixture while eliminating the influence of mechanical factors common to the SAI method. It is known that the presence of mineral powders influences cement hydration and compressive strength of blended cement in ways other than pozzolanic reaction (Ballim and Graham, 2009; Kadri et al, 2010; Berodier, 2015, Nwaubani, 2018) and therefore the SAI test requires additional tests to validate pozzolanic reaction. The chemical shrinkage measurement applied the dilatometry technique to record volume changes in cement mortar resulting from chemical processes that are associated with the hydration and pozzolanic reactions. The chemical shrinkage test results were compared with results from heat of hydration, thermogravimetric analysis (TGA) and compressive strength and were found to be consistent.

Chemical shrinkage tests were applied on test samples following a mix design presented in Table 4.10. The hydration process between cement and water results into hydration products that are less in volume than the absolute volume of the reactants (Tazawa, Miyazawa and Kasai, 1995; Mounanga et al.,2004). Stoichiometric quantification of hydration processes can help in understanding the effects of blending Portland cement on pozzolanic activity and hydration progression (Tazawa, Miyazawa and Kasai, 1995; Mounanga et al.,2004; Berodier, 2015). This process is however only possible if the hydration reaction mechanisms in cement systems are known (Tazawa, Miyazawa and Kasai, 1995; Mounanga et al.,2004). While the hydration reactions in plain Portland cement are reported complex to establish (Tazawa, Miyazawa and Kasai, 1995; Wild, Khatib and Roose, 1998; Mehta and Monteiro, 2006), addition of mineral admixtures into plain Portland cement systems increases on this level of uncertainty in establishing the reaction mechanisms that go on in the cement paste hydration processes. Tazawa, Miyazawa and Kasai, 1995, however, found that experimental results predicted well the chemical shrinkage property of hydrating cement paste.

Table 4.10: Mix design for the different mortars used in the chemical shrinkage experiments

Sample No.	Sand (g)	CEM 1 52.5R (g)	Test Pozz (g)	FA (g)	Water (ml)	Remarks
1	200.0	200.0	-	-	100	Control 1
2	170.0	200.0	30.0	-	100	Poz-1
3	170.0	200.0	30.0	-	100	Poz-2
4	170.0	200.0	30.0	-	100	Poz-3
6	170.0	200.0	-	30.0	100	Control 2 (Fly ash)
7	170.0	200.0	30.0	-	100	Poz-1 Calcined 825^{o}C
8	170.0	200.0	30.0	-	100	Poz-2 Calcined 825^{o}C
9	170.0	200.0	30.0	-	100	Poz-3 Calcined 825^{o}C

The current study applied the dilatometry principle as an experimental approach to generate chemical shrinkage results that guided on identifying the possible hydration reaction mechanisms ongoing in the kamafugites and carbonatites blended Portland cement paste. Adopting previous experimental procedures (Berodier, 2015; Yodsudjai and Wang, 2013) and protocols in Ballim, 1983, a cheap instrumental setup was improvised to include a 500ml glass container with a rubber-cushioned watertight metallic cover and a 50 mls graduated glass burette. A small hole was drilled in the center of the metallic cover and the 2mls graduated burette was fitted with clear silicon to ensure water tightness (Figure 4.13). The setup provides continuous manual measurements in volumetric changes due to chemical shrinkage. To minimize variables in the hydration reaction, the cement content in all samples was kept constant and the test pozzolans were introduced to partially replace sand for its particle size less than 150µm. The three test pozzolans (Poz-1, 2 & 3) were all tested in raw and calcined state to further characterise the effect of the carbonate minerals and volatile alkalis (results presented in Section 4.3). Table 4.10 gives the mix proportioning of all the test samples and experimental setup used.

Figure 4.13: Chemical shrinkage measurement apparatus and experimental setup

4.2.5.1 Preparation of samples for chemical shrinkage test

All the samples were pre-weighed and, together with distilled water, kept in a room at controlled temperature (20±2ºC) for 24 hours before starting the experiment. The cement, sand and test pozzolans were placed in a stainless steel bowl and using a spoon blended together in a dry state for a minute and distilled water was then added. Mixing of the blend with water was done by hand and for a period of 3 minutes with one minute of rest in between. The mix proportioning is as presented in Table 4.10. After establishing homogeneity in the mortar mix, a sample of the mix was placed in a pre-weighed glass bottle shown in Figure 4.13. Care was taken to limit the amount of the test sample placed in the glass bottle to less than 10mm in thickness to eliminate the possibility of self-desiccation (Wild et al., 1998). The samples were weighed and then placed under partial vacuuming for 2 minutes to eliminate entrapped air. The sample was weighed again and this weight after compaction was used in chemical shrinkage calculation. Distilled water was slowly and carefully poured on top of the sample in the glass container ensuring that the paste was not disturbed. The water was filled to the brim of the glass container and the whole sample container was carefully immersed

into a bucket full of distilled de-aired water that was maintained at the same room temperature as set throughout this experiment (20±1ºC). The covers of the glass container with 50mls graduated burettes fitted on them (Figure 4.13) that had spent 24 hours soaked in the distilled de-aired water to minimize any water absorption of the silicon glue and rubber material were then used to seal the sample under water. The sealing of the sample was done in such a way that the water meniscus was about 1mls below the highest reading on the fitted burette to facilitate long term readings. To avoid water loss to evaporation, a layer of a non-emulsifying oil (hydraulic oil) was placed above the water level in the burette. The whole setup was finished within 25 minutes from the start of mixing. The time when water was added into the sand-cement-pozzolan mixture was recorded and considered as the start of the test and the first shrinkage reading was taken at one hour after the start time.

4.2.5.2 Measurement of chemical shrinkage

The meniscus readings were taken for the different experiments following the format provided in Table 4.11. Figure 4.14 presents a typical graphical presentation of the results generated

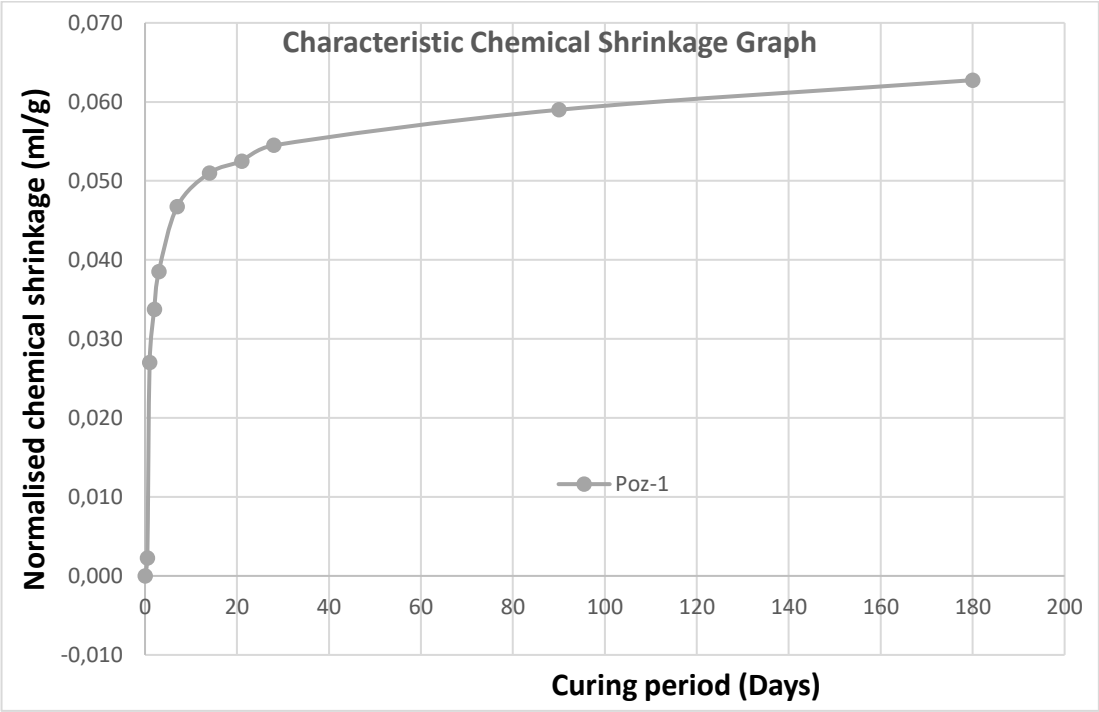

Figure 4.14: Characteristic chemical shrinkage graph

Table 4.11: Characteristic chemical shrinkage test analysis

Experiment: Chemical shrinkage of blended Portland cement (Pycnometer test)							
Sample Name: Poz-3 CALCINED		**Weight: (W2-W1)=**		**59.80**	**Sample Number: 10**		
Start date for Experiment: 17-11-2015				**Start time for Experiment: 1:37 PM**			
Date	**Curing period (days)**	**Day Time**	**Time Unit**	**Water mark (ml)**	**Oil Mark (ml)**	**Room Temp (^oC)**	**Normalised reading (ml/g)**
17-Nov-15	0	2:37PM	1				
		3:37PM	2				
		4:37PM	3				
		6:37PM	5				
		8:37PM	7				
		11:37PM	10				
18-Nov-15	1	7:30AM	17				
		4:00PM	25				
		10:00PM	31				
19-Nov-15	2	9:00AM	42				
		3:30PM	49				
		8:00PM	53				
20-Nov-15	3	9:00AM	61				
		2:30PM	67				
		8:15PM	72				
24-Nov-15	7	8:00AM	84				
		2:00PM	90				
		9:00PM	97				
1-Dec-15	14	8:00AM	108				
		3:00PM	115				
		8:00PM	120				
15-Dec-15	28	9:00AM	672				
12-Jan-16	56	9:00AM	1344				
15-Feb-16	90	9:00AM	2160				
16-May-16	180	9:00AM	4320				

4.2.5.3 Results

Figure 4.15 is a graphical representation of chemical shrinkage values presented in Table 4.12. The observed volume change is normalized to cement content and variabilities evaluated for compositional effects and pozzolanic reaction. The results show the control sample blended with fly ash, and Poz-1 a carbonatite and Poz-2 a kamafugite, to have higher chemical shrinkage values than the control sample that

was blended with andesite powder. Both Poz-1 and Poz-2 are silica undersaturated and with high contents of calcite. Poz-3, an ultrapotassic and silica saturated kamafugite with relatively low content of carbonate minerals gave the least values in chemical shrinkage ranking lower than the andesite powder blended control sample for the whole test period up to 180 days.

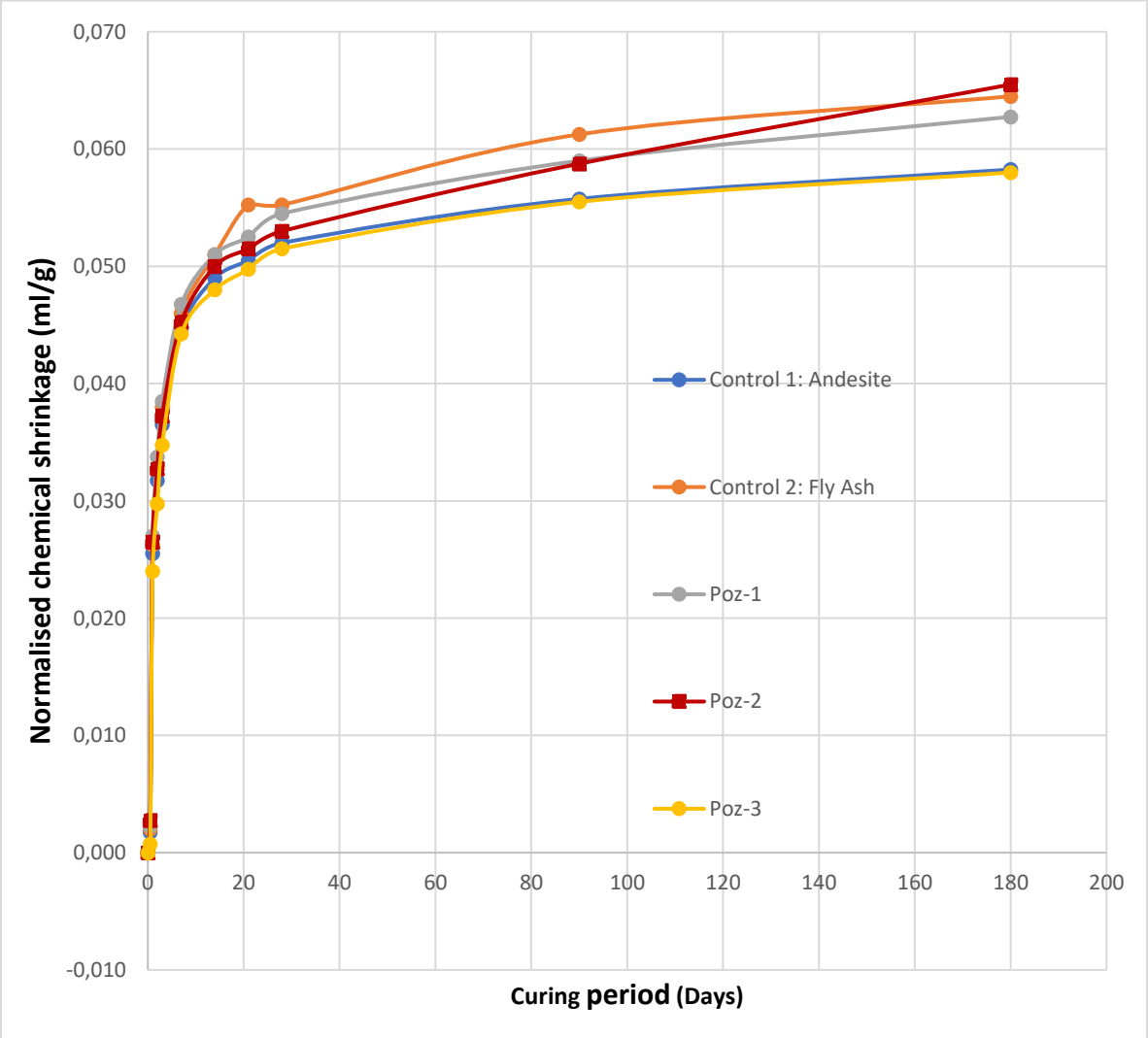

Figure 4.15**:** Chemical shrinkage results for raw test pozzolans (results normalized to cement content).

Table 4.12**:** Chemical shrinkage results

Curing (Days)	Control 1: Andesite (mL/g)	Control 2: Fly Ash (mL/g)	Poz-1 Raw (mL/g)	Poz-2 Raw (mL/g)	Poz-3 Raw (mL/g)
0	0.000	0.000	0.000	0.000	0.000
0.5	0.002	0.002	0.002	0.003	0.001
1	0.026	0.026	0.027	0.027	0.024
2	0.032	0.033	0.034	0.033	0.030
3	0.037	0.038	0.039	0.037	0.035
7	0.045	0.046	0.047	0.045	0.044
14	0.049	0.051	0.051	0.050	0.048
21	0.051	0.055	0.053	0.052	0.050
28	0.052	0.055	0.055	0.053	0.052
90	0.056	0.061	0.059	0.059	0.056
180	0.058	0.065	0.063	0.066	0.058

4.2.6 Thermalgravimetric Analysis (TGA) tests

To characterize hydration products, pozzolanic reactions and degree of hydration of the different phases in the hydrating cement paste, the Thermogravimetric analysis/Differential thermal analysis (TGA/DTG) instrumental technique was applied on paste samples at 0 hours, 7 hours, 7 days, and 56 days from the start of hydration following the experimental design presented in Table 4.13.

Table 4.13: Paste mix proportioning for TGA and XRD tests

<table>
<tr><td colspan="7">W/C=0.35</td></tr>
<tr><td>Sample ID</td><td>Fineness level</td><td colspan="3">Replacement level/ Sample No.</td><td>Calcined Sample</td><td>Remarks</td></tr>
<tr><td rowspan="2">CEM 1 52.5R</td><td rowspan="2">Control</td><td>10%</td><td>20%</td><td>30%</td><td>20%</td><td rowspan="9">Only 2 fineness levels F1 and F3 considered</td></tr>
<tr><td colspan="3">1</td><td></td></tr>
<tr><td rowspan="2">Poz-1</td><td>F1</td><td>2</td><td>8</td><td>14</td><td></td></tr>
<tr><td>F3</td><td>3</td><td>9</td><td>15</td><td>20</td></tr>
<tr><td rowspan="2">Poz-2</td><td>F1</td><td>4</td><td>10</td><td>16</td><td></td></tr>
<tr><td>F3</td><td>5</td><td>11</td><td>17</td><td>21</td></tr>
<tr><td rowspan="2">Poz-3</td><td>F1</td><td>6</td><td>12</td><td>18</td><td></td></tr>
<tr><td>F3</td><td>7</td><td>13</td><td>19</td><td>22</td></tr>
</table>

TGA/DTG applies mass loss with increase in temperature to identify composition properties of a sample by comparing the observed trends with thermal data of pure minerals that are predicted to be present in the test samples. In this thesis, the TGA technique is applied in quantification of cement hydration products and how they relate with anhydrous phases (esp. carbonates, MgO, alkalis and silicates of test pozzolans) within the hydrating paste system. Numerical models that quantify the degree of hydration (α), the degree of pozzolanic activity (β) and the net SCM benefit (λ) of SCMs are generated for the test pozzolans which further helps in understanding the mechanisms of hydration of cements blended with carbonatites and kamafugites.

4.2.6.1 Preparation of samples

Plain and blended cement samples were mixed in a 0.35 water to cement ratio and cast in a watertight cylindrical plastic container of diameter 30mm and height 750mm. Four curing periods, 0hrs, 7hrs, 7 days and 56 days, were selected under this study. The samples prepared according to the experimental design in Table 4.13 were stored under controlled temperature of 20°C ±2. A total of 22 samples were prepared to address fineness property, effect of replacement level, and the role of calcite and volatile alkalis as compositional variables. Sampling processes involved taking slices from the cylindrical samples for both the TGA and XRD tests (discussed in Chapter 3 of this thesis) at the same time. Three disk samples were taken per sampling event using a water-cooled diamond saw to slice through the sample and its plastic housing. The plastic housing was important in keeping the rigidity of the samples at 7 days of hydration. The hydrating paste sample for 7 hours was drawn from the same mix that was cast in the cylindrical plastic container but separately placed and properly sealed in a plastic sample bag. The sample was then crushed after 7 hours of hydration and subjected to hydration stoppage protocols that were applied uniformly to all samples at all testing periods except the anhydrous samples.

4.2.6.2 Hydration stoppage

The sliced samples, about 2mm thick disks made for the 7 and 56 days and the crushed samples for the 7 hrs of curing, were placed in isopropanol to stop hydration process by the solvent exchange mechanism. The samples were kept in isopropanol for 48

hours, replacing the isopropanol liquid with a fresh one after 6 hours and 24 hours. The samples were then dried under vacuum conditions at 40°C for another period of 48 hours before testing them.

4.2.6.3 Measurement and analysis

Thermogravimetric analysis was performed on both anhydrous and hydrated samples, unblended and blended, to understand phase compositions and how they change with hydration progression. The parameters tested included fineness, replacement level, age of curing and carbonate minerals for the three test pozzolans. All tests were performed on powder samples in a Mettler Thermogravimetric Analyzer equipment model TGA/DSC1 accessed at Afrisam South Africa (PTY) Ltd at their Center for Products Excellence, Rooderport. Samples from vacuum drying were milled using a mortar and pestle to fine powder. Samples weighing between 50 and 70 grams were placed in aluminium crucibles as sample container (Figure 4.16) in a furnace cell. Temperature in a furnace cell was increased to the starting temperature of 100°C before starting measurements. The samples were then heated and their thermal decomposition features observed from 100°C to 950°C at a heating rate of 20°C/min while the chamber gas used was air flowing at 200ml/min.

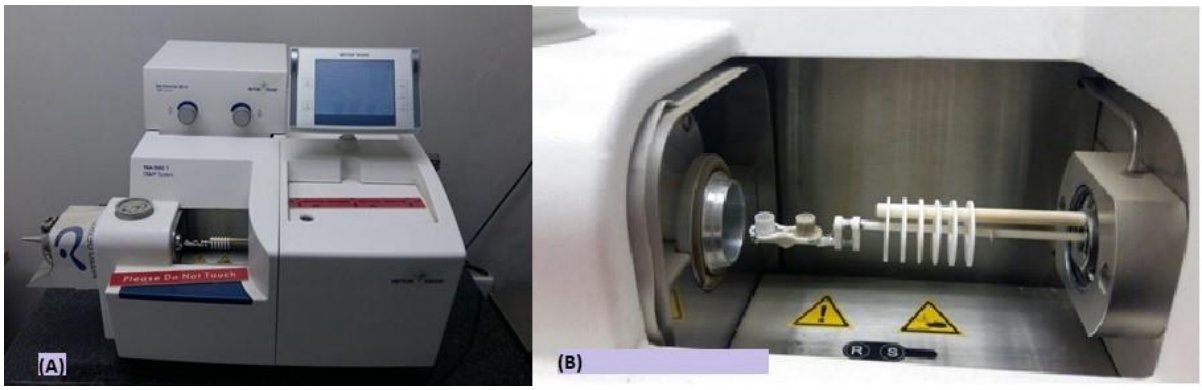

Figure 4.16: (A) Thermogravimetric analysis instrument (B) Furnace Cell of the TGA showing the sample and control cells

Typical results of TGA are presented in form of a mass loss vs temperature graph, and its first derivative as the DTG graph shown in Figure 4.17. The graph shows three endothermic peak zones of dehydration, dihydroxylation and decarbonation at temperature ranges of 105°C-400°C, 400°C-600°C, and 600°C-800°C respectively.

Text data was also generated from the analysis software (STARe Evaluation) for the purpose of estimation of hydration products. The digital data generated by the software provides weight values against temperature at intervals of approximately 0.2 of a degree.

Through observation of the changes in the 1st derivative curves with varying parameters, consideration is made for the nature of hydration products made and how these products are changing with time, replacement level, composition, and fineness. The 1st derivative curves are applied in estimation of CH consumption, characterisation of hydration products and changes in the carbonate phases against the parameters studied.

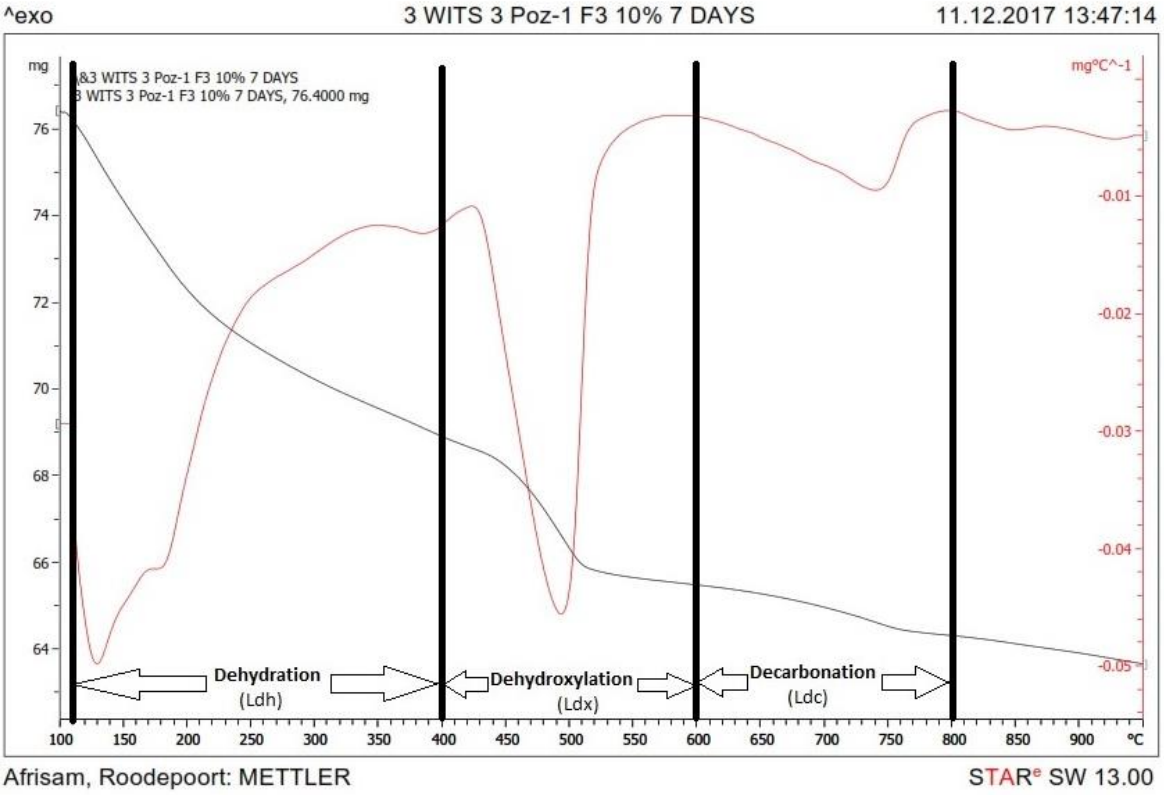

Figure 4.17: Characteristic TGA/DTG graph for a blended cement (CEM I 52.5R with a carbonatite at 10% level of replacement).

4.2.6.4 Estimation of the degree of hydration(α) and pozzolanic activity (β) by TGA method

Free calcium hydroxide (CH), being one of the hydration products of the silicate phases in Portland cement systems, reacts with pozzolanic materials to form extra hydrates with cementing properties. As a result, Portland cements that are blended with pozzolanic materials have reduced CH content over a long curing period because of its involvement in the pozzolanic reactions. Therefore, quantification of CH content in hydrating Portland cements blended with pozzolanic materials facilitates characterisation of pozzolanic reactivity of pozzolanic materials (Ramachandran, 1979). Thermogravimetric analysis instrumental technique was applied in pozzolanic characterisation of kamafugites and carbonatites. The TGA graph presents three major phases, the dehydration phase (Ldh), the dihydroxylation phase (Ldx) and the decarbonation phase (Ldc), each phase presenting unique properties as follows (Lothenbach and Wieland, 2006; Monteagudo et al, 2014; Deboucha et al, 2017)

1. The dehydration phase (Ldh) considered on the TGA temperature scale to range from 105°C to 400°C represents mass loss due to decomposition of chemically bound water onto C-S-H, ettringite, hydrotalcite and aluminate hydrate phases in a cement paste.

2. The dihydroxylation phase (Ldx) (400°C to 600°C) characterizes mass loss due to the decomposition of CH precipitated from the hydration of silicate phases in cement. It is this CH that combines with the aluminosilicate phases in an SCM to cause a pozzolanic reaction (Equation 2.12). The same portlandite is prone to carbon dioxide attack through a reaction process known as carbonation, a condition that demands consideration of the decarbonation phase in the estimation of the CH content in a hydrating cement.

3. The decarbonation phase (Ldc) (600°C to 800°C) accounts for mass loss due to decomposition of carbonates to form CaO and CO_2 gas. In a plain Portland cement, carbonates are normally considered to be absent as shown by Bhatty, 1986, in his model of estimation of degree of hydration of cement. The TGA model by Bhatty, 1986, considers mass loss in the decarbonation phase of plain cement to be from the decomposition of carbonates which are formed by carbonation of the CH associated with the dihydroxylation phase. However, plant inefficiencies and cement handling can

result in plain Portland cement containing carbonates. Blended cements can also contain carbonates contributed by the mineral admixtures, mainly of volcanic origin as is the case in this thesis. Therefore, estimation of CH in the dihydroxylation phase must be sensitive to the two sources of carbonates. CH results that only consider the dihydroxylation phase are exposed to significant levels of error in their quantification.

Following TGA/DTG procedures, the reaction mechanisms in blended cement are assessed using chemically bound water in hydrated cement as a proxy variable since the reactions are predominantly hydration reactions, but also by monitoring changes in the mineral phases of the kamafugites and carbonatites. The observed changes with test variables clarify the actual mechanisms of interaction between the test pozzolans and Portland cement and, as a result, quantification of the degree of hydration (α) and the degree of pozzolanic activity (β).

4.2.6.5 Results

The TGA results for the dehydration (105°C to 400°C), dehydroxylation (400°C to 600°C) and decarbonation (600°C to 900°C) phases of thermo decomposition of test blended cement systems are presented in Table 4.14 as an extract of the file “TGA results” saved on the attached DVD. Test samples were water cured for 0 hrs, 7 hrs, 7 days and 56 days. The replacement level of test pozzolans was fixed at 20% to facilitate comparison in pozzolanic activity between the different samples. The results are presented as a fraction of a milligram (mg/mg) for each of the cementitious materials tested. This normalization simplifies estimation of lost water due to dehydroxylation and decarbonation of the total CH phases produced by the cement silicate phases in the hydrating cement systems. Normalization also enables stoichiometric estimation of the CH content and the amount of non-evaporable water. Accordingly, the results of the stoichiometric estimations are applied in comparison across all the test samples for the CH content.

The results normalized to cementitious material content show proxy values that, with a scale factor, can be used to estimate CH accumulation in hydrating cement.

Table 4.14: Mass loss due to thermo decomposition of test samples in TGA between 105 °C and 900 °C

Test sample and variables	**Curing (Days)**	**Mass readings**				Ldh (mg/mg)%	Ldx (mg/mg)	Ldc (mg/mg)
		105°C	**400°C**	**600°C**	**900°C**			
Poz-1 **Plain**		100.046	98.0234	97.0881	87.5844	2.022	0.935	9.499
Poz-2 **Plain**		100.002	96.9879	95.8639	86.0937	3.014	1.124	9.770
Poz-3 **Plain**		100.08	97.0388	95.9089	91.4042	3.039	1.129	4.501
Control (CEM I 52.5R)	0	61.3918	60.8237	60.6646	60.483	0.925	0.259	0.296
	0.3	61.2456	60.3096	59.7939	59.2752	1.528	0.842	0.847
	7	100.147	93.1442	88.6378	86.4686	6.993	4.500	2.166
	56	99.48	88.8905	83.0699	82.1948	10.645	5.851	0.880
Poz-1, **F3-20%**	0	47.7865	47.4045	47.2035	46.19	0.799	0.421	2.121
	0.3	51.2194	50.4102	50.014	48.7171	1.580	0.774	2.532
	7	45.0531	41.4878	39.9877	38.5859	7.914	3.330	3.111
	56	99.4968	88.2111	83.4544	80.5571	11.343	4.781	2.912
Poz-2, **F3 -20%**	0	78.7048	77.7612	77.3656	75.5	1.199	0.503	2.370
	0.3	62.0155	60.789	60.0782	58.0975	1.978	1.146	3.194
	7	44.5225	40.9238	39.2617	37.8914	8.083	3.733	3.078
	56	69.1876	62.3479	59.7674	56.9482	9.886	3.730	4.075
Poz-3, **F3-20%**	0	100.109	98.9594	98.5236	97.4701	1.148	0.435	1.052
	0.3	56.5422	55.0758	54.3332	53.2633	2.593	1.313	1.892
	7	60.9968	56.433	54.0594	52.7353	7.482	3.891	2.171
	56	75.067	66.6843	63.4955	60.597	11.167	4.248	3.861

4.2.7 X-ray diffraction tests

Both TGA and XRD tests track changes in CH content with curing and therefore characterize CH consumption as pozzolanic activity of the paste system. While quantification of the CH content was done following TGA procedures, XRD was applied as a validation tool to establish consistencies with the results of the TGA. XRD tests on three samples were further done to establish changes in hydration products with age.

4.2.7.1 Preparation of samples

The sample preparation and hydration stoppage followed procedures like those of TGA experiments described in Section 4.2.6 of the current chapter.

4.2.7.2 Measurement and analysis (XRD)

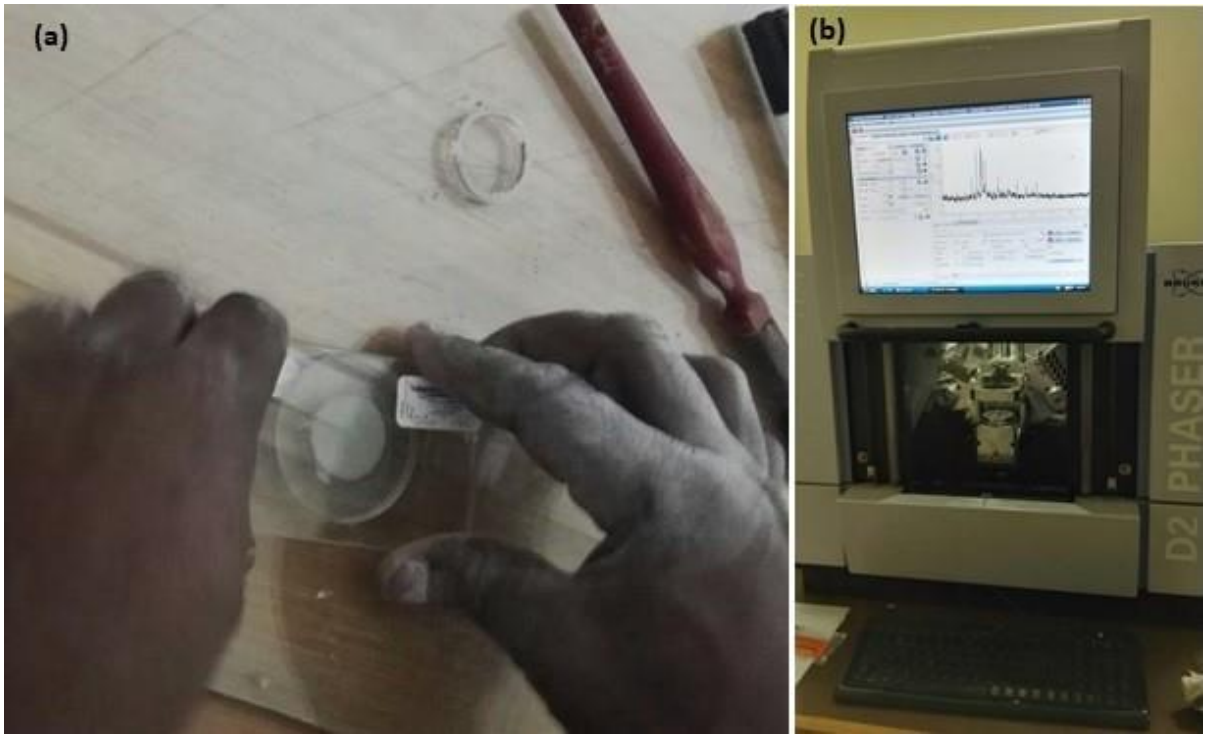

Figure 4.18: (a) placement of sample into the sample holder, (b) XRD machine with sample loaded onto the sample stage.

For each test, a sample powder was placed in a plastic XRD sample holder and straight glass plate was used to press the sample into the holder, trim its surfaces and finish it

flat to the brim of the sample holder so as to create a specimen face in the focusing angle of the diffractometer (see Figures 4.18 (a) and (b)).

XRD patterns generated were compared with reference XRD patterns for the different variables studied to identify the relative changes in crystalline phases. Of interest was the changes in crystalline peaks of calcite, ettringite, portlandite and other mineral phases of the test pozzolans on the XRD spectra while considering the parameters tested.

4.2.7.3 Results

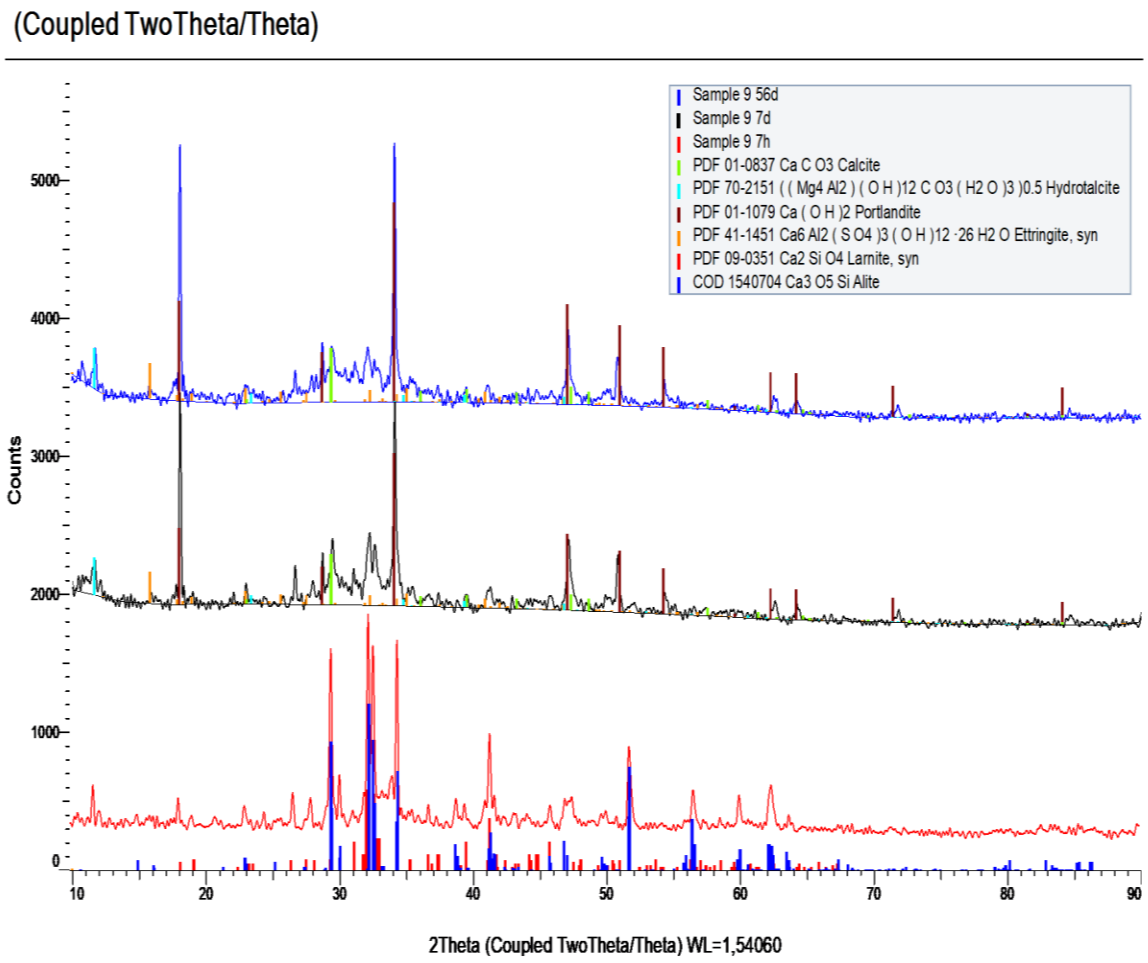

Figure 4.19: Diffraction patterns for Poz-1 blended Portland cement at 7hrs, 7 days and 56 days of curing

Figures 4.19, 4.20 and 4.21 show the XRD patterns of Poz-1, Poz-2 and Poz-3 respectively. The patterns are compared for the 7 hrs, 7 days and 56 days. The

samples at 7 hrs are still dominated by alite and belite phases. At 7 days, the C-S-H hump is evolded and the anhydrous silicate phases have significantly hydrated. The C-S-H hump doesn't show significant change at 56 days.

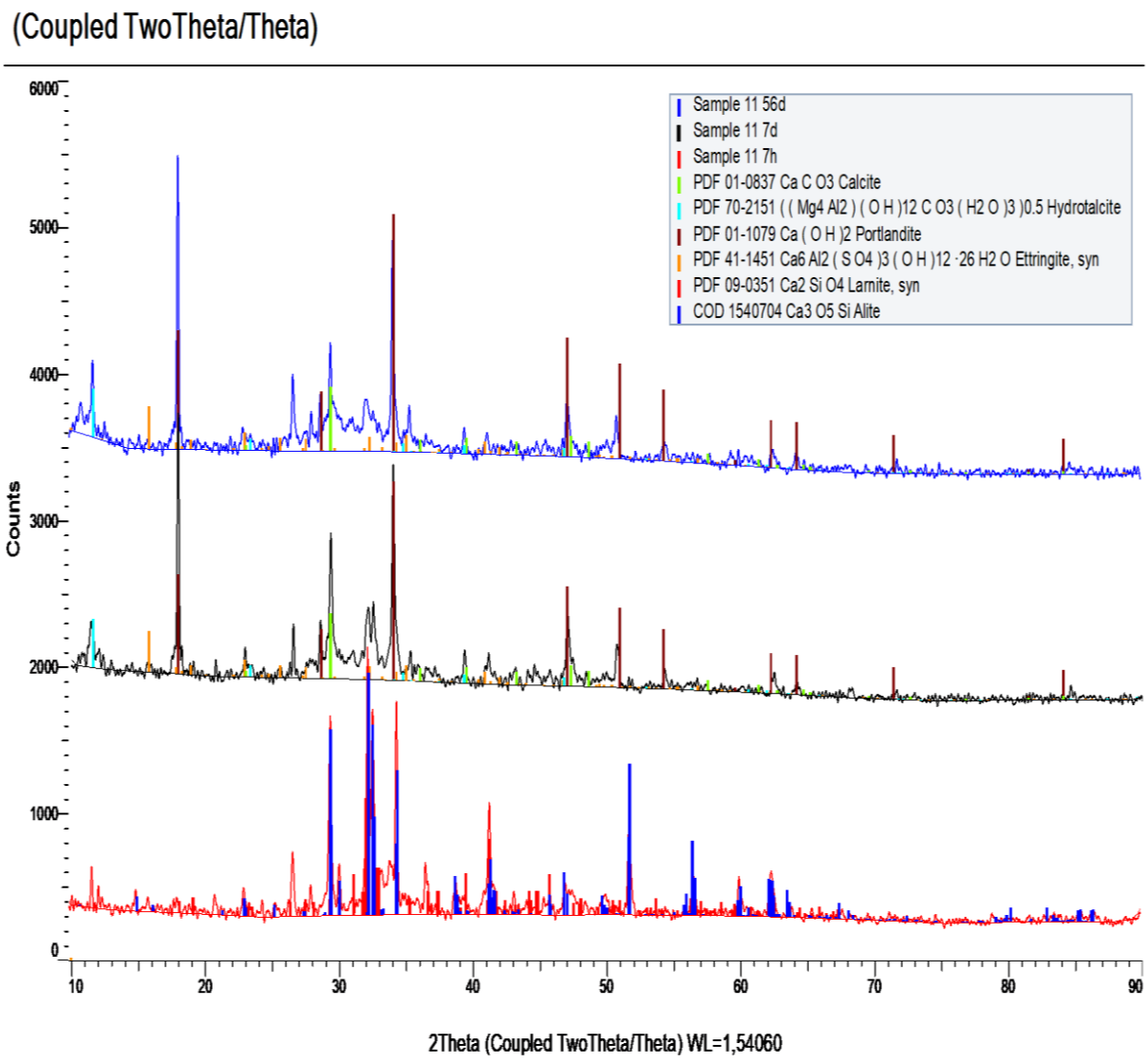

Figure 4.20: Diffraction patterns for Poz-2 blended Portland cement at 7hrs, 7 days and 56 days of curing

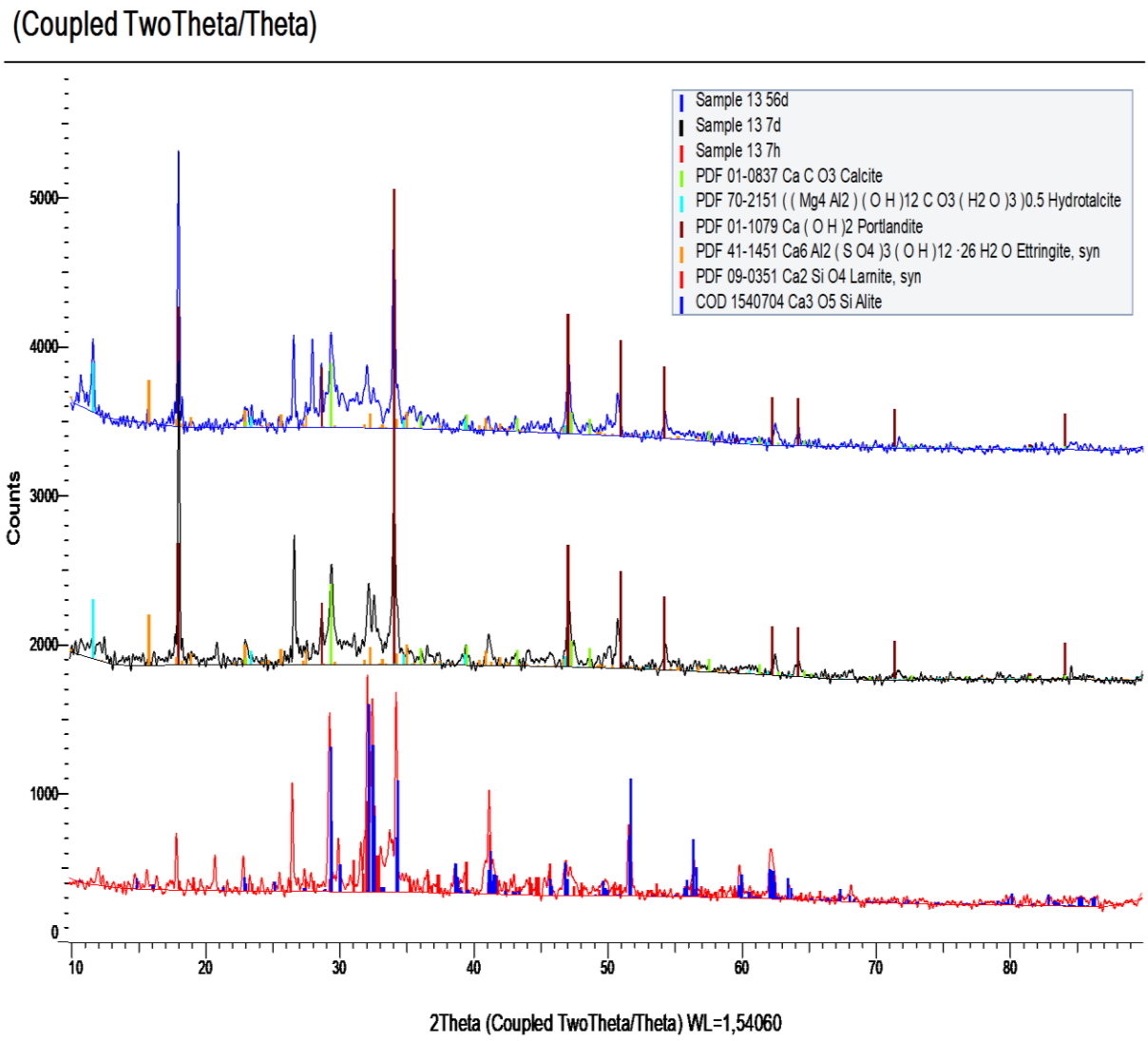

Figure 4.21: Diffraction patterns for Poz-3 blended Portland cement at 7hrs, 7 days and 56 days of curing

4.2.8 Comparison of test methods for pozzolanic activity characterisation

Test methods for characterisation of pozzolanic activity of mineral admixtures measure different parameters and, as such, were applied collectively to test performance of pozzolanic materials. On top of SAI, Frattini, XRD, TGA, isothermal calorimetry instrumental techniques and chemical shrinkage were applied in characterisation of pozzolanic activity of kamafugites and carbonatites. Both the SAI and the Frattini tests are well established in international standards as methods for testing pozzolanicity of mineral admixtures and the procedures for their application were followed as stated in the standards. There have been significant advances in characterising the TGA and

XRD instrumental technique for applications in characterisation of Portland cements blended with mineral admixtures and the author has applied the tools in accordance with standard procedures for use and useful results were generated. The tools demand high capital and maintenance costs and their access in Sub-Saharan Africa is limited. Isothermal calorimetry is applied by research mainly to study early age properties of hydrating cement, especially at a time when pozzolanic activity is not yet pronounced, a trend that has kept its application in characterising pozzolanic activity limited to a few research (Kocaba, Gallucci and Scrivener, 2012). Isothermal calorimetry also relies on sophisticated equipment that demands high capital and maintenance costs, a reason the tool is also not common in sub-Saharan Africa. The author studied chemical shrinkage of Portland cement blended with kamafugites and carbonatites based on the dilatometry principle. A low cost and simple experimental set up was realized and the intention of this section of the thesis is, firstly, to establish correlations between the different parameters applied in the study of pozzolanic activity of SCMs and, secondly, to show that the dilatometry method for measuring chemical shrinkage of cement is a plausible tool for characterising pozzolanic activity of Portland cement concrete.

Of the six methods applied in pozzolanic activity study, results generated from four of the pozzolanic tests, the compressive strength (SAI), the heat of hydration, the chemical shrinkage, and the thermogravimetric analysis (TGA) tests are considered for comparison. It was assumed that the progression of the tested parameters for the different methods would correlate for similar curing periods. The base parameter considered for this comparison was compressive strength. It is established that pozzolanic reactions result into strength giving hydration products. Accordingly, the choice of compressive strength was the most appropriate of all the parameters for the different test methods.

4.2.8.1 Correlation of compressive strength and chemical shrinkage

As shown in Figure 4.22, there is a significant correlation between strength and chemical shrinkage results for all the test samples, all the samples giving very high coefficients of determination (R^2>0.98). The mathematical relationship between chemical shrinkage and compressive strength is represented by Equation 4.4.

$$y_1 = Ax_1 \qquad \text{Equation 4.4}$$

Where y_1, is chemical shrinkage in mL/g, x_1 represents compressive strength, and A a scale factor.

Figure 4.23 presents a plot of all the data points on chemical shrinkage against strength. A general trend is observed establishing A in the equation to a scale factor of 0.001. The trend shows a plausible coefficient of determination with an R^2 value of 0.99.

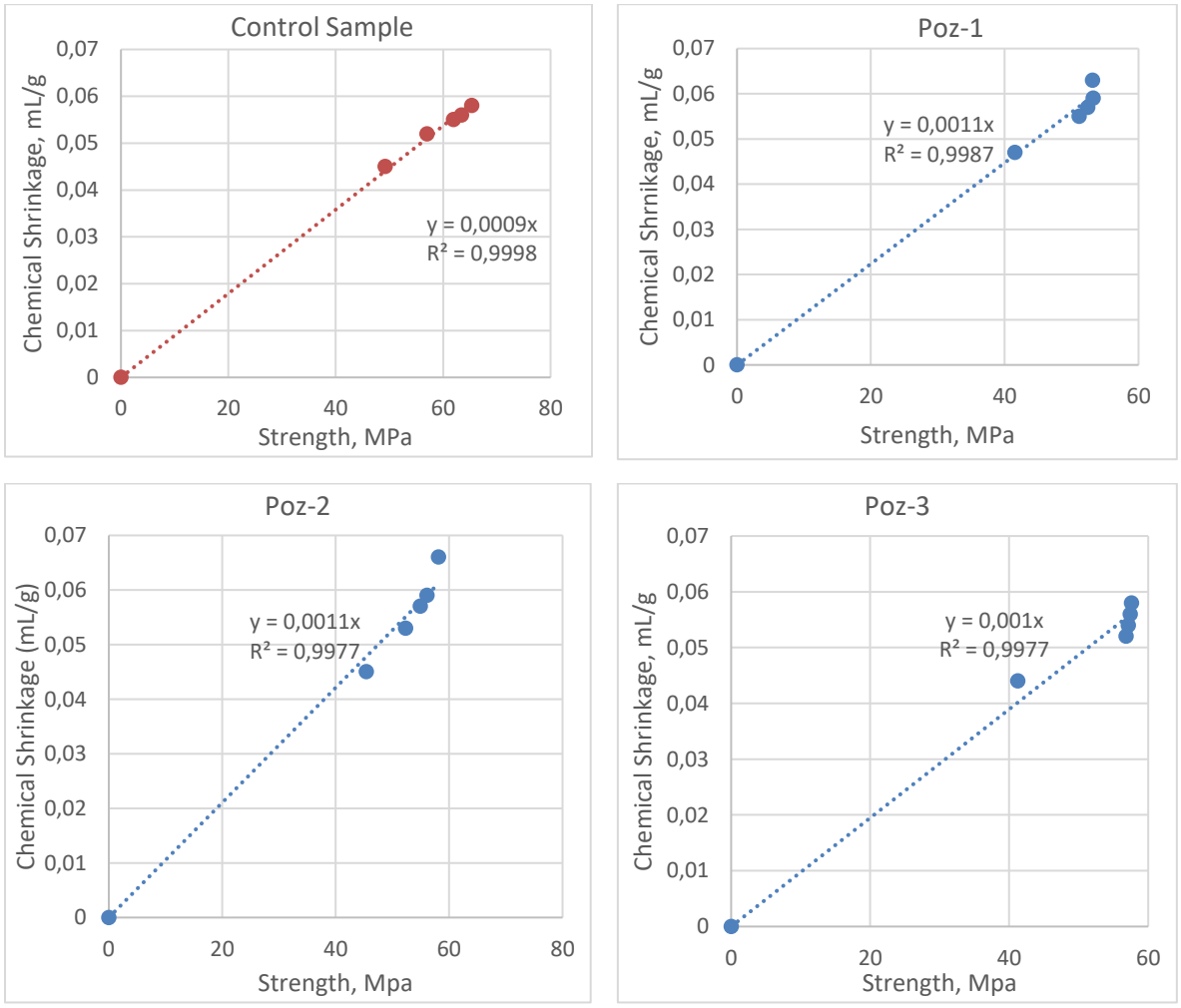

Figure 4.22: Correlation between compressive strength and chemical shrinkage results for pozzolanic activity tests for control sample (CEM I 52.5R), Poz-1, Poz-2 and Poz-3 blended cement samples.

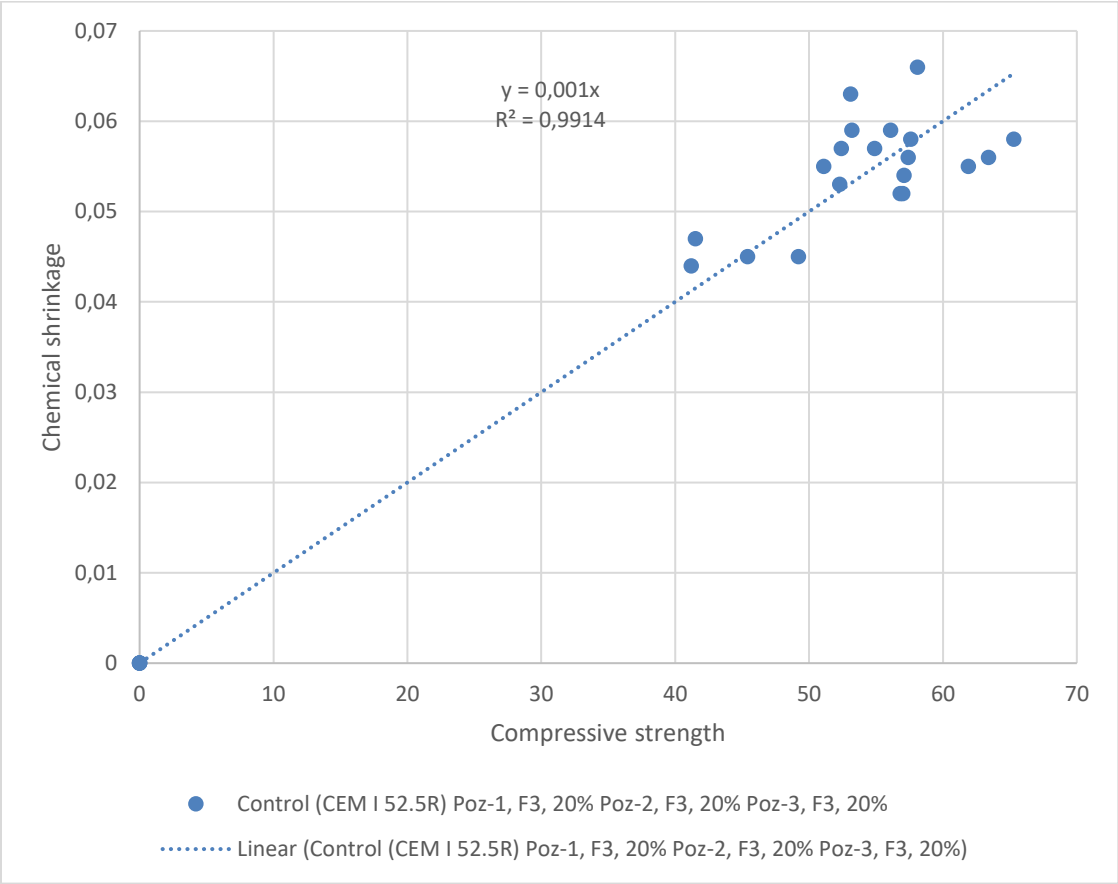

Figure 4.23: Correlation of the combined chemical shrinkage data ploted against strength for all the test pozzolans and cement control sample.

4.2.8.2 Correlation of compressive strength and TGA results

Figure 4.24 shows comparison between compressive strength and TGA results. The TGA decomposition temperature profiles are divided into three phases that reporesent dehydration (Ldh), dihydroxylation (Ldx) and decarbonation (Ldc). The Ldh and Ldx phases represent weight lost due to chemically bound water while Ldc represents weight loss due to decomposition of carbonates. Ldh spans the temperature range for decomposition of the silicate and aluminate hydrates in cement while Ldx, the dehydroxylation phase, spans the portlandite decomposition temperatures. The current work argues for consideration of the decomposition phase that is responsible for the strength giving hydrates, the dehydration phase, when comparing TGA results with other hydration properties. It is established that the CH does not significantly contribute to the strength of hydrating cement paste because of its low surface area property (Mehta and Monteiro, 2006) and therefore considering them in correlation studies

would advance inaccurate models. Results show the dehydration phase of the TGA results profile to correlate strongly with compressive strength giving a very high coefficient of determination (R^2>0.97). The results present a mathematical relationship that can be used to predict strength performance from blended cements following Equation 4.5.

$$y_2 = Ax_1 + B \qquad \text{Equation 4.5}$$

Where, y is the weight loss parameter due to the dehydration phase of the TGA test, x is the compressive strength, A, the scale factor, and B the intercept which represents the initial weight loss value due to the dehydration phase of the TGA test on an anhydrous cement test sample. The trend intercepts are theoretically at zero, but the intercepts of the plot are far from the zero point. This is because cement recorded a non-zero measurement at anhydrous state for the TGA test. The hygroscopic nature of anhydrous cement phases (Gabrovšeka, Vuk and Kaučiča, 2006) leads it to absorb water from the atmosphere and formation of hydration products for the period the cement is exposed prior to casting.

Figure 4.25 presents a general trend for all the results provided in Figure 4.27. The general trend presents the correlation constants A and B provided in Equation 4.5 to 0.1633 and 0.9571 respectively. The general correlation is strong with a high coefficient of determination (R^2=0.957). The model is therefore a plausible tool in predicting strength from the dehydration phase (105°C to 400°C) of a hydrating cement paste.

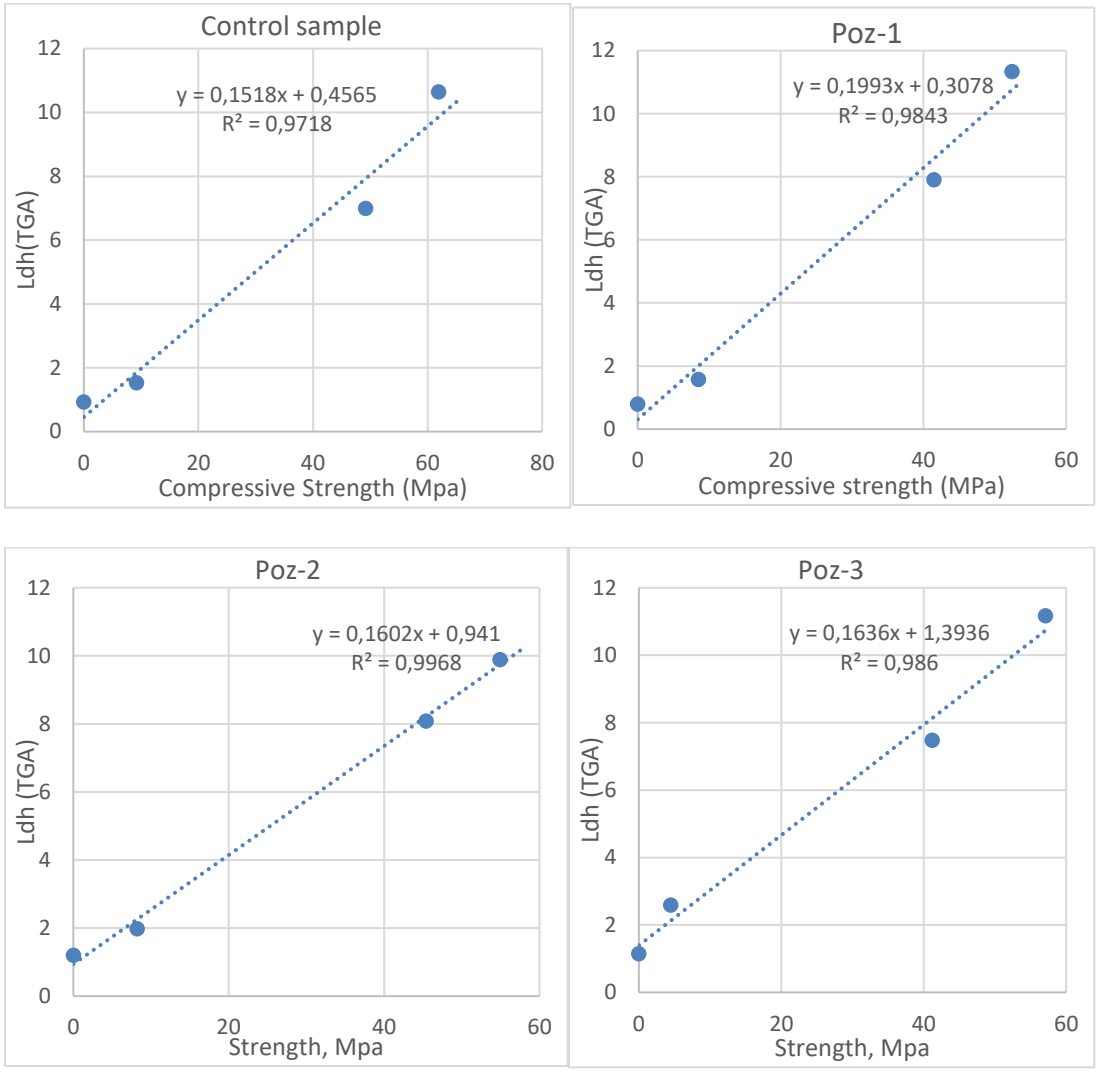

Figure 4.24: Correlation between compressive strength and TGA results for pozzolanic activity tests for control sampe (CEM I 52.5R), Poz-1, Poz-2 and Poz-3 blended cement samples.

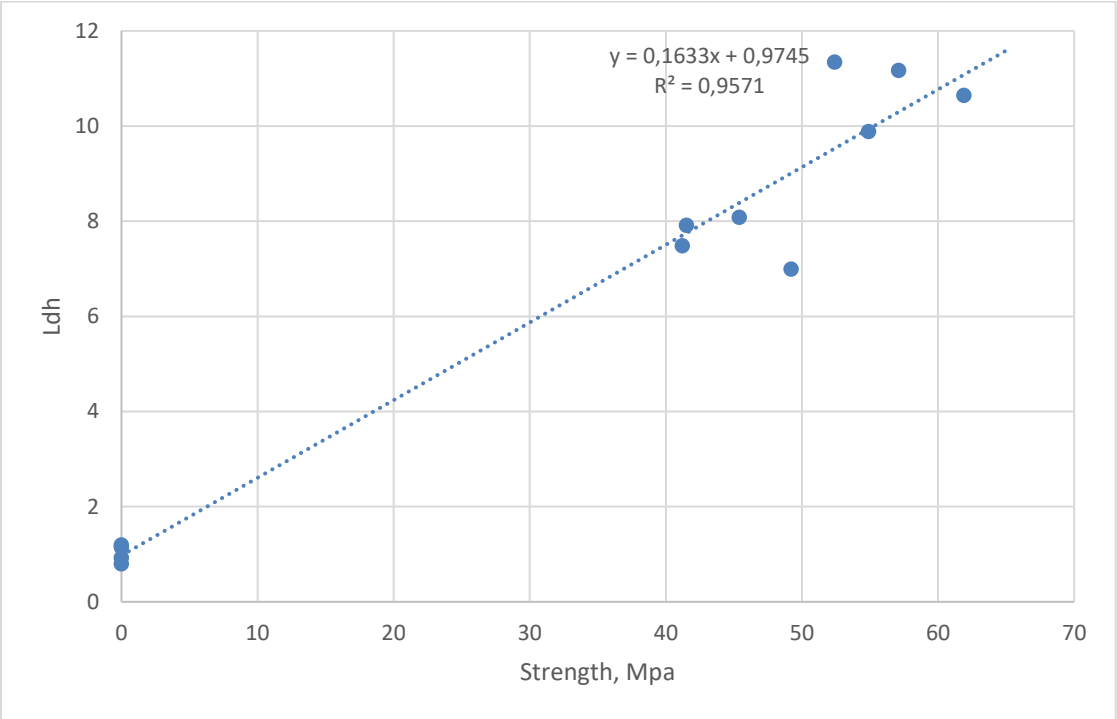

Figure 4.25: Correlation of the TGA data for Ldh phase ploted against strength for all the test pozzolans and cement control sample.

4.2.8.3 Correlation of chemical shrinkage and heat of hydration

The chemical shrinkage and heat of hydration correlation was done to check the consistency of the heat of hydration results with other hydration propreties. The chemical shrinkage data was most appropriate to correlate with the heat of hydration since they are both continuous parameters and had the most shared data points. Results show a strong correlation between heat of hydration and chemical shrinkage supporting observations in other published work (Lura, Winnefeld and Klemm, 2010). The results show chemical shrinkage can be used to predict heat of hydration following a mathematical relationship in Equation 4.6.

$$y_3 = Cx_2 \qquad \text{Equation 4.6}$$

Where C is a scale factor that is unique to the test pozzolan, x is chemical shrinkage in mL/g and y is the heat of hydration in J/g.

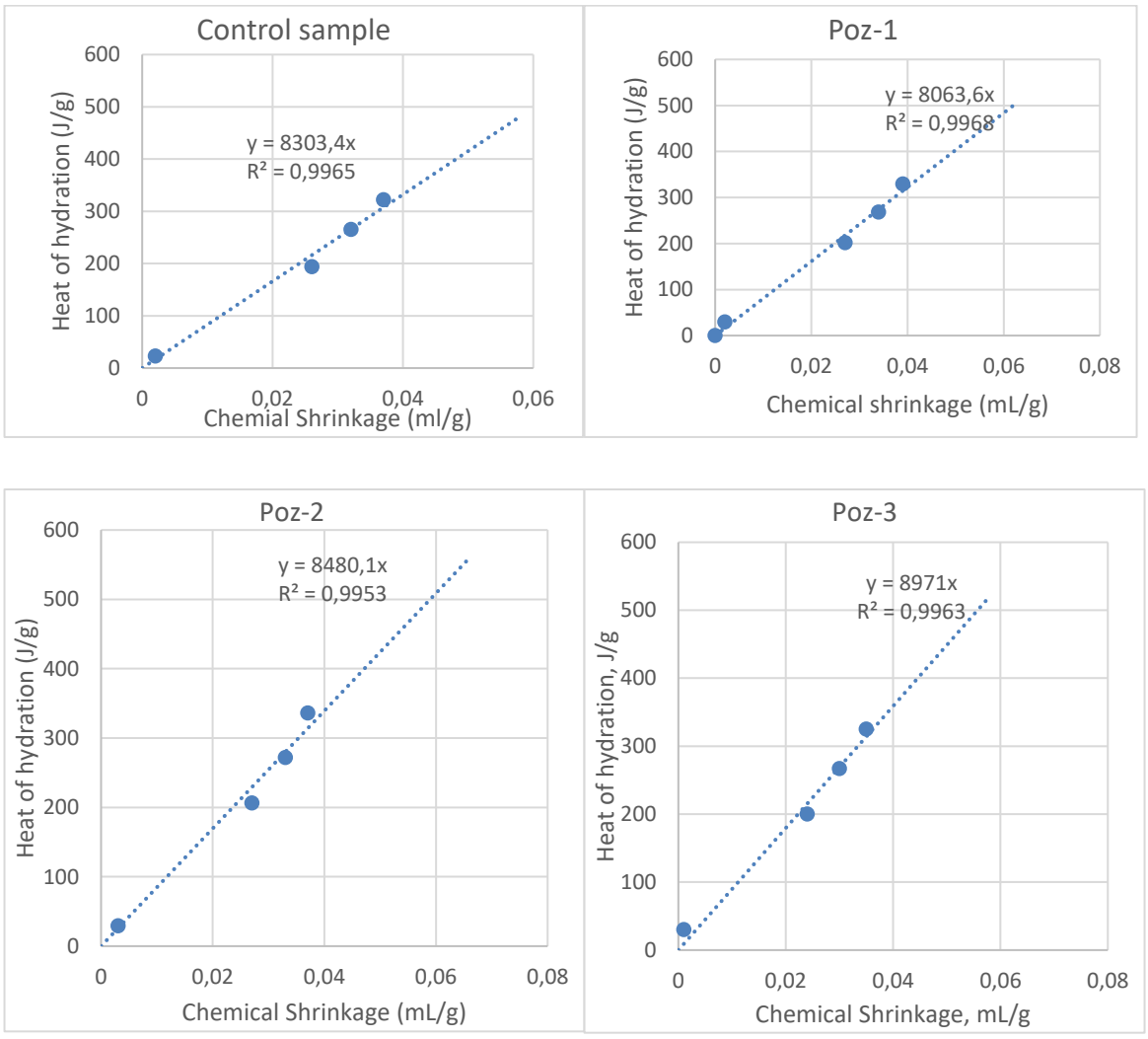

Figure 4.26: Correlation between chemical shrinkage and heat of hydration results for pozzolanic activity tests for control sampe (CEM I 52.5R), Poz-1, Poz-2 and Poz-3 blended cement samples.

The relationship between chemical shrinkage and heat of hydration (Figure 4.26) is similar to that between chemical shrinkage and compressive strength. Accordingly, heat of hydration can be correlated with compressive strength following Equation 4.7.

If $x_2 = y_1$, then $y_3 = Cy_1$

Therefore,

$y_3 = CAx_1$ Equation 4.7

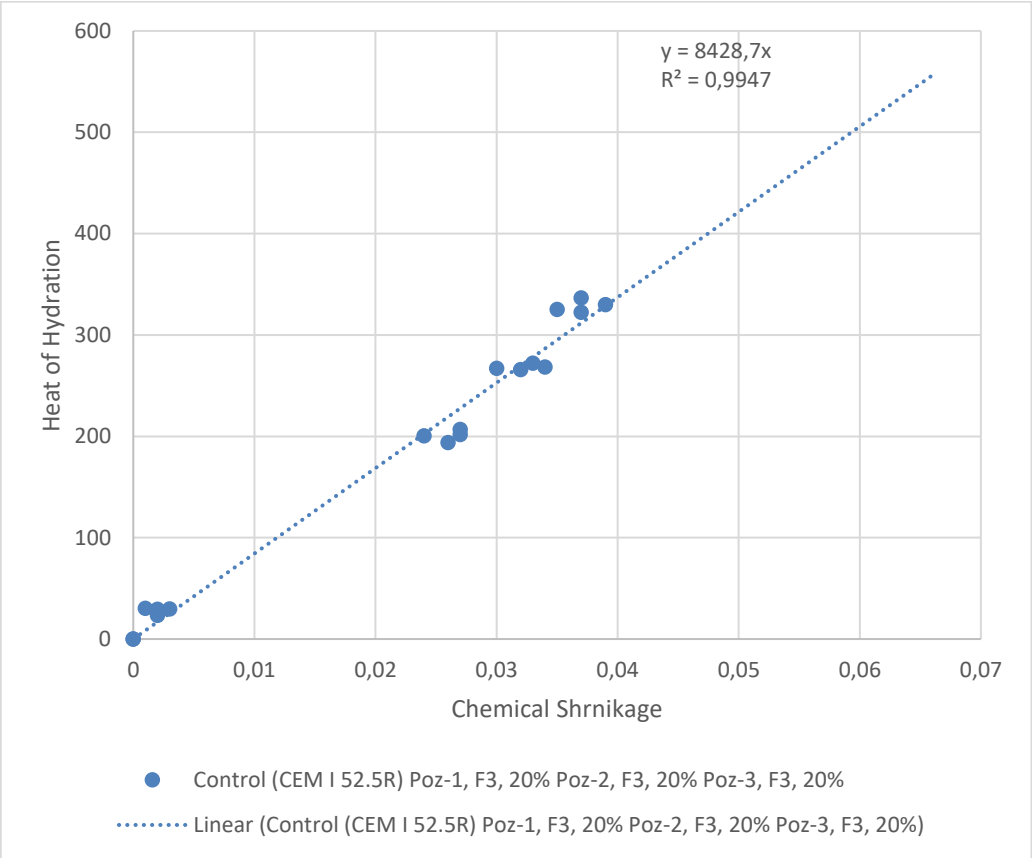

Figure 4.27: Correlation of the heat of hydration data ploted against chemical shrinkage for all the test pozzolans and cement control samples.

Indeed, Figure 4.24 that provides a general correlation of the results in Figure 4.27 gives the value of CA as 8428.7 for a very high coefficient of determination (R^2=0.983). The value A is known and therefore C can be established.

4.2.8.4 Correlation of chemical shrinkage and TGA results

Results comparing chemical shrinkage and TGA are presented in Figure 4.28 and show a strong correlation with high R^2 values, Poz-3 ranking least with an R^2 value of 0.95. The results present a mathematical relationship shown in Equation 4.8 which is similar to the one presented in Equation 4.5.

$$y_2 = Dy_1 + E \qquad \text{Equation 4.8}$$

Where, y_2 is the weight loss parameter due to the dehydration phase of the TGA test, y_1 is the chemical shrinkage, D the scale factor and E the intercept which represents

the initial weight loss value due to the dehydration phase of the TGA test on an anhydrous cement test sample.

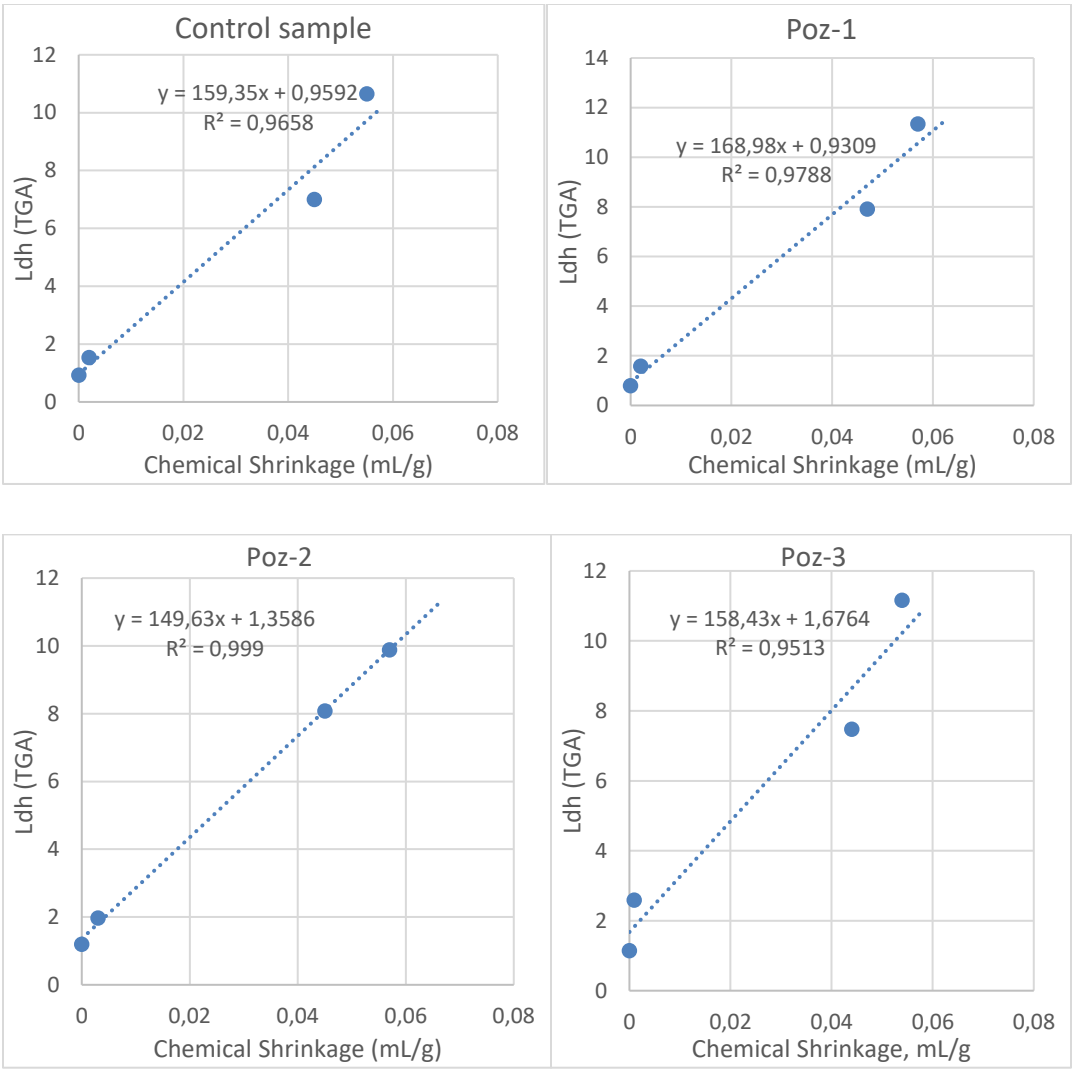

Figure 4.28: Correlation between chemical shrinkage and heat of hydration results for pozzolanic activity tests for control sampe (CEM I 52.5R), Poz-1, Poz-2 and Poz-3 blended cement samples.

Figure 4.29 presents a correlation of the combined results presented in Figure 4.28. The general correlation equation provides the correlation coefficient, D, in Equation 4.7 as 159.05 and the intercept value, E, as 1.2334, all at a coefficient of determination of 0.967.

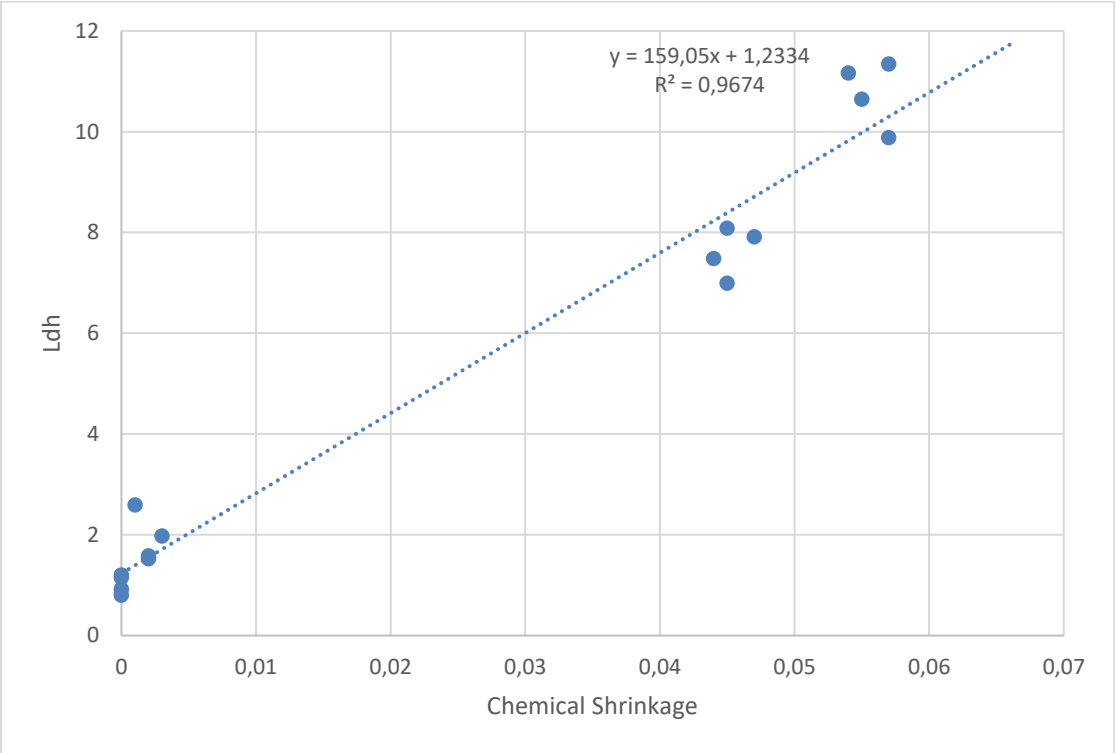

Figure 4.29: Correlation of the heat of hydration data ploted against chemical shrinkage for all the test pozzolans and cement control samples.

4.3 Studies on calcination of carbonatites and kamafugites

4.3.1 Results on the effect of calcination on chemical composition

Table 4.15**:** Comparison of the chemical composition and water-soluble alkalis of raw and calcined kamafugites and carbonatites

Oxides	**% composition**						
	Poz-1		Poz-2		Poz-3		Control
	Raw	Calcined	Raw	Calcined	Raw	Calcined	CEM I 52.5R
LOI	13.8	1.01	16.5	1.06	13.2	1.3	0.09
SiO_2	27.3	31.7	32	38.38	46.9	52.95	20.33
Al_2O_3	6.71	7.86	6.9	8.17	8.23	8.86	4.41
Fe_2O_3	11.4	13.15	10	11.99	7.37	8.82	2.53
CaO	29.2	32.92	21.2	24.08	9.78	11.33	65.19
MgO	4.15	4.82	5.37	6.73	6.21	6.9	1.8
K_2O	1.05	1.25	2.93	3.59	4.61	5.59	0.48
Na_2O	1.06	1.34	0.68	0.95	0.2	0.26	0.09
P_2O_5	2.67	2.81	1.57	1.79	0.93	1.04	0.08
TiO_2	1.79	2.17	2.33	2.79	2.23	2.59	0.41
Mn_2O_3	0.48	0.57	0.3	0.34	0.2	0.23	0.1
Cr_2O_3	0.02	0.02	0.02	0.03	0.05	0.06	
V_2O_5	0.05	0.06	0.1	0.03	0.03	0	
SO_3	0.1	0.31	0.06	0.07	0	0.04	
Cl	0.02	0.04	0.01	0	0	0	
XRF Total	99.9	100.03	100	100	100	99.97	95.51
Water Soluble Alkalis -AAS							
Mg^{2+}	737	863	775	858	875	870	
K^{1+}	48	43	125	60	105	48	
Na^{1+}	6	*bdl*	23	*bdl*	8	*bdl*	
Ca^{2+}	*Concentrations too high for AAS detection*						

bdl - below detection limit

The experimental study for the effect of calcination on chemical composition of kamafugites and carbonatites followed test procedures presented in Chapter 3 of this thesis. Table 4.15 presents oxide composition and Loss on Ignition (LOI) results for the natural pozzolans in raw and calcined states. Two test natural pozzolans, a kamafugite and a carbonatite, failed the ASTM C618 minimum composition requirement of 70% for

the sum of the acidic oxides (Si, Al and Fe) to be used as pozzolanic materials in Portland cement concrete. The test pozzolans had a relatively low silica and alumina content due to carbonates and potassic alkalis enrichment. All the three test pozzolans exceeded the 10% maximum requirement for volatile elements (LOI) as required in ASTM C618, 2005.

4.3.2 Results on the effect of calcination on mineralogical composition

XRD mineralogical composition characterisation results are shown in Table 4.16 and Figures 4.30, 4.31 and 4.32. The experimental setup for these tests has been shared in Section 3.4 in Chapter 3 of this thesis. The kamafugites and carbonatites were effectively decarbonated at 850 °C. A new mineral, Augite, is raised to detectable levels in calcined test pozzolans possibly due to increase in its concentration after the decomposition of the carbonates. Augite is a mineral of the pyroxene family and is generally associated with low silica igneous rocks. Figures 4.30, 4.31 and 4.32 show calcination to have minimal effect on the structure and composition of the other minerals present in the kamafugites and carbonatite.

Table 4.16**:** A comparison of the mineralogical composition of kamafugites and carbonatites (XRD) for both natural (raw) and calcined samples.

Minerals present	**Poz-1**		**Poz-2**		**Poz-3**		**Chemical Formula**
	Raw	**Calcined**	**Raw**	**Calcined**	**Raw**	**Calcined**	
Calcite	√	*x*	√	*x*	√	*x*	$(Mg_{0.03}Ca_{0.97})(CO_3)$
Pigeonite	√	√	√	√	√	√	$(Ca,Mg,Fe)(Mg,Fe)Si_2O_6$
Quartz	√	√	√	√	√	√	SiO_2
Muscovite	√	√	√	√	√	√	$KAl_2(AlSi_3O_{10})(F,OH)_2$
Olivine	√	√	√	√	√	√	$Na_2(SiO_4)$
Apatite	√	√	√	√	√	√	$Ca_{10}(PO_4)_6(OH)_2$
Augite	*x*	√	√	√	x	√	$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$
Kaolinite	*x*	*x*	√	√	√	√	$Al_4(OH)_8(Si_4O_{10})$
Epidote	*x*	*x*	*x*	*x*	√	√	$Ca_2Al_{2.4}Fe_{0.6}(SiO_4)_3(OH)$

√- Mineral detected; x- Mineral not detected

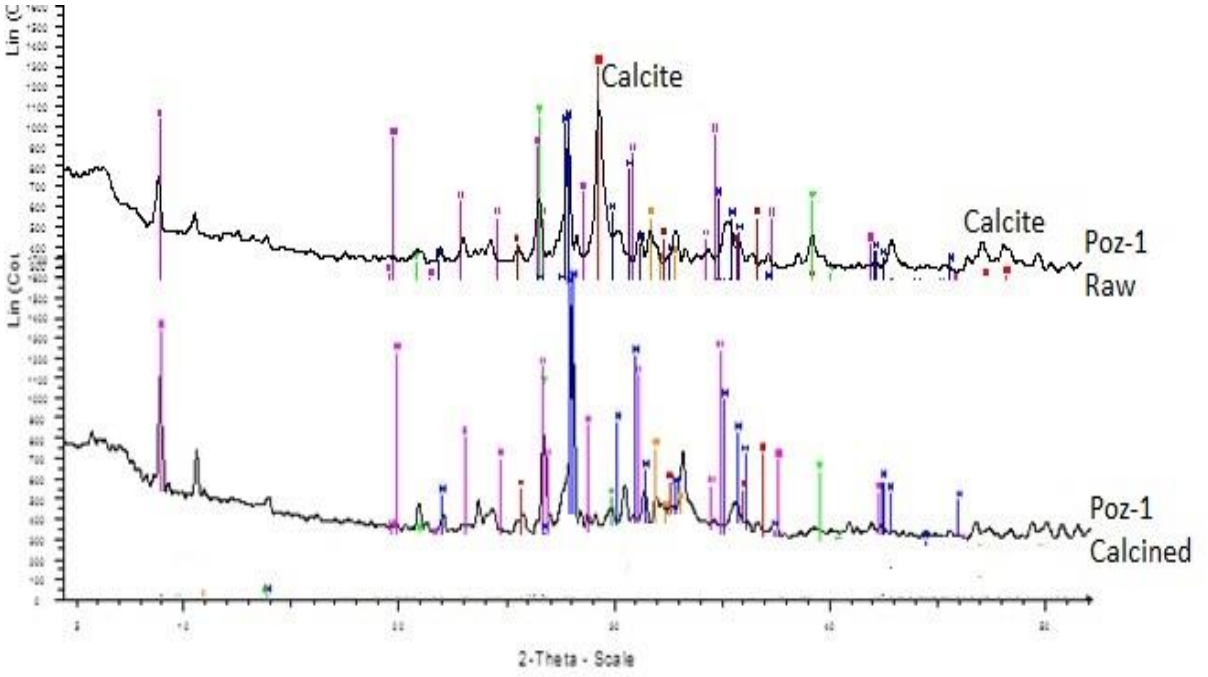

Figure 4.30: Mineralogy of Poz-1 in both raw and calcined states

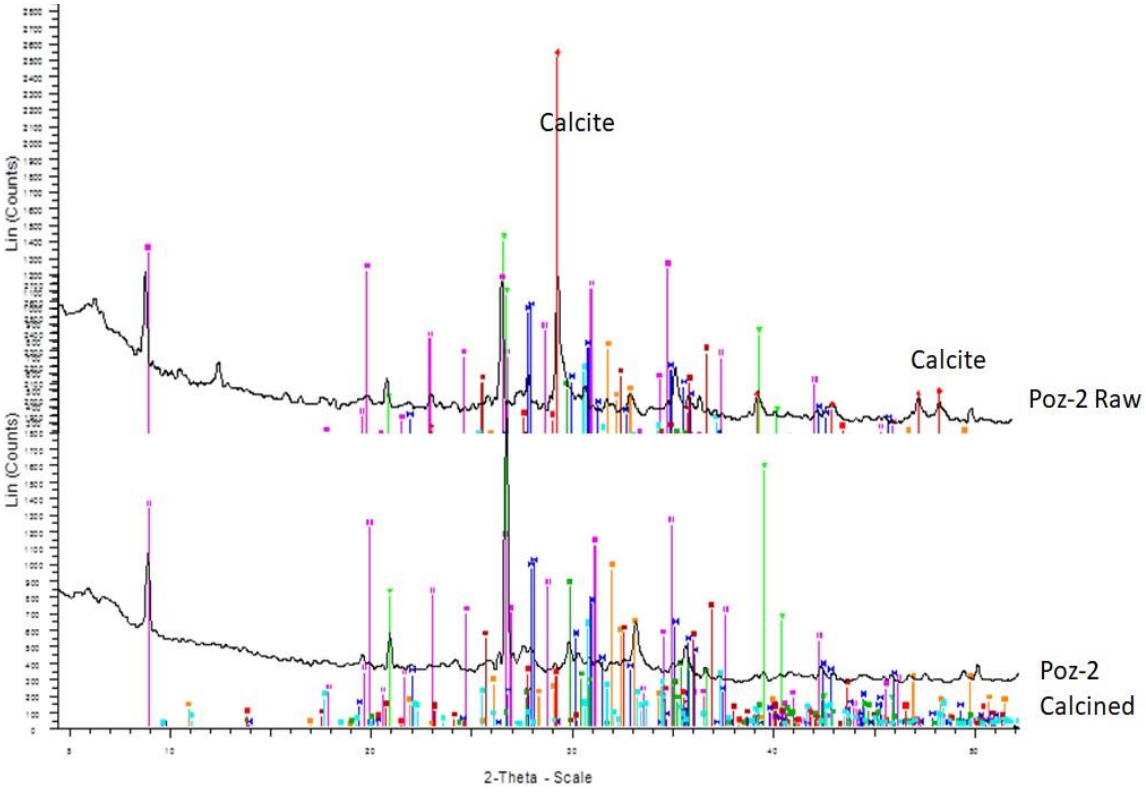

Figure 4.31: Mineralogy of Poz-2 in both raw and calcined states

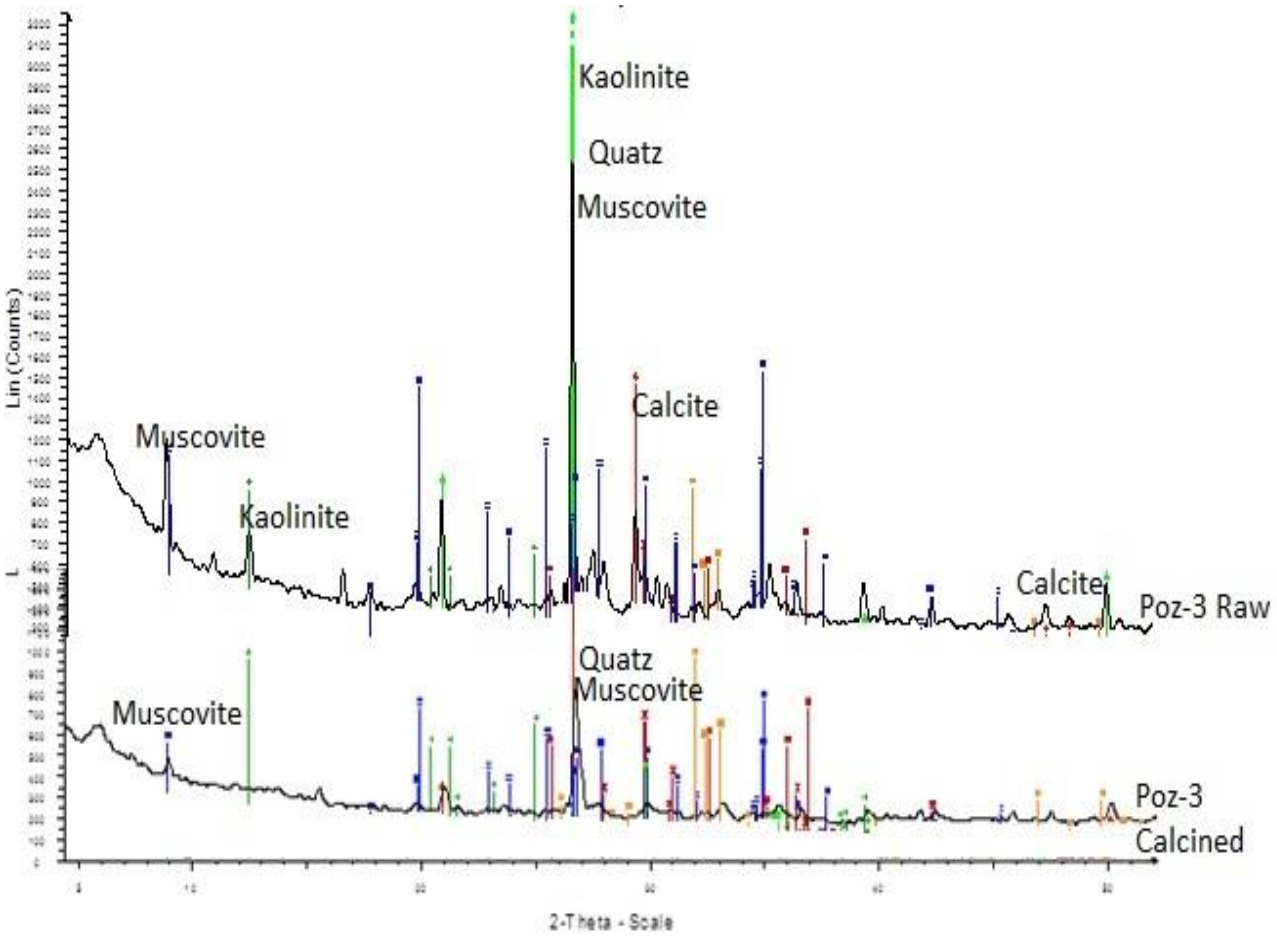

Figure 4.32: Mineralogy of Poz-3 in both raw and calcined states

4.3.3 Results on the effect of calcination on relative density

Table 4.17 shows relative density results for both the raw and calcined test pozzolans. Calcining test pozzolans resulted in increase in specific weight, Poz-1 showing the highest gain.

Table 4.17**:** Effect of calcination on the densities of the test pozzolans

Treatment	**Relative density of powders**			
	Poz-1	Poz-2	Poz-3	CEM I 52.5R
Raw	2.69	2.52	2.41	3.14
Calcined at 850°C	3.19	3.12	2.84	

4.3.4 Results on the effect of calcination on fresh properties of cement paste and mortar

Table 4.18 presents results on setting time, water demand, slump flow and soundness tests of the test pozzolans in raw and calcined forms. The tests followed procedures already discussed in Section 4.2.1 of the current chapter. All samples led to acceleration of setting, increased water demand and reduced slump flow, poz-3 showing a relatively higher influence on the fresh properties of Portland cement than Poz-2 and Poz-1. On calcination, these effects were pacified significantly. The test pozzolans showed no reportable effect on the soundness property of cement.

Table 4.18**:** Properties of fresh cement paste and mortar

Parameters	**Control**	**Poz-1**		**Poz-2**		**Poz-3**	
	CEM I 52.5R	Raw	Calcined	Raw	Calcined	Raw	Calcined
Initial Setting (min)	215	200	217	200	210	190	205
Final Setting (min)	286	245	291	255	280	246	269
Water demand (%)	29.2	30.7	29.5	32.3	30.2	33.1	30.5
Slump flow (%)	100.0	95.3	98.0	92.1	95.9	87.9	98.0
Soundness (mm)	0	0	1	0	1	0	0

4.3.5 Results on the effect of calcination on heat of hydration

Figures 4.33-4.35 present heat of hydration results measured following isothermal conduction calorimetry methods (TAM Air calorimeter, TA Instruments) and normalised to unit weights of all the cementitious materials. The presented results are for Poz-1, Poz-2 and Poz-3 respectively.

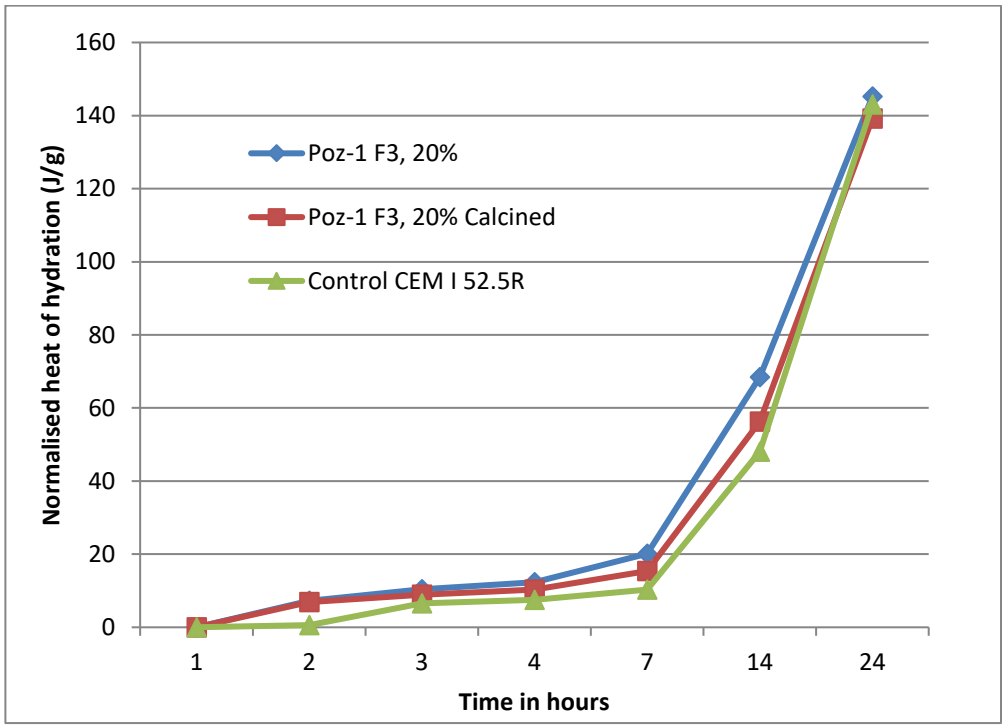

Figure 4.33: Heat of hydration progression for the first 24 hours for Poz-1 raw and calcined test pozzolans at 20% replacement level.

Table 4.19**:** Heat activity index (HAI) results for normalized heat of hydration (J/g)

Curing (Hrs)	Poz-1 F3, 20%	Control CEM I 52.5R	HAI, Poz-1	HAI, Poz-2	HAI, Poz-3
1	0.007	-0.001	-631	171	-21
2	7.258	7.913	92	150	6
3	10.416	10.742	97	137	138
4	12.345	12.357	100	132	150
7	20.111	18.689	108	125	170
14	68.490	68.253	100	111	130
24	145.193	164.188	88	102	97
48	217.425	258.562	84	100	87
72	245.958	295.155	83	102	85
90	262.607	316.603	83	103	85
120	285.317	343.714	83	104	85
139	296.756	356.302	83	104	85
162	308.704	369.053	84	104	85
164	309.582	369.988	84	104	
167	310.921	371.400	84		

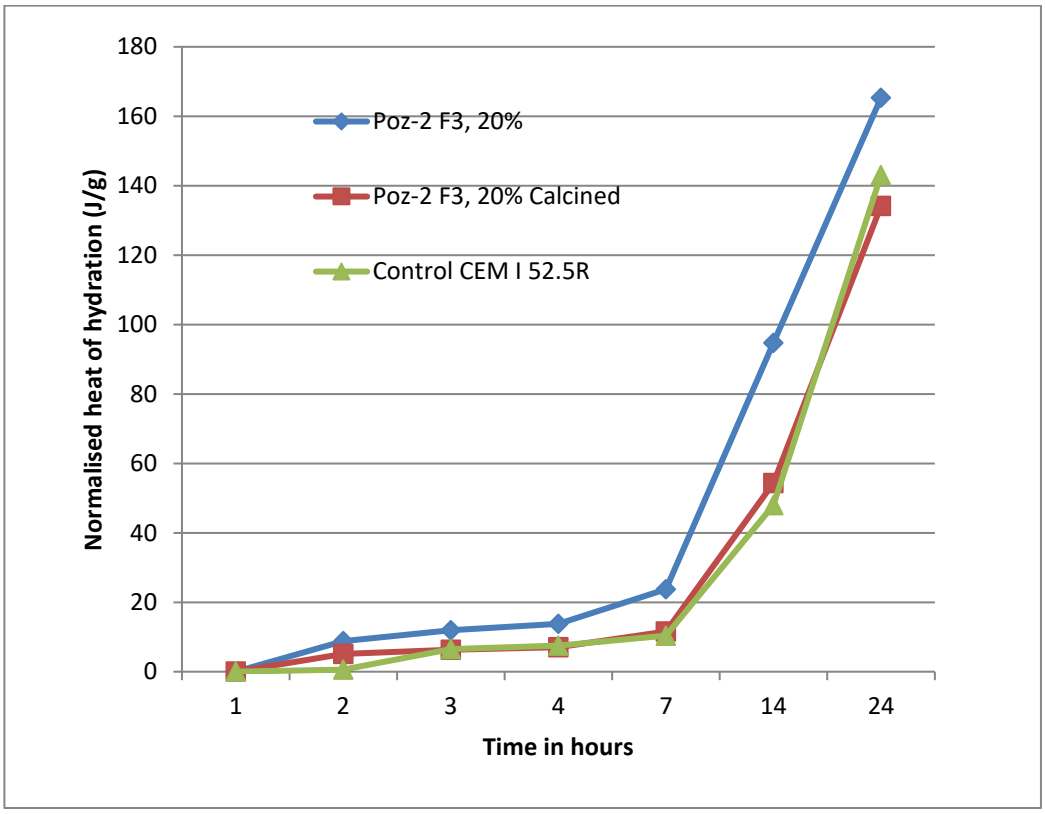

Figure 4.34: Heat of hydration progression for the first 24 hours for Poz-2 raw and calcined test pozzolans at 20% replacement level.

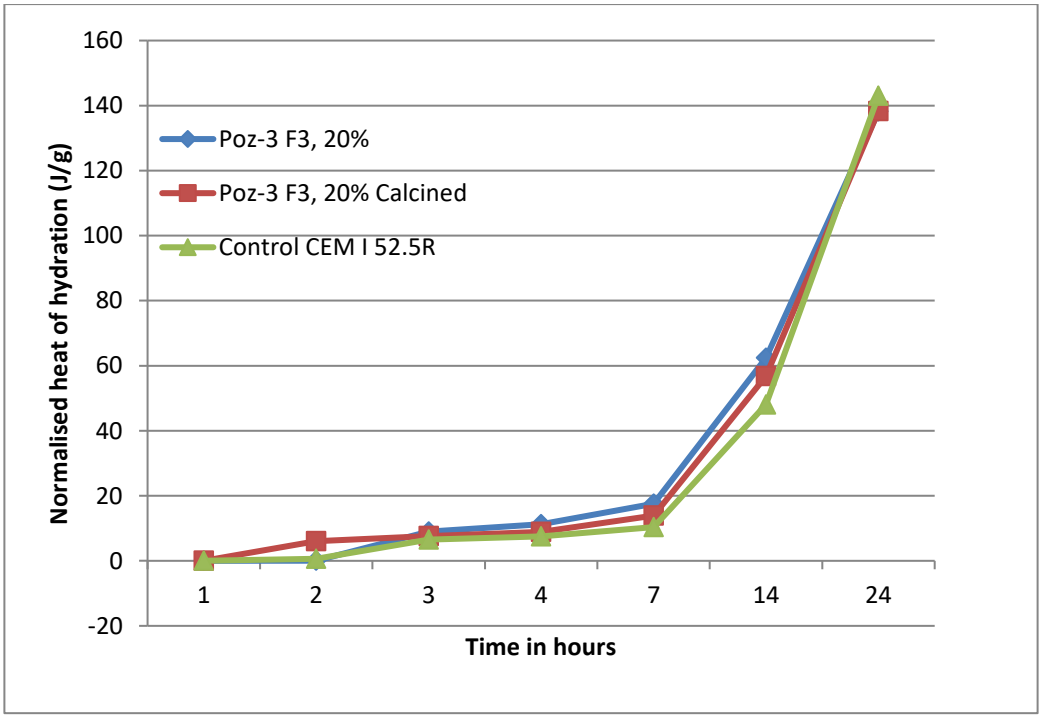

Figure 4.35: Heat of hydration progression for the first 24 hours for Poz-3 raw and calcined test pozzolans at 20% replacement level.

Table 4.19 presents a summary of the progression of heat of hydration results for a period up to 162 hours. To facilitate comparison of the results, considering that each sample was cast on a different day and had its independent control, a form of normalisation, the heat activity index is introduced. The Heat Activity Index (HAI) is defined as a ratio of total heat generated by a unit mass of a test sample to heat generated by a unit mass of a control sample at a fixed time, *t*. The raw data on heat of hydration is stored under a file name "heat of hydration data" as part of the DVD copy submitted with the thesis.

$$HAI = \frac{Q_{(t)SAMPLE}(\frac{J}{g})}{Q_{(t)CONTROL}(\frac{J}{g})} \times 100\% \qquad \text{Equation 4.9}$$

Table 4.20**:** Heat activity index (HAI) and normalised heat of hydration (J/g) results for calcined samples

Control 2-FA	HAI, Control 2-FA	Poz-1 F3, 20% Calcined	HAI, Poz-1	Poz-2 F3, 20% Calcined	HAI, Poz-2	Poz-3 F3, 20% Calcined	HAI, Poz-3	Control CEM I 52.5R
0.003604	-47	0.007543	-98	0.013622	-177	0.017171	-224	-0.00768
5.741601	63	6.894056	76	5.165611	57	5.989418	66	9.10477
7.531462	65	8.897811	77	6.295923	55	7.614608	66	11.54529
8.844331	66	10.30521	77	7.085879	53	8.844501	66	13.46471
13.44269	60	15.36344	69	11.59443	52	13.90809	63	22.22878
51.88805	71	56.23531	76	54.32558	74	56.81288	77	73.53697
135.5555	90	139.2214	92	134.1719	89	138.2901	92	150.8425
217.7706	98	215.5204	97	214.5229	97	218.2218	98	221.7806
248.1946	99	245.0267	98	243.5786	97	246.5223	98	251.1644
266.0384	99	262.3216	98	260.5444	97	262.5981	98	268.4009
290.2594	99	285.8307	98	283.3857	97	283.7627	97	292.0521
302.4415	99	297.728	98	294.7808	97	294.1049	97	304.1708

The heat activity index (Equation 4.9) helps in comparison of the extent of gain in heat of hydration between the control sample (plain Portland cement) and the test sample (plain Portland cement blended with test pozzolans at 20% replacement level). Results on pozzolanic reactivity by TGA revealed the pozzolanic activity to be pronounced at 7 days of curing. Accordingly, the 162-hour heat of hydration captures the initial stages of the pozzolanic reaction. Results show a rebound in heat of hydration measurement

at 72 hours but only for Poz-2. The experiment terminates when Poz-1 and Poz-3 have a stable trend in relation to the control samples as indicated by a fixed value of HAI.Table 4.20 presents heat of hydration results for the calcined kamafugites and carbonatites compared against two controls, class F fly ash (FA) and CEM I 52.5R. The results are also processed to include the heat activity index (HAI) values to aid comparison with those of the raw samples.

4.3.6 Results on the effect of calcination on compressive strength

The compressive strength parameter has been used to study the pozzolanic performance of the test natural pozzolans. The results are compared against results of two control samples, CEM I 52.5R and class F Fly Ash. Fly ash is a pozzolanic material that has passed the testing and development stage and, therefore, a reasonable control in characterisation of pozzolanic properties of natural pozzolans. In fact, Fly Ash and natural pozzolans share the same ASTM C 618, 2005, characterisation standard. Results presented in Table 4.21 were generated following experimental procedures discussed in Section 4.2.2 of this theisis. The results show the raw natural pozzolans to perform better than their calcined equivalents up to 28 days. The hydration reactions in the samples blended with raw natural pozzolans appear to have stopped by 90 days of curing implying either depletion of reactants or a conversion mechanism with rates exceeding the pozzolanic reaction mechanisms. The calcined samples continue to gain in strength after 90 days of curing, a trend they share with both FA and CEM I control samples. There is a 3.4% and 7.6% gain in compressive strength with calcination for Poz-1 and Poz-3 respectively. The gain in compressive strength does not show any correlation with the change in composition of the test natural pozzolans after calcination (Table 4.15). Poz-3 however has a clay mineral, Kaolinite, which exhibits pozzolanic properties when thermally destabilized at temperatures as low as 350°C (Habert et al, 2008).

Table 4.21**:** Results showing the effect of calcination of kamafugites and carbonates on compressive strength of mortar prisms

Curing (Days)	**Control 1** CEM 1 52.5R	**Control 2** Class F Fly Ash	**Poz-1**		**Poz-3**	
			Raw	Calcined	Raw	Calcined
7	49.2	40.0	41.5	40.9	41.2	41.0
28	57.0	54.2	51.1	49.6	56.8	55.0
90	63.4	69.7	53.2	54.4	57.4	58.2
180	65.3	72.1	53.1	54.9	56.6	60.9

Table 4.22 presents calculated values of the strength activity index (SAI) based on Equation 4.1. All values at all curing times are above the minimum of 80% required for a material to be considered pozzolanic according to ASTM C617, 2005. The calcined samples have higher long-term SAI values in comparison with the raw samples showing a better pozzolanic performance.

Table 4.22**:** Strength activity index (SAI) test for pozzolanic activity

Curing (Days)	Control 1 CEM 1 52.5R	Control 2 Class F Fly Ash	Poz-1		Poz-3	
			Raw	Calcined	Raw	Calcined
7	100	81	84.4	83.3	83.8	83.4
28	100	95	89.6	87.1	99.6	96.4
90	100	110	83.9	85.8	90.6	91.8
180	100	110	81.3	84.1	86.7	93.2

4.3.7 Results on the effect of calcination on chemical shrinkage

To characterise the governing reactions in chemical shrinkage of Portland cement blended with kamafugites and carbonatites, calcination was performed on the test pozzolans to decarbonate and remove volatile alkalis. Andesite powder was used in the experimental setup as a control sample to help characterise the pozzolanic reactions from the other hydration mechanisms associated with blended cements. The chemical shrinkage results are presented in Table 4.23

Table 4.23**:** Chemical shrinkage results for raw and calcined test pozzolans

Curing (Days)	Control 1: Andesite (mL/g)	Control 2: Fly Ash (mL/g)	Poz-1 Raw (mL/g)	Poz-2 Raw (mL/g)	Poz-3 Raw (mL/g)	Poz-1 Calcined (mL/g)	Poz-2 Calcined (mL/g)	Poz-3 Calcined (mL/g)
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.5	0.002	0.002	0.002	0.003	0.001	0.003	0.003	0.002
1	0.026	0.026	0.027	0.027	0.024	0.025	0.026	0.027
2	0.032	0.033	0.034	0.033	0.030	0.030	0.032	0.033
3	0.037	0.038	0.039	0.037	0.035	0.035	0.036	0.038
7	0.045	0.046	0.047	0.045	0.044	0.041	0.043	0.045
14	0.049	0.051	0.051	0.050	0.048	0.046	0.047	0.049
21	0.051	0.055	0.053	0.052	0.050	0.047	0.048	0.051
28	0.052	0.055	0.055	0.053	0.052	0.049	0.050	0.052
90	0.056	0.061	0.059	0.059	0.056	0.054	0.055	0.057
180	0.058	0.065	0.063	0.066	0.058	0.058	0.059	0.059

4.3.8 Results on the effect of calcination on hydration products development with TGA

The effect of carbonates, volatile alkali and calcination of test kamafugites and carbonatites were tested by fixing the cement replacement level and casting blended cement paste samples of identical mixes for each test pozzolan in raw and calcined states. The hydration products assemblage and pozzolanic performance properties are discussed based on results from both the TGA and XRD experiments following the experimental plan presented in Sections 4.2.6 and 4.2.7 of this thesis.

4.3.8.1 Thermogravimetric analysis (TGA) results

Thermogravimetric analysis results for study of the effect of calcination on hydration products and pozzolanic performance are presented in Figures 4.36-4.44. The results are presented at a fixed curing time of 7 hours, 7 days and 56 days to facilitate comparison.

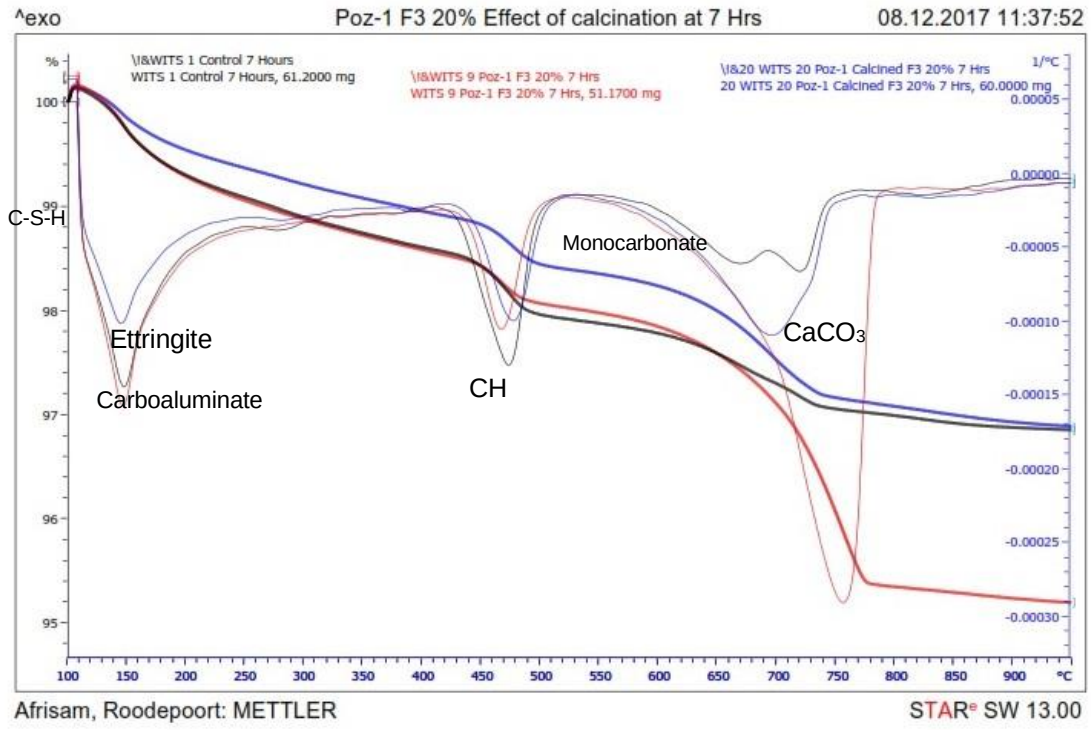

Figure 4.36: Effect of calcination of Poz-1 on hydration products and pozzolanic performance at 7 hours.

The results at 7 hours of hydration for Poz-1, poz-2 and Poz-3 are presented in Figures 4.36, 4.37 and 4.38 respectively. All the three test pozzolans show the paste sample blended with raw kamafugites and carbonatites to have more hydration products in the first phase of the TGA profile, the dehydration phase (105°C-400°C), than both the calcined and control samples, Poz-3 leading in the magnitude followed by Poz-2 and Poz-1 showing marginal increase in the hydration products. The calcined sample trailed the control sample in hydration products accumulation since calcination inactivates the acceleratory effects of the test pozzolans. The dehydration phase is associated with the silicate hydrates as the most pronounced hydration products but also the AFt

phases together with carboaluminates phases (Lothenbach et al, 2008; Taylor, 1997; Ramachandran et al., 2002; Hewlett, 2004; Gabrovšek, Vuk and Kaučič, 2006). The observed trend is attributed to the acceleratory effects of the test kamafugites and carbonatites. The acceleratory effect has been reported in other sections of this thesis and is attributed to the calcite and water soluble alkalis.

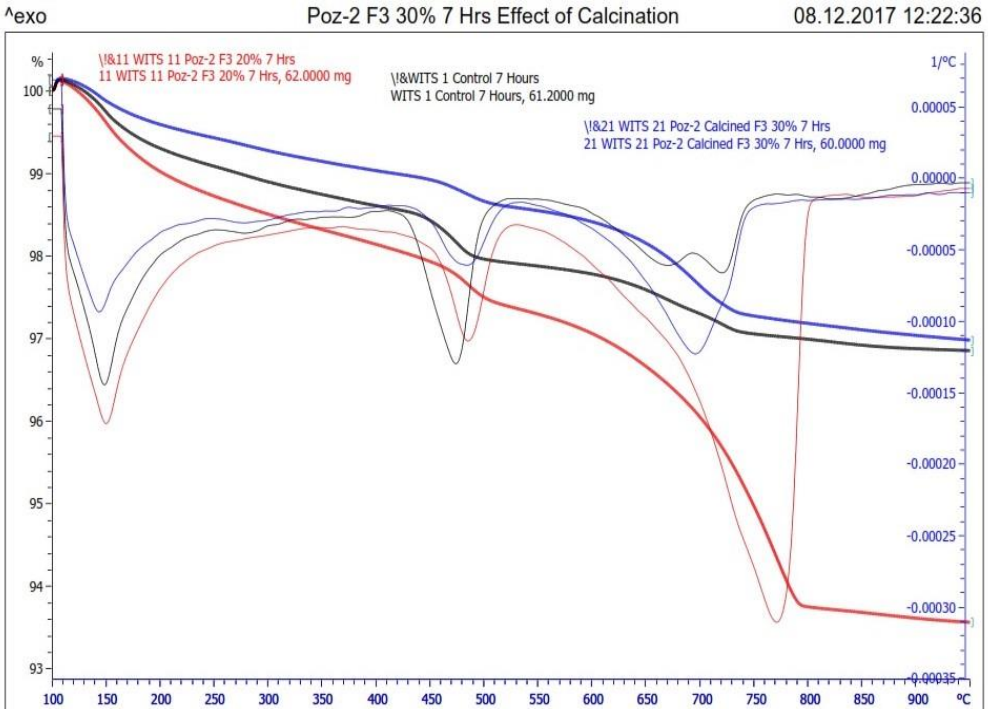

Figure 4.37: Effect of calcination of Poz-2 on hydration products and pozzolanic performance at 7 hours.

It is expected that accelerated hydration of the silicate phases would reflect on the deposition of the CH hydrates in the dihydroxylation phase (400°C-600°C) but, as observed with paste samples blended with Poz-1 and Poz-2, the control sample presented more CH hydrates than the test pozzolans, both raw and calcined. This observation serves to indicate that the increase in volume of the hydration products is based on non-silicate hydrates. The formation of high density carboaluminates phases is a plausible hypothesis for Poz-1 and Poz-2 test pozzolans that are higher in the carbonates content. It is however observed that the accelerated hydration in Poz-3 is dominated by the hydration of the silicate phases as observed in the high content of CH. The CH phase of the raw test pozzolan blended paste is relatively higher than that of the control sample paste and paste made with calcined kamafugite.

There is no pozzolanic activity traceable at the 7 hour hydration state.

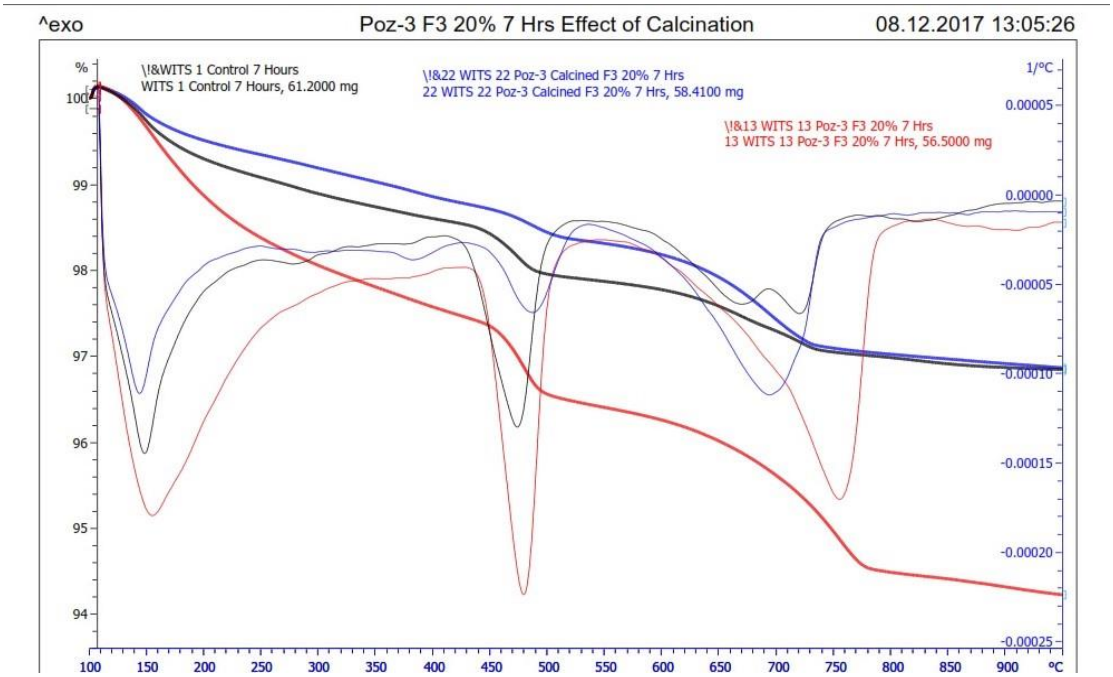

Figure 4.38: Effect of calcination of Poz-3 on hydration products and pozzolanic performance at 7 hours.

The decarbonation phase shows the test samples to have carbonated in the process of handling and sample preparation for TGA testing. The formed carbonates are principally monocarbonates (Lothenbach and Wieland, 2006) with lower decomposition temperatures in relation to the calcite phase in the raw test pozzolan blended cement paste. The blended sample shows a higher rate of carbonation than the control sample (CEM I 52.5R), a trend that is observed in all the three samples. The process of carbonation is probably accelerated by the hydrated CaO that is present in the test pozzolans leading to the reversing of the decarbonation previously achieved through thermal decomposition.

Figures 4.39, 4.40 and 4.41 represent the TGA profiles at 7 days of curing for Poz-1, Poz-2 and Poz-3 respectively. The results show the increase in hydration products in the dehydration phase of the TGA thermodecomposition profile sustained. The dominant phases in the dehydration phase are C-S-H, Ettringite and carboaluminates phases. The acceleratory effect of Poz-3 is minimized at 7 days of curing.

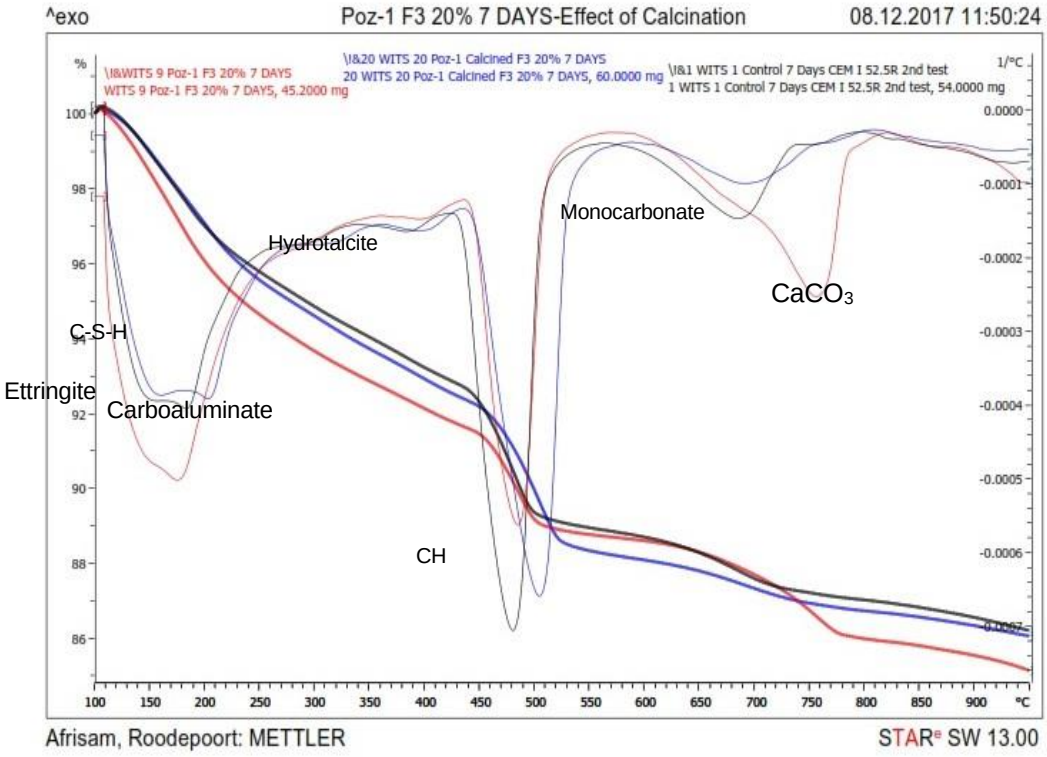

Figure 4.39: Effect of calcination of Poz-1 on hydration products and pozzolanic performance at 7 days.

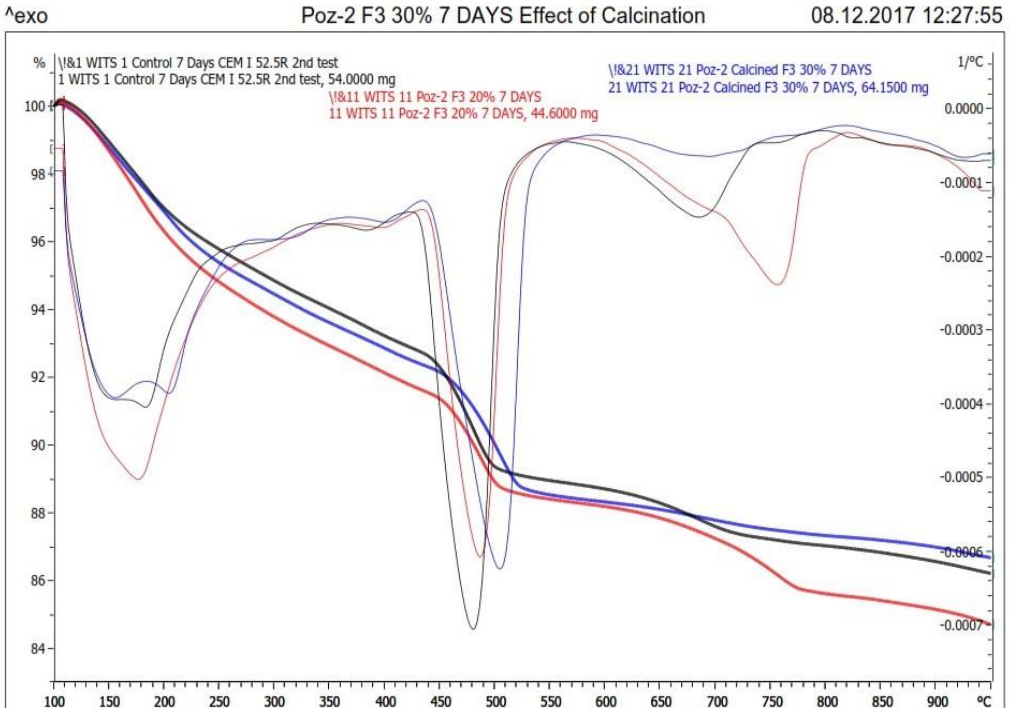

Figure 4.40: Effect of calcination of Poz-2 on hydration products and pozzolanic performance at 7 days.

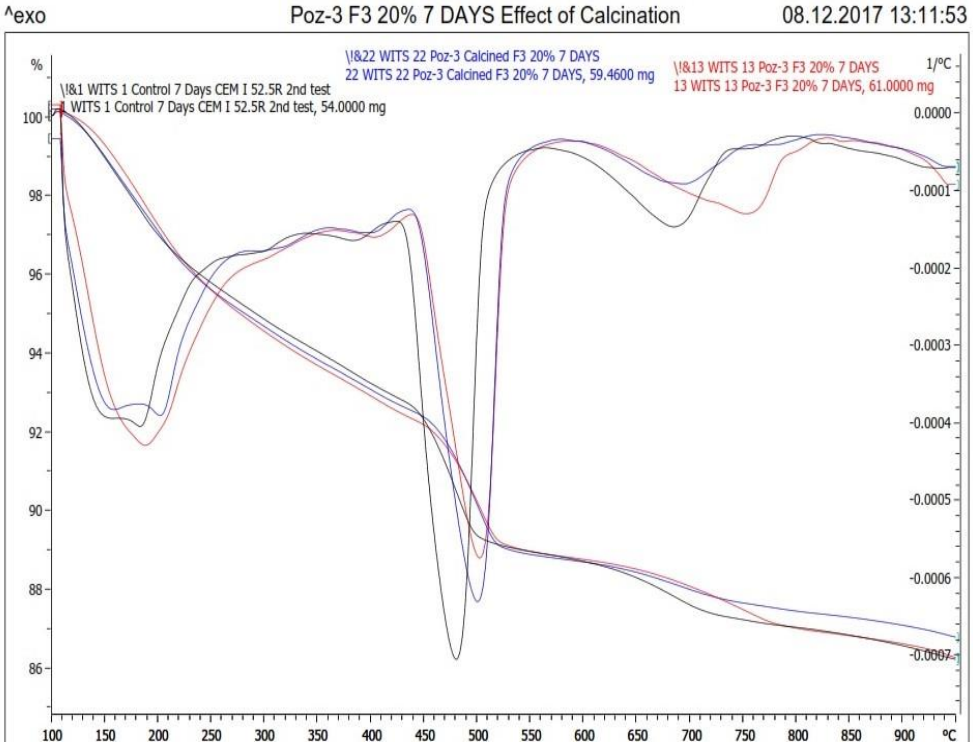

Figure 4.41: Effect of calcination of Poz-3 on hydration products and pozzolanic performance at 7 days.

The dihydroxylation phase results show calcination to reduce the pozzolanic activity of the test kamafugites and carbonatites. A slight shift in the DTG dihydroxylation profile indicates that calcination led to deposition of CH hydration products that are more stable, demanding a higher decomposition temperature than those formed by the control sample and the paste sample blended with the raw test pozzolan.

The decarbonation phase of paste samples at 7 days show the existence of both monocarbonates and calcite phases. The results also reveal a reduction in the carbonate phases indicating a consumptive reaction that converts carbonates to bond with hydration products. Lothenbach and Wieland, (2006) observed carbonates to be fixed in hydration reactions over a long period of curing. It is considered that the carbonates take part in the hydration reactions that take place within the dehydration phase. The XRD results that characterize hydration products indicated the presence of hydrotalcite, a Mg-Al-OH-CO_3(H_2O) mineral that is formed through reactive $Mg(OH)_2$ where some of the magnesium ions are substitutes by Al ions with the water molecules and carbonates correcting the created charge imbalance (Taylor, 1997). Hydrotalcite

acts together with the carboaluminates phases to bond some of the carbonates from the blended test pozzolans.

Figures 4.42, 4.43 and 4.44 present results of the TGA decomposition profiles for samples cured up to 56 days. The trends were similar to those observed at 7 days of curing with similar observations for the three thermal decomposition phases of dehydration, dihydroxylation and decarbonation. The rate of carbonation was high between 7 hours and 7 days but reduced to negligible levels relative to other hydration products at 56 days of curing. The samples blended with raw test pozzolans sustained increased hydration products through up to 56 days of curing.

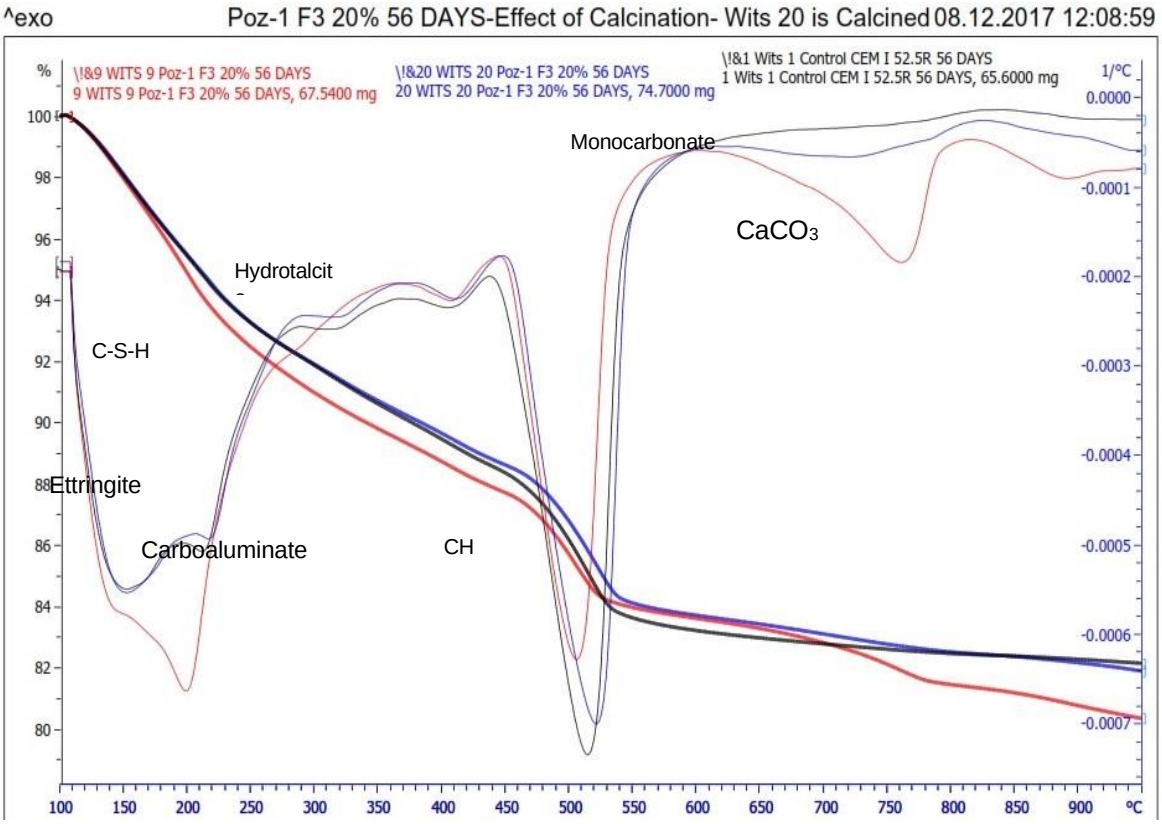

Figure 4.42: Effect of calcination of Poz-1 on hydration products and pozzolanic performance at 56 days.

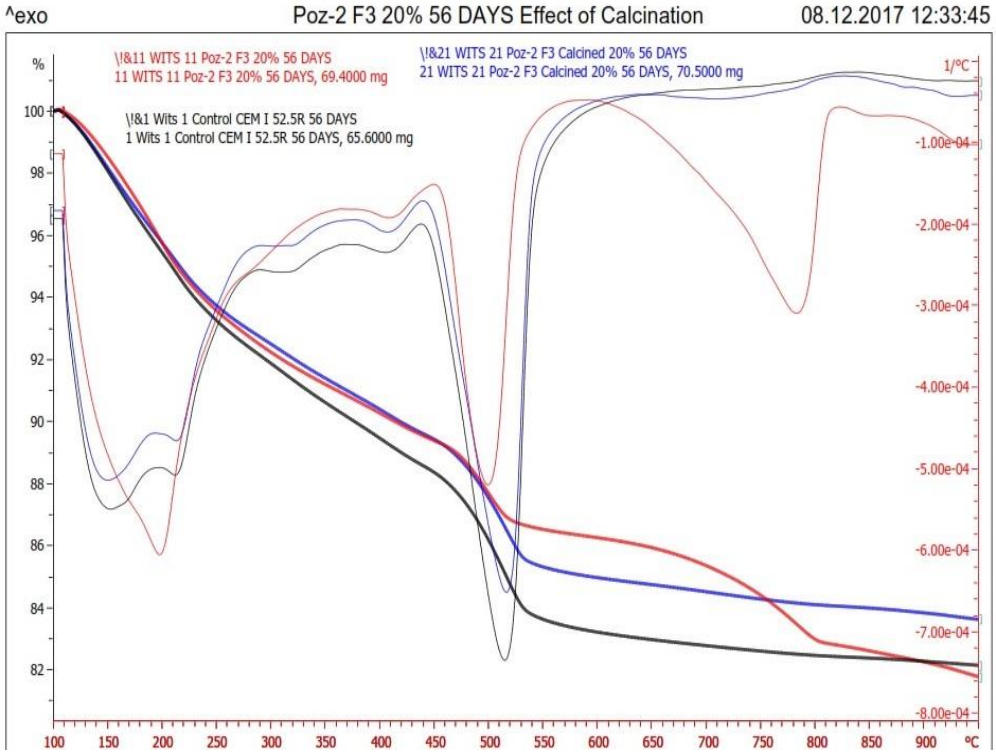

Figure 4.43: Effect of calcination of Poz-2 on hydration products and pozzolanic performance at 56 days.

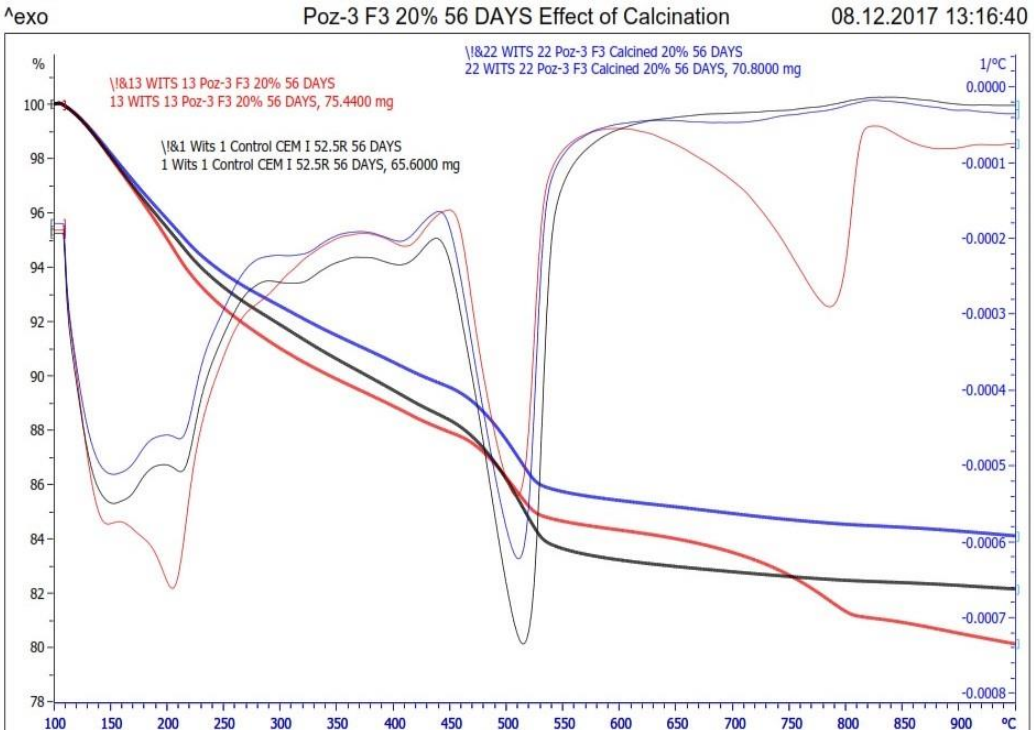

Figure 4.44: Effect of calcination of Poz-3 on hydration products and pozzolanic performance at 56 days.

4.3.9 Results on the effect of calcination on hydration products with XRD

The XRD patters for the three pozzolans showed similar trends as presented in Figures 4.45, 4.46 and 4.47. The samples were reviewed for effects of calcination of kamafugites and carbonatites on hydration products at 7 days. As indicated in Section 4.3.2 of the current thesis chapter, calcination of the test kamafugites at anhydrous state effectively decarbonated the samples and also volatilized their water soluble alkali content. Volatilization of water soluble alkalis has a direct effect on the composition of pore fluids while decarbonation pacifies the effects of calcine in the hydrating cement system. Calcination had no significant effect on the other mineral phases in the kamafugites and carbonatites.

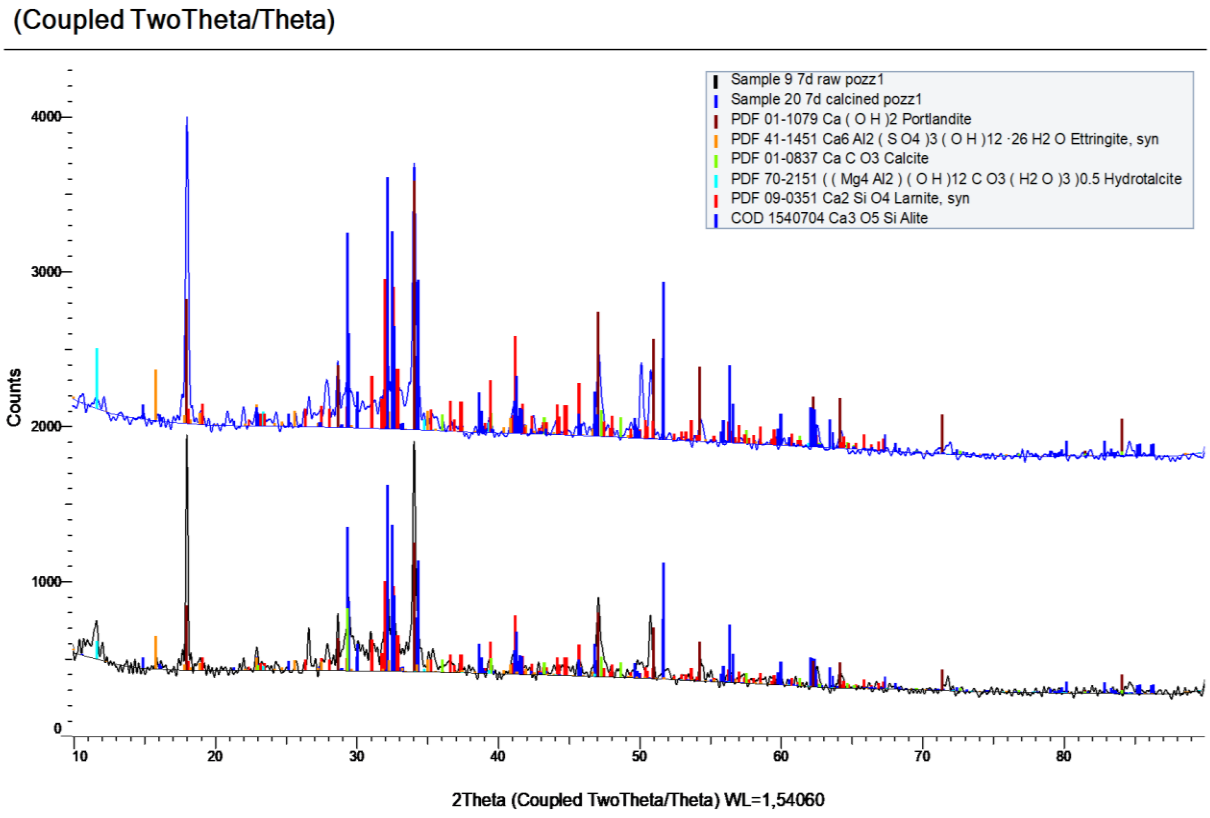

Figure 4.45: Effect of calcination of carbonatites on hydration products development-Poz-1 at 7 days

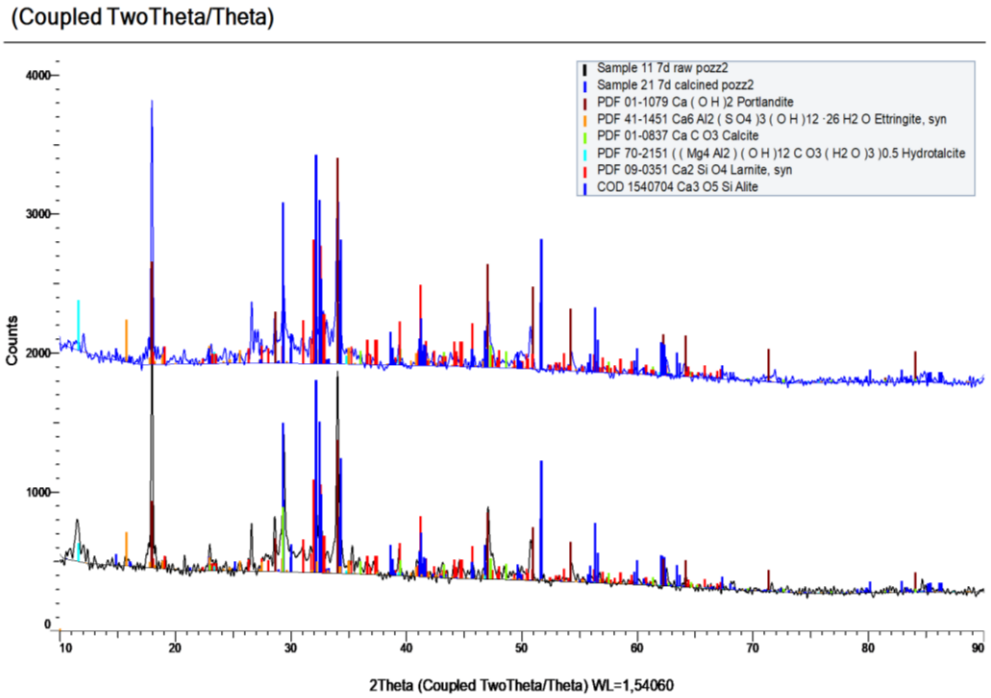

Figure 4.46: Effect of calcination of a kamafugite on hydration products development-Poz-2 at 7 days

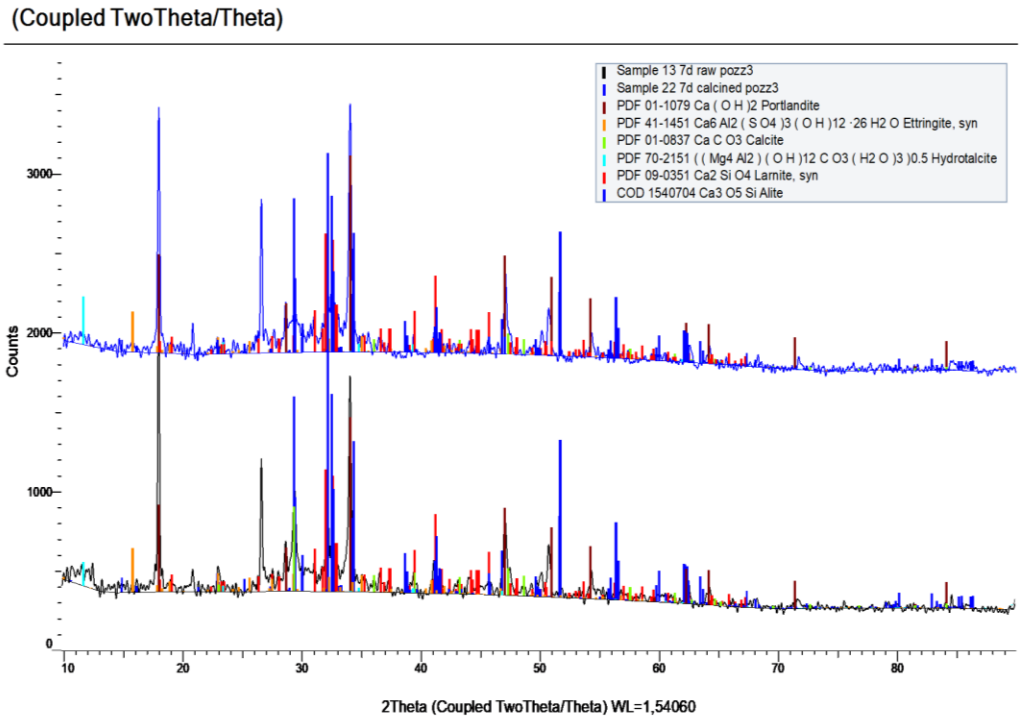

Figure 4.47: Effect of calcination of a kamafugite on hydration products development-Poz-3 at 7 days

4.4 Results on the effect of physical properties

Detailed results for the effect of replacement levels of the test kamafugites and carbonatites on heat of hydration are saved under the folder name “heat of hydration” on the DVD submitted together with this thesis. The folder contains subfolders that show specific results against the different properties of kamafugites and carbonatites tested. The TGA results on hydration products development are saved on the same DVD under the folder name “TGA_DTG results” and with subfolder names “TGA_effect of fineness” reporting data on the effect of fineness on hydration products development. All subfolders are named appropriately for the specific properties of kamafugites and carbonatites reported in this thesis. The results on the effect of fineness and replacement level on compressive strength of blended cements are presented in Appendix 2 of this thesis. All results were generated following experimental procedures presented in Section 4.1 and 4.2 of the current chapter.

4.5 Chapter summary

The experimental procedures followed in the study of the effects of compositional properties of kamafugites and carbonatites as SCMs in Portland cement pastes and mortars have been presented together with the results generated from the experimental processes. The discussion and conclusion about the results presented in Chapter 4 are presented in Chapter 5 of this thesis. The following observations can be made from the comparative study on results from the different pozzolanicity tests applied to kamafugites and carbonatites in this study.

1. The chemical shrinkage test method correlates well with other test methods and is considered feasible for application in characterisation of pozzolanic activity of SCMs in regions that have difficulty accessing more sophisticated methods. The setup for the chemical shrinkage method following the dilatometry technique is affordable and easy to reproduce in different environments.
2. Theoretically, the intercepts for TGA are at zero. This is because there is no hydration reaction at zero time before water is added and accordingly there is no strength at zero. However, exposure of cement to the atmosphere leads to absorption of water from the environment by the hygroscopic anhydrous cement compounds leading to

formation of hydration products that are picked by the TGA method. Therefore, hydration products exist at zero time for cement exposed to the atmosphere.

3. Because the C-S-H hydration products dominate in contributing to the strength of hydrated cement, the TGA phase associated with decomposition of the silicate hydrate phase, the dehydration phase, was considered in comparison studies with results from other pozzolanic tests. This improved on the correlation coefficient further promoting the negation of the Ldx and Ldc phases in development of numerical methodologies since these parameters do not easily correlate with other hydration parameters.
4. Finally, the strong correlations that exist between the different sets of results shows that the 4 test methods, compressive strength, heat of hydration, chemical shrinkage and TGA can all be independently applied in characterisation of pozzolanic activity to directly give reliable results. The correlations also show that the data generated by the different experiments is an actual representation of the chemical processes taking place in the hydration of blended cements as represented by the different parameters applied in the test programs. The two general equations established for prediction of paste properties are as follows.

i. $y = Ax, Where\ A\ is\ a\ scale\ factor\ and\ x\ a\ predictor\ variable.$ This model is applicable in Chemical Shrinkage-Heat of hydration-Strength relationships

ii. $y = Bx + C, Where\ B\ is\ a\ scale\ factor, C\ an\ intercept.$ This model is applicable in Chemical Shrinkage-Degree of hydration-Strength relationships.

CHAPTER 5

ANALYSIS AND DISCUSSION OF RESULTS

The current chapter presents an analysis and discussion of results obtained from experimental procedures reported in chapters 3 and 4 of this thesis. The work characterizes compositional parameters of kamafugites and carbonatites as SCMs and their pozzolanic activity, long-term compressive strength development, influence on hydration kinetics, chemical shrinkage, and hydration products assemblage. The results are grouped in three parts that discuss; pozzolanic and other SCM properties; the role of calcite and volatile alkalis in carbonatites and kamafugites on compressive strength development, hydration kinetics and hydration products development; and the effect of fineness and replacement levels of carbonatites and kamafugites on pozzolanic activity, compressive strength development and hydration kinetics when the natural pozzolans are blended with Portland cement in paste and mortar. In order to report coherently following the objectives set for this research, a discussion of results that follow the experimental plans that test compositional effects and the role of physical properties of kamafugites and carbonatites is presented in sections 5.2 and 5.3 of this chapter. Accordingly, the results discussed in section 5.1 are mainly those conducted at a fixed replacement level of 20% for the test SCMs using CEM I 52.5R as a control sample. A fixed replacement level is important for comparative analysis of results of the different test SCMs.

5.1 Pozzolanic activity and other SCM effects of carbonatites and kamafugites

5.1.1 Fresh properties of blended cement

Results presented in Table 4.2 in Chapter 4 showed that the addition of kamafugites and carbonatites in Portland cement led to a reduction in the setting time, increased water demand, reduced slump flow, and had no measurable influence on soundness property of cement. To understand the obtaining mechanisms, each of the three fresh cement paste and mortar property - water demand, setting time and soundness – are discussed as follows.

5.1.1.1 Cement paste consistency and water demand

Studies on natural pozzolans that produced similar results (Turanli, Uzal and Bektas, 2004) attributed the loss in slump flow of natural pozzolan blended cements and their increase in water demand to microscopic pores and shape features of natural pozzolans. However, microstructure observations of the carbonatites and kamafugites (Figure 3.7 on page 3-13) could not identify micro-pores attributed to most zeolitised tuffs and pumices. Perhaps, the closest hypothesis that can be advanced to explain the water demand-SCM relationship for the kamafugites and carbonatites is one advanced by Ulusoy and Yekeler, 2005. Ulusoy and Yekeler, 2005, studied the influence of surface roughness of typical industrial minerals (calcite, barite, talc, quartz) on hydrophilicity (wettability) and found a clear linear relationship with a high coefficient of determination (R^2>0.93). The hydrophilicity property increased with increase in surface roughness and was independent of the grinding conditions of the different minerals tested. From the images in Figure 3.7, it is observed that both angular-shaped and rough spherical particles exist.

5.1.1.2 Setting time

The kamafugites and carbonatites generally reduced the setting time of the cement system. Factors such as the temperature and relative humidity that influence setting time (Neville, 2002) and the amount of pozzolanic admixture were controlled and monitored through the experimental process. This left the setting time to be influenced by the interaction between the test SCM materials and cement phases and water. The factors mainly attributed to affecting setting time of natural pozzolan blended cement systems include fineness, presence of water-soluble alkalis, and reactive mineral phases in the pozzolanic materials. Different studies on natural pozzolans report contradicting results, the majority reporting a delayed setting trend. Turanli, Uzal and Bektas, 2004, however found a reduction in setting time while studying Turkish volcanic tuffs but the cause of this reduction was not established. A similar observation by Targan et al., 2003, suggested a higher surface area of natural pozzolan, a mechanism that is not explained in their work. The results observed in the current study did not show any relationship between setting time and fineness levels of the kamafugites and carbonatites.

In order to understand the possible causes of set acceleration effect of the kamafugites and carbonatitic lavas, one needs to evaluate their composition and powder properties. Important to note is that a reduction in setting time was observed to increase with increase in kamafugites and carbonatites content. Two mechanisms discussed in Section 2.4.2 of the literature review chapter of this thesis can be advanced here, the dilution mechanism and the physio-chemical activation mechanism. The dilution mechanism presents a paste with a higher water cement (clinker) ratio and less cement content. The effect of increasing the water cement ratio and reducing cement content is known to increase the setting time. The reduction in setting time of the kamafugites and carbonatites blended Portland cements is therefore governed by a physio-chemical mechanism. The physio-chemical activation as presented in literature is mainly based on the filler effect (nucleation sites model) and alkali activation of the cement hydration models.

The mineral phases responsible for pozzolanic reaction are in a latent state at the time of cement paste setting (Berodier, 2015). Berodier, 2015, studied hydration kinetics of blended cements focusing on the third phase, the acceleration phase, on a calorimetry curve. She used an inert material (quartz powder) for reference in this study. Both the initial and final setting times are reported to occur in the acceleration stage on a calorimetric curve. Her work found the filler effect to accelerate the hydration process of blended cements, but the common explanation associated with provision of extra nucleation sites for hydrates was not adequate to explain the observed acceleration. Limestone was found to have the highest accelerating effect in relation to other SCMs and inert material (quartz powder). The observed denser nucleation sites with limestone were hypothesized to be associated with a fundamentally preferential mineral surface structure for precipitation of the silicate hydrates. The carbonates in the kamafugites and carbonatitic lava are, therefore, a plausible candidate for a similar effect on hydration of cement.

Additionally, alkalis are known to influence the hydration and setting properties of cement. Jawed and Skalny, 1978, and later Odler and Wonnemann, 1983, both studied the effect of alkalis and found them to accelerate early hydration and setting of cement pastes. Odler and Wonnemann, 1983, found that the Na^+ based alkalies

delayed setting time while the K^+ based alkalis accelerated the setting time of cement. The Na^+ based alkalis were observed to delay the hydration of the aluminate phases in the cement paste. Indeed, the hydration of the aluminate phases and gypsum is responsible for the setting property of cement. A look at the oxide composition data for the Turkish natural pozzolan samples studied by Turanli, Uzal and Bektas, 2004, and Targan et al., 2003, show that the natural pozzolan samples are predominantly potassic (Table 5.1). The natural pozzolan sample used by Targan et al., 2003, had no Na^+ based alkalies. Their explanation of the role of natural pozzolan on setting time of cement did not evaluate the influence of the potassic alkali type of the Turkish natural pozzolans studied. Moreover, the ultrapotassic kamafugite with the least content of carbonates of the three test pozzolan ranked highest on the set accelerating property.

Table 5.1: Alkali composition of Turkish natural pozzolans associated with accelerating setting time (Turanli, Uzal and Bektas, 2004; Targan et al., 2003)

Compostion	Pozzolan (Kula – Turkish) Targan et al 2003	Nozzolan P1, Turanli, Uzal and Bektas, 2004	Pozzolan P2 Turanli, Uzal and Bektas, 2004	Pozzolan P3 Turanli, Uzal and Bektas, 2004
Na_2O %	-	3.90	1.50	3.50
K_2O %	2.47	4.10	2.10	2.4

5.1.1.3 Soundness property

The soundness results are also presented in Table 4.2, Chapter 4. The kamafugites and carbonatites blended cements registered no volume change. The influence of SCMs on the soundness property of cement paste is controlled by the rate at which the important constituents of SCMs react in a mix. The constituents that react and form stable hydrates before the cement paste has set do not cause the problem of unsoundness. Lime as a cement admixture is reported to react rapidly completing its hydration reaction before the paste has acquired any form of rigidity (Neville, 2002). Therefore, the carbonates in kamafugites and carbonatites are hypothesized to hydrate rapidly and their reactions to be completed before the setting time of the paste. A study of the microstructure of the hydration products, especially the mono- and hemicarboaluminate phases, would reveal the role of the carbonates in the hydration reaction. In studies on cement-limestone microstructure, ettringite and

monocarboaluminates were observed and no monosulfates were observed (Chowaniec, 2012). This study showed that increased C_3A did not lead to the breakdown of ettringite to monosulfates, but rather reacted with limestone to form more monocarboaluminates. The TGA and XRD results in the later sections of the current thesis chapter further reveal the hydration products formed.

On MgO which forms a significant part of the composition of the kamafugites and carbonatites, the only dangerous form of MgO is periclase which is a crystalline form of MgO formed through the clinkering process of cement (Neville, 2002). MgO reacts with silicate hydrates in the presence of water to form magnesium silicate hydrates (M-S-H), a reaction process that forms hydrates with a larger volume than the decalcified silicate hydrates (C-S-H and C-A-S-H). The increase in volume leads to internal stresses and expansion of cement paste that has already set. The MgO in natural pozzolans generally exists in amorphous form and is considered not to take part in the expansion causing hydration reactions. However, Kupwade-Patil et al., 2016, studied microstructure of Portland cement blended with natural pozzolans and found that the Mg^{2+} ions substituted Ca^{2+} ions of the C-S-H and C-A-S-H hydration products forming more porous M-S-H hydration products. This study observed the M-S-H causing reactions to depend on the level of substitution, increase in substitution leading to increase in the M-S-H hydrates. M-S-H phases are inferior in strength compared to the decalcified hydration phases in hydrating cement microstructure (Bonen, 1992), a condition that may lead to conversion effect considering that the decalcification reaction is a delayed reaction in the hydration process.

The other aspect of soundness is that of delayed hydration of gypsum that is caused by excess gypsum above the amount required to react with the aluminate phases in cement (Neville, 2002). The interaction of calcium sulfate and calcium sulfoaluminate phases with pozzolans has been studied by Ioannou et al., 2014, using fly ash. The presence of fly ash led to fast absorption of the sulfate phase leading to ettringite formation. Chowaniec, 2012, also studied cement and limestone systems and reported an increase in hydration products. This was explained by the absorption of C_3A in its reaction with limestone which led to formation of monocarboaluminates while limiting gypsum to hydrate to ettringite. The natural pozzolans studied are

known to have $CaCO_3$, alumina and silica phases which are considered to contribute to the hydration of blended cements and, consequently, are likely to present similar hydration reactions.

The addition of the kamafugites and carbonatitic lavas did not cause any negative change to the soundness property of cement. The absence of expansion as shown in Table 4.2 implies that the carbonatitic phases in the natural pozzolans react to completion before setting takes place. The MgO component in the natural pozzolans appears not to significantly participate in the hydration reaction to form expansive hydration products. No variation of gypsum was conducted to test the effect of excess gypsum in delayed ettringite formation and, especially, how the presence of the natural pozzolans would affect this reaction. The variation of natural pozzolana content (20% and 35% CEM I replacements with natural pozzolans) showed no effect on the soundness results.

5.1.2 Compressive strength development

A known pozzolan, a class F Fly Ash was included in the experimental design as a second control. It is observed that, whereas compressive strength of the fly ash test sample increases to compensate for the cement content replaced in the blended mixes, all the test natural pozzolans did not show any relative gain in strength beyond 28 days of curing. However, the SAI test shows that the test samples exhibit values above the minimum of 80% of the control sample (CEM I 52.5R) required in EN 197-1, 2000, declaring the kamafugites and carbonatites to be beneficial SCMs. The reduction in the SAI values with curing age after 28 days indicates either depletion of pozzolanic reactions or the possibility of a conversion effect (a chemical process that leads to modification or disintegration of the already formed strength giving hydration products). The argument that pozzolanic reactions in natural pozzolans are depleted at 28 days of curing is farfetched considering that pozzolanic reactions tend to progress way beyond 28 days (Mehta and Monteiro, 2006). The conversion effect therefore stays the most viable argument. Poz-3 ranks highest in the rate of reduction in the SAI which is followed by Poz-1 and Poz-2 showing stability in SAI values from 56 days to 180 days of curing. The stability seen in Poz-

2, however, does not prove absence of a conversion mechanism but, rather, that the rate of gain in strength due to pozzolanic reaction is discounted by the conversion effect.

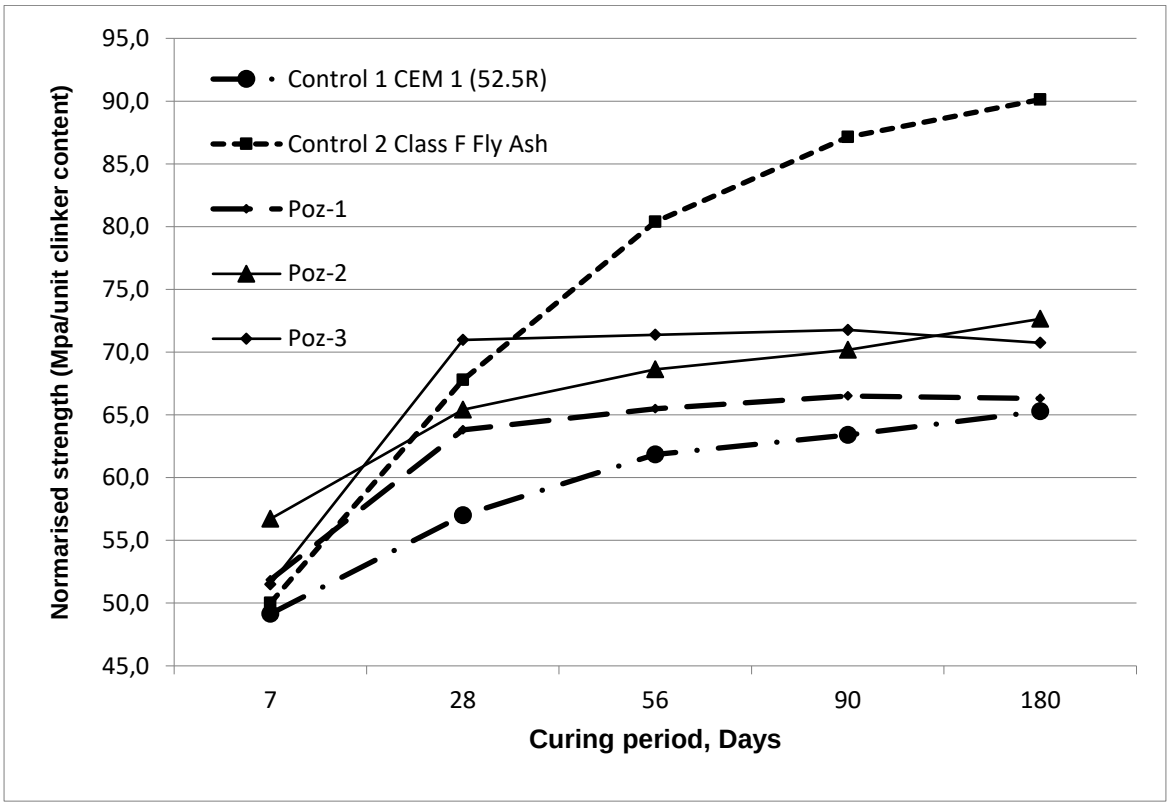

Figure 5.1**:** Results of compressive strength tests for test natural pozzolans and control samples normalized to Portland cement content

Figure 5.1 is a graphical presentation of strength development for the three natural pozzolans and two control samples, all normalized to cement content. The figure further helps in characterizing compositional effects on strength development. The addition of carbonatites and kamafugites shows a time dependent influence on strength in relation to the unit Portland cement content possibly due to a combined effect of hydration acceleration and pozzolanic effect. The gain in strength for Poz-1 and Poz-3 terminates at 28 days indicating either a depletion of reactive compounds in the matrix or a strength development retardation reaction mechanism (conversion effect). The reactive silica content seems to be the determinant in pozzolanic activity at 28 days of curing, but its effect is minimized after 90 days of

curing. Poz-2 shows better pozzolanic activity at longer curing times than Poz-3 yet the later has more reactive silica, an occurrence this study hypothesizes to be a conversion reaction that discounts the pozzolanic benefits of the silicate phases in the test pozzolans. Poz-1 and Poz-3 appear to have a more pronounced conversion effect on the hydrating cement after 28 days as their strength activity index values reduce with curing time.

Based on the specifications presented in EN 197-1, 2000, and a test program adopted to composition specifications in ASTM C618, 2005, all the test pozzolans fulfill the requirement for the strength activity index. The standards limit these tests to only 28 days of curing but strength activity over longer periods (up to 180 days of curing) reveal no significant gain in strength after 28 days for the test kamafugites and carbonatites. The pozzolanic activity of the kamafugites and carbonatites is therefore less pronounced.

1. Compositional effects on compressive strength of mortar prisms

The chemical composition of all the test samples, and soluble SiO_2, CaO and PH of the kamafugites and carbonatites are all evaluated in relation to other observed properties of the samples and to requirements by international standards. Contrary to the ASTM C618, 2005, requirement of the sum of silica, alumina and iron oxides to be above 70%, the pozzolanic property of the natural pozzolans as observed by the SAI did not sustain consistencies with chemical composition requirement for the sample to achieve the 80% strength in relation to the strength of the control sample. Similar contradictions were observed by Pourkhorshidi et al., 2010, while testing consistencies of the ASTM C618, 2005, method on four (4) Iranian natural pozzolans. It is, however, noticed that the mechanisms driving hydration reactions are beyond the acidic oxide content though its role can be observed in the 90 days sample as shown in Figure 5.2. The loss of correlation between strength and silica content at 7 days and 180 days of curing indicate presence of other mechanisms that are affecting formed hydration products.

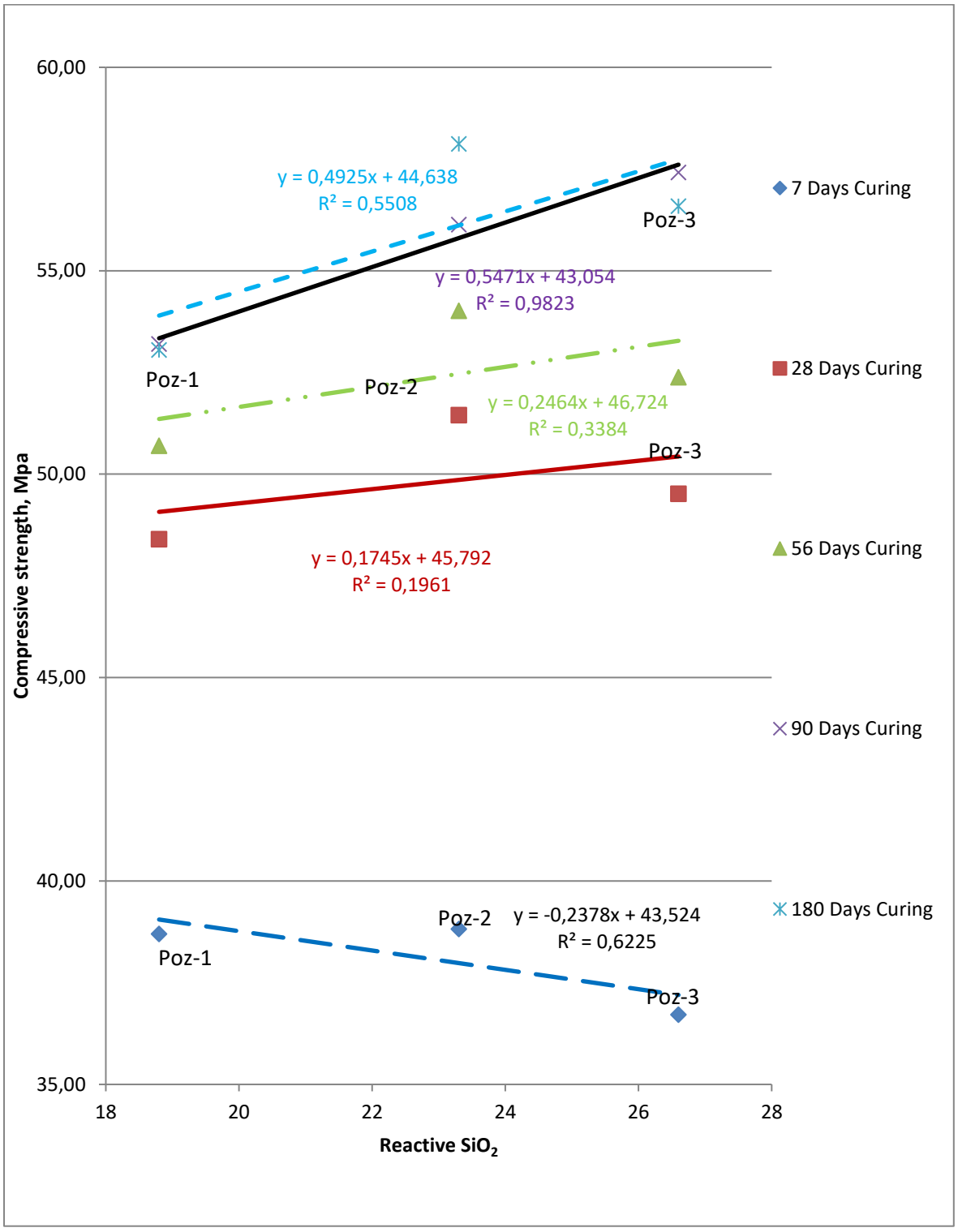

Figure 5.2: Dependence of strength on reactive SiO_2 in the natural pozzolan samples.

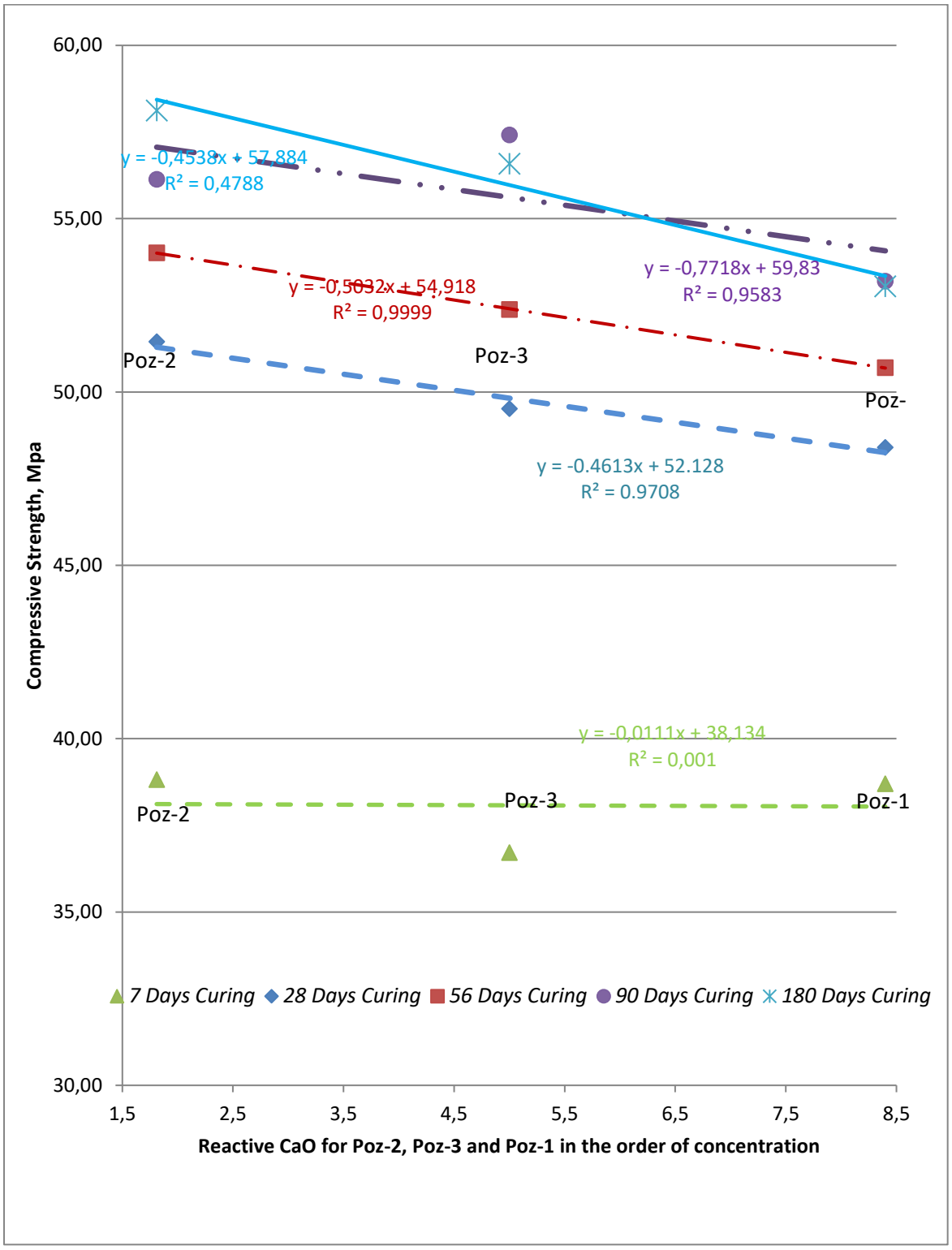

Figure 5.3**:** Dependence of strength on reactive CaO in the natural pozzolan samples.

Reactive silica (exchangeable cation content) and amorphous content of natural pozzolan are reported to be the drivers of a pozzolanic reaction in a blended cement paste (Snellings, Mertens and Elsen, 2012; Malhotra and Mehta, 1996; Özen et al., 2016). Most of this research used pozzolanic materials that are characteristically high in silica content. Malhotra and Mehta, 1996, stress the importance of the amorphous state of the minerals and morphological properties of the pozzolanic materials over the chemical composition in determining their performance as SCMs in concrete. These studies however focus on the silica and alumina phases and do not address the role of the carbonatite minerals and other compositional parameters in a cement-natural pozzolan blended system. The dependence trend on the reactive silica content in the current research as shown in Figure 5.2 appears distorted with low coefficients of determination at all curing ages except for the 90 days test. This advances the possibility that there are other significant reaction mechanisms in the blended cement systems. Figure 5.3 presents strength to be more dependent on the reactive CaO content with high coefficients of determination for 28, 56 and 90 days of curing. The negative trend between compressive strength and reactive CaO content of the natural pozzolanic materials is strongest at 56 days of curing presenting a linear correlation with a very high coefficient of determination (R^2=0.999). The linear trends at 28 and 90 days of curing are equally very strong with their coefficients of determination, R^2, at 0.9708 and 0.9583 respectively. The sample with the highest reactive CaO content showed least “pozzolanic activity” as presented in strength parameters, a condition this research is hypothesizing as the influence of reactive carbonate minerals in the blended cement samples. Habert et al., 2008, calcined two natural pozzolans and observed contradicting trends, one decarbonating at 600ºC and showing improvement in strength while the other showed a negative trend in strength development when subjected to temperatures above 350ºC for 28 days compressive strength. The work by Habert et al., 2008, attributed the gain in strength experienced in one of the samples to the Ca^+ ions made available by the action of decarbonation. The work, however, did not explain the role the carbonates have in influencing strength, hydration products and hydration kinetics. The negative trend observed between reactive CaO and

compressive strength was not answered in the current research and has been recommended for future studies. The observed conversion effect discussed under the long-term compressive strength results is probably associated with the carbonates in the test kamafugites and carbonatites.

It is further observed in Figures 5.2 and 5.3 that the mechanisms influencing strength development at early stages (7 days) and later stages (180 days of curing) are not dominated by the calico-silicate phases in the test pozzolans. Therefore, the hydration progression and strength development mechanisms in cements blended with Kamafugites and carbonatites cannot be sufficiently appraised on the Si and CaO content in the test pozzolans. The importance of alkalis, MgO and other minerals in the test pozzolans is justified.

5.1.3 The Frattini test for pozzolanicity

The results of the Frattini test are presented in Figure 4.10 on 19 of Chapter 4 in this thesis. Natural pozzolans with reactive CaO lead to test results showing no pozzolanic activity because of a Ca^{2+} ionic concentration higher than the expected at saturation point. This was the case for the kamafugites and carbonatitic lavas. The varying composition of reactive CaO in the different natural pozzolans (See Table 4.6 on Page 4-19 of this thesis) makes the Frattini test an unreliable test for pozzolanicity of the kamafugites and carbonatites. This same rationale limits all other estimation methods that seek to quantify the amount of CaO and water consumed by the aluminosilicates in the pozzolanic materials. The other methods affected include thermogravimetric analysis (TGA) and saturated lime test. The Frattini test method has however been applied successfully in pozzolanicity tests for natural pozzolans whose CaO composition is very low compared to silica composition (Pourkhorshidi et al., 2010). The strength activity index, microstructure image analysis, long term chemical shrinkage measurement, modified TGA and prolonged heat of hydration measurements are more adapted methods for testing pozzolanic activity of carbonatitic lavas and kamafugites.

5.1.4 Heat of hydration progression

The results from the heat of hydration experiments for 92 hours testing period are presented in Table 4.9. The results show samples blended with kamafugites and carbonatites and GGBS to have a higher heat release per unit cement content compared to the control sample (CEM I 52.5R). Various research (Malhotra and Mehta, 1996; Schöler et al., 2017) reveal the pozzolanic reaction to be more evident in concrete mixes after 28 days. The intention for characterisation of the early age heat of hydration of OPC blended with test pozzolans was therefore to review their effect on the important hydration processes that are responsible for the transition of concrete through setting, hardening and strength development stages. Moreover, highly pozzolanic SCMs may contribute to strength gain at an earlier age. Riding et al., 2012, stresses the importance of early hydration in influencing the micro-characteristics of concrete that are responsible for its strength, vulnerability to delayed ettringite formation and development of internal residual stresses that would compromise concrete durability.

Figure 5.4 presents isotherms that show heat discharge rates normalized for cement content while Figures 5.5, 5.6 and 5.7 represent different parts of the isotherms in Figure 5.4. Table 4.9 shows total heat released at 1, 2, 3, 7, 24, 48 and 92 hours from start of hydration reactions. Total heat has been normalized to Portland cement content in the paste mixture. The figures show typical hydration curves of cement with all the five (5) stages (the rapid initial peak, the dormant period, the acceleration period, the retardation period and the long-term hydration reaction, typical of Portland cement hydration (Neville, 2002)) indicating that the presence of carbonatites and kamafugites did not significantly alter the hydration reactions of the cement phases.

Figure 5.5 shows the rapid initial peak after addition of water into the test samples and the beginning of the second stage of hydration, the dormant stage. The initial peak is associated with dissolution of ions and initial hydration of cement phases (Taylor, 1997). All blended samples show a higher heat rate than the CEM I 52.5 R control sample, test pozzolans ranking higher than cement samples blended with GGBS. The test pozzolans do not cause any peculiar trends at the dormant stage.

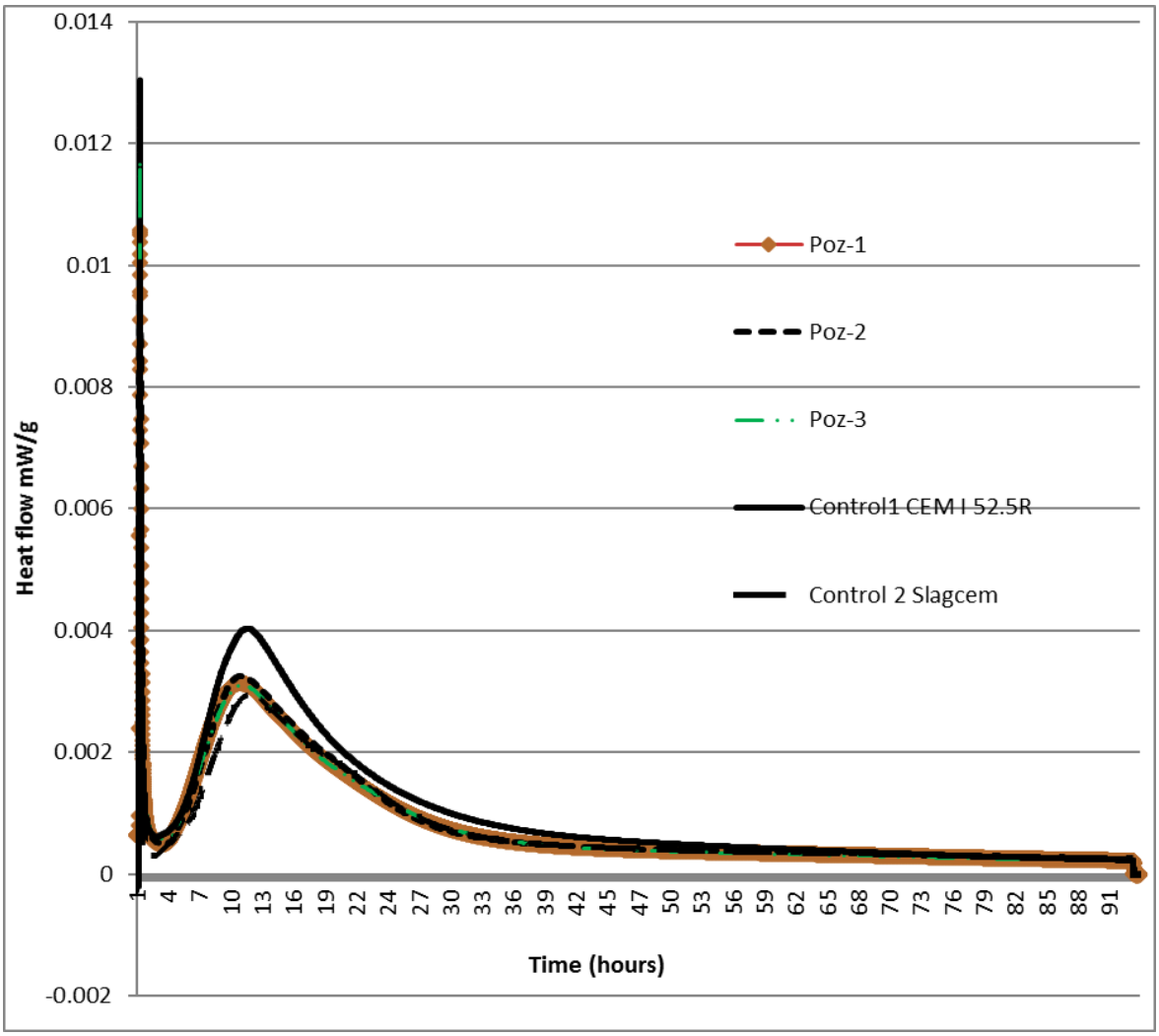

Figure 5.4**:** Effect of test pozzolans on heat of hydration in isothermal conduction calorimetry: Heat flow rate for 90 hours.

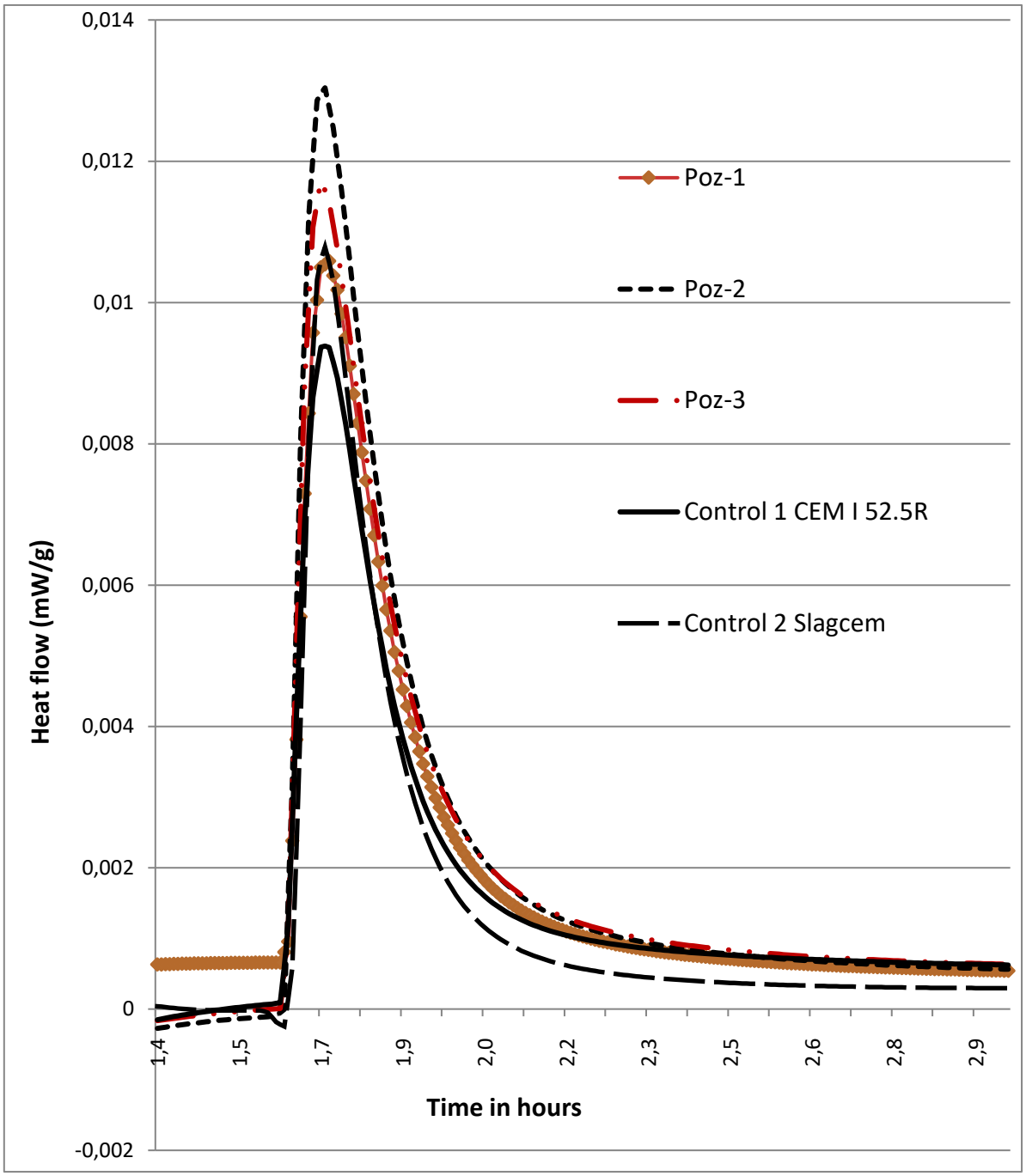

Figure 5.5**:** Effect of test pozzolans on heat of hydration in isothermal conduction calorimetry: The rapid initial peak after addition of water.

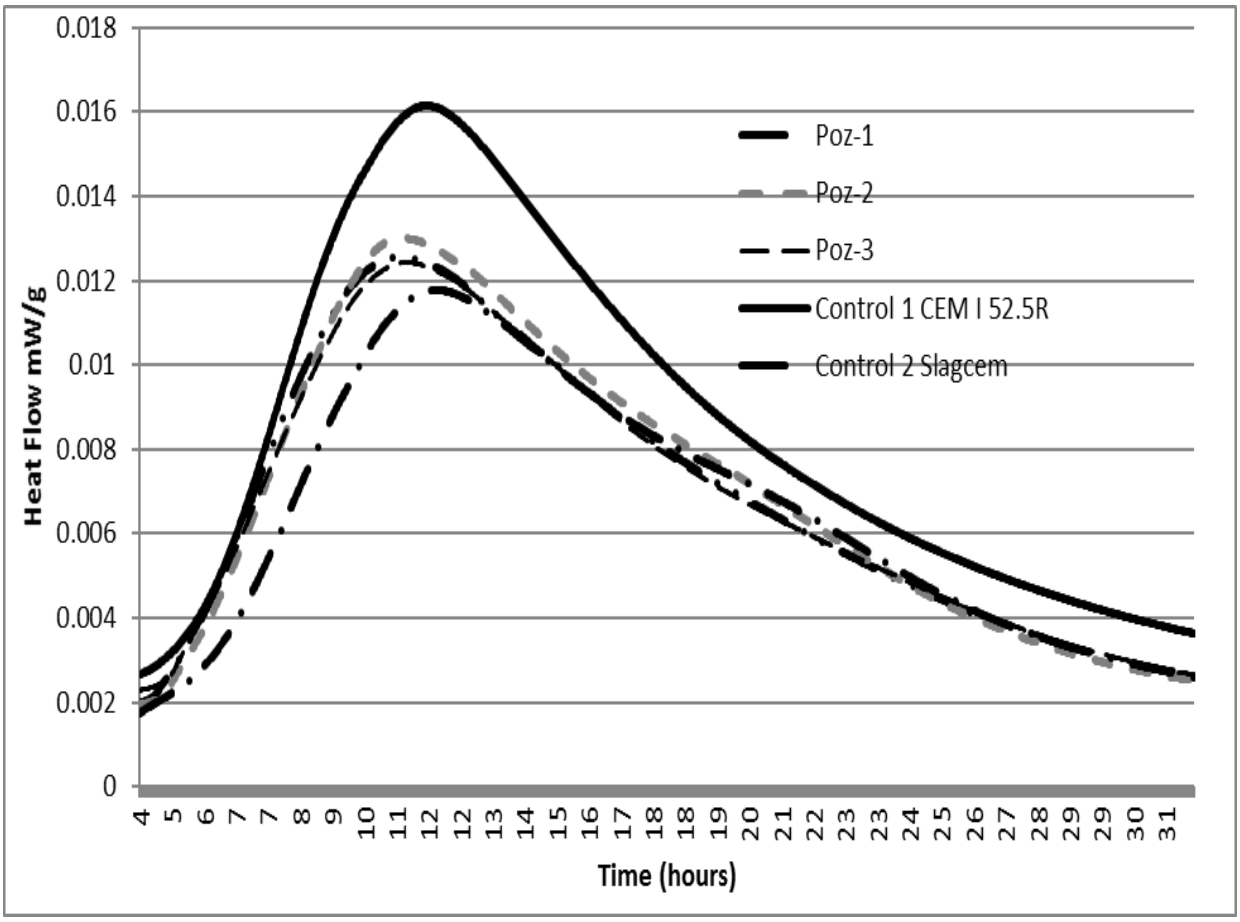

Figure 5.6**:** Effect of test pozzolans on heat of hydration in isothermal conduction calorimetry: Acceleration and retardation stages of hydration

Figure 5.6 shows the acceleration and retardation periods with the second peak coming early for cement blended with test pozzolans. The accelerating effect of carbonatites and kamafugites is observed with blended samples peaking earlier than the control samples. This is consistent with setting time results (Table 4.2, Chapter 4 of this thesis).

Heat of hydration is a proxy parameter used to predict the rate and extent of hydration of cement compounds. Deviations in these properties can therefore be applied in characterisation of cement admixtures and additives. Increased heat release observed in blended samples can be attributed to the accelerating phenomena of SCMs attributed to the filler effect (Berodier, 2015; Berodier and Scrivener, 2014; Kakali et al., 2000; Lothenbach et al., 2008; Matschei, Lothenbach and Glasser 2007;

Ipavec et al., 2011; Mohamed, Elsalamawy and Ragab, 2015; Scrivener et al., 2015; Schöler et al., 2017) and other hydration accelerating mechanisms attributed to the alkalis in Portland cement systems (Odler and Wonnemann, 1983; Thongsanitgarn et al., 2012). The two accelerating mechanisms advanced in this study are the preferential filler effect of calcite and the influence of the potassic alkalis on the aluminate phases of cement. Berodier and Scrivener, 2014, reveal that the filler effect is a function of mineral types in SCMs, calcite/limestone performing better than other common SCMs. This appears to agree with the results in Table 4.9 as the calcite bearing test natural pozzolans led to a higher heat release compared to a cement sample blended with GGBS. This effect is sustained for the first 7 hours of hydration when the filler effect is considered important (Berodier and Scrivener, 2014; Scrivener et al., 2015; Schöler et al., 2017). Furthermore, studies on the effect of alkalis on hydration of aluminate phases report an accelerating effect with potassic leaning alkalis and a retarding effect with sodic leaning alkalis. The chemical composition of the test kamafugites and carbonatites (Table 3.3) shows the samples to be enriched in mainly potassic alkalis. However, the trends observed beyond 7 hours cannot be explained through the acceleratory mechanisms above.

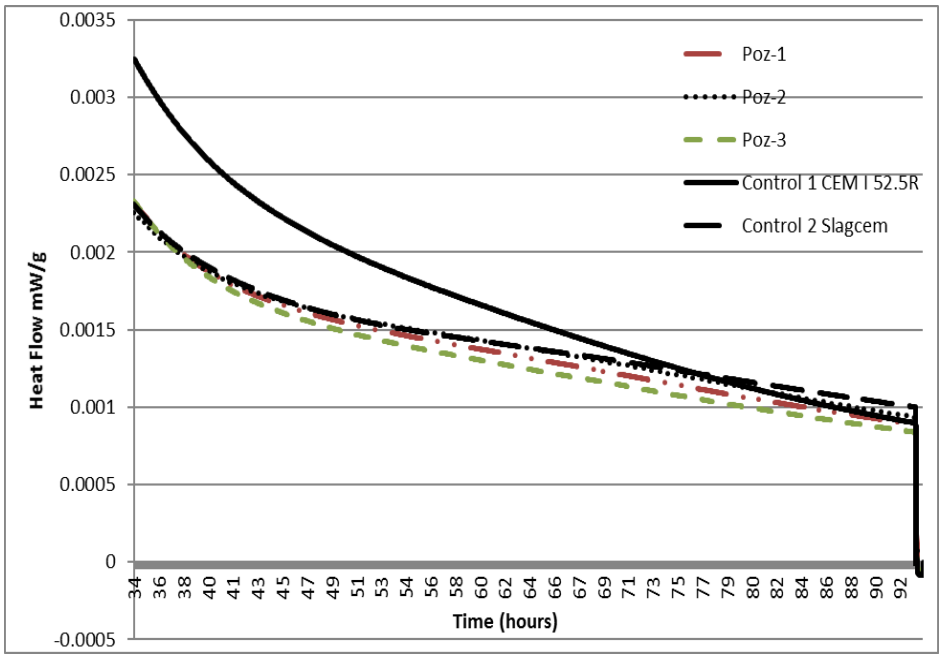

Figure 5.7**:** Effect of test pozzolans on heat of hydration in isothermal conduction calorimetry: The start and progression of the long-term hydration reactions.

Figure 5.7 shows the beginning of the fifth stage, the long-term reactions. There is a distinct beginning of this phase at about 36 hours indicating a start of pozzolanic reactions between SCMs and Portland cement phases. The heat rates of SCMs blended cements gain on the CEM I 52.5R control sample with Poz-2 and Poz-1 presenting superior heat rates than the cement control at about 90 hours. The results show Poz-2 to perform better just below the slag blended control sample and followed by Poz-1 and Poz-3 trailing. This trend correlates well with the strength results at early stages of hydration as shown in Table 4.4 indicating that heat of hydration is a good predictor of strength development in blended cement systems. At 36 hours after the start of hydration, the cement has set, and the reaction mechanisms are diffusion controlled as the free movement of ions is constrained. The acceleratory effect attributed to the filler effect of SCMs is also less important for the same reason of constrained movement of ions on the cement matrix. The reaction mechanisms in blended cement systems that generate heat are therefore hydration reactions accelerated probably because of equilibrium shifts due to fixation of CH in a pozzolanic reaction. Therefore, the pozzolanic reactions of kamafugites and carbonatites are hypothesized to start as early as 36 hours after the start of the hydration reactions.

5.1.5 Chemical shrinkage

Chemical shrinkage measurement came as a sequel to characterisation of the kamafugites and carbonatites as pozzolans in Portland cement after inconsistencies appeared in the previous results from two test methods. Two standard test methods for pozzolanicity, one direct, the Frattini test, (EN 196-5) and one indirect, the strength activity index (SAI), (BS 3982), used to characterize pozzolanicity of kamafugites and carbonatites yielded contradicting results. The direct method which relies on estimation of free Ca^{2+} ions in a test solution resulted in a higher concentration of the ions indicating a lack of pozzolanic reaction of the kamafugites and carbonatites while the indirect method, the strength activity index, showed the kamafugites and carbonatites to be pozzolanic with strength gain against the control sample up to 28 and 90 days of curing. It was hypothesized that the presence of free Ca^{2+} ions in the kamafugites and carbonatites limited the application of the direct

test method (EN 196-5, 2005). The EN 196-5, 2005, standard method assumes that test pozzolans, which are mostly silicic, do not significantly contribute to Ca^{2+} ions concentration in the test solution (BS EN 196-5, 2005; Donatello, Tyrer and Cheeseman, 2010). Carbonatites are primarily composed of calcite and minor quantities of dolomite minerals (Stoppa and Schiazza, 2013) that can be a source of extra Ca^{2+} ions above these supplied by the hydrating cement leading to circulation levels beyond the maximum expected for a pozzolanic cement and therefore causing the EN 196-5, 2005, standard method to fail to detect pozzolanic properties. To strengthen the basis for testing the hypothesis above, a third pozzolanicity test method, the chemical shrinkage measurement, was proposed to characterize the pozzolanic nature of carbonatites. The chemical shrinkage method presents the advantage of indirectly assessing chemical processes in a water-cement mixture while eliminating the influence of mechanical factors common to the SAI method. It is known that the presence of mineral powders influences cement hydration and compressive strength of blended cement in ways other than pozzolanic reaction (Ballim and Graham, 2009; Kadri et al, 2010; Berodier, 2015, Nwaubani, 2018) and therefore the SAI test requires additional tests to validate pozzolanic reaction. The chemical shrinkage measurement applied the dilatometry technique to record volume changes in cement mortar resulting from chemical processes that are associated with the hydration and pozzolanic reactions. The chemical shrinkage test results were compared with results from heat of hydration, thermogravimetric analysis (TGA) and compressive strength and were found to be consistent.

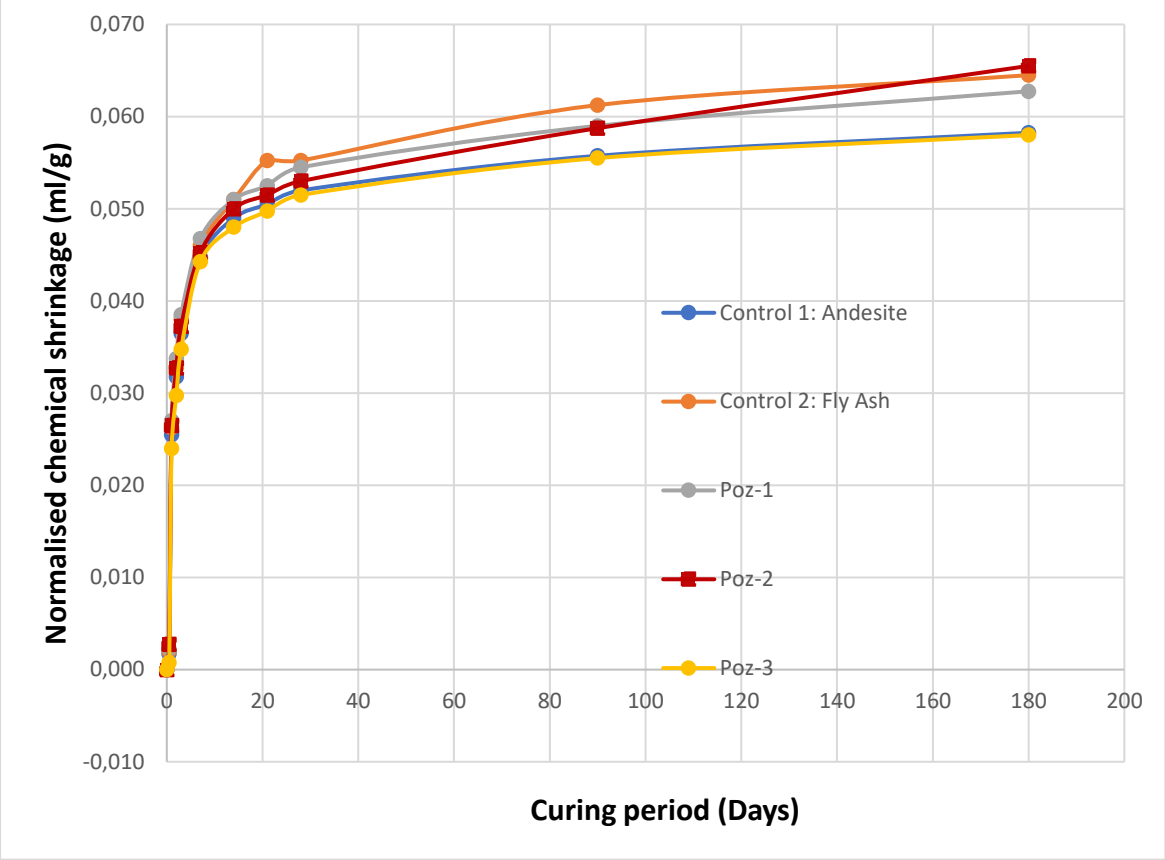

Figure 5.8**:** Chemical shrinkage analysis of results for raw test pozzolans (results normalized to cement content).

Figure 5.8 is a graphical representation of chemical shrinkage values presented in Table 4.12, Chapter 4 of this thesis. The observed volume change is normalized to cement content and variabilities evaluated for compositional effects and pozzolanic reaction. The results show the control sample blended with fly ash, and Poz-1 a carbonatite and Poz-2 a kamafugite, to have higher chemical shrinkage values than the control sample that was blended with andesite powder. Both Poz-1 and Poz-2 are silica undersaturated and with high contents of calcite. Poz-3, an ultrapotassic and silica saturated kamafugite with relatively low content of carbonate minerals gave the least values in chemical shrinkage ranking lower than the andesite powder blended control sample for the whole test period up to 180 days.

To characterise the contribution of pozzolanic reactions to chemical shrinkage, stoichiometric quantification of the pozzolanic reactions is performed. The equation

of the pozzolanic reaction (Equation 2.9) enables the stoichiometric calculation of reactants and products as follows.

Molar mass of $Ca(OH)_2$; 40.078 + 2(15.999) + 2(1.008) = 74.092 g/mol

Molar mass of SiO_2; 28.085 + 2(15.999) = 60.083 g/mol

Molar mass of $(CaO)_3(SiO_2)_2(H_2O)_3$;

3(40.078) + 3(15.999) + 2(28.085) + 4(15.999) + 6(1.008) + 3(15.999) = 342.442 g/mol

In a pozzolanic reaction, for every 3 moles of $Ca(OH)_2$, 2 moles of SiO_2 are needed to form 3 moles of the cementitious reaction product($3CaO.2SiO_2.3H_2O$). Considering $n = \frac{m}{M}$ $where\ n = number\ of\ moles, m = mass\ and\ M = molar\ mass,$ and assuming 1.00 grams as mass of the primary reactant ($Ca(OH)_2$) in the pozzolanic reaction, the volume of the reactants and reaction product of a pozzolanic reaction is calculated basing on densities of the pure compounds in the reaction process (Table 5.2).

Table 5.2: Stoichiometric changes in a pozzolanic reaction.

Pozzolanic reaction	$3Ca(OH)_2$ +	$2SiO_2$ →	$3CaO.2SiO_2.3H_2O$
Molar mass (g/mol)	74.092	60.083	342.442
Mass (g)	222.276	120.166	342.442
Mass (g) for 1 g CH	1.00	0.54	1.54
Density (g/ml)	2.251*	2.641*	2.12**
Volume (ml)	0.444	0.204	0.727
Volume increase due to Chemical expansion = 12% expansion			

* Balonis and Glasser, 2009; ** Zhang et al., 2013

A similar approach has been used and reported by different authors (Tazawa, Miyazawa and Kasai,1995; Mehta and Monteiro, 2006) to estimate chemical shrinkage of Portland cement compounds. Mehta and Monteiro, 2006, report work of Justness et al., 1998, that presented chemical shrinkage of C_3S for total hydration as 7.2% and 8.5% of the sum volume of initial reactants for two probable hydration products. Tazawa, Miyazawa and Kasai, 1995, reports chemical shrinkage of Portland cement to rise up to 10% of total volume at complete hydration. The works above used dilatometry techniques to measure chemical shrinkage alongside stoichiometric calculations. These studies however do not discuss the effects of pozzolanic reactions on chemical shrinkage of Portland cement.

Bouasker et al., 2008, quoting others advance two explanations, the role of the filler effect in accelerating hydration and the chemical reactions with hydrating cement leading to formation of high density products. The accelerating effect is anticipated to cause a higher normalized shrinkage at an early age since more hydration products are formed due to the accelerating effect. Studies show the accelerating effect of SCMs is only important in the first three days (Berodier, 2015) and therefore the final shrinkage measurements for the blended samples and the controls can be compared since the cement content in the experimental setup is the same (Table 4.10).

Given that the pozzolanic reactions happen by consumption of the CH precipitate from the hydrating cement phases to produce C-S-H, considering that the reactions are governed by saturation levels of reactants and products (Taylor, 1997), the reduction in the CH precipitate may further accelerate hydration of the silicate phases in cement to replace the consumed CH precipitate. This being a preferred reaction mechanism, the total shrinkage at any time is therefore a function of the degree of hydration of the cement paste and pozzolanic reaction of the test blend. The anticipated difference in chemical shrinkage between the cement paste and test pozzolans is net shrinkage compensating for the effect that results out of the expansive pozzolanic reaction (Table 5.2). Moreover, the estimated value of 12% expansion due to the pozzolanic reaction is only limited to a fraction of the reactive silica in a test blended pozzolan. The shrinkage compensating effect is therefore

less significant in relation to shrinkage magnitudes generated by the dominating hydration reactions.

The results imply the reaction mechanisms of cements blended with kamafugites and carbonatites to be more complex with other reaction mechanisms more significant than the pozzolanic reaction hypothesis. It is possible that calcite governed acceleration of hydration reactions resulting in higher chemical shrinkage values for the test kamafugites and carbonatites while the pozzolanic reactions govern chemical shrinkage of fly ash blended cement.

5.1.5.1 Compositional factors influencing chemical shrinkage

1. Reactive Silica in kamafugites and carbonatites

Figure 5.9 shows a trend between reactive silica in the test pozzolans and chemical shrinkage values. It is observed that the increase in reactive silica leads to a reduction in chemical shrinkage. The trend is observed to be strong at 7 and 28 days, the period that is consistent with strength results that showed pozzolanic activity to be accelerated in all the samples. This trend weakens from a coefficient of determination (R^2 value) of 0.99 at 28 days to 0.3 at 180 days indicating that the long term dominant reaction mechanisms are non pozzolanic. Wyllie and Huange (1976) reports carbonates enrichment in kamafugites and carbonatites to have happened at the expense of the silicates. Accordingly, the lower the silica content, the higher the calcite content in the test pozzolan. It appears that calcite driven reactions advanced higher magnitudes of chemical shrinkage than the pozzolanic reactions. Moreover, the trend peaks at 28 days and diminishes at 180 days of curing contrary to trends of typical pozzolanic materials that influence later reactions. This trend is also observed in the strength results (Table 4.4) with strength activity index values reducing after 28 days of curing. A detailed analysis of the influence of calcite minerals and pozzolanic reactions on chemical shrinkage of Portland cement is presented in Chapter 5 of this thesis.

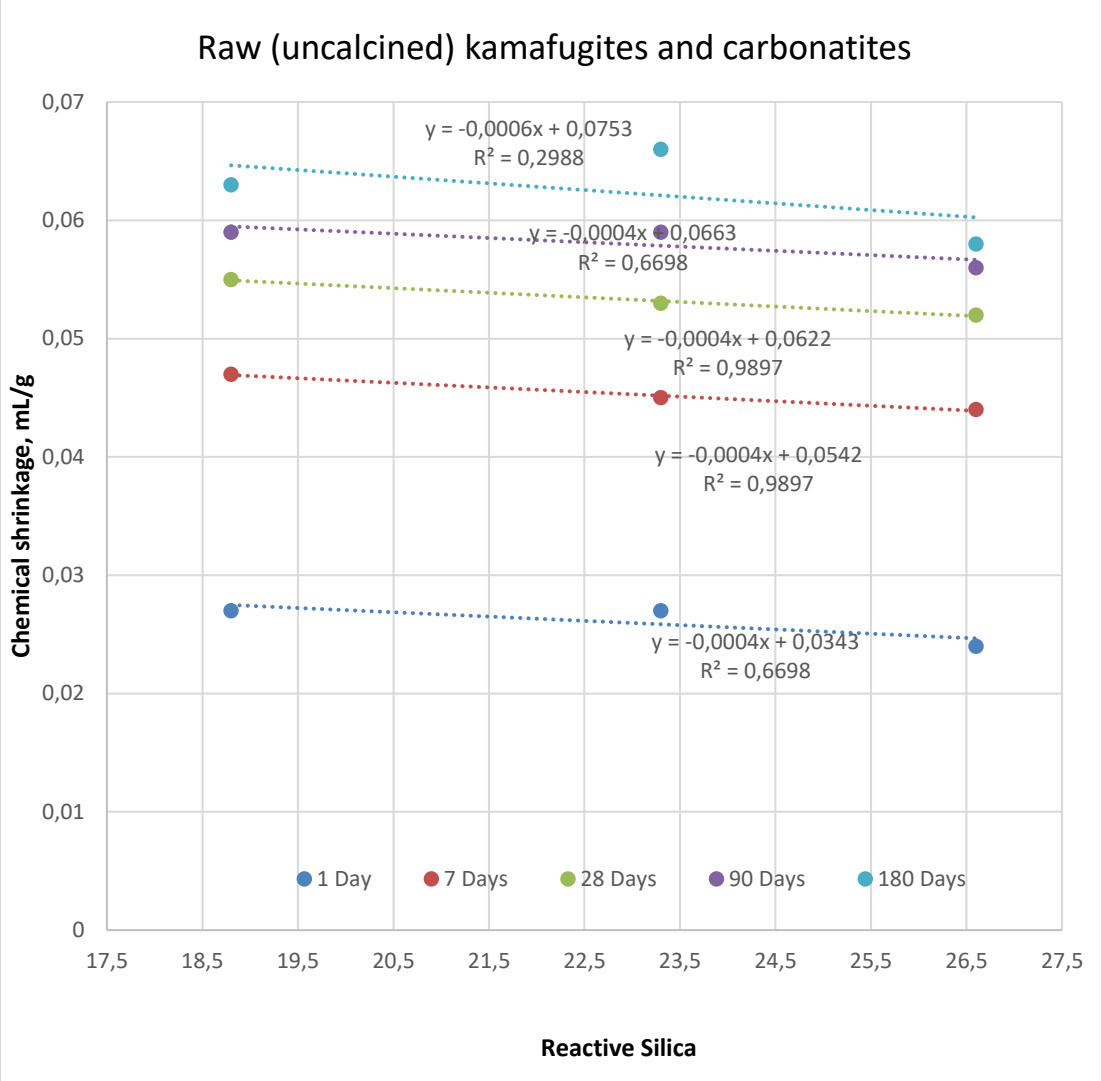

Figure 5.9**:** Relationship between reactive silica and chemical shrinkage of kamafugites and carbonatites (uncalcined)

2. Calcium oxide (CaO) content in the test kamafugites and carbonatites

Figure 5.10 shows the relationship between CaO and chemical shrinkage of kamafugites and carbonatites blended Portland cement. Calcium oxide values presented in the XRF oxide composition result (Table 3.3) are because of carbonate composition in the test kamafugites and carbonatites. Therefore, CaO was projected to represent calcite. Research done by Berodier (2015) proved the accelerating effect of mineral additives in Portland cement giving calcite a dominant role in accelerating hydration. The research, however, limited the accelerating effect to

about 3 days after the start of hydration. The trends observed cannot all be explained by the enhanced accelerating effect on hydration by the calcite minerals. The high coefficients of determination at 7, 28 and 90 days (0.85, 0.85, and 0.9 respectively) indicate that the carbonates participate in the hydration reaction to form hydration products that bond water. Indeed, Bouasker et al, (2008) reports on the preferential deposition of carboaluminates against AFm phases in a calcite blended hydrating cement. The work by Bouasker et al, (2008), shows the reaction of the sulfate phases in cement to end at ettringite letting the aluminates to react with carbonates in the system. The carboaluminates are known to have a higher density than the AFm sulfate phases hence an increase in chemical shrinkage. The trend observed in Figure 5.9 is that of increase in chemical shrinkage which further supports the data presented in Figure 5.8.

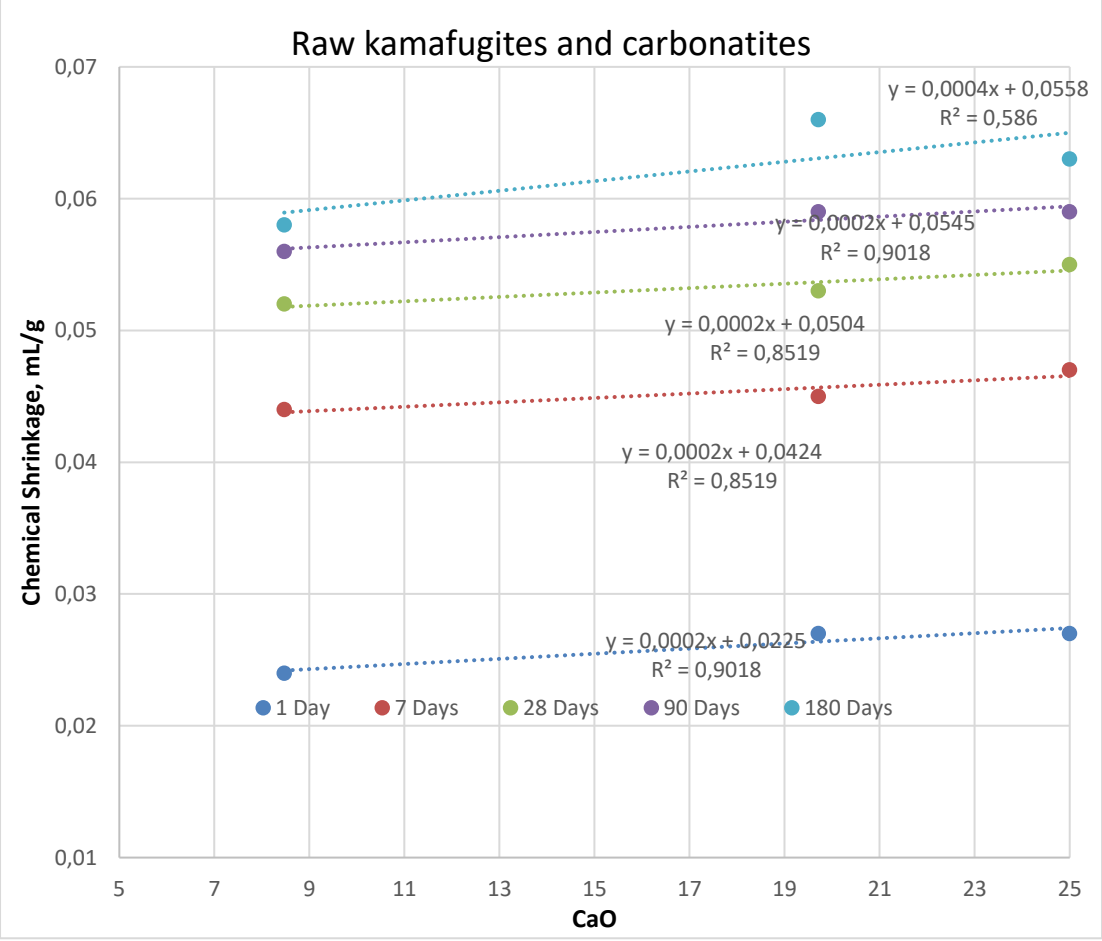

Figure 5.10**:** Relationship between CaO and Chemical Shrinkage for the raw sample

3. Magnesium oxide (MgO %) content in the test kamafugites and carbonatites

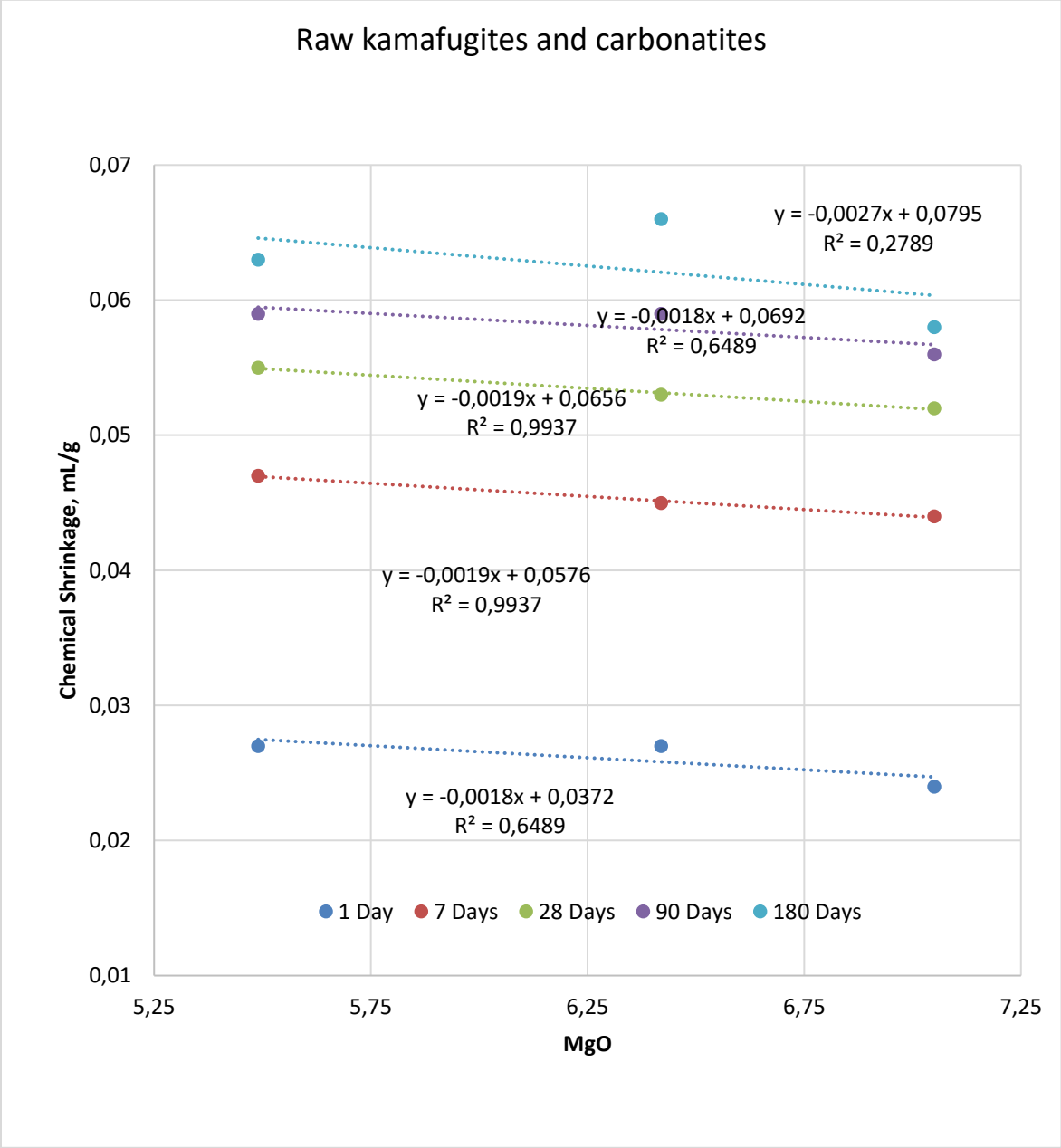

Figure 5.11**:** Relationship between MgO and Chemical Shrinkage for the raw sample

Figure 5.11 presents the relationship between the MgO composition and chemical shrinkage of test kamafugites and carbonatites. The MgO trend is strongest at 7 and 28 days with a coefficient of determination of 0.99. The trend weakens with age to a coefficient of determination of 0.3 at 180 days. The trend is like that of reactive silica indicating a relationship in the reaction mechanisms and also a possibility that the

MgO in the kamafugites and carbonatites is involved in the hydration reactions of Portland cement. It is normally considered that MgO that is not in the form of periclase is not reactive in cement (Neville, 2002). Howerer, Kupwade-Patil et al (2016) reported Ca^{2+} ions substitution by Mg^{2+} ions in the C-S-H and C-A-S-H hydration products leading to more porous, high volume, M-S-H hydration products. The observed negative trend in Figure 5.11 is hypothesized to be due to MgO driven conversion of C-S-H hydration products. The strength conversion effect was reported in the compressive strength results in section 4.3 of this report.

4. K_2O and Na_2O alkalis in the test kamafugites and carbonatites

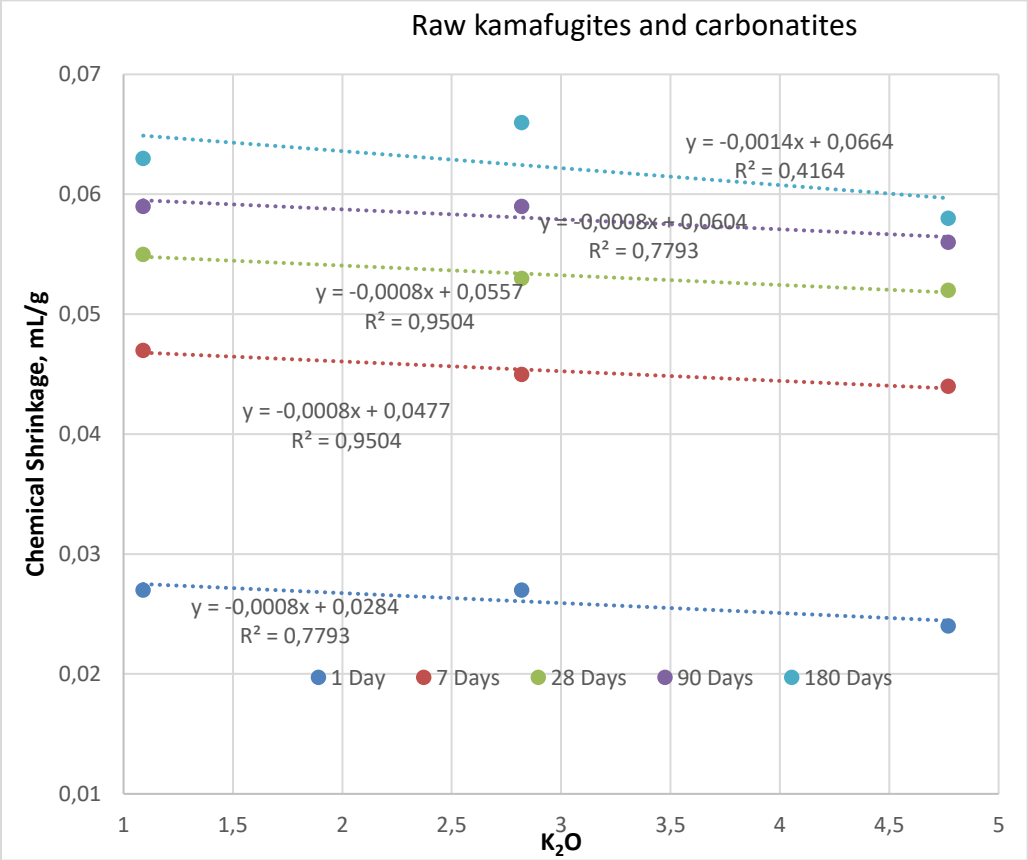

Figure 5.12**:** Relationship between K2O and Chemical Shrinkage for the raw samples

Figures 5.12 and 5.13 show the relationship between the alkalis in the test pozzolans and chemical shrinkage. As observed, the alkalis drive differing trends to chemical shrinkage, potassic alkalis showing a reduction in chemical shrinkage with increase

in concentration while sodic alkalis showed a positive trend. Studies on the role of alkalis report them to influence the rates of hydration of cement phases (Neville, 2002). Jawed and Skalny (1978) and Odler and Wonnemann (1983) both studied the effect of alkalis and found them to accelerate early hydration and setting of cement pastes. Odler and Wonnemann (1983) found that the Na^+ based alkalis delayed setting time while the K^+ based alkalis accelerated the setting time of cement. The Na^+ based alkalis were observed to delay the hydration of the aluminate phases in the cement paste. The current work could not explain the observed trends. Probably, the alkalis interact differently with different phases of cement, potassic alkalis leading to shrinkage compensating reactions in the cement systems.

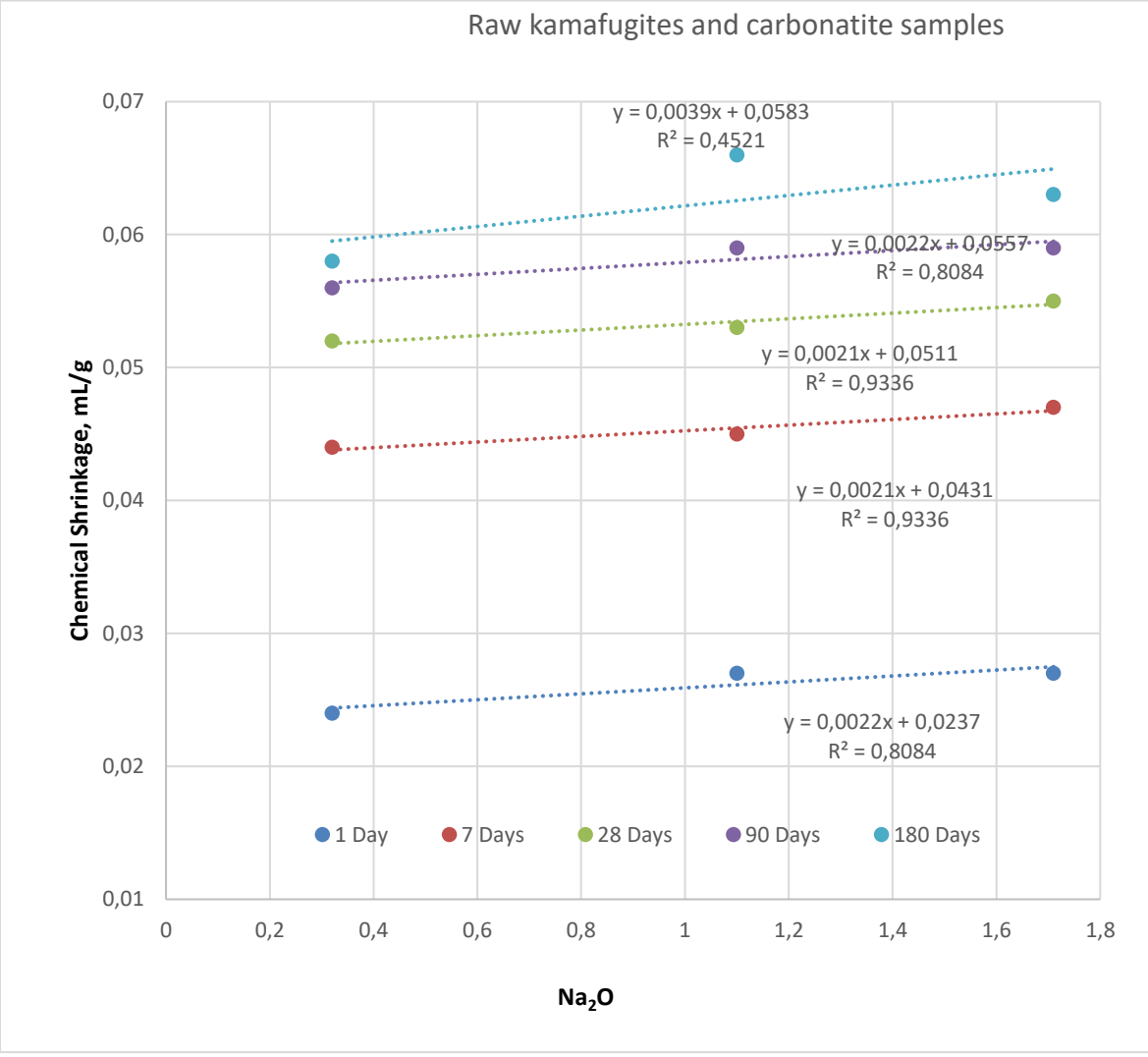

Figure 5.13**:** Relationship between Na_2O and Chemical Shrinkage for the raw samples

5.1.6 Hydration products development with TGA

Figures 5.14, 5.15 and 5.16 give graphical presentation of TGA results in Table 4.14 and show the hydrates content variation with curing age for the three decomposition phases, while Figures 5.17, 5.18 and 5.19 provide graphical presentations of the decomposition profiles (both TGA and DTG profiles) for full spectrum of reaction products from 105°C to 950°C. The results normalized to cementitious material content show proxy values that, with a scale factor, can be used to estimate CH accumulation in hydrating cement.

The dehydration (Ldh) graphs show blended cement samples to generate more hydration products than the control sample. This is due to the acceleratory effects, the formation of carbonate dozed hydration products and pozzolanic reaction products deposition in the dehydration phase as observed previously in the heat of hydration, chemical shrinkage and studies on setting time of Portland cement blended with the test pozzolans. The increase in quantity of hydration products, however, does not correlate to strength performance of the different test pozzolan samples as shown in Section 4.3.2 of this thesis.

The dehydroxylation phase (Ldx) graphs shown in Figure 5.15 show the control sample (CEM I 52.5R) to have the highest quantity of CH precipitates compared to blended samples, understandably because CH produced by cement in blended cement systems is consumed by the pozzolanic reaction and other hydration reactions. Also, from the profiles presented in Figures 5.17, 5.18 and 5.19, it is evident that CH content increases with curing age for Poz-1, reduces for Poz-2 and Poz-3 at 56 days of curing. Whereas the reaction of silicate phases in cement leads to deposition of free calcium hydroxide, a reduction in deposition rate informs on reaction mechanisms that consume the CH. Generally, the CH peaks in the decomposition profiles (Figures 5.17, 5.18 and 5.19) in all test pozzolans shift to higher temperatures with curing age indicating improvement in the crystallization structure with age of hydrated cement (Gabrovšek, Vuk & Kaučič, 2006) leading to a more stable form of CH crystals.

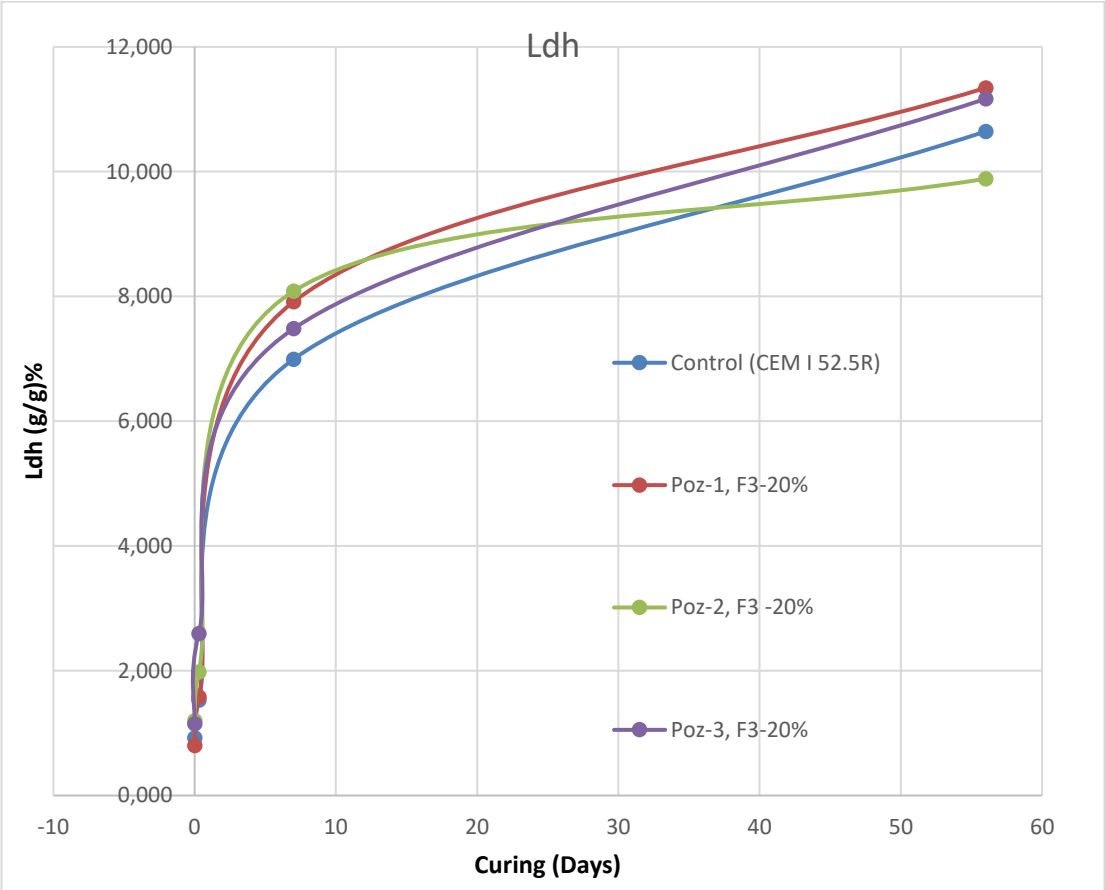

Figure 5.14: Change in mass of chemically bound water at different curing time for CEM I 52.5R cement blended with kamafugites and carbonatites at 20% replacement level. The mass change is due to decomposition of C-S-H and aluminate based hydration products.

Two mechanisms, the carbonation and pozzolanic reaction mechanisms are generally considered important in estimation of CH in cement systems (Kim and Olek, 2012). Studies report the CH reactions in Portland cements blended with pozzolans to be predominantly pozzolanic (Ramachandran, 1979; Kim and Olek, 2012). Moreover, the decarbonation phases in Table 4.14 (Ldc) on page 4-37 of this thesis show the carbonate phases to generally increase with age which further validates the carbonation of CH hypothesis. The extent and rate of carbonation appear to depend on the amount of CH in the hydrating cement system. The consumption of CH in blended cements is therefore attributed to both the pozzolanic reaction (Equation 2.9) and the carbonation reaction (Equation 2.19).

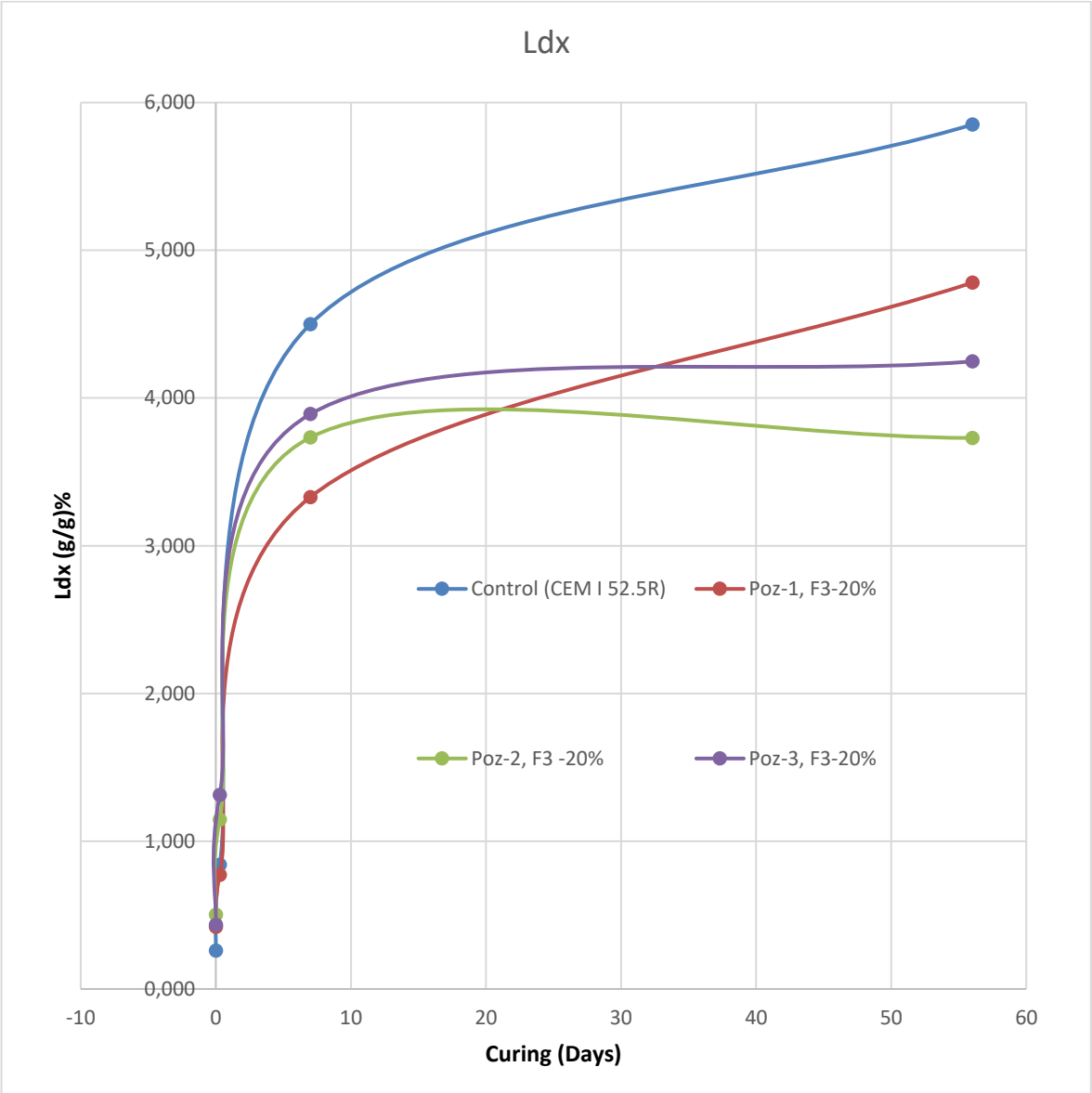

Figure 5.15: Change in calcium hydroxide (CH) content with curing age for CEM I 52.5R cement blended with test pozzolans at 20% replacement level.

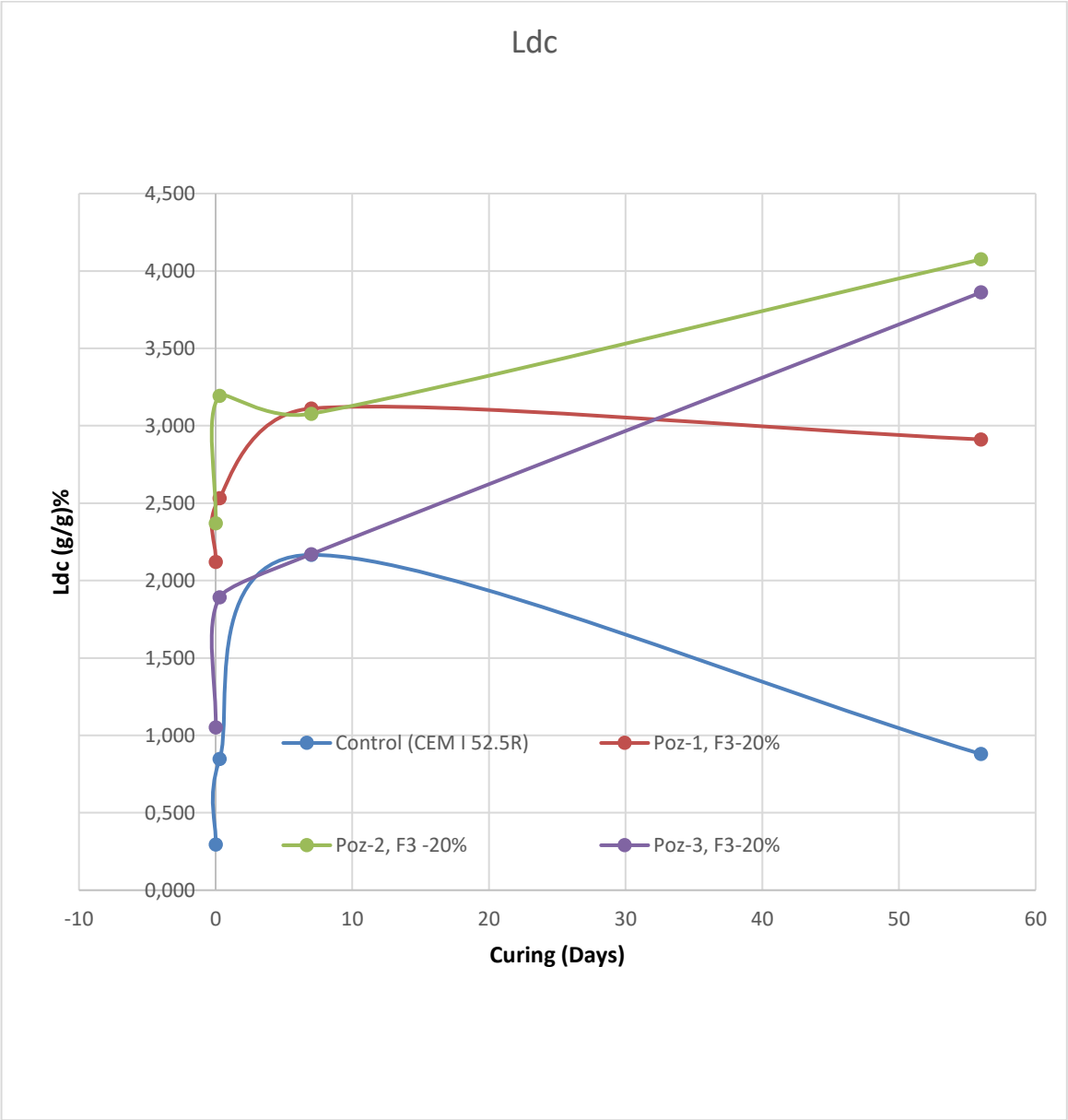

Figure 5.16: Change in mass with curing age due to TG decomposition of carbonates for CEM I 52.5R cement blended with test pozzolans at 20% replacement level.

To characterize the change in CH content, results of the blended cement samples are compared against those of the control sample. Figures 5.20 and 5.21 show the comparison between the control sample (CEM I 52.5R) and the test pozzolans (Poz-1, Poz-2 and Poz-3) for the 7hrs and the 56 days curing age. The results covering the whole scope of the pozzolanicity test are presented in Appendix 5. The CH deficit between the control and test blended cement samples at 0 hrs, 7 hrs, 7 days and 56 days was calculated following a procedure modified from the degree of hydration

calculation advanced by Monteagudo et al (2014). Monteagudo et al (2014) proposed a numerical relationship that quantifies the total equivalent CH bound water in a hydrating cement as follows.

$$W_{total\ CH} = Ldx + 0.41(Ldc - Ldc_a) \quad \text{Equation 5.1}$$

Where, Ldx is mass loss due to CH decomposition and $0.41(Ldc - Ldc_a)$ is the equivalent water lost by the CH phase in the process of carbonation. $Ldc\ and\ Ldc_a$ are the mass losses due to decarbonation of the test sample after hydration and at anhydrous state simultaneously. The coefficient of 0.41 is considered as a stoichiometric factor for converting the decarbonation mass loss to an equivalent chemically bound water for the carbonated CH (Monteagudo et al, 2014). This equation is part of a general equation for estimation of degree of hydration of a single cement (Equation 2.16). However, characterisation of pozzolanic activity is achieved by comparing two samples, a control sample, which is normally a plain Portland cement, and a test sample that is blended with a test pozzolanic material. The formula in Equation 4.3 is therefore modified as follows.

$$W_{poz} = (W_{CH\ cement} - W_{CH\ poz}) - 0.41(Ldc - Ldc_a) \quad \text{Equation 5.2}$$

$$W_{poz} = \left(Ldx_c - Ldx_p\right) - 0.41(Ldc - Ldc_a) \quad \text{Equation 5.3}$$

Where W_{poz} represents chemically bound water in the CH involved in a pozzolanic reaction, Ldx_c and Ldx_p represent the mass loss in the dihydroxylation phase for the control (CEM I 52,5R) and test cement sample respectively. Ldc and Ldc_a respectively represent decarbonation mass loss of the test sample hydrated to the time of testing and anhydrous. Results of the chemically bound water due to pozzolanic reactions for the different pozzolans are presented in Table 5.3.

The observed negative quantities of CH water at 0 and 7 hrs shown in Table 5.3 are due to the accelerating effect of the test pozzolans as presented in heat of hydration and chemical shrinkage studies and as shown in Figure 5.20. Figure 5.20 shows the sample blended with Poz-3 to have a more rapid accumulation of CH precipitate while Poz-1 and Poz-2 show increased carbonation rate of the CH precipitates. Accelerated hydration leads to test samples having more CH precipitate than the control sample

hence negative values. The results, however, show pozzolanic activity at 7 days after the hydration accelerating effect has diminished. The pozzolanic reaction results in production of extra C-S-H cement hydrates that are considered to contribute extra strength to the hydrated paste. Indeed, Poz-2 and Poz-3 show a plausible SAI, Poz-2 ranking highest, while Poz-1, a carbonatite, ranks inferior in the SAI.

Table 5.3: Calculations for the mass loss due to the pozzolanic reaction of blended cements

Test sample and variables	Curing (Days)	Ldh (mg/mg)%	Ldx (mg/mg)	Ldc (mg/mg)	$(Ldx_c - Ldx_p)$	$0.41(Ldc - Ldc_a)$	W_{poz}
Control (CEM I 52.5R)	0	0.925	0.259	0.296	0.000	0.000	0.000
	0.3	1.528	0.842	0.847	0.000	0.226	-0.226
	7	6.993	4.500	2.166	0.000	0.767	-0.767
	56	10.645	5.851	0.880	0.000	0.239	-0.239
Poz-1, **F3-20%**	0	0.799	0.421	2.121	-0.161	0.000	-0.161
	0.3	1.580	0.774	2.532	0.068	0.169	-0.100
	7	7.914	3.330	3.111	1.170	0.406	0.764
	56	11.343	4.781	2.912	1.070	0.324	0.746
Poz-2, **F3 -20%**	0	1.199	0.503	2.370	-0.243	0.000	-0.243
	0.3	1.978	1.146	3.194	-0.304	0.338	-0.642
	7	8.083	3.733	3.078	0.767	0.290	0.477
	56	9.886	3.730	4.075	2.121	0.699	1.423
Poz-3, **F3-20%**	0	1.148	0.435	1.052	-0.176	0.000	-0.176
	0.3	2.593	1.313	1.892	-0.471	0.344	-0.816
	7	7.482	3.891	2.171	0.608	0.459	0.150
	56	11.167	4.248	3.861	1.603	1.152	0.451

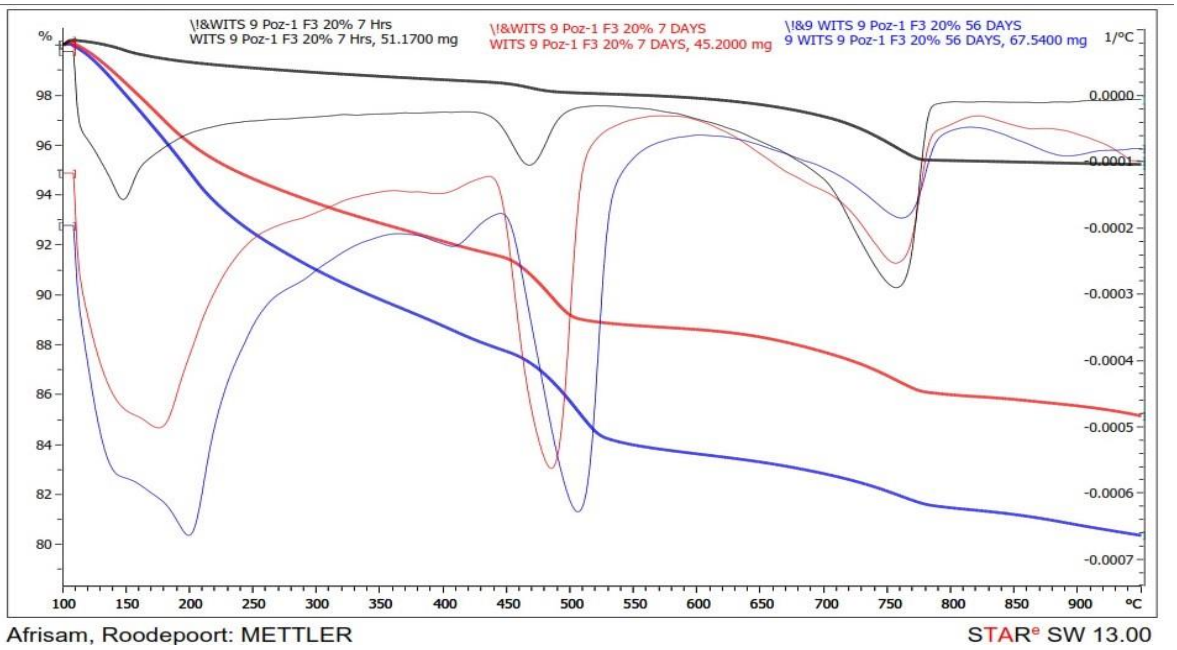

Figure 5.17: TGA results showing hydration progression of Portland cement sample blended with Poz-1 at 20% level of replacement.

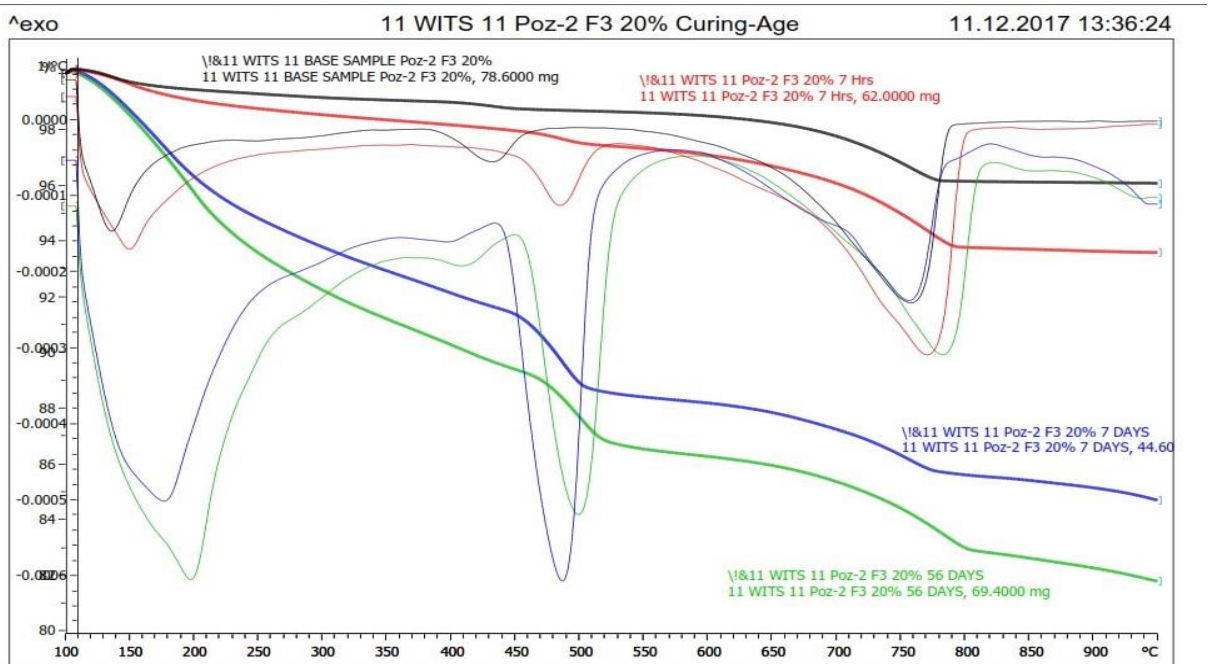

Figure 5.18: TGA results showing hydration progression of Portland cement sample blended with Poz-2 at 20% level of replacement.

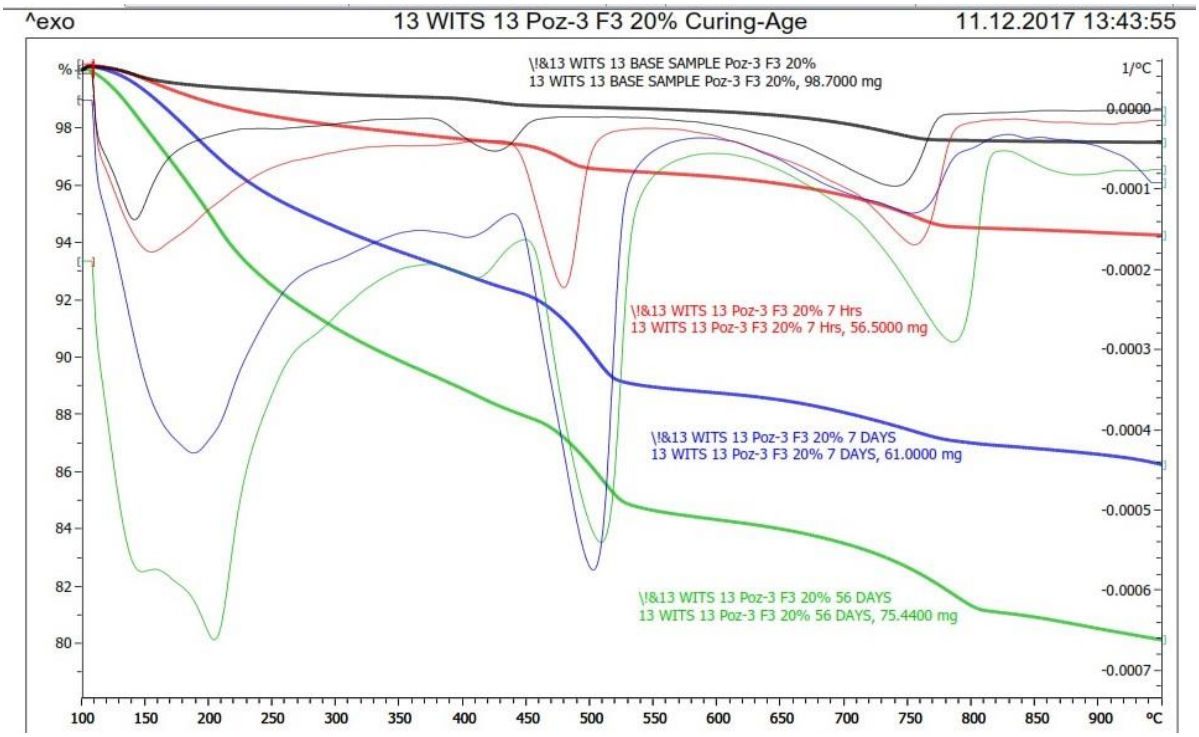

Figure 5.19: TGA results showing hydration progression of Portland cement sample blended with Poz-3 at 20% level of replacement.

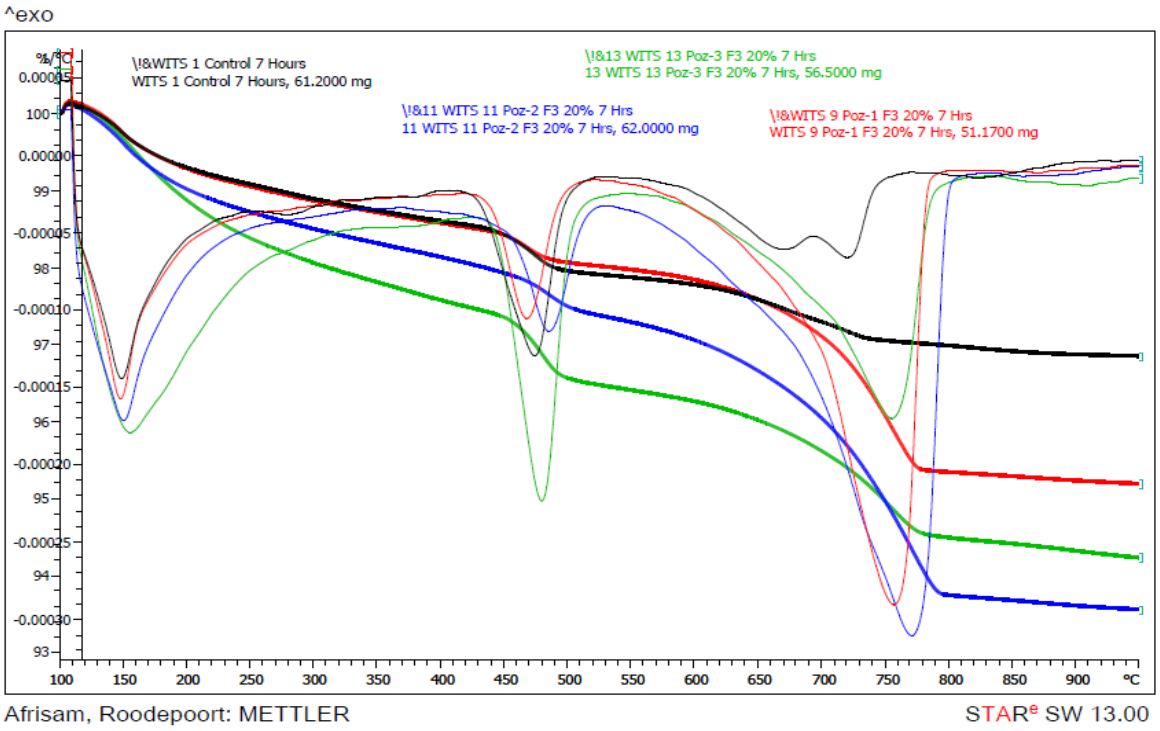

Figure 5.20: 7 hour TGA results showing hydration progression of Portland cement sample and test samples at 20% level of replacement.

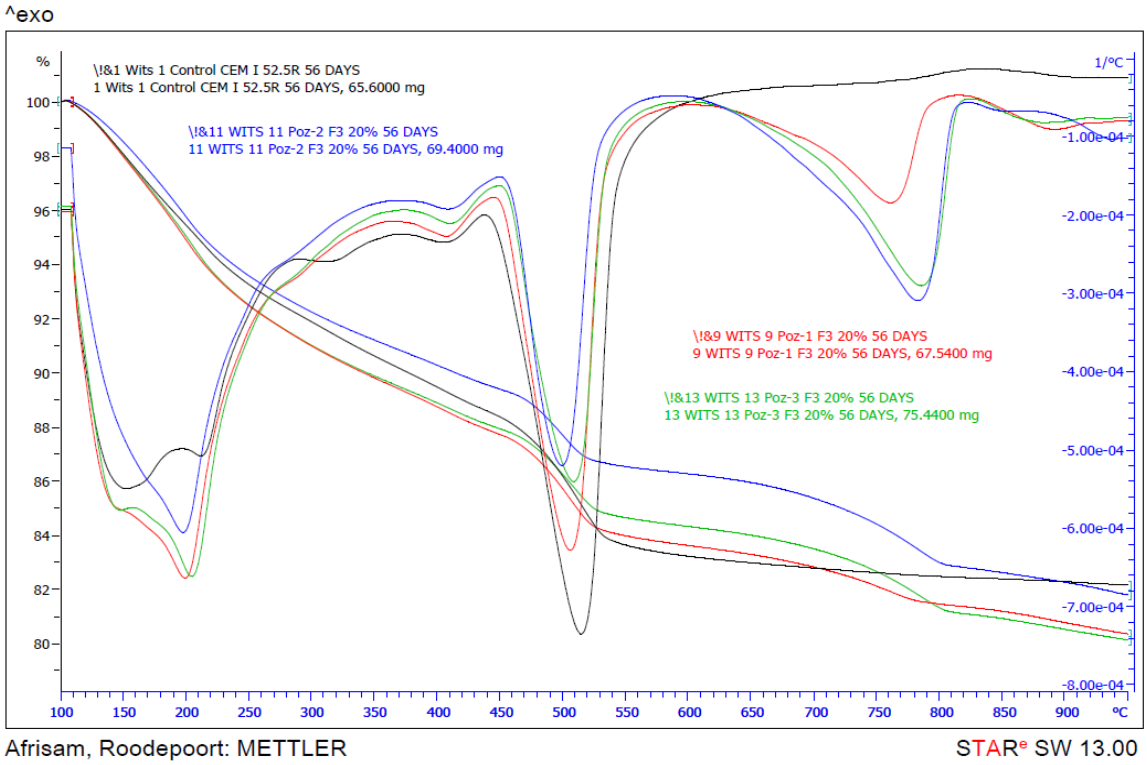

Figure 5.21: 56 Days TGA results showing hydration progression of Portland cement sample and test samples at 20% level of replacement.

5.1.7 Calcium Hydroxide consumption with XRD

To clearly understand changes in the CH content with curing, CH main phase was filtered and superimposed according to the time of curing of samples. Figures 5.22, 5.23, and 5.24 show the superimposed trends for the CH main phase, with the peak intensity reflecting the concentration. The XRD patterns show consumption of CH in all samples, Poz-2 ranking highest followed by Poz-3 and Poz-1 trailing. Poz-2 and Poz-3 are able to reduce the CH content at 56 days to be lower than that at 7 days while Poz-1 shows weaker pozzolanic property only observed by suppression of CH trend from what is expected at 56 days. The XRD results are consistent with observation in TGA, chemical shrinkage and strength activity index results.

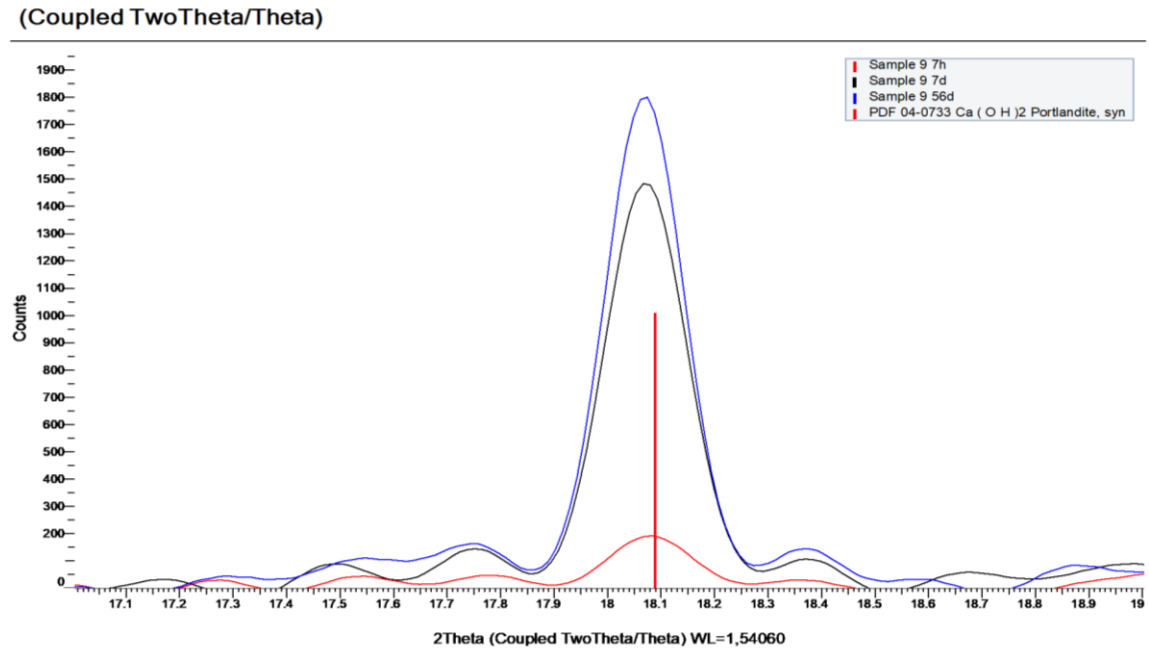

Figure 5.22: Superimposed positions for the CH main phase showing changes in intensities with time, the red colour indicating 7 hrs, black 7 days and blue 56 days for Poz-1.

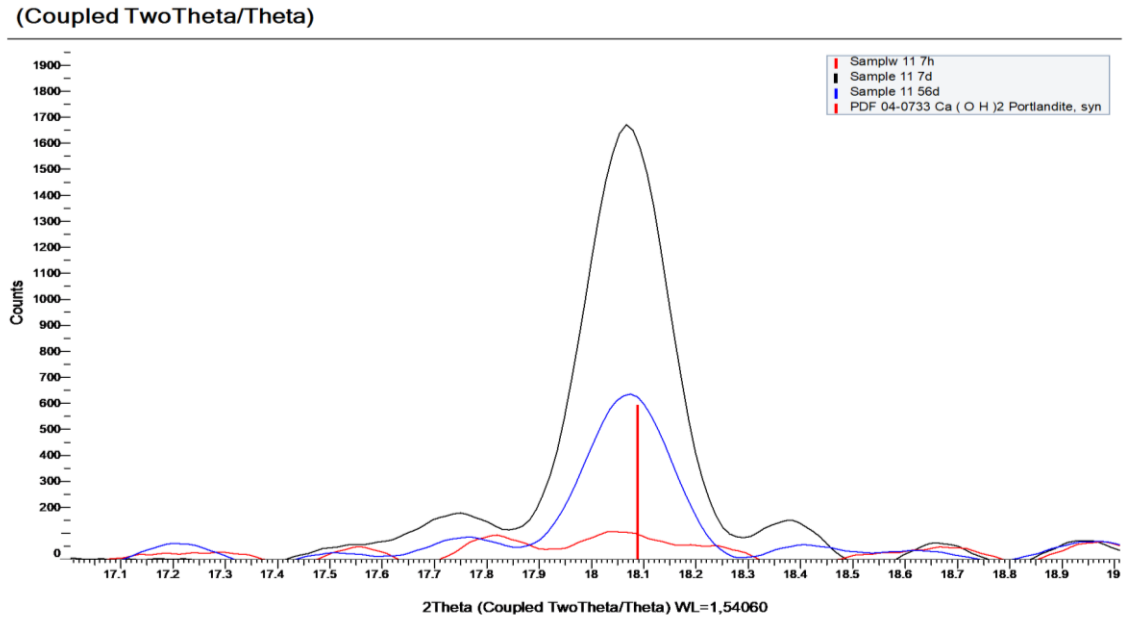

Figure 5.23: Superimposed positions for the CH main phase showing changes in intensities with time, the red colour indicating 7 hrs, black 7 days and blue 56 days for Poz-2.

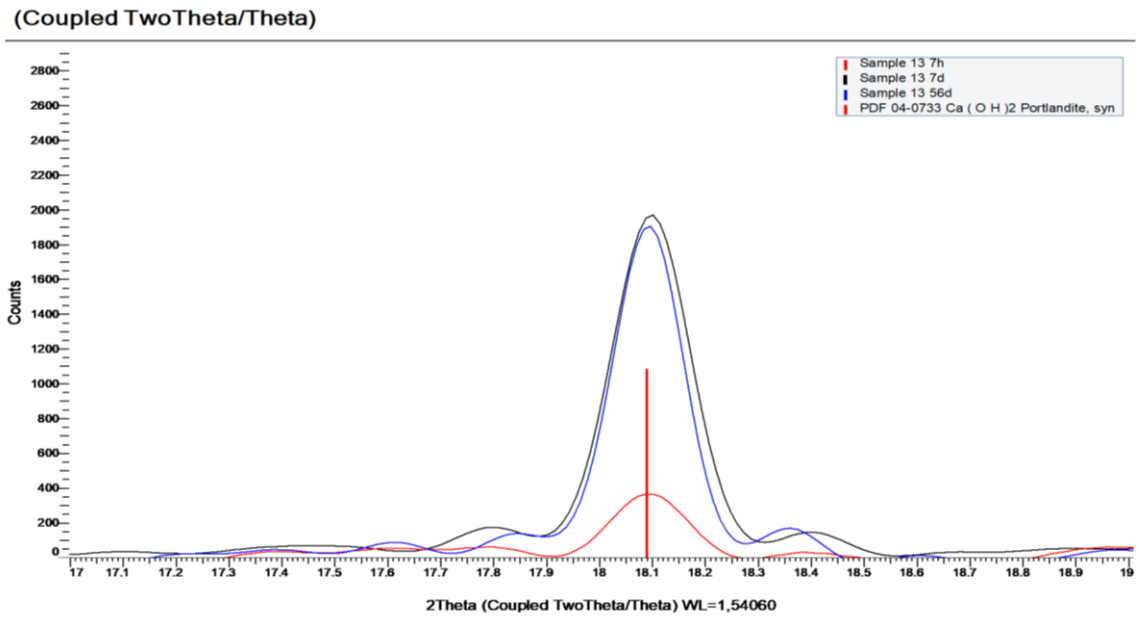

Figure 5.24: Superimposed positions for the CH main phase showing changes in intensities with time, the red colour indicating 7 hrs, black 7 days and blue 56 days for Poz-3.

5.2 Carbonate minerals and volatile alkalis as compositional parameters

This section discusses the effect of carbonate minerals and alkalis in the kamafugites and carbonatites and calcination on setting time, standard consistency, workability, soundness, CH consumption (pozzolanic reaction), chemical shrinkage, early heat of hydration, type and amount of hydration products and strength development of blended Portland cements. Portland cement pastes and mortars blended with kamafugites and carbonatites that were studied in the current thesis advanced strong correlations in the above listed properties with the calcite minerals and alkalis (Chapter 4). It became important to characterize the role of both calcite and volatile alkalis in influencing the different properties of blended Portland cement pastes and mortars. Calcination of kamafugites and carbonatites made it possible to deactivate the carbonate minerals and to volatilize the water-soluble alkalis. The three (3) samples, Poz-1, a carbonatite, and Poz-2 and Poz-3, both kamafugites, sourced from deposits located in the Toro-Ankole geological region of the East African rift system were calcined in a furnace at 850 °C for one hour. The samples were then subjected to XRD analysis for mineralogical composition characterisation and to establish the effect of calcination at 850 °C on mineralogy. Setting time, standard consistency, workability, soundness, hydration products assemblage, chemical shrinkage, heat of hydration, chemically bound water and strength development were studied following instrumental techniques and standard procedures for testing blended Portland cements, all discussed in Chapter 4.

5.2.1 Analysis of calcination effects on composition

Calcite is a primary mineral in all the kamafugites and carbonatites. To test its effects on hydration activity, chemical shrinkage, hydration products assemblage, and strength development, the kamafugites and carbonatites were calcined in a furnace at 850°C for an hour. Calcined samples were further checked for mineralogical composition following XRD test procedures discussed in Chapter 3 of this thesis.

Calcination at 850°C led to an increase in oxides concentration, increase in water solube Mg^{2+} ion concentration and volatilisation of water soluble K^{+} and Na^{+} alkalis. The carbonate minerals in the test carbonatite and kamafugite are the primary reason

for a high LOI value as demonstrated in Figures 3.10, 3.11 and 3.12 on pages 3-19 and 3-20 of this thesis. As a result, their decomposition by calcination led to an increase in the densities of the different mineral and oxide components of the test pozzolans. It is feasible that this increase in the concentration of mineral and oxide components of the test pozzolans led to availability of more reactants per unit of batching and hence a higher relative gain in strength and better performance in the ASTM C618, 2005, minimum composition requirement of the sum of the silica, alumina, and Iron oxides. The gain in strength discussed in Section 4.3.6 of this thesis, however, did not show any correlation with the relative change in oxide composition after calcination.

Kaolinite, a secondary mineral formed through alteration of the primary rock minerals (Habert et al, 2008), was detected in Poz-3, a kamafugite. Habert et al., 2008, reports a higher strength with thermal destabilisation of kaolinite enriched volcanic materials. Kaolinite, a clay mineral, is known to have pozzolanic properties when thermally destabilised. Extensive work on pozzolanic nature of kaolinite and how it influences Portland cement properties is presented in the RILEM book series on Calcined Clays for Sustainable Concrete (Scrivener and Favier, 2015). Calcination of a kaolinite enriched Poz-3 is therefore a considered factor in increasing its compressive strength.

5.2.2 Analysis of calcination effects on density

Calcining test pozzolans resulted in increase in specific weight, Poz-1 showing the highest gain. The gain in specific weight correlates well with the carbonates content which is associated with the CaO content in the XRF results (Table 4.15). Density is a parameter that is known to influence strength performance of concrete. Consequently, gain in density of the test pozzolans on calcination elevates their strength performance.

5.2.3 Analysis of calcination effects on fresh properties of blended cement

5.2.3.1 Setting time

The accelerating effect of the test pozzolans is in agreement with the results of a tuff from central Turkey studied by Turanli and others (Turanli, Uzal and Bektas, 2005) whose alkalis are predominantly potassic. Although Turanli and coworkers did not report on the possible cause of the trend, work by Jawed and Skalny (Jawed and Skalny, 1978) and Odler and Wonnemann (Odler and Wonnemann, 1983) show K+

ions to have an accelerating effect on the aluminate phase while Na+ alkali ions have a retarding effect. Considering the ultrapotassic nature of Poz-3, the sample's relative effect on the setting time is higher than that of Poz-1 and Poz-2. Calcination completely stopped the set accelerating effect of Poz-1 and Poz-2 but partially for Poz-3 indicating presence of other contributing mechanisms. The ultrapotassic nature of the kamafugite (Poz-3) is advanced as a factor in its superior set accelerating property.

Works on the effect of calcite/limestone on physical properties of Portland cement blended with limestone, too, report accelerating effect on setting time and a small increase in water demand that is governed by the limestone fineness (Odler and Wonnemann, 1983; Ipavec et al, 2011). Calcite modifies paste microstructure by reacting with the aluminate and sulfate phases to form carboaluminates and AFm respectively (Ipavec et al, 2011; Mohamed, Elsalamawy, and Ragab, 2015) with a consequence of accelerating early hydration mechanisms, especially hydration of alite phases (Matschei, Lothenbach, and Glasser, 2007). The accelerating phenomena is partly attributed to the "filler effect", which Berodier and Scrivener (Berodier and Scrivener, 2014) explain to be driven by the interparticle distance and not the previous belief that mineral admixtures provide extra surfaces for nucleation sites of hydrates (Mohamed, Elsalamawy and Ragab, 2015). Indeed, Kadri et al., 2009, advance the filler effect to be driven by the particle size and chemical nature of the SCMs. Also, a recent review by Scrivener, Juilland and Monteiro (Scrivener et al 2015) advance two mechanisms namely, clinker bulk density reduction effect and a dispensation of extra sites for precipitation and growth of hydration products. The filler effect, therefore, is still an open area of study. Berodier and Scrivener, 2014, report calcite to have a higher filler effect compared to other SCMs. This, therefore, increases the importance of calcite composition in the kamafugites and carbonatites.

Also, the filler effect is the concern of the first few hours of hydration (up to the final setting of cement paste) which is a very important stage of concrete responsible for paste microstructure prognosis and resulting macrostructure properties. Accordingly, the carbonate minerals in the kamafugites and cabonatites are a plausible consideration in accelerating the setting time of blended samples.

5.2.3.2 Water demand and slump flow

The mechanisms that control water demand and slump flow are relatable and depend on both the physical characteristics of the finer particles in test pozzolans and early hydration reactions. Given that all the test pozzolans have d(0.1) particle size values in the same range (details of particle size characterisation of kamafugites and carbonatites are discussed in Chapter 3 of this thesis), the difference in water demand and slump flow readings can therefore be attributed to the effect of composition of the test pozzolans on cement early hydration progression. The relationship in trends of the water demand and slump flow results with setting time results further validates the role of the mineralogical composition of the test pozzolans. The accelerating effect of $CaCO_3$ is present in all the test pozzolan blended cements. The high K+ alkali content in Poz-3 is considered a factor in causing higher water demand values in relation to Poz-1 and Poz-2.

5.2.3.3Soundness

On soundness property, the Le Chatelier's soundness tests recorded no expansion for all raw test pozzolans blended with Portland cement at a 20% replacement level. On calcination of the test pozzolans, Poz-1 and Poz-2 registered a 1 mm expansion possibly due to hydration of calcium oxide made available by the de-carbonation of the calcite minerals in the test pozzolans. Both Poz-1 and Poz-2 have relatively higher calcite content (29.2% and 21.2% respectively) than Poz-3 (9.78%) and consequently more CaO content on calcination.

5.2.4 Analysis of calcination effects on heat of hydration

Heat release in cement hydration process is considered as a proxy indicator to the progression of the hydration reactions. Heat release recorded for 24 hours show the raw test pozzolans to have a higher heat release than the control sample (CEM I 52.5R). Calcination of the test pozzolans pacified the trend and led to early heat of hydration to be less than that of the control sample. The role of calcite and volatile alkalis in accelerating early hydration reactions is further revealed through heat of hydration. Considering that Poz-3 has significantly lower concentrations of calcite

(9.78%) compared to Poz-1 and Poz-2 (29.2 and 21.2 respectively), the influence of the Poz-3 on heat of hydration is less pronounced.

The heat activity index helps in comparison of the extent of gain in heat of hydration between the control sample (plain Portland cement) and the test sample (plain Portland cement blended with test pozzolans at 20% replacement level). Previous results on pozzolanic reactivity by TGA revealed the pozzolanic activity to be pronounced at 7 days of curing. Accordingly, the 162-hour heat of hydration captures the initial stages of the pozzolanic reaction. Results show a rebound in heat of hydration measurement at 72 hours but only for Poz-2. The experiment terminates when Poz-1 and Poz-3 have a stable trend in relation to the control samples as indicated by a fixed value of HAI.

The results show calcined samples to have low initial heat of hydration but this changed after 24 hours (Figures 5.25 and 5.26). The heat of hydration trends follows those of fly ash, a known pozzolan that is considered to have already passed the development and testing stages. The trends observed show calcination to pacify the acceleratory effects of the kamafugites and carbonatits, possibly emphasizing the role of calcite in the hydration acceleration mechanism of blended cements. Topical works show the presence of SCMs in a cement paste to affect the rate of hydration of clinker phases and consequently lead to an accelerated gain in mortar strength at an early age, a condition they also attribute to the “filler effect”. Scrivener et al., 2015, advanced two mechanisms that explain the filler effect which include clinker bulk density reduction effect and a dispersion of extra sites for precipitation and growth of hydration products.

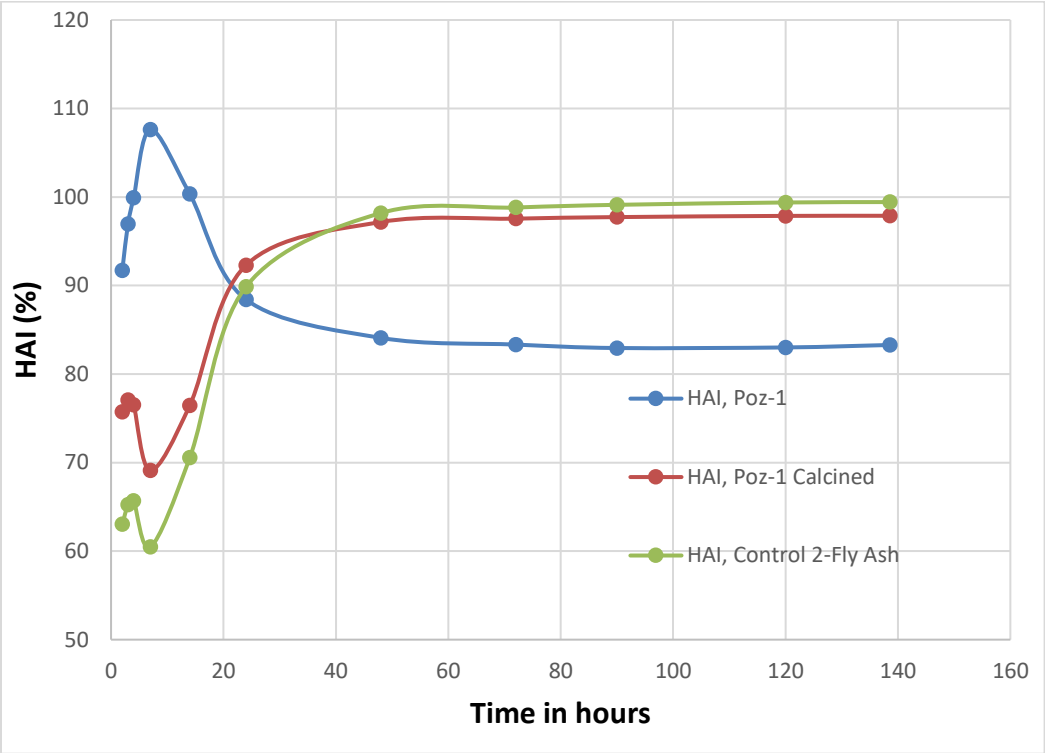

Figure 5.25: Heat activity index (HAI) for raw, calcined and FA blended cements for Poz-1

The clinker bulk density reduction effect as a result of partial replacement of Portland cement with an SCM leads to availability of more space for clinker hydration products to form unconfined. Space is one of the parameters that control the rate of hydration of clinker phases (Berodier and Scrivener, 2015). The hydrates are known to cause an increase in volume in relation to the cement anhydrous phases and therefore require extra space for the hydration reaction to take place. Berodier (2015) refers to this filler effect mechanism as the dilution effect; however, the current discussion chose to limit the term ‘dilution effect’ to only apply in relation to mixing water. The precipitation and growth of hydrates is reported to be heterogeneous (grows on surfaces of both cement and SCM grains in the paste) with some SCM types providing more sites than others, an observation Kaid et al (2010) attributed to the chemical nature of SCMs. A study by Kaid et al (2010) showed limestone to provide more sites for precipitation than quartz (used in the tests as an inert material) and ground granulated blastfurnace slag (ggbs).

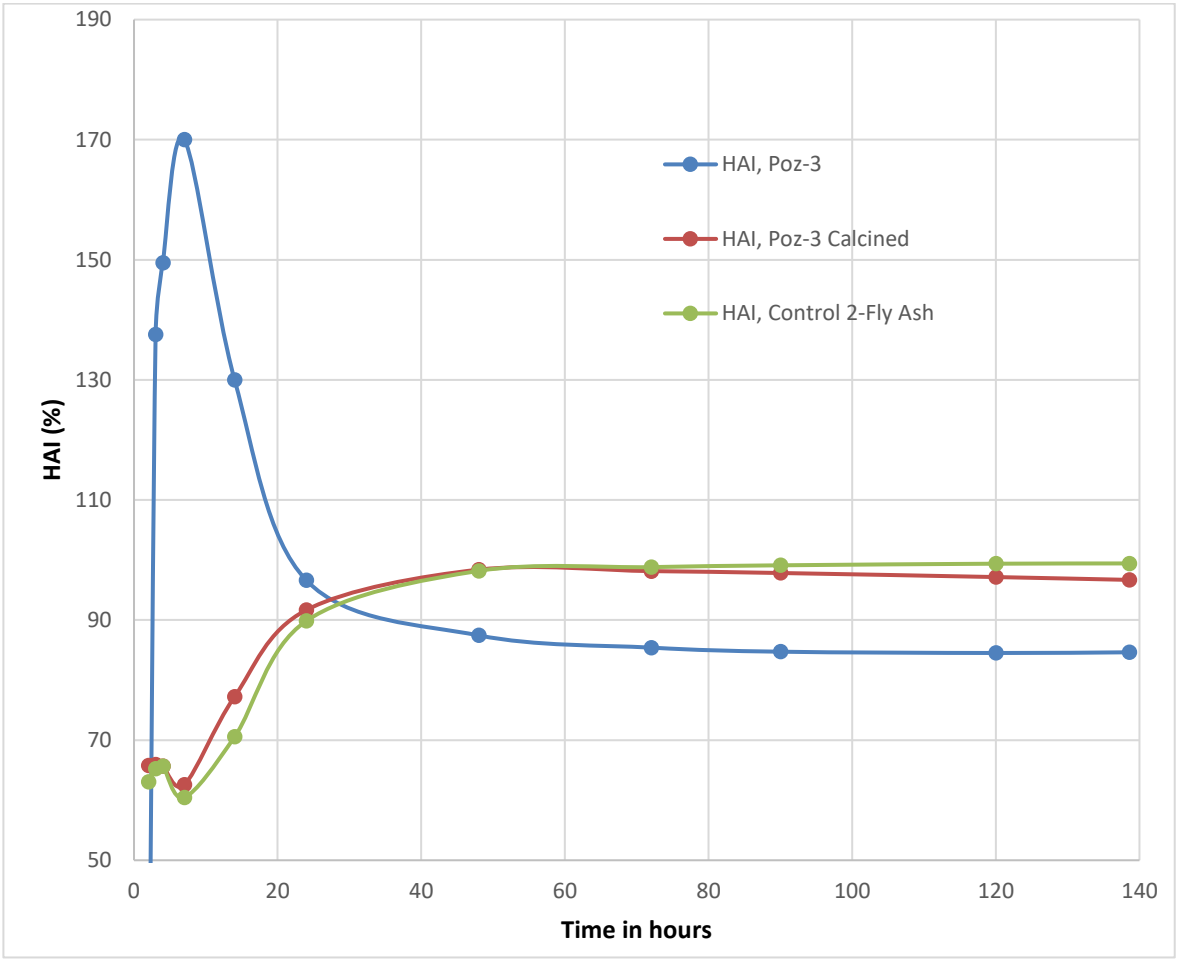

Figure 5.26: Heat activity index for raw, calcined and FA blended cements for Poz-3

The filler effect is seen to end at about 24 hours after the beginning of the hydration reaction for the raw samples (Figures 5.25 and 5.26). The relatively stable relationship observed up to 162 hours for the raw samples reveal the carbonatites and kamafugites to be relatively low in their pozzolanic property. The HAI index is however sustained above the minimum for all the replacement levels indicating the kamafugites and carbonatites to have a beneficial level of participation in the hydration of Portland cement.

The heat of hydration results for the calcined samples show a relative gain in heat up to 97% of the control sample at 162 hours indicating that calcination improves on the hydration reactions in the test kamafugites and carbonatites blended cement.

5.2.5 Analysis of calcination effects on compressive strength

The results presented in Section 4.3.2 showed raw natural pozzolans to perform better than their calcined equivalents up to 28 days. The hydration reactions in the samples blended with raw natural pozzolans appeared to have stopped by 90 days of curing implying either depletion of reactants or a strength conversion mechanism with rates exceeding the pozzolanic reaction mechanisms. The calcined samples continued to gain in strength after 90 days of curing, a trend they share with both FA and CEM I control samples. There is a 3.4% and 7.6% gain in compressive strength with calcination for Poz-1 and Poz-3 respectively. The gain in compressive strength does not show any correlation with the change in composition of the test natural pozzolans after calcination (Table 4.15 on page 4-42). Poz-3 however has a clay mineral, Kaolinite, which exhibits pozzolanic properties when thermally destabilized at temperatures as low as 350°C (Habert et al, 2008).

5.2.6 Analysis of calcination effects on chemical shrinkage

Figure 5.27 presents a comparison of the results of chemical shrinkage for the calcined samples while Figures 5.28, 5.29 and 5.30 provide a comparison of chemical shrinkage results for raw and calcined test pozzolans. It is observed that calcination enhanced the pozzolanic property of Poz-3. The results also show that the governing mechanisms in Poz-1 and Poz-2 are based on the carbonates and alkalis interactions with a possibility of alkali activation leading to fixation of the silicates by the cement hydrate phases. It should also be understood that Poz-1 and Poz-2 have relatively higher content of carbonate phases and are silica undersaturated, a condition that limits the extent of their pozzolanic reactions. The possibility of formation of high density carboaluminates hydrates instead of monosulfates in the blended kamafugites and carbonatites is supported.

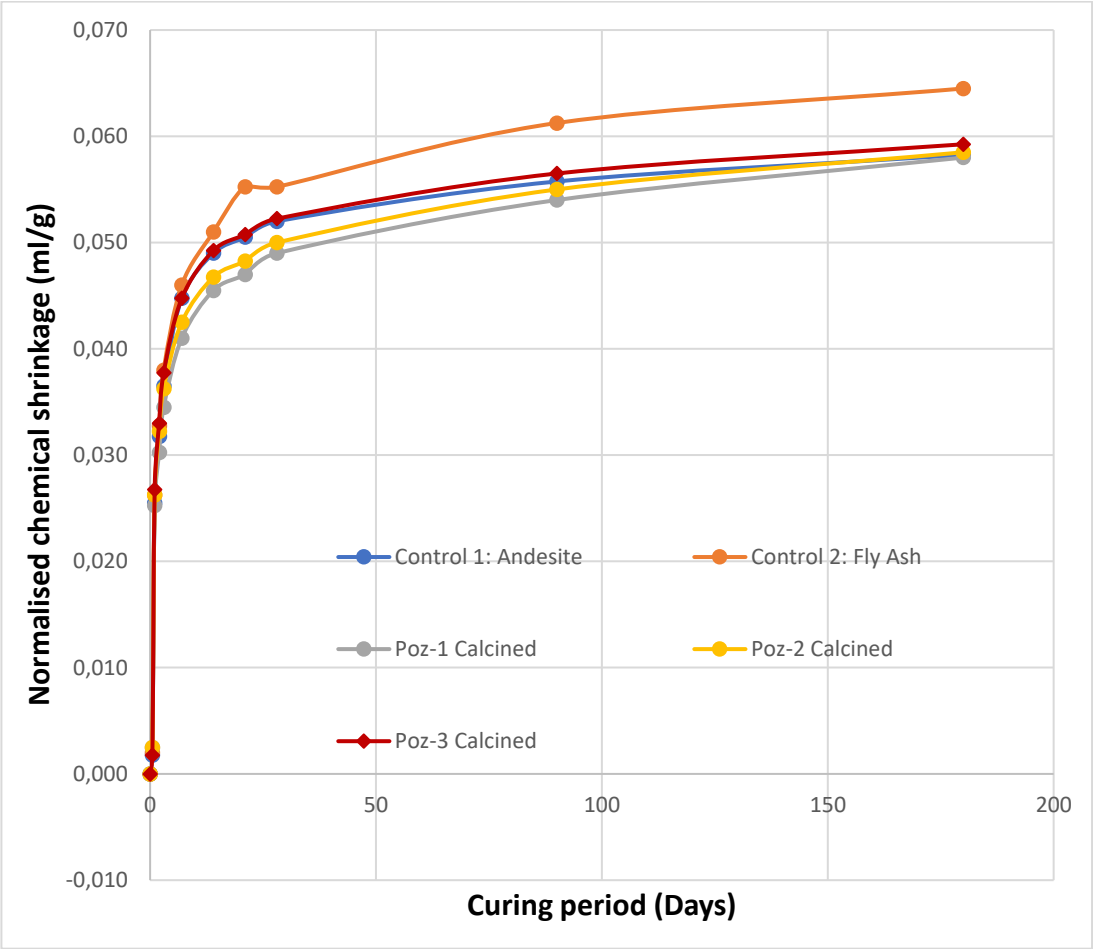

Figure 5.27: Chemical shrinkage results for calcined test pozzolans (results normalized to cement content).

While chemical shrinkage is driven primarily by the hydration reactions of the cement phases, the pozzolanic reaction results into chemical expansion as demonstrated in Table 5.2. As a result, the chemical shrinkage property can favorably characterise pozzolanic performance on the basis of how the pozzolanic reaction shifts equilibria and accelerates the hydration reactions of cement phases. Indeed, cements blended with pozzolanic materials give higher degrees of hydration of cement phases due to early hydration acceleration and creation of extra spaces for deposition of hydration products (Scrivener et al., 2015). Accordingly, the increased chemical shrinkage values in blended cements acts as a proxy indicator of the pozzolanic reaction to the extent that the pozzolanic materials advance no other reaction mechanisms that influence the hydration kinetics of the cement hydrating phases. Calcination revealed that both calcite and volatile alkalis in the kamafugites and carbonatites increased chemical

shrinkage more significantly compared to the pozzolanic reaction. It is observed that Poz-3, a kamafugite with relatively lower concentrations of calcite and high silica saturation advanced minimal influence to chemical shrinkage in its raw state but plausible values after calcination. The observed inclease in chemical shrinkage values after calcination of Poz-3 is considered driven by the pozzolanic reactions. The trend is also similar to that of the control sample that was blended with class F fly ash which is a known pozzolan.

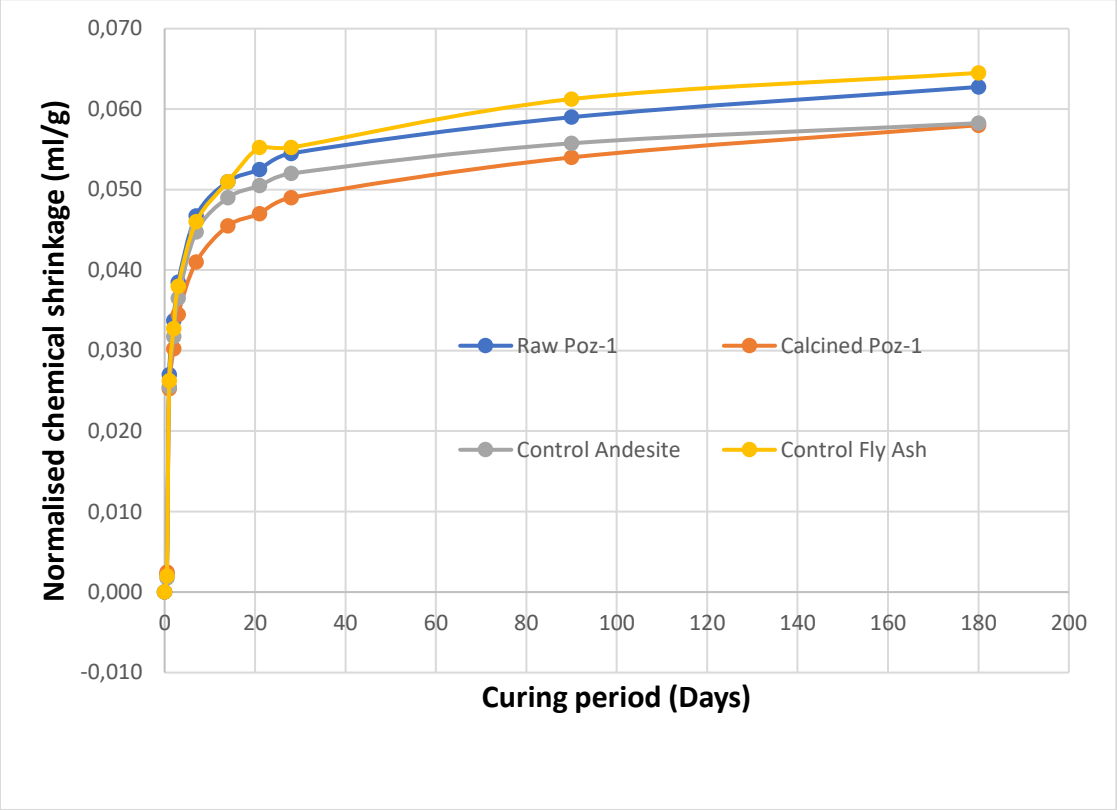

Figure 5.28: Chemical shrinkage results comparison for Poz-1 in raw and calcined states

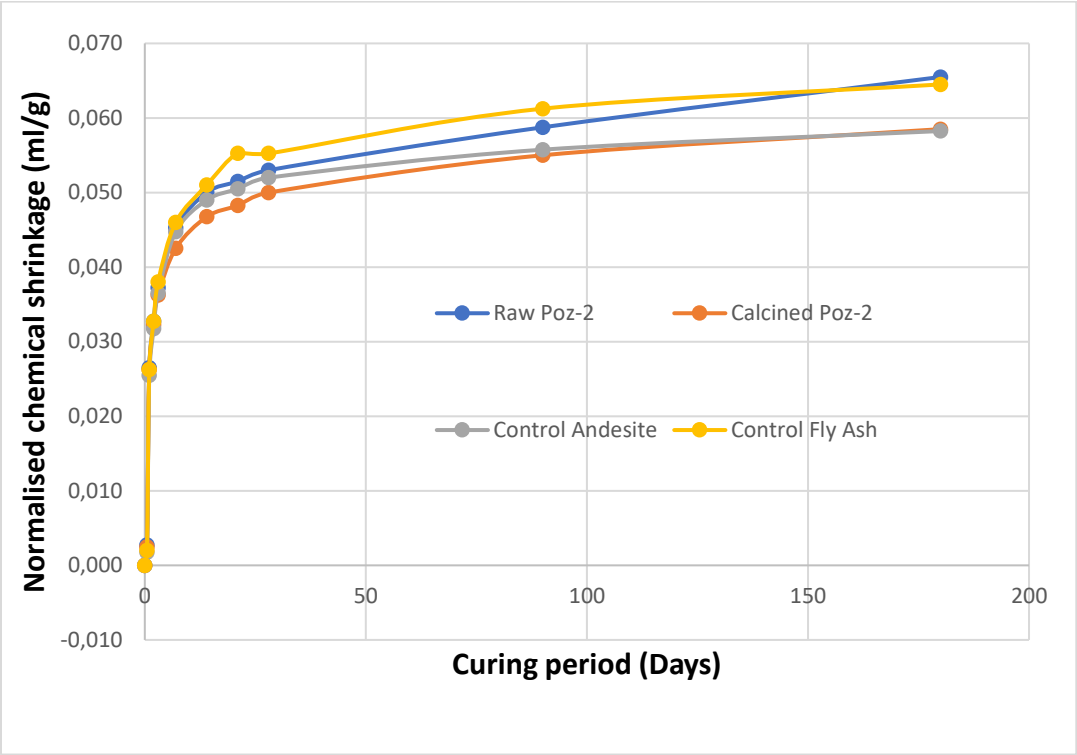

Figure 5.29: Chemical shrinkage results comparison for Poz-2 in raw and calcined states

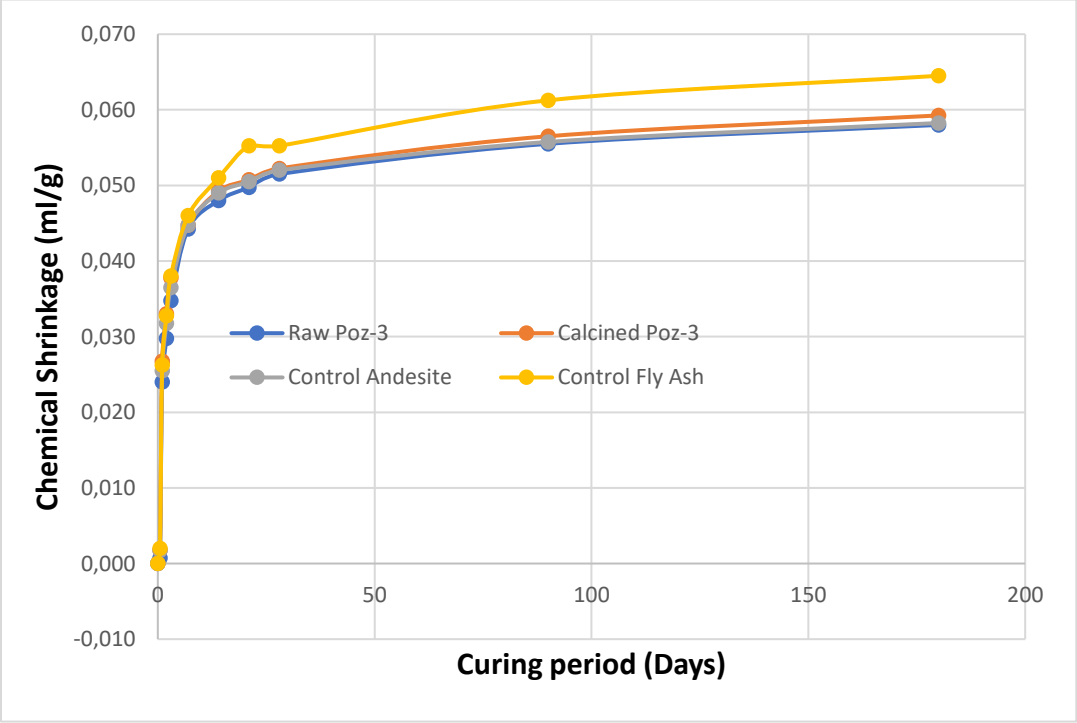

Figure 5.30: Chemical shrinkage results comparison for Poz-3 in raw and calcined states

5.2.7 Compositional factors influencing chemical shrinkage

5.2.7.1 Reactive Silica in the kamafugites and carbonatites

Chemical shrinkage results at 1, 7, 28, 90 and 180 days are compared with reactive silica content of the kamafugites and carbonatites as presented in Figures 5.31 and 5.32 for raw and calcined samples respectively. It is observed that, whereas the trend for the reactive silica in the raw sample is a negative one, the calcined samples showed increase in chemical shrinkage with increase in reactive silica. The cause of the negative trend in the raw samples is attributed to the acceleratory effect the carbonate minerals have on cement hydration (Berodier, 2015). Moreover, enrichment of carbonate minerals in the carbonatites and kamafugites occurred at the expense of the silicates (Stoppa and Schiazza, 2013; Tappe, Foley and Pearson, 2003; Wyllie and Huange, 1976). The observed difference in the chemical shrinkage and reactive silica trends show the reaction mechanisms associated with calcite to be more pronounced than the pozzolanic reactions in cement systems that are blended with kamafugites and carbonatites. The level of determination of this trend (R^2 values), however, drop from 0.99 at 7 and 28 days to 0.3 at 180 days of curing indicating that carbonates are less pronounced in long-term hydration reactions.

The trend observed in the calcined samples present high coefficients of determinations for the whole test period (R^2=0.99 at 7 days and 0.82 at 180 days of curing). This indicates that the pozzolanic mechanism is the dominant mechanism in the calcined samples. The pozzolanic reactions depend on reactive silica in a test pozzolan (Mehta and Monteiro, 2006) and, as a consequence, in the absence of the calcite minerals, the pozzolanic reactions are more pronounced.

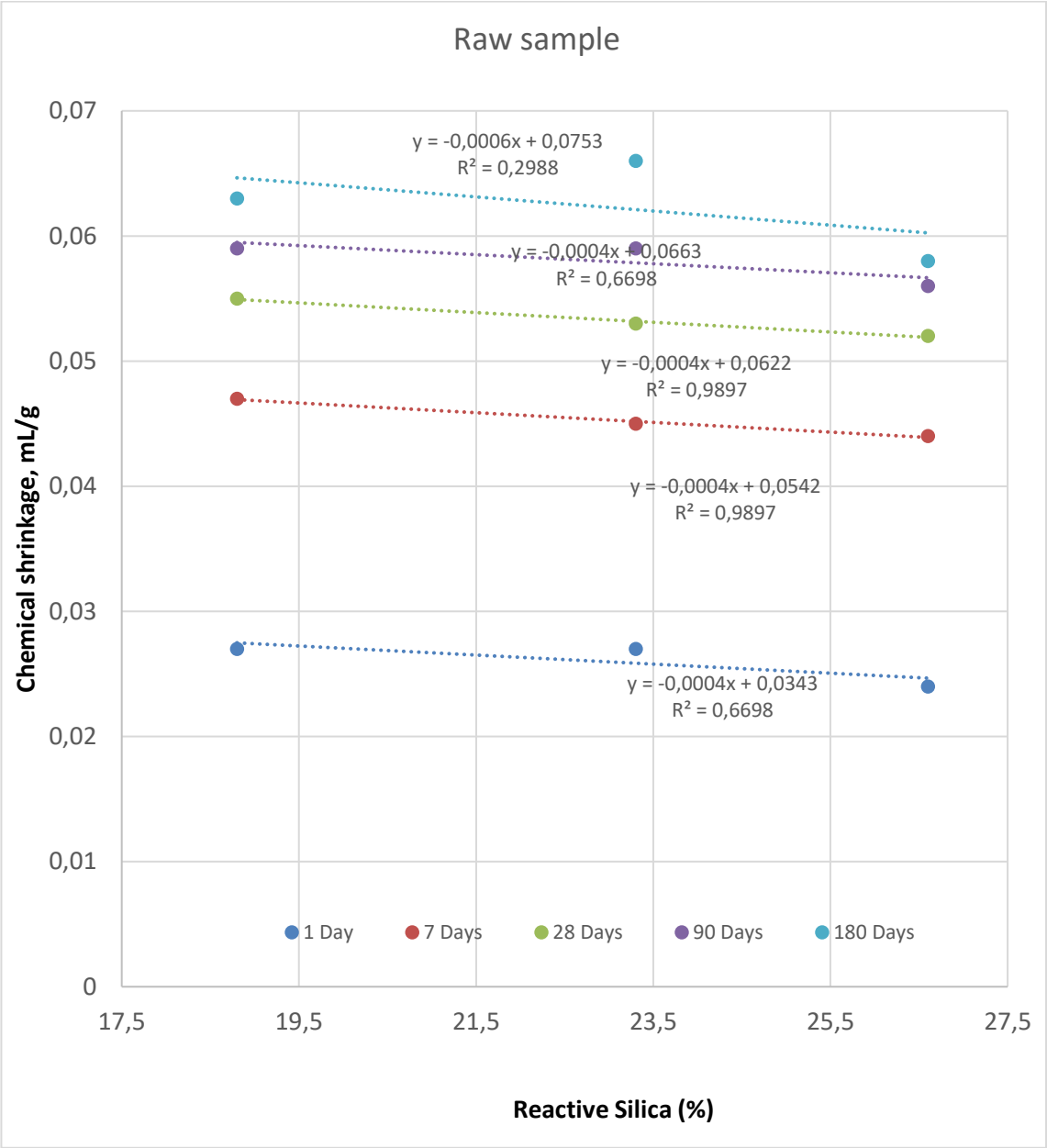

Figure 5.31: Relationship between reactive silica and chemical shrinkage of kamafugites and carbonatites (uncalcined)

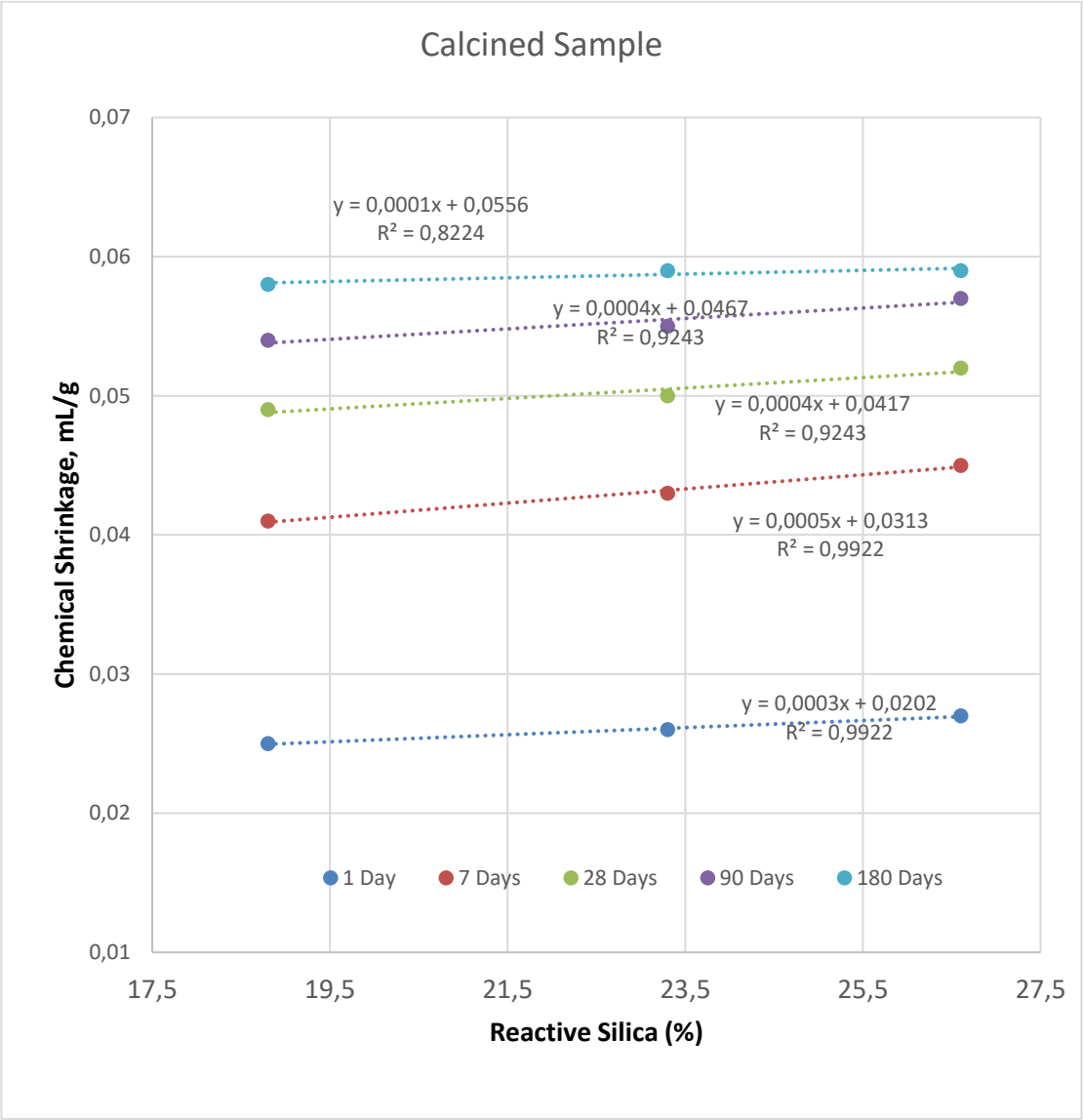

Figure 5.32: Relationship between reactive silica and chemical shrinkage of kamafugites and carbonatites (calcined)

5.2.7.2 CaO content in the kamafugites and carbonatites

Calcium oxide (CaO) content in the kamafugites and carbonatites as shown in the XRF results (Table 3.3) is considered to represent the calcite minerals. As is in the case of reactive silca above, the samples with higher calcite content are low on silica saturation. The trend is therefore a positive one for an increase in CaO content (Figure 5.33). Calcination pacified the effects of calcite leading to a negative trend as in Figure 5.34. Because of the dependence relationship between silica and calcite enrichment in the carbonates and kamafugites (Stoppa and Schiazza, 2013; Tappe, Foley and Pearson, 2003; Wyllie and Huange, 1976), the influence of chemical shrinkage on one is echoed

on the other. Figures 5.33 and 5.34 further advance the calcite reactions with cement phases to dominate chemical shrinkage compared to pozzolanic reactions.

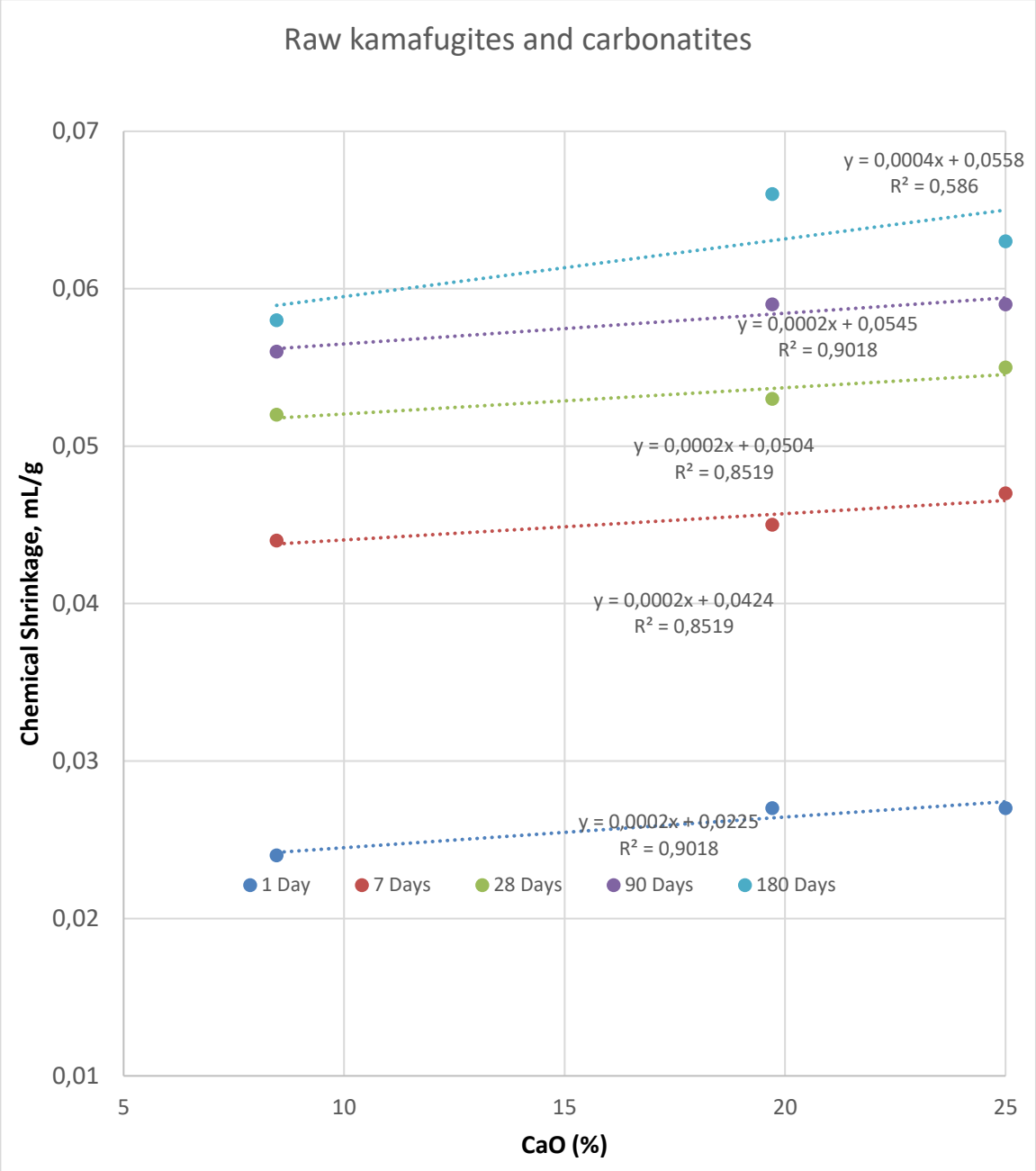

Figure 5.33: Relationship between CaO and Chemical Shrinkage for the raw sample

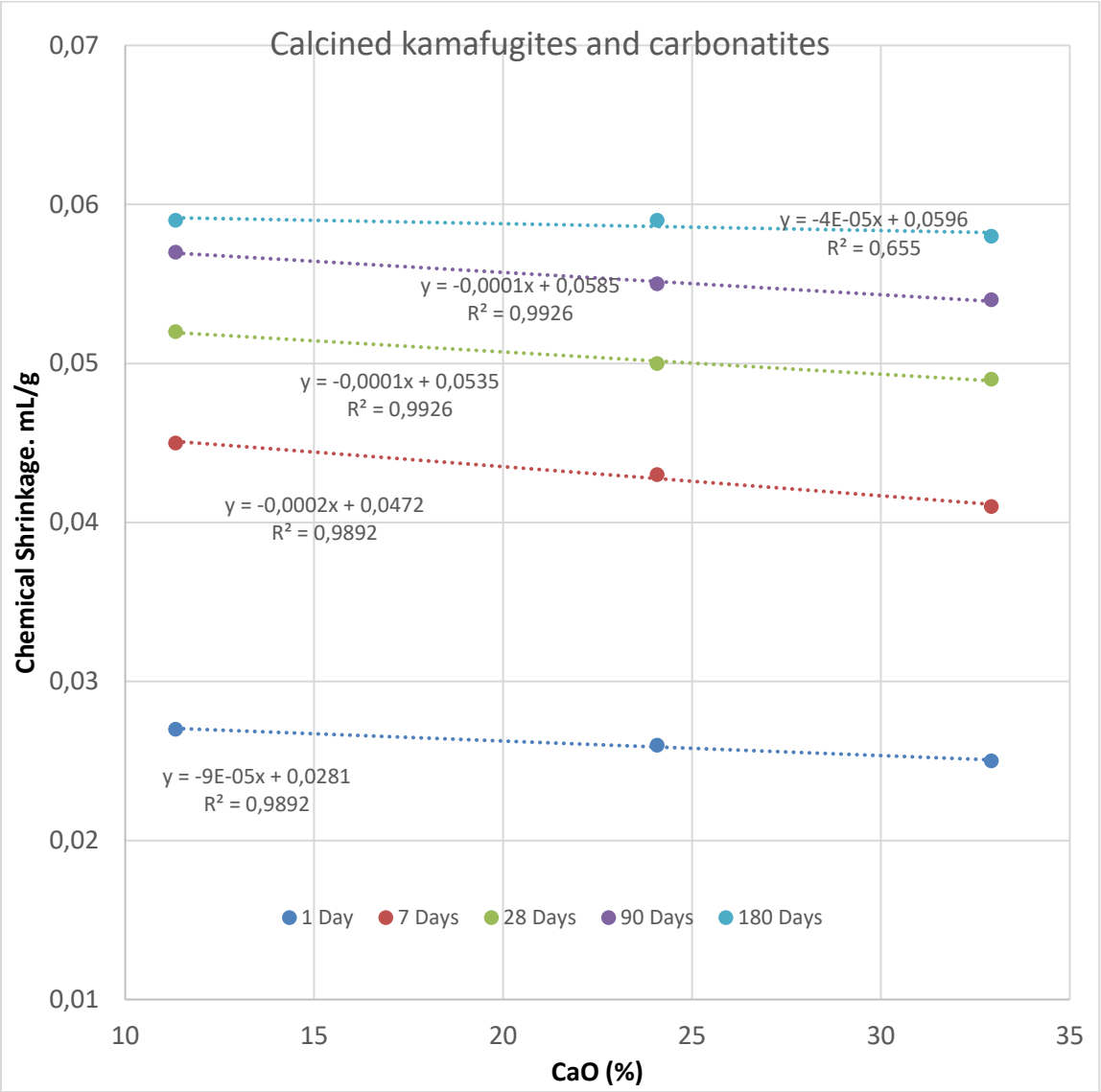

Figure 5.34: Relationship between CaO and Chemical Shrinkage for the calcined sample

5.2.7.3 Magnesium oxide content in the kamafugites and carbonatites

Figures 5.35 and 5.36 advance a comparison in chemical shrinkage trends with MgO content for the kamafugites and carbonatites in both raw and calcined states. While the trends in the raw samples are negative, calcination resulted in increase in chemical shrinkage with increase in MgO concentration for all the testing period. The observed trends are similar to those of silica content in Figures 5.31 and 5.32. The trends show Magnesium to participate in the hydration reactions.

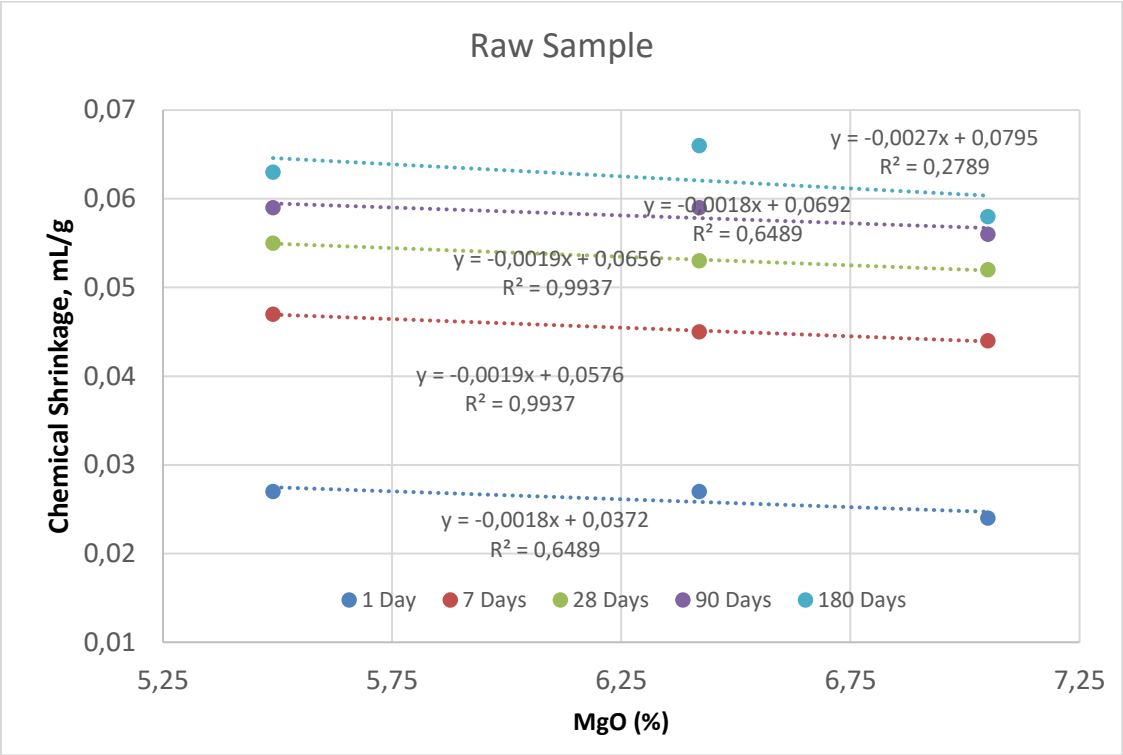

Figure 5.35: Relationship between MgO and Chemical Shrinkage for the raw sample

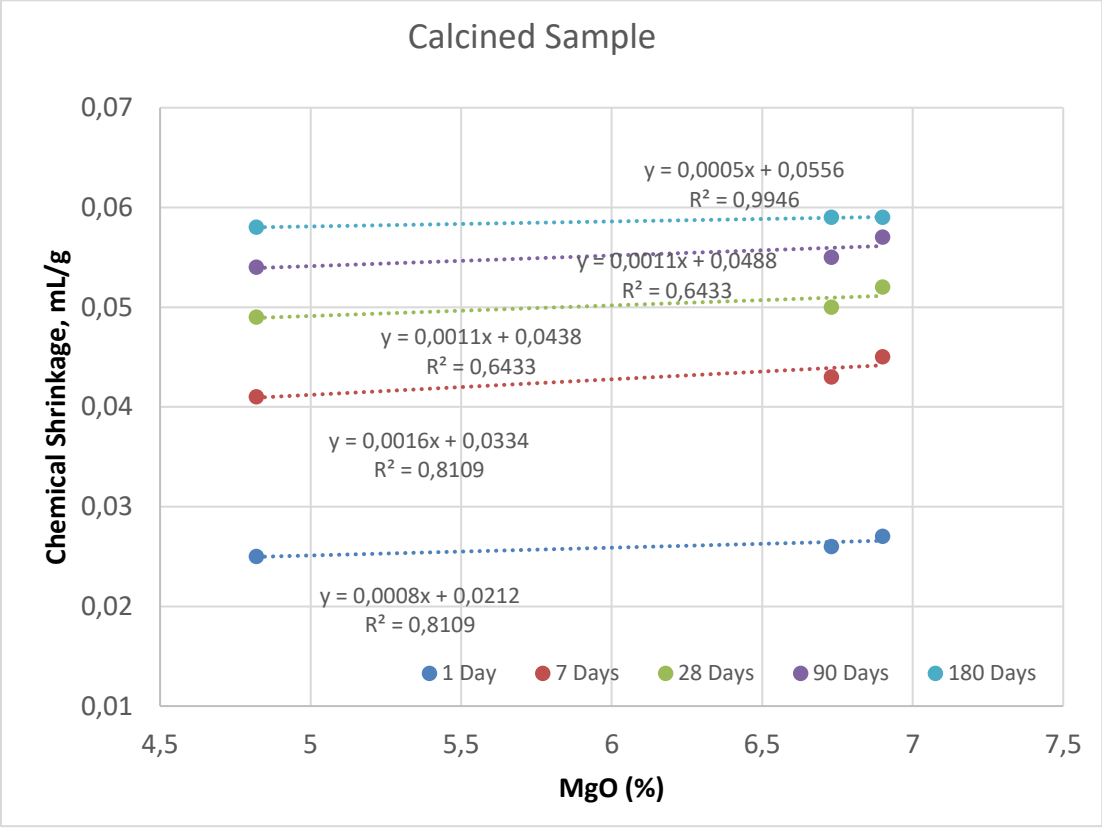

Figure 5.36: Relationship between MgO and Chemical Shrinkage for the calcined sample

5.2.7.4 K_2O and Na_2O alkalis in the kamafugites and carbonatites

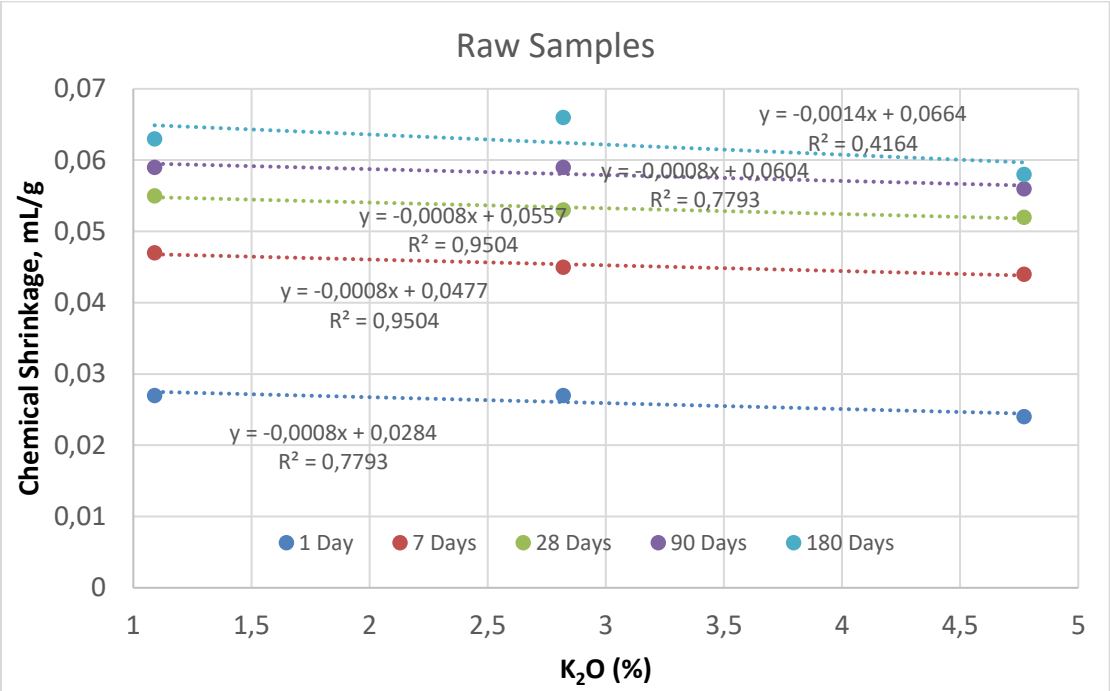

Figure 5.37: Relationship between K_2O and Chemical Shrinkage for the raw samples

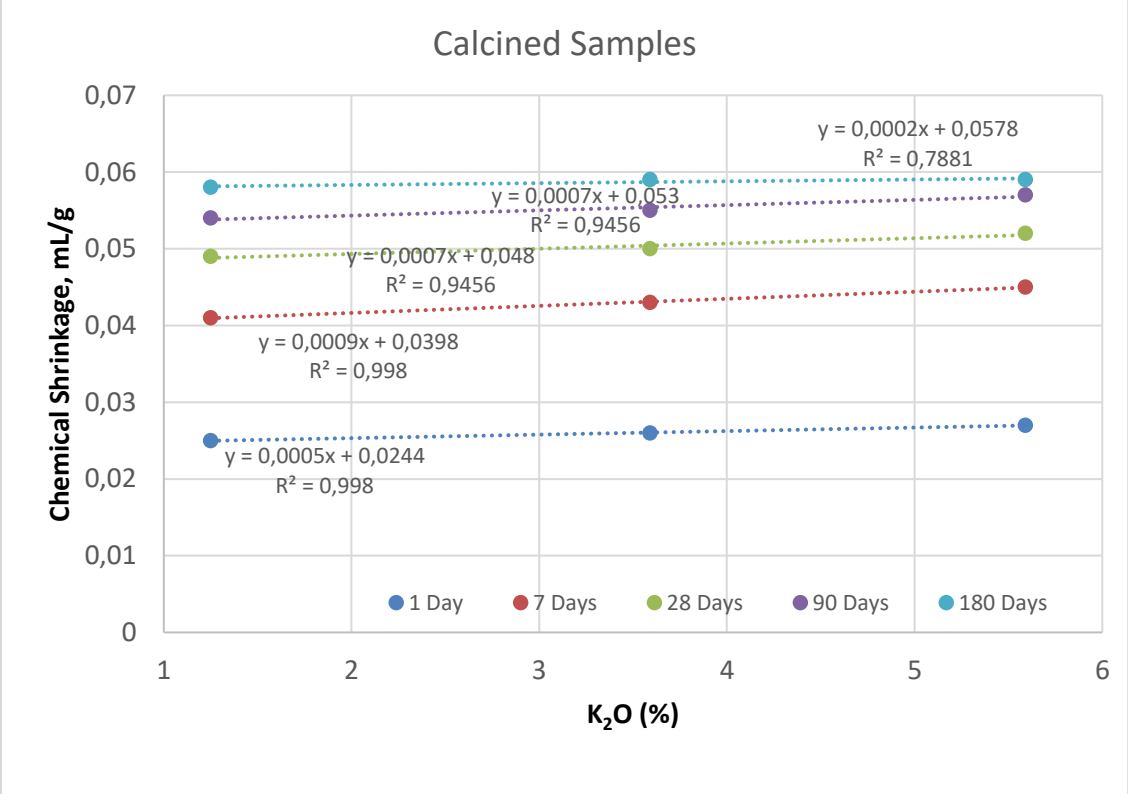

Figure 5.38: Relationship between K_2O and Chemical Shrinkage for the calcined kamafugites and carbonatites

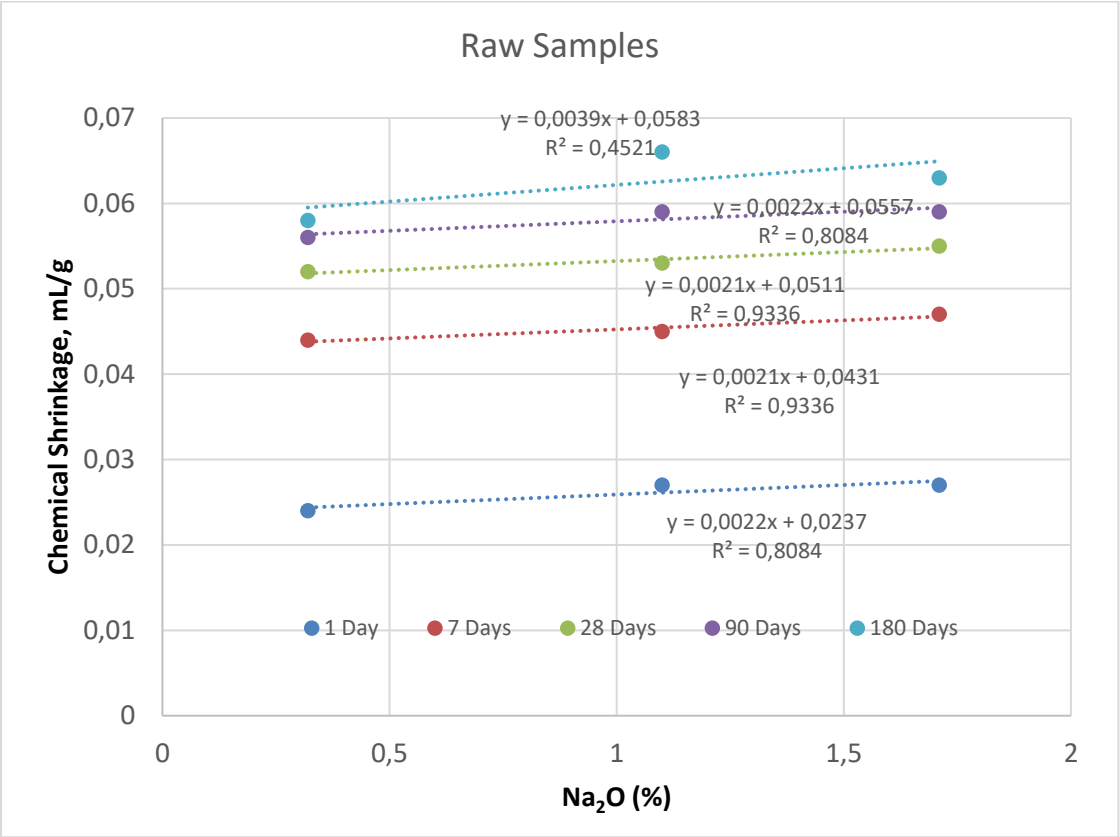

Figure 5.39: Relationship between Na_2O and Chemical Shrinkage for the calcined sample

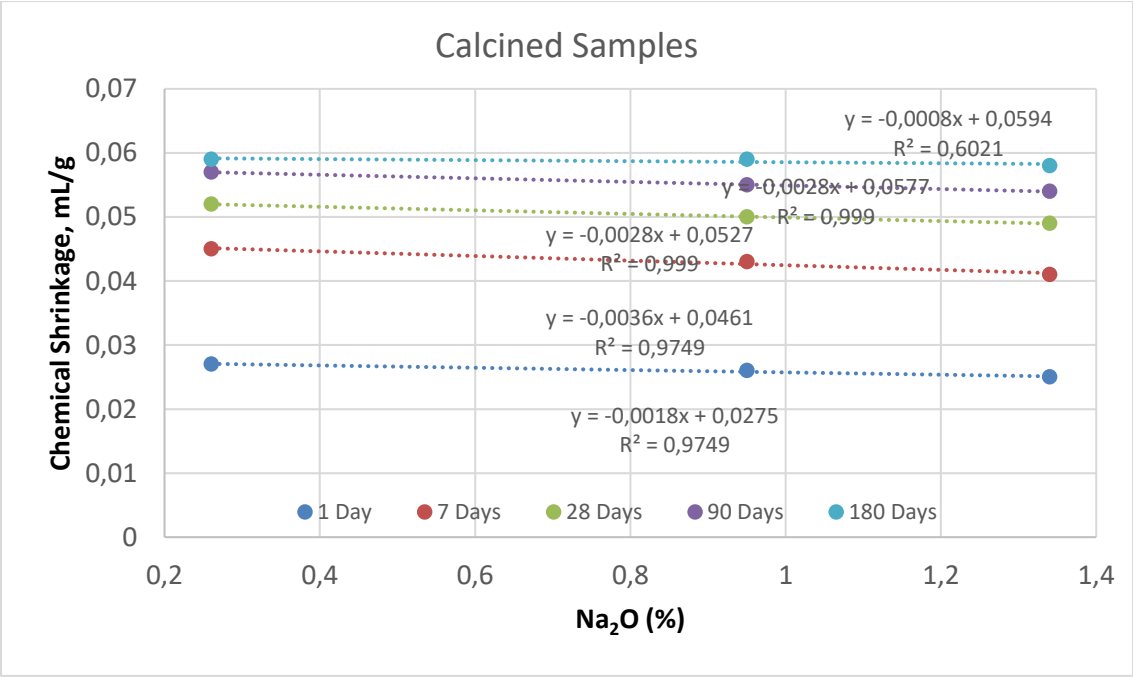

Figure 5.40: Relationship between Na_2O and Chemical Shrinkage for the calcined sample

Alkalis are known to have an acceleratory role on hydration of cement phases (Neville, 2002) but there is limited research (Odler and Wonnemann, 1983) that separates the effect of sodic alkalis from that of the potassic alkalis in cement hydration. Calcination of kamafugites and carbonatites resulted in volatilization of water soluble alkalis and, therefore, provided an opportunity to characterise the unique effects of the different alkalis on cement hydration. Figures 5.37 and 5.38 show the trends between chemical shrinkage and water soluble potassic alkalis for both the raw and calcined samples respectively, while Figures 5.39 and 5.40 show the trends for sodic alkalis with chemical shrinkage for the raw and calcined test pozzolans respectively. From the Figures 5.37-5.40, it is observed that the potassic alkalis influence cement hydration differently from the sodic alkalis. Whereas calcination reversed the negative trend in chemical shrinkage with increase in concentration of potassic alkalis, calcination resulted in reduction of chemical shrinkage with increase in concentration of sodic alkalis. These trends were not explained by the current study.

5.2.8 Hydration products and pozzolanic activity of calcined samples

5.2.8.1 Thermogravimetric analysis (TGA) results

Thermogravimetric analysis results for study of the effect of calcination on hydration products and pozzolanic performance are presented in Figures 5.41-5.49. The results are presented at a fixed curing time of 7 hours, 7 days and 56 days to facilitate comparison.

The results at 7 hours of hydration for Poz-1, Poz-2 and Poz-3 are presented in Figures 5.41, 5.42 and 5.43 respectively. All the three test pozzolans show the paste sample blended with raw kamafugites and carbonatites to have more hydration products in the first phase of the TGA profile, the dehydration phase (105°C-400°C), than both the calcined and control samples, Poz-3 leading in the magnitude followed by Poz-2 and Poz-1 showing marginal increase in the hydration products. The calcined sample trailed the control sample in hydration products accumulation since calcination inactivates the acceleratory effects of the test pozzolans. The dehydration phase is associated with the silicate hydrates as the most pronounced hydration products but also the AFt phases together with carboaluminates phases (Lothenbach et al, 2008; Taylor, 1997;

Ramachandran et al., 2002; Hewlett, 2004; Gabrovšek, Vuk and Kaučič, 2006). The observed trend is attributed to the acceleratory effects of the test kamafugites and carbonatites. The acceleratory effect has been reported in other sections of this thesis and is attributed to the calcite and water soluble alkalis.

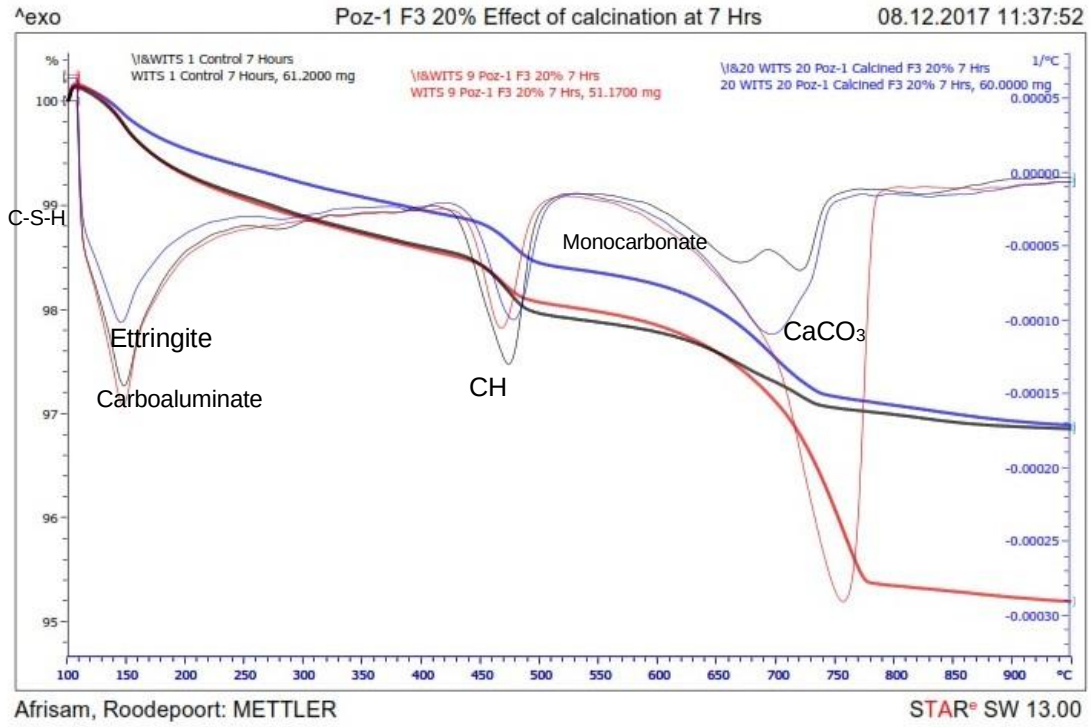

Figure 5.41: Effect of calcination of Poz-1 on hydration products and pozzolanic performance at 7 hours.

It is expected that accelerated hydration of the silicate phases would reflect on the deposition of the CH hydrates in the dihydroxylation phase (400°C-600°C) but, as observed with paste samples blended with Poz-1 and Poz-2, the control sample presented more CH hydrates than the test pozzolans, both raw and calcined. This observation serves to indicate that the increase in volume of the hydration products is based on non-silicate hydrates. The formation of high density carboaluminates phases is a plausible hypothesis for Poz-1 and Poz-2 test pozzolans that are higher in the carbonates content. It is however observed that the accelerated hydration in Poz-3 is dominated by the hydration of the silicate phases as observed in the high content of

CH. The CH phase of the raw test pozzolan blended paste is relatively higher than that of the control sample paste and paste made with calcined kamafugite.

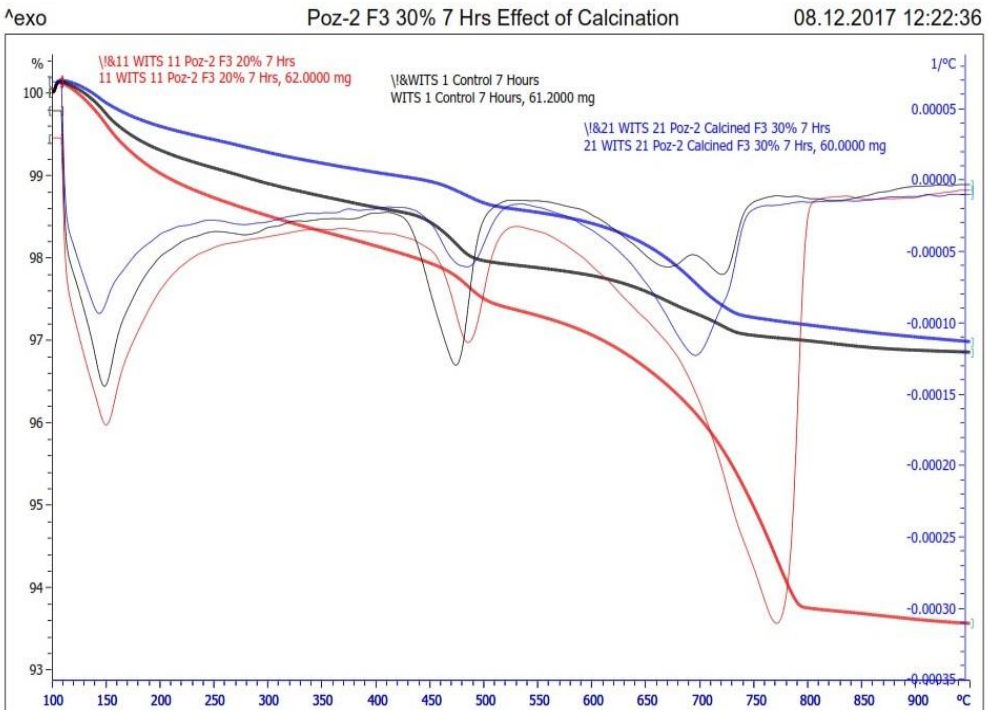

Figure 5.42: Effect of calcination of Poz-2 on hydration products and pozzolanic performance at 7 hours.

The decarbonation phase shows the test samples to have carbonated in the process of handling and sample preparation for TGA testing. The formed carbonates are principally monocarbonates (Lothenbach and Wieland, 2006) with lower decomposition temperatures in relation to the calcite phase in the raw test pozzolan blended cement paste. The blended sample shows a higher rate of carbonation than the control sample (CEM I 52.5R), a trend that is observed in all the three samples. The process of carbonation is probably accelerated by the hydrated CaO that is present in the test pozzolans leading to the reversing of the decarbonation previously achieved through thermal decomposition.

There is no pozzolanic activity traceable at the 7 hour hydration state.

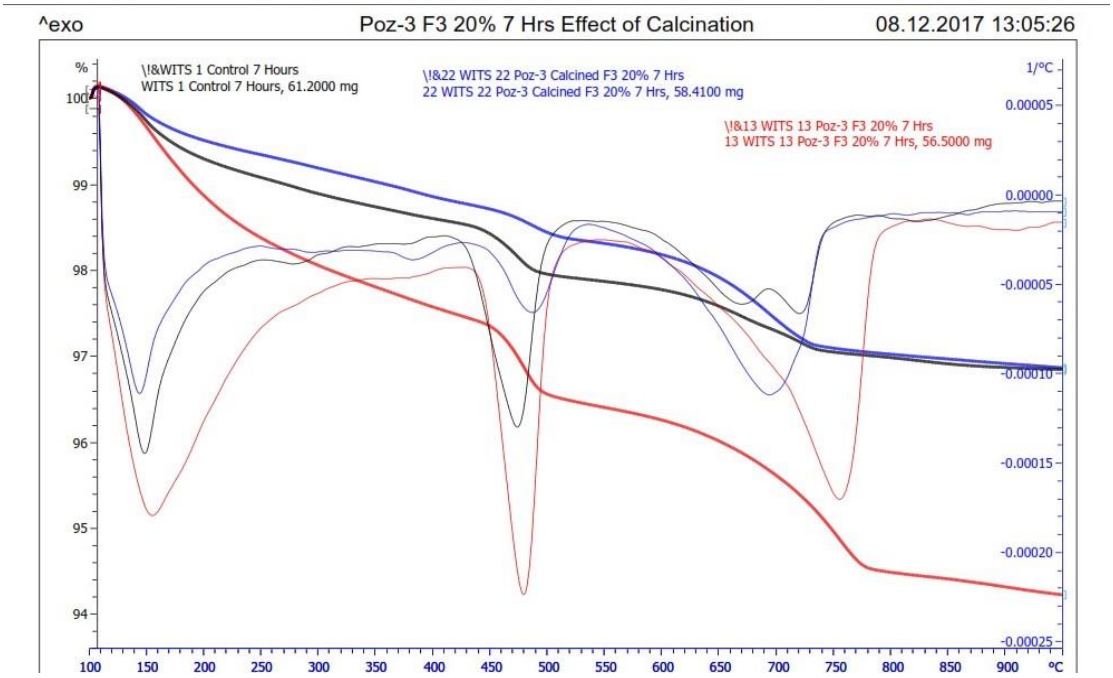

Figure 5.43: Effect of calcination of Poz-3 on hydration products and pozzolanic performance at 7 hours.

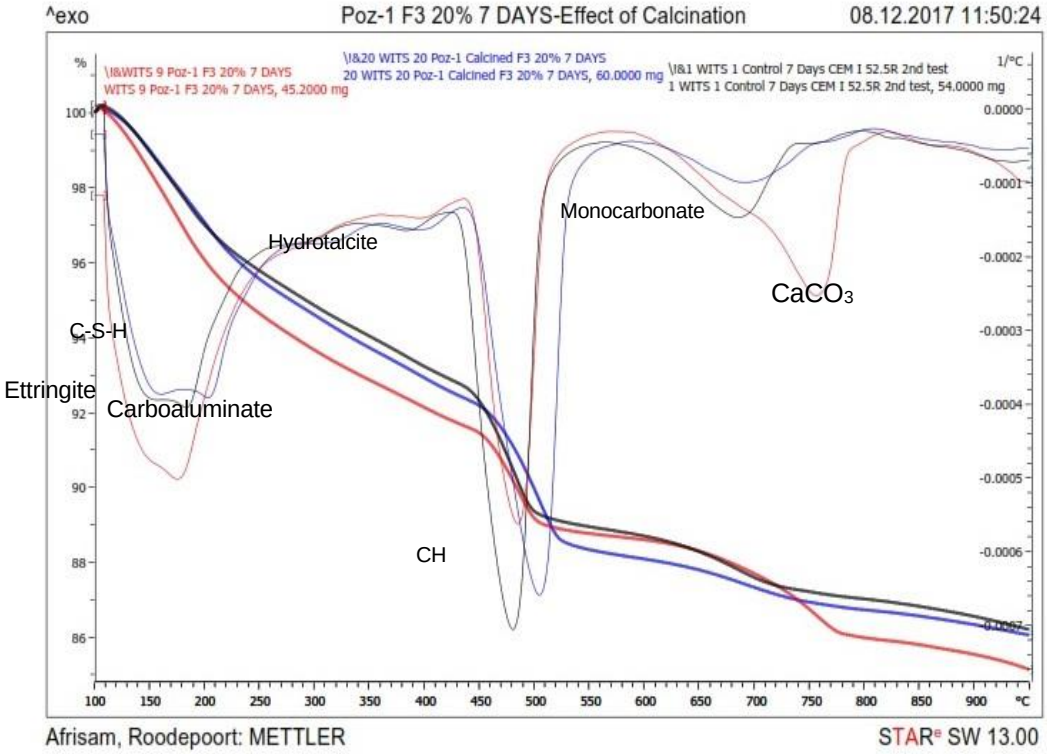

Figure 5.44: Effect of calcination of Poz-1 on hydration products and pozzolanic performance at 7 days.

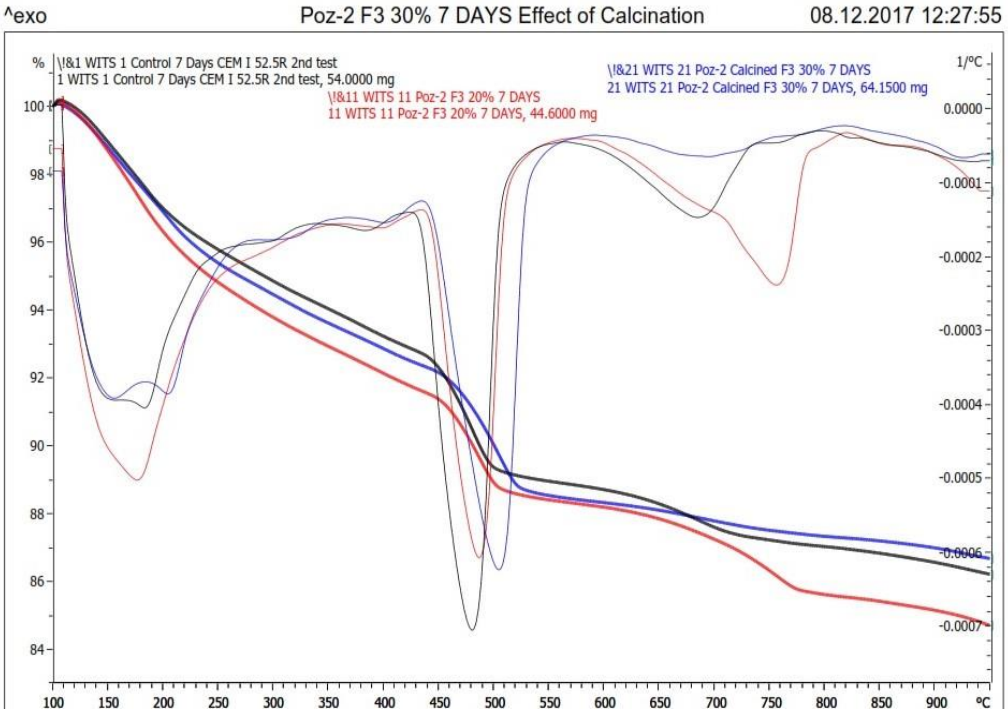

Figure 5.45: Effect of calcination of Poz-2 on hydration products and pozzolanic performance at 7 days.

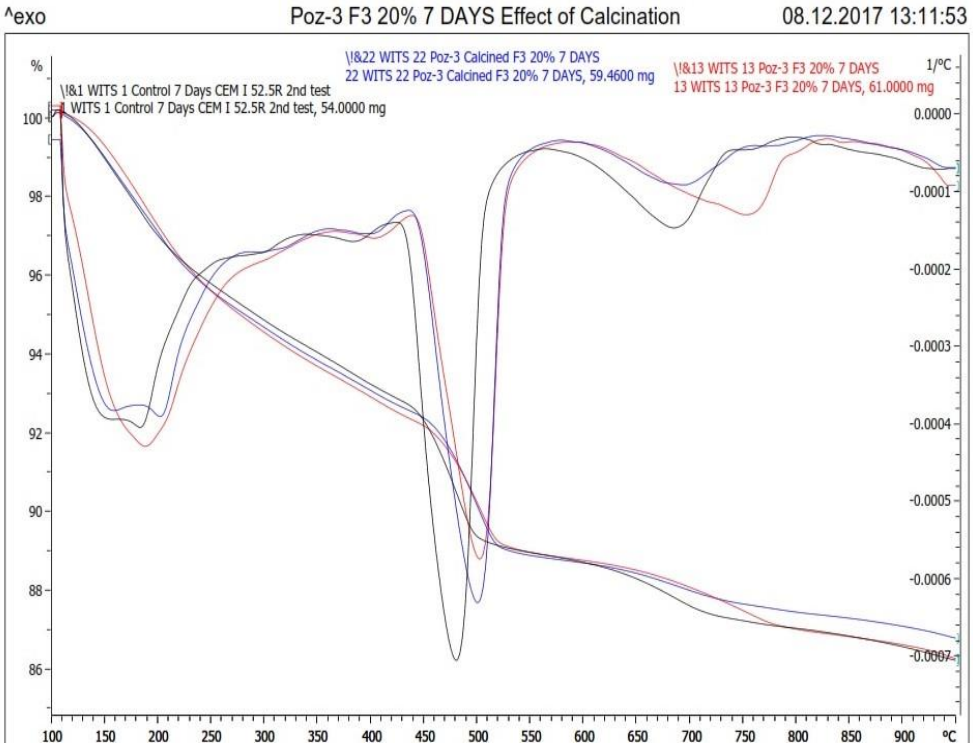

Figure 5.46: Effect of calcination of Poz-3 on hydration products and pozzolanic performance at 7 days.

Figures 5.44, 5.45 and 5.46 represent the TGA profiles at 7 days of curing for Poz-1, Poz-2 and Poz-3 respectively. The results show the increase in hydration products in the dehydration phase of the TGA thermodecomposition profile were sustained. The dominant phases in the dehydration phase are C-S-H, Ettringite and carboaluminates phases. The acceleratory effect of Poz-3 is minimized at 7 days of curing.

The dihydroxylation phase results show calcination to reduce the pozzolanic activity of the test kamafugites and carbonatites. A slight shift in the DTG dihydroxylation profile indicates that calcination led to deposition of CH hydration products that are more stable, demanding a higher decomposition temperature than those formed by the control sample and the paste sample blended with the raw test pozzolan.

The decarbonation phase of paste samples at 7 days show the existence of both monocarbonates and calcite phases. The results also reveal a reduction in the carbonate phases indicating a consumptive reaction that converts carbonates to bond with hydration products. Lothenbach and Wieland, (2006) observed carbonates to be fixed in hydration reactions over a long period of curing. It is considered that the carbonates take part in the hydration reactions that take place within the dehydration phase. The XRD results that characterize hydration products indicated the presence of hydrotalcite, a Mg-Al-OH-CO_3(H2O) mineral that is formed through reactive $Mg(OH)_2$ where some of the magnesium ions are substitutes by Al ions with the water molecules and carbonates correcting the created charge imbalance (Taylor, 1997). Hydrotalcite acts together with the carboaluminates phases to bond some of the carbonates from the blended test pozzolans.

Figures 5.47, 5.48 and 5.49 present results of the TGA decomposition profiles for samples cured up to 56 days. The trends are similar to those observed at 7 days of curing with similar observations for the three thermal decomposition phases of dehydration, dihydroxylation and decarbonation. It is observed that the rate of carbonation of samples that is observed high in samples at 7 hours and 7 days reduces to negligible levels relative to other hydration products. The samples blended with raw test pozzolans sustain increased hydration products through up to 56 days of curing.

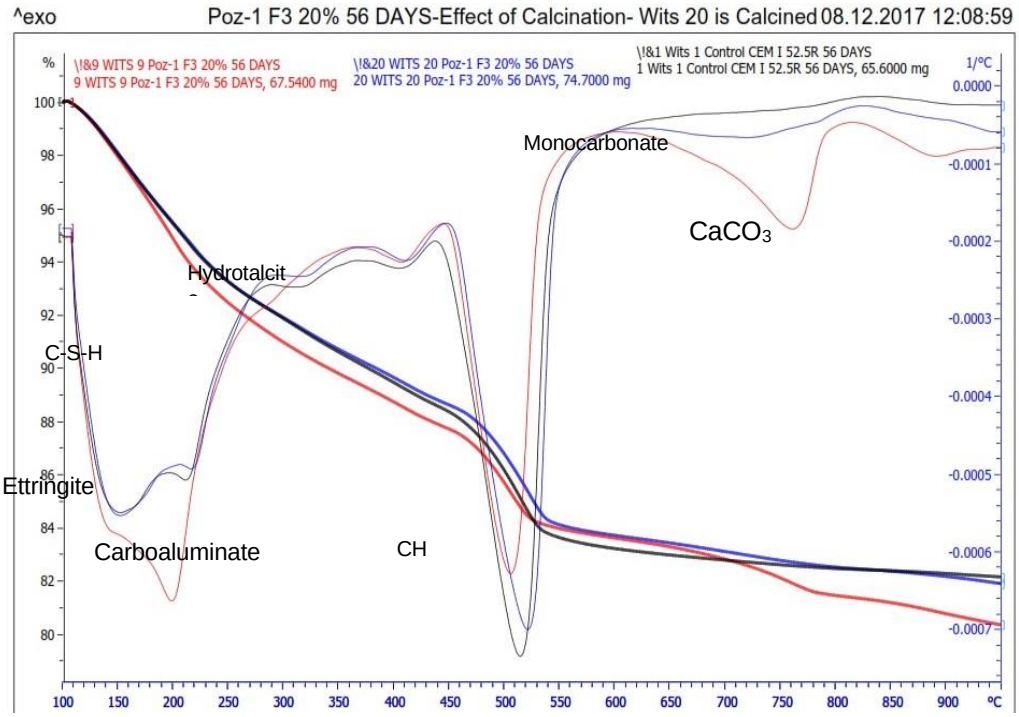

Figure 5.47: Effect of calcination of Poz-1 on hydration products and pozzolanic performance at 56 days.

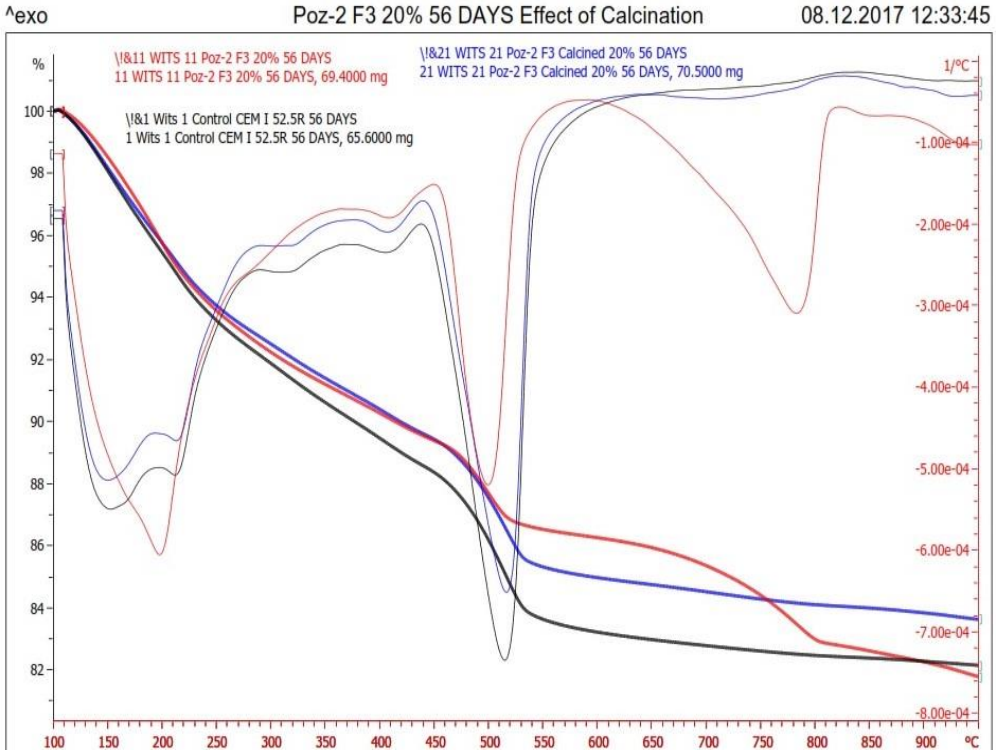

Figure 5.48: Effect of calcination of Poz-2 on hydration products and pozzolanic performance at 56 days.

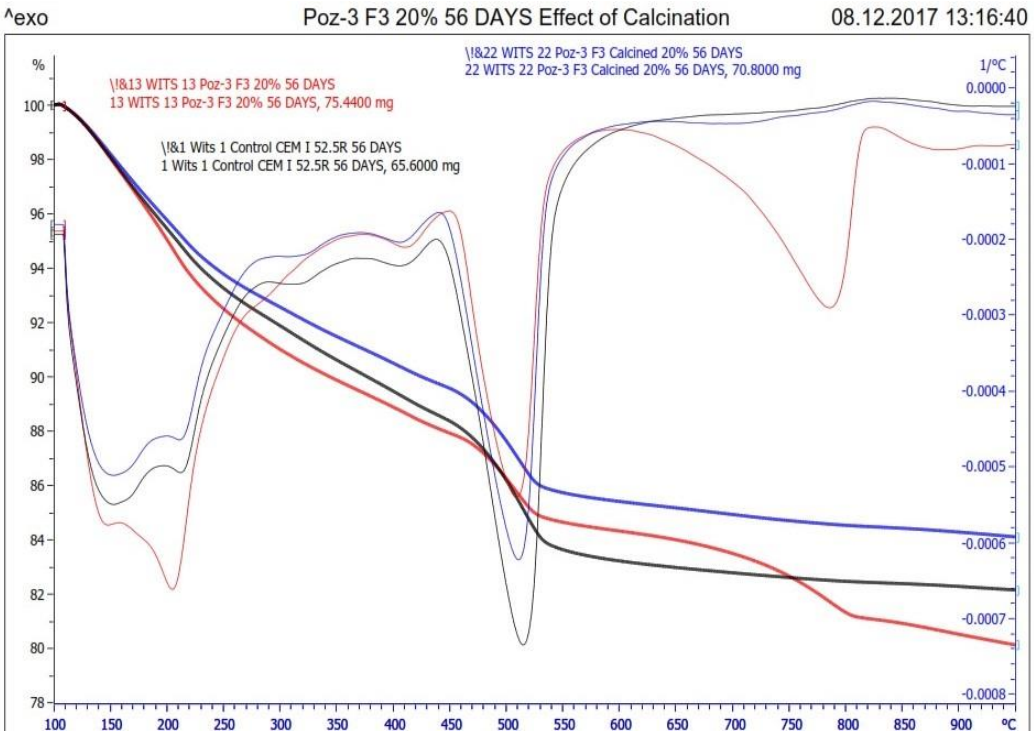

Figure 5.49: Effect of calcination of Poz-3 on hydration products and pozzolanic performance at 56 days.

5.2.9 Effect of calcination on X-ray Diffraction results

As indicated in Section 4.3.2 in Chapter 4 of this thesis, calcination of the test kamafugites at anhydrous state effectively decarbonated the samples and volatilized their water soluble alkali content. Volatilization of water soluble alkalis has a direct effect on the composition of pore fluids while decarbonation pacifies the effects of calcine in the hydrating cement system. Calcination had no significant effect on the other mineral phases in the kamafugites and carbonatites. As a result, the type of hydration products formed in cements blended with raw samples are similar to those formed by the calcined samples. However, the following general observations are made on the different cement phases and hydrates of hydrating blended cements at 7 days.

1. The calcined sample is seen to have more CH content than the raw sample. This is an indication that calcination reduces the pozzolanic activity rate of the kamafugites and carbonatites at early stages of hydration. Accumulation of CH for the calcined sample is as a result of a reduced rate of their consumption in the hydration and pozzolanic reactions.

2. Calcination also reduced the amount of ettringite formed in the cement hydrates at 7 days. Works by Bouasker et al., 2008, report suppression of sulfo-aluminate reactions by the carbonates in cement paste in favor of monocarbonates. The higher amounts of ettringite in the raw sample is an indication that the carbonates in the blended cements preferentially react with aluminates to form carboaluminate products at the expense of monosulfates.

3. Traces of calcite are observed in the hydrating paste blended with the kamafugites and carbonatites. This is as a result of carbonation of the paste that took place in the sample handling process. The magnitudes are, however, minimal compared to the calcite content in the pastes blended with raw kamafugites and carbonatites.

4. An Mg-hydrotalcite phase is observed in the paste samples blended with raw and calcined kamafugites and carbonatites. Calcination led to increase in hydrotalcite deposition confirming that the Mg^{2+} ions in the test kamafugites and carbonatites participate in the hydration reactions. It is observed in the results of Table 4.15 that calcination increased water soluble Mg^{2+} ions. Calcination therefore increases the reactivity of Mg in the kamafugites and carbonatites.

5. Calcination slows the consumption of silicate phases in the hydration reactions.

The effects listed above apply to all the test pozzolans as presented in Figures 4.44, 4.45 and 4.46 on pages 4-72 of Chapter 4 with Poz-3 showing less effects in intensity in the observed changes indicating that the observed changes are driven by the calcite composition in the carbonatites and kamafutites. Poz-3 is a kamafugite that is silica saturated and relatively lower in calcite composition compared to the other test natural pozzolans.

5.3 Fineness and replacement level of kamafugites and carbonatites

The two physical properties tested were fineness and replacement level. Whereas replacement level was a simple parameter to set, fineness parameters could not be unified for the two test pozzolans. The samples milled in a lab scale ball mill for 20 min (F1), 30 min (F2) and 40 min (F3) at fixed mass loads showed variations in their properties as presented in Table 3.1 and discussed in Section 3.4.1 of this thesis. Though the variations in the specific surface area parameters are distinct for comparative studies, the d_{10} values for the F3 fineness level are nearly similar for the two test pozzolans. Also, the particle size spread between d_{10} and d_{90} for the test pozzolans is much wider in comparison with the cement control sample. This is possibly due to the heterogeneous nature of the kamafugite and carbonatite petrographic composition. The different minerals within the test pozzolans have different hardness values which, as a result, lead to different rates of disintegration. This assumption agrees with a study by Turanli, Uzal and Bektas, 2004, on three Turkish natural pozzolans which reports dependence of particle size parameters on the level of hardness of the natural pozzolan materials. The closeness of the d_{10} values for F3 fineness level of both Poz-1 and Poz-3 is likely a compositional property than a dependence on the milling. The spread of fineness levels from F1 to F3 show Poz-1, a carbonatite, to be softer than Poz-3, a kamafugite. Note that the specific surface area of the control sample (1.75 m^2/g) is significantly lower than for the test pozzolans at the highest fineness level, F3. This is probably due to a much lower d_{10} value for the test pozzolans in relation to the control sample. The chemical composition and physical properties are as reported in Tables 3.1-3.4 and Figures 3.1-3.6 of this thesis. Poz-1 has a very high content of CaO (25%) which is responsible for its silica undersaturation. Poz-3 is silica saturated and ultrapotassic but also with a relatively high CaO content (8.47%). Both samples have high LOI values primarily due to decomposition of the carbonate minerals between 600°C and 800°C as discussed in Section 3.2 of this thesis. Poz-3 has a higher value of water soluble alkalis than Poz-1.

5.3.1 Analysis of fineness effect on heat of hydration

The effect of fineness of carbonatites and kamafugites on the heat of hydration progression is shown in Figure 5.50 for Poz-1 and Figure 5.51 for Poz-3. The results are normalized for cementitious materials content. Both experiments run for 170 hours (7 days) and were tested against CEM I 52.5R as a control sample. The results show no variation in heat of hydration with fineness levels of the test pozzolans for the 170 hours of testing.

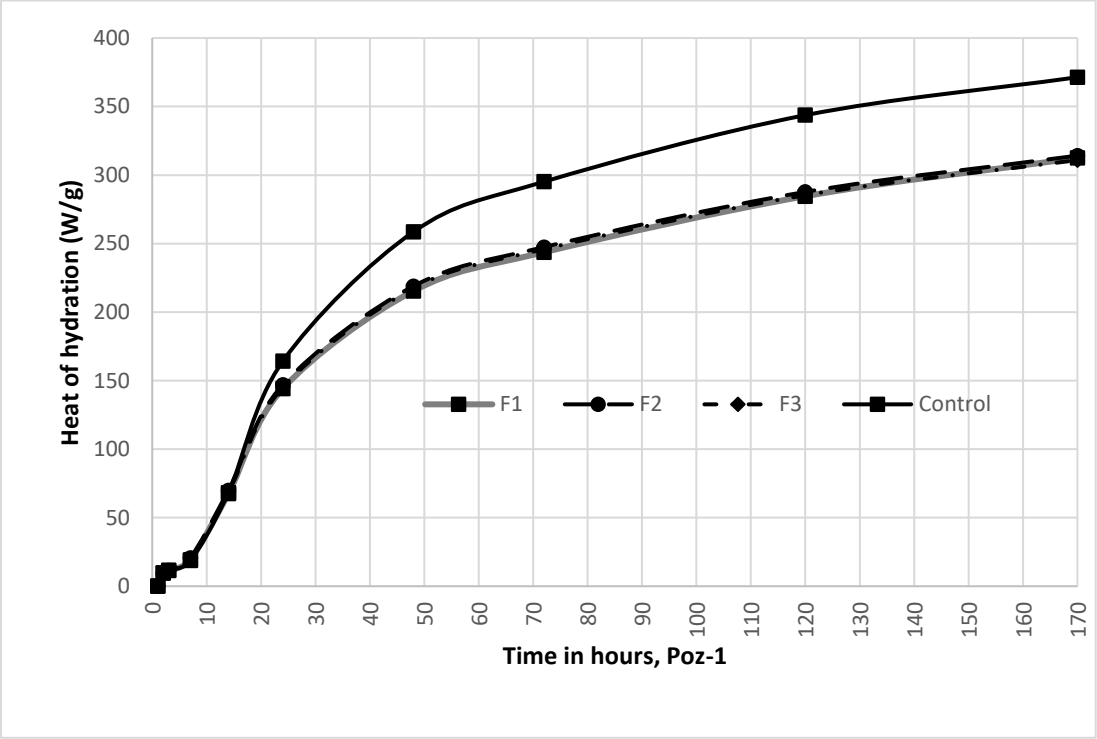

Figure 5.50: Effect of fineness on heat of hydration for Poz-1

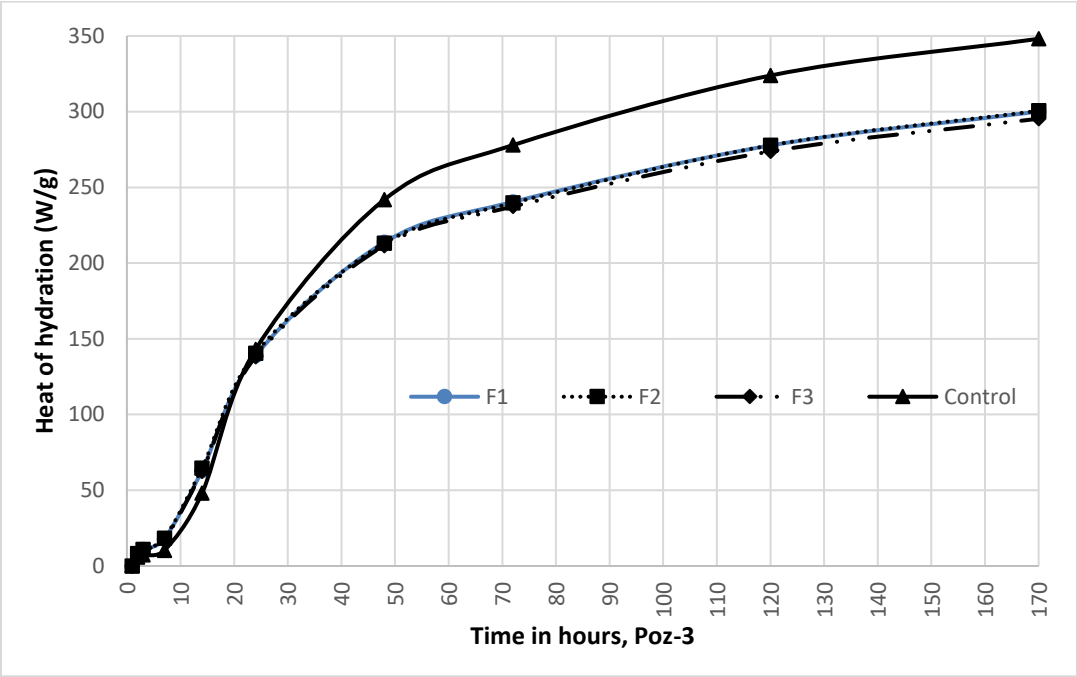

Figure 5.51: Effect of fineness on heat of hydration for Poz-3

It is anticipated that, considering the role the filler effect (explained in Section 2.4.2) has on hydration progression of blended cements (Ogawa, Uchikawa and Takemoto, 1980; Berodier and Scriverner, 2014), increase in fineness would have a hydration accelerating effect on cement phases. This accelerating effect is expected to reflect on the amount of heat of hydration generated. Since the results in this study showed no dependence of heat of hydration on fineness, it would imply that the fineness parameter has no influence. However, this is not true as fineness is observed to influence the strength parameter as presented in Section 2.4.2 of this thesis. The author takes two assumptions in explaining the observed results; 1. That the reactant components from the test pozzolans are required in relatively minimal quantities and below the fineness influences of solubility rates for the fineness range studied. Moreover, Blanco et al., 2006, using a chemical method for testing pozzolanic performance of two volcanic samples from Cuba, established dependence on readily soluble silica content and not on fineness property of the test pozzolans. This assumption could not be tested. 2. That the different hydration reaction mechanisms in the blended cement samples are simultaneously accelerating and retarding. This second assumption is plausible considering that it is supported by the TGA data (discussed later in Section 5.3.3) which shows similar trends between chemically bound water and fineness of test pozzolans.

The conversion reactions are therefore established in Kamafugites and Carbonatites blended Portland cement from the start of hydration and their reaction rates are dependent on the level of fineness of the test pozzolans.

5.3.2 Analysis of fineness effect on compressive strength development

Figures 5.52 and 5.53 present analysis of results on the effect of fineness of test pozzolans on compressive strength development. The influence of fineness on strength development is at its highest at 28 days of curing and diminishes up to 90 days when fineness differences cease to cause any significant benefit to the test pozzolans. It is also observed that the pozzolanic performance of Poz-3 is better compared to Poz-1 in relation to the control sample, an observation the author attributes to a higher content of reactive silica in Poz-3. The relationship between fineness level and compressive strength for Poz-1 appears not distinct and, probably, is because of low pozzolanic activity in the test pozzolan. The effect of fineness of the test pozzolans is more significant in Poz-3 which is significantly more pozzolanic.

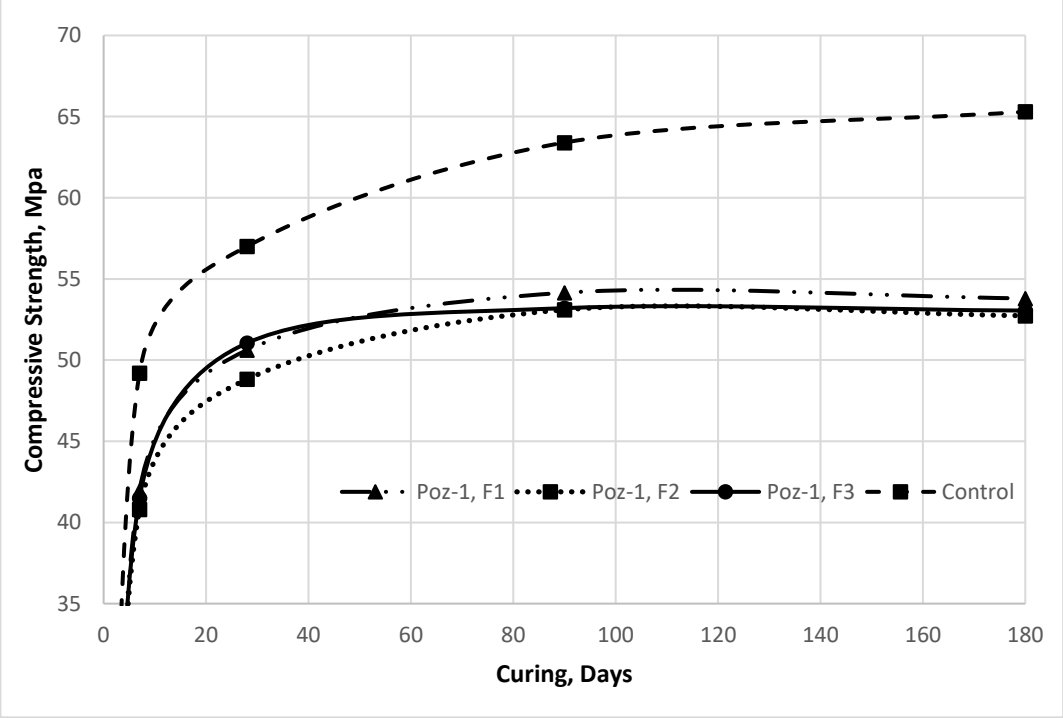

Figure 5.52: Effect of fineness on compressive strength development for Poz-1

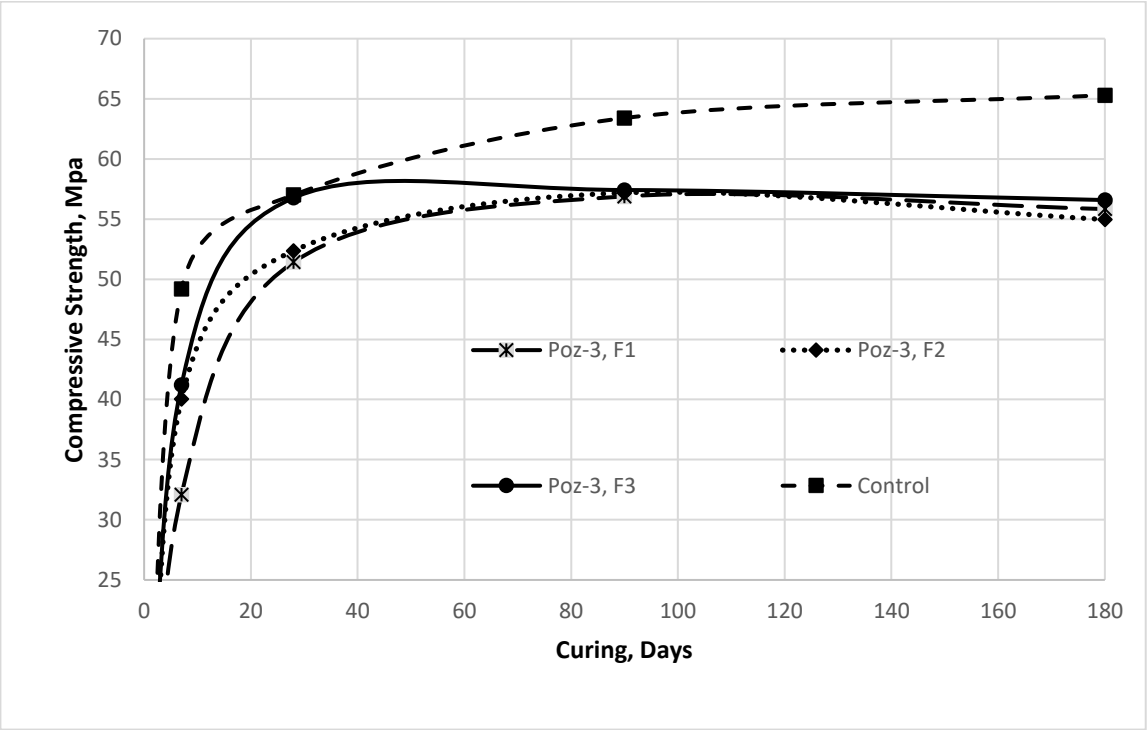

Figure 5.53: Effect of fineness on compressive strength development for Poz-3

The reaction mechanisms advanced to influence hydration of pozzolan blended cements are the filler effect and the pozzolanic reactions (Berodier and Scrivener, 2014; Scrivener et al., 2015; Oey et al., 2013). The filler effect is a physical mechanism that explains the role that dilution and particle surface characteristics may have on the hydration progression of Portland cement. The presence of pozzolanic and other supplementary cementitious materials (SCMs) provide surfaces as nucleation sites for precipitation and growth of cement hydration products. Ogawa, Uchikawa and Takemoto, 1980, and others (Berodier and Scriverner, 2014; Scrivener et al., 2015; Oey et al., 2013) advance the filler effect as acceleratory and, as an important process in the early stages of hydration, responsible for provision of extra sites for precipitation of primarily C-S-H hydrates. The studies by Oey et al., 2013, and Berodier and Scriverner, 2014, advance the dependence of the filler effect on the interparticle distances of SCM particles, shorter interparticle distances giving higher precipitation densities of hydrates. The works above further observe the rate of growth of nucleation sites to depend on the mineral type forming an SCM, calcium carbonates performing better than quartz, slag and fly ash. It is therefore anticipated that both the increase in fineness, which leads to a reduction in interparticle distances of test pozzolans

(Berodier and Scriverner, 2014), and presence of calcite in the test pozzolans would lead to accelerated hydration and strength development. The filler effect is however limited to the early stages of hydration, though its influence on microstructure prognosis and long term compressive strength performance cannot be downplayed.

Fineness increased the compressive strength up to 90 days, peaking at 28 days of curing. The fineness sensitivity appears to be further strengthened by pozzolanic reactions as observed consistent in a silica saturated sample (Poz-3). The composition of Poz-1 is primarily carbonates with reactive silica at 18.8% and, as a consequence, its pozzolanic performance is less pronounced compared to Poz-3, a kamafugite whose reactive silica is above the required minimum of 25%. Other than the filler effect that explains early hydration processes (first 3 days), fineness appears to have accelerated hydration reactions up to 28 days of curing. The effect of fineness diminished after 90 days of curing indicating that the slow reacting coarse samples later react and compensate for the strength deficit due to accelerated hydration of the finer samples. It also appears that the fineness parameter can be used as an indicator of pozzolanic activity considering that the dependence of compressive strength on fineness increases up to 28 days and appeared consistent for the sample with a higher pozzolanic activity.

5.3.3 Analysis of fineness effect on hydration products assemblage

The extent of deposition of hydration products with varying fineness of test pozzolans was studied at a fixed replacement level of 20% test pozzolan in a Portland cement paste. Figures 5.54 and 5.55 show the TGA/DTG graphs for Poz-1 for 7 hours and 56 days of curing while Figures 5.56-5.58 show the TGA/DTG graphs for Poz-3 for 7 hours, 7 days and 56 days of curing respectively. All the data files are saved under the subfolder name “TGA_effect of fineness” in the folder name “TGA_DTG results” on the DVD submitted together with this thesis.

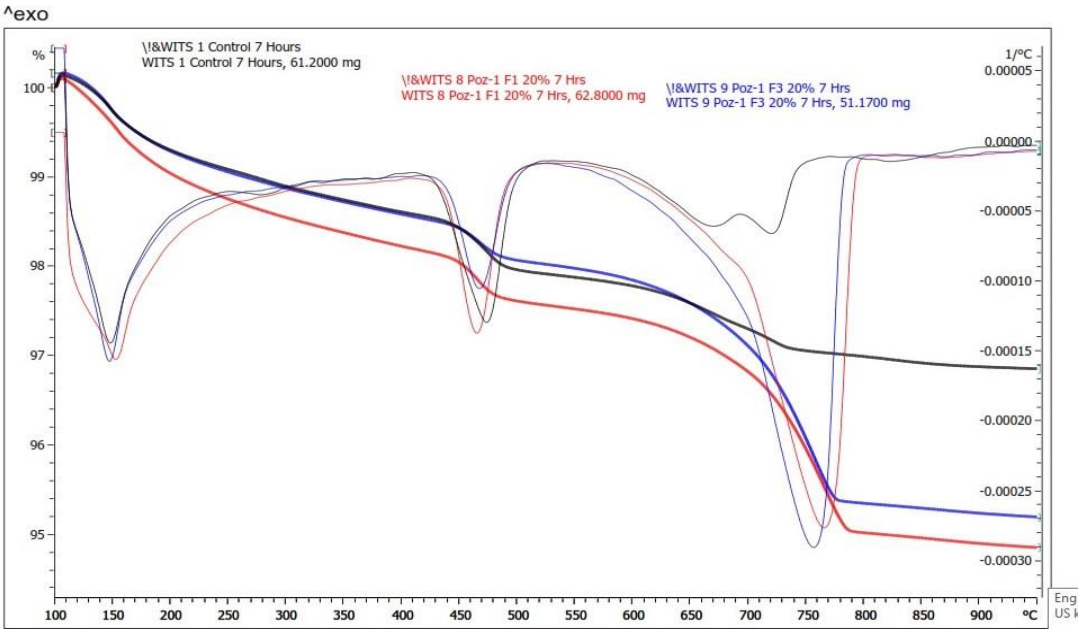

Figure 5.54: TGA/DTG graphs showing effect of fineness of Poz-1 on hydration products development at 7hrs

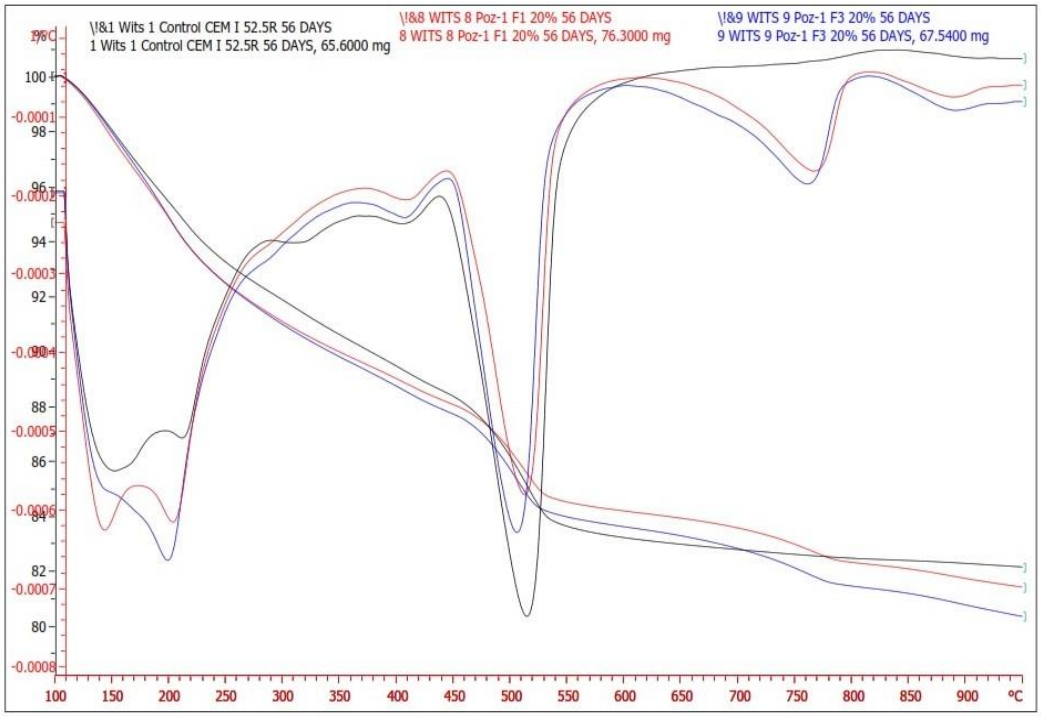

Figure 5.55: TGA/DTG graphs showing effect of fineness of Poz-1 on hydration products development at 56 days

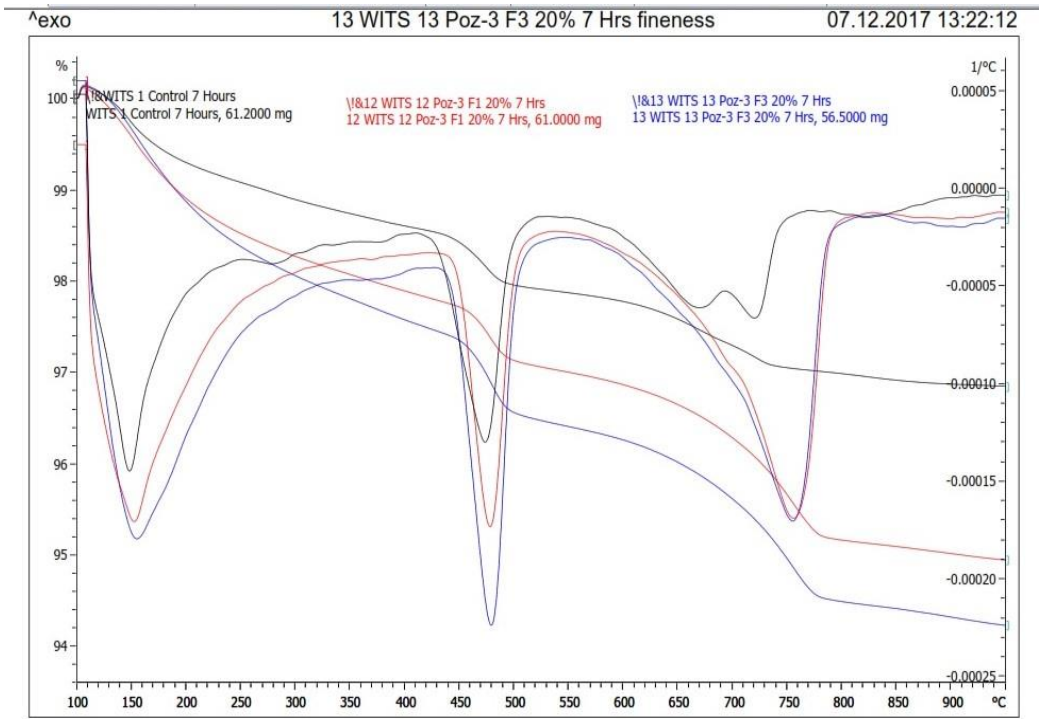

Figure 5.56: TGA/DTG graphs showing effect of fineness of Poz-3 on hydration at 7 hours

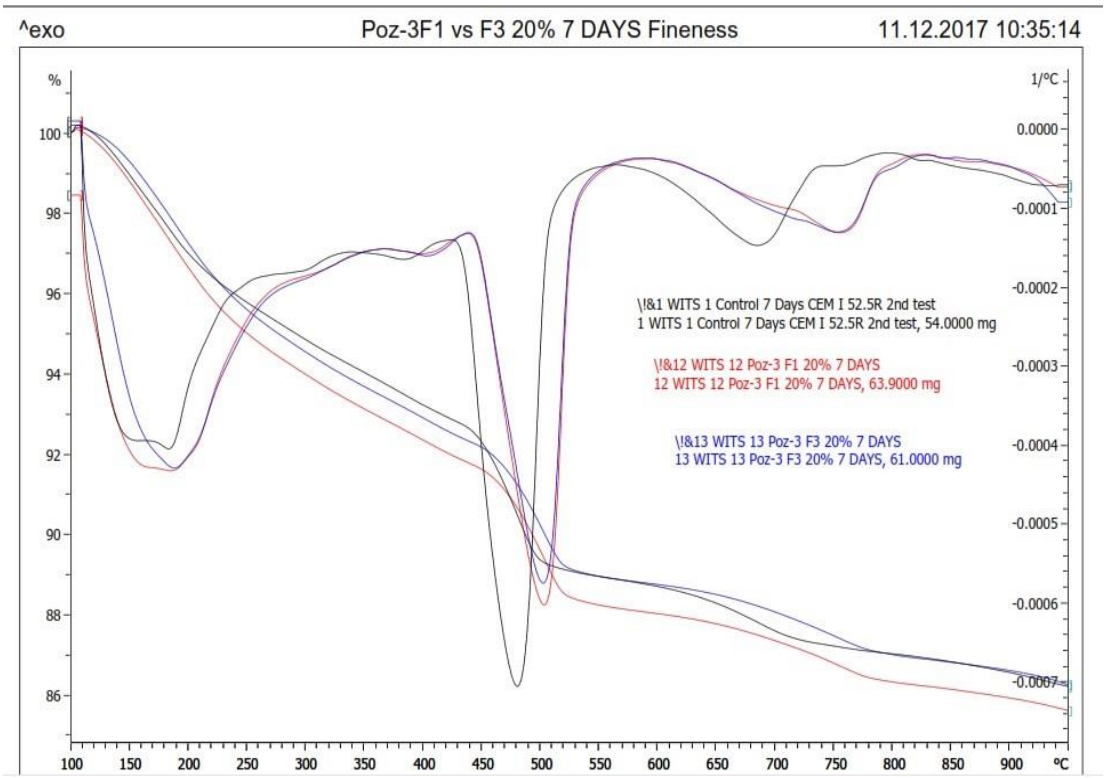

Figure 5.57: TGA/DTG graphs showing effect of fineness of Poz-3 on hydration at 7 days

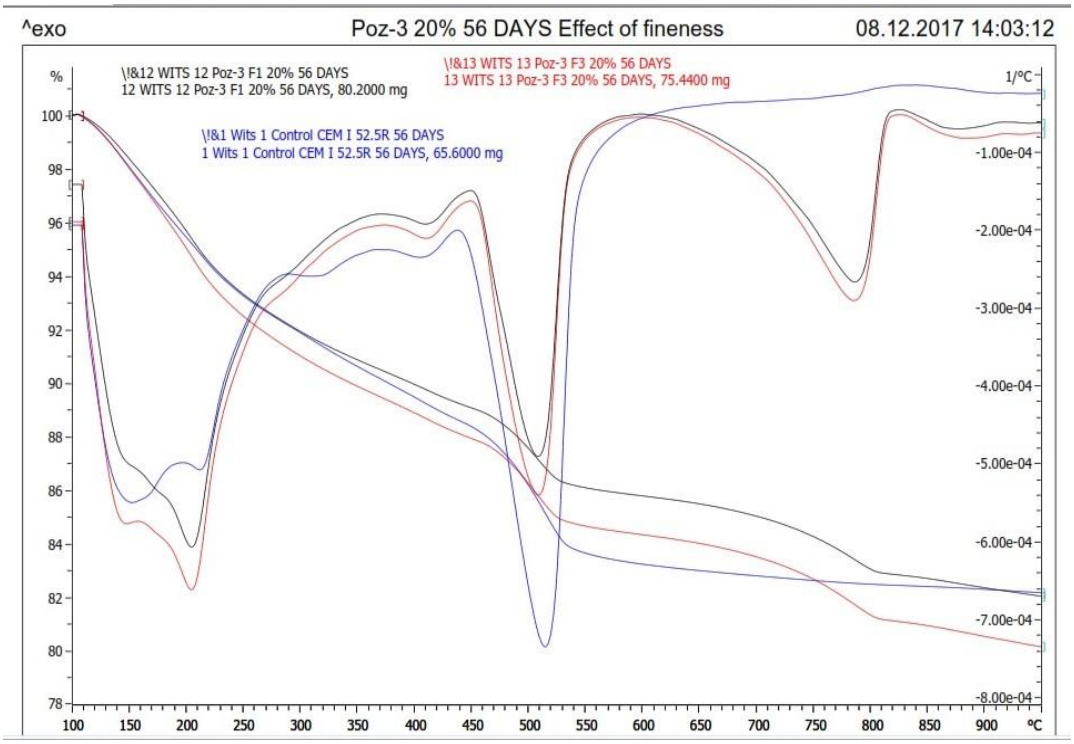

Figure 5.58: TGA/DTG graphs showing effect of fineness of Poz-3 on hydration at 56 days

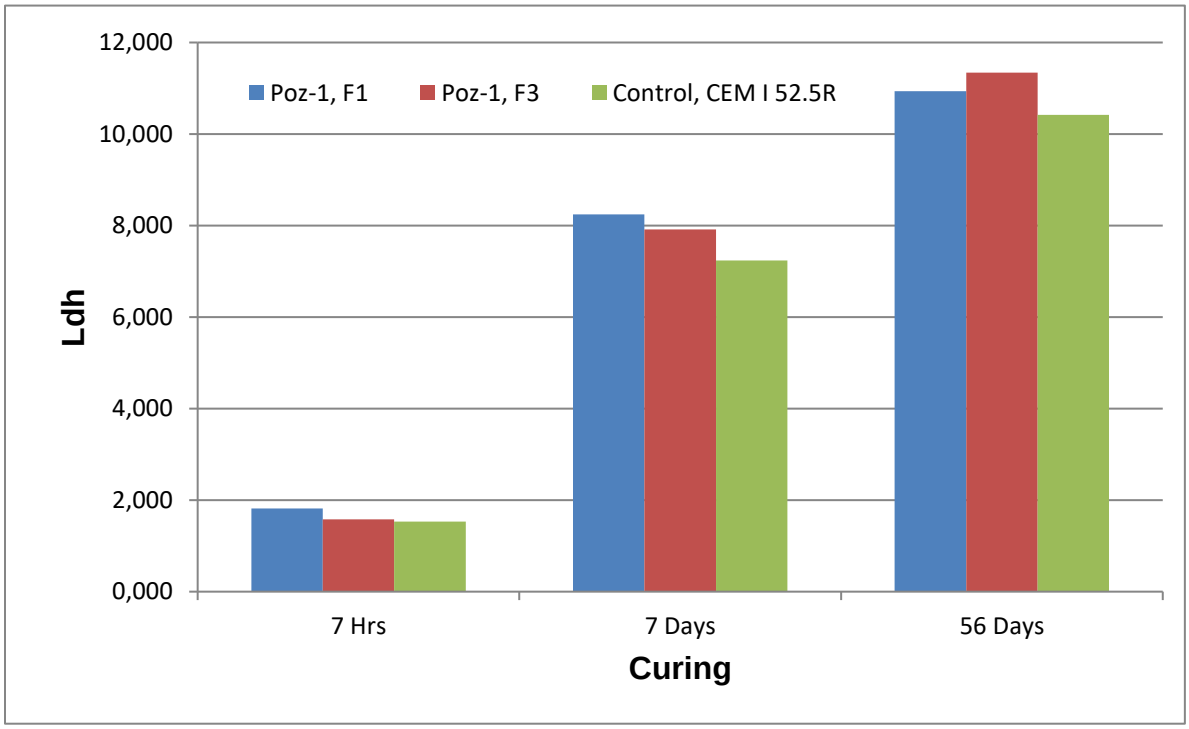

Figure 5.59: Effect of fineness on non-evaporable water (Ldh) at 7hrs, 7 days and 56 days curing for Poz-1

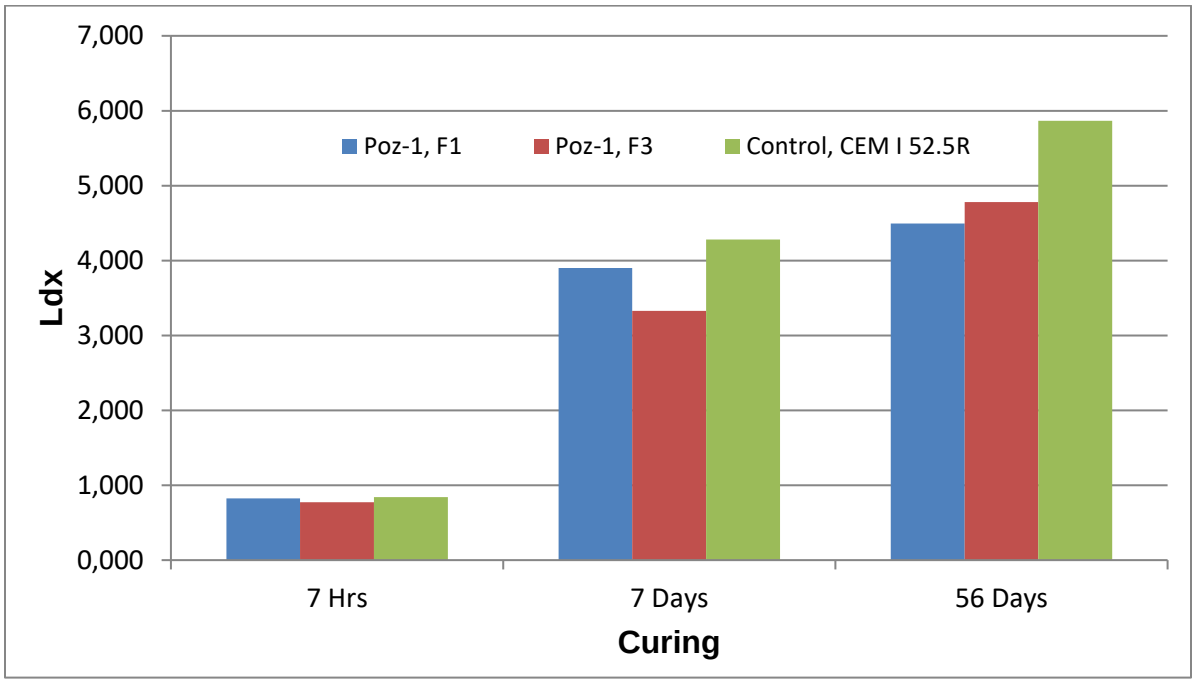

Figure 5.60: Effect of fineness on non-evaporable water (Ldx) at 7hrs, 7 days and 56 days curing for Poz-1

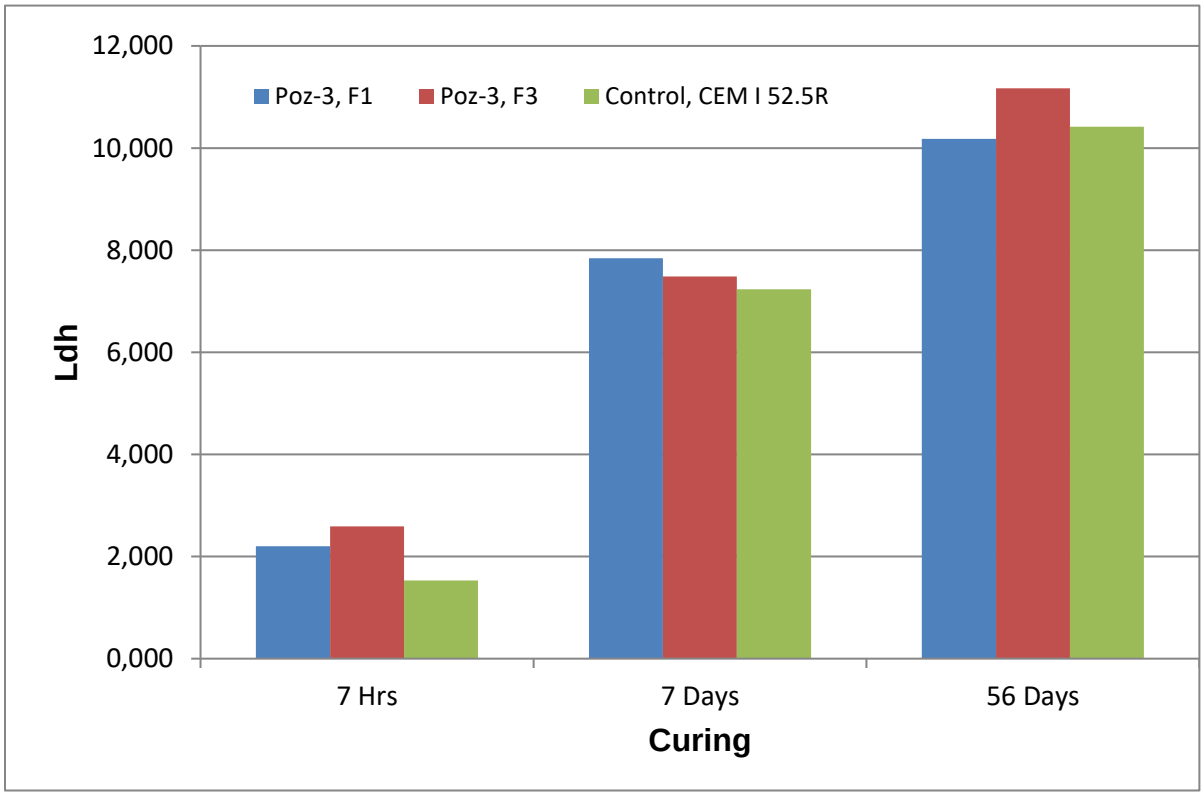

Figure 5.61: Effect of fineness on non-evaporable water (Ldh) at 7hrs, 7 days and 56 days curing for Poz-3

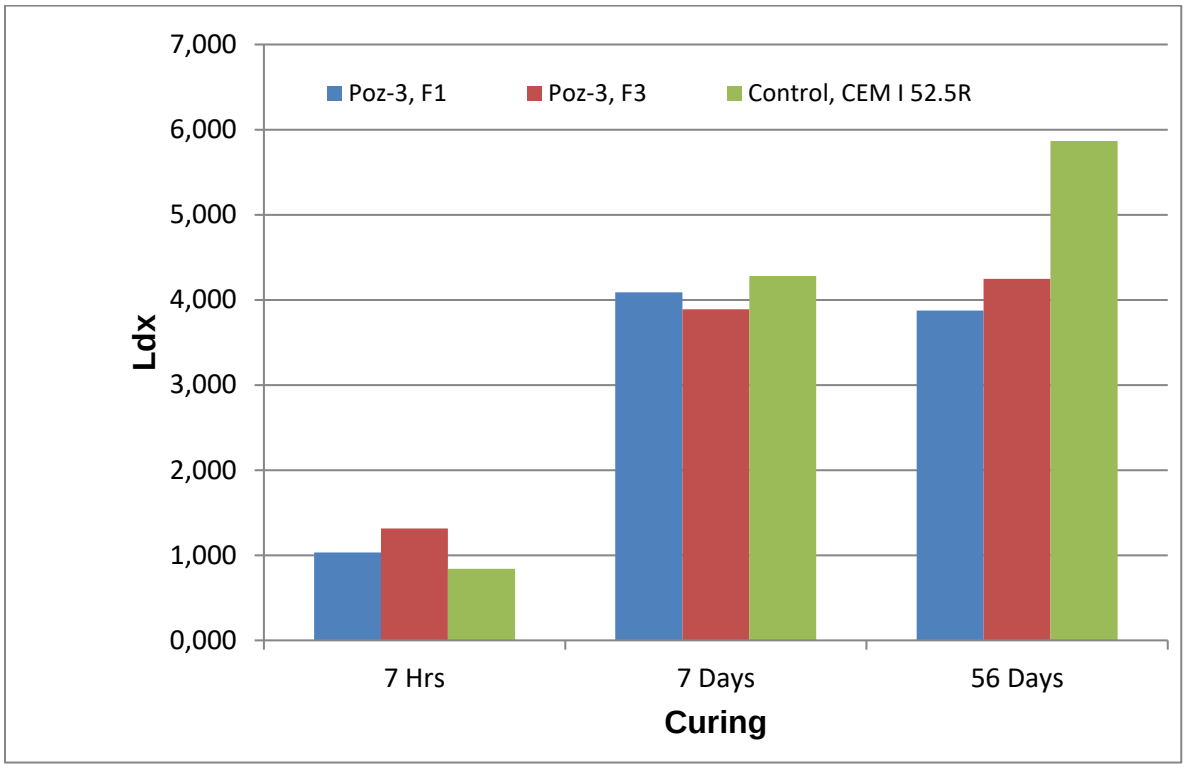

Figure 5.62: Effect of fineness on non-evaporable water (Ldx) at 7hrs, 7 days and 56 days curing for Poz-3

The different phases on a TGA/DTG graph are defined in Chapter 4 of this thesis to include the dehydration phase (Ldh) at a temperature range from 105°C to 400°C, the dehydroxylation phase (Ldx) at a temperature range from 400°C to 600°C, and the decarbonation phase (Ldc) at a temperature range from 600°C to 800°C. For the purpose of quantifying the effect of fineness of the test pozzons, the phases Ldh and Ldx that are directly related to the hydration reactions are considered. Figures 5.59, 5.60, 5.61 and 5.62 present the quantified values of Ldh and Ldx for the TGA/DTG graphs at the two fineness levels F1 and F3 as defined in Chapter 3.

It is observed that the fineness property has a time dependent effect on reaction rates and deposition of hydration products. For Poz-1, fineness is seen to have a significant influence at a later stage, 56 days, the finer pozzolan leading to deposition of more hydrates and increase in consumption of the CH precipitates. Different studies show pozzolanic reactions to progress slowly compared to hydration reactions and, as a result, are more prominent after 28 days of curing (Mehta and Monteiro, 2006;

Massazza, 1993; Massazza, 2002). It is considered that the later consistency in hydration products assemblage with fineness is governed by the pozzolanic reactions.

Poz-3 showed a consistent dependence on fineness with the test pozzolans of a higher fineness level leading to increased volume of hydration products at 7 hours and 56 days of curing. There is an inverse relationship at 7 days for Poz-3 which is consistent with the results of Poz-1. This trend is also observed in the other properties of blended cement (strength and heat of hydration) studied in this thesis. The peculiar trend confirms presence of retarding reaction mechanisms at early stages of hydration which, probably due to other parallel hydration and pozzolanic reaction mechanisms, are relatively minimized after 7 days of hydration.

5.3.4 Alaysis of replacement levels effect on heat of hydration

Detailed results for the effect of replacement levels of the test kamafugites and carbonatites on heat of hydration are saved under the file name “heat of hydration” on the DVD submitted together with this thesis. The results have been summarized as presented in Figures 5.63 and 5.64. A time dependent influence of replacement level on heat of hydration is observed in both the kamafugites and carbonatites. For the period from the start of the experiment up to 14 hours, the heat of hydration increased with increase in replacement level of both Poz-1 and Poz-3. The trend changed to a decrease in heat of hydration with increase in replacement level at 24 hours reaching stability at 120 hours. The trend in heat of hydration in the first 14 hours shows Poz-1, a carbonatite, to be slightly less reactive than Poz-3, a kamafugite. The 14-hour trend in Poz-1 is considered to increase given that increase in replacement level reduces cement content yet there is no indication in reduction in the amount of heat released for the total paste system at all replacement levels. The change in trend at 24 hours appears to stabilize at 120 hours advancing a parallel trend with the 170 hours data which indicates that the earlier reaction mechanisms are suppressed completely after 120 hours.

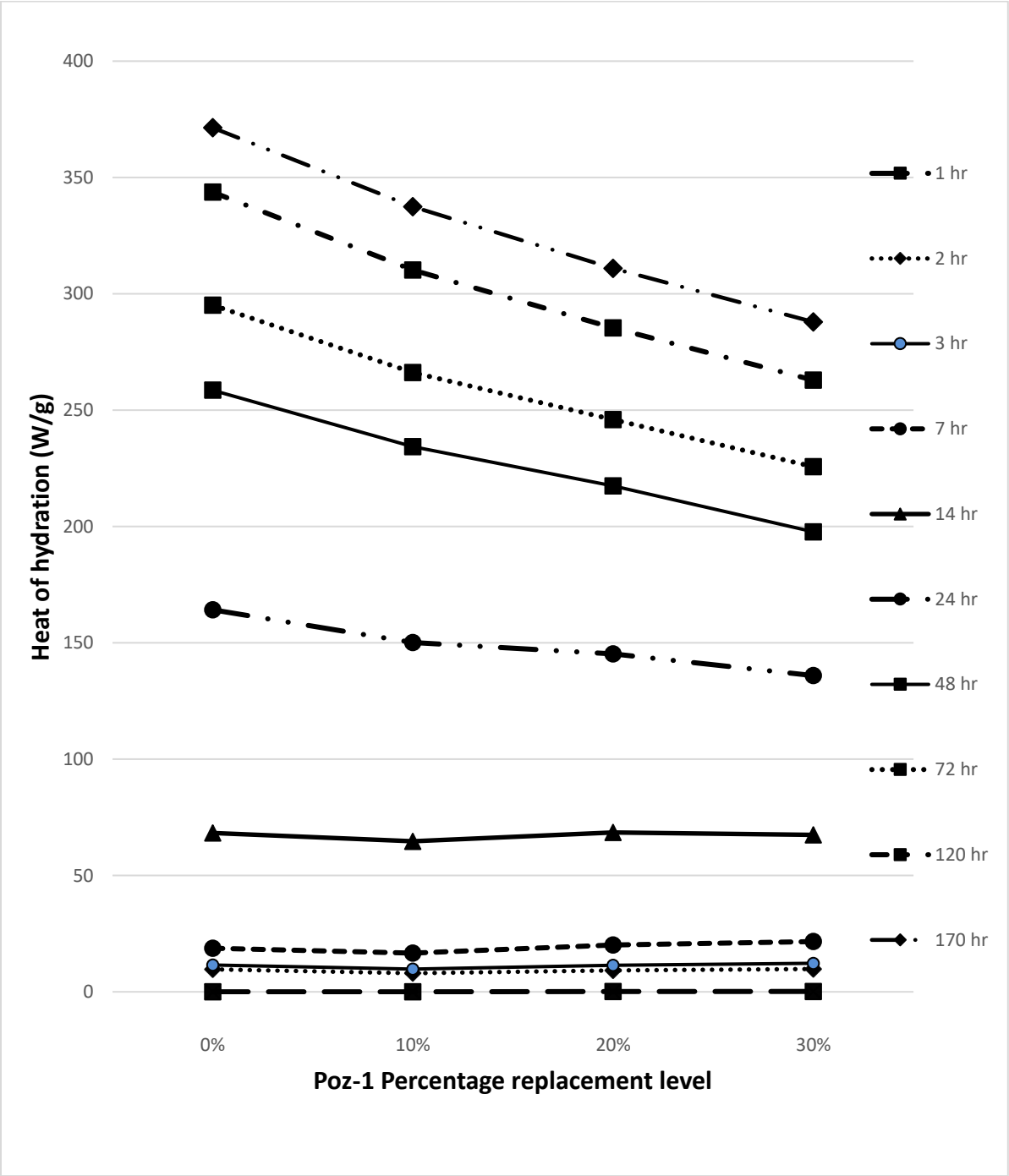

Figure 5.63: Effect of replacement level on heat of hydration for Poz-1

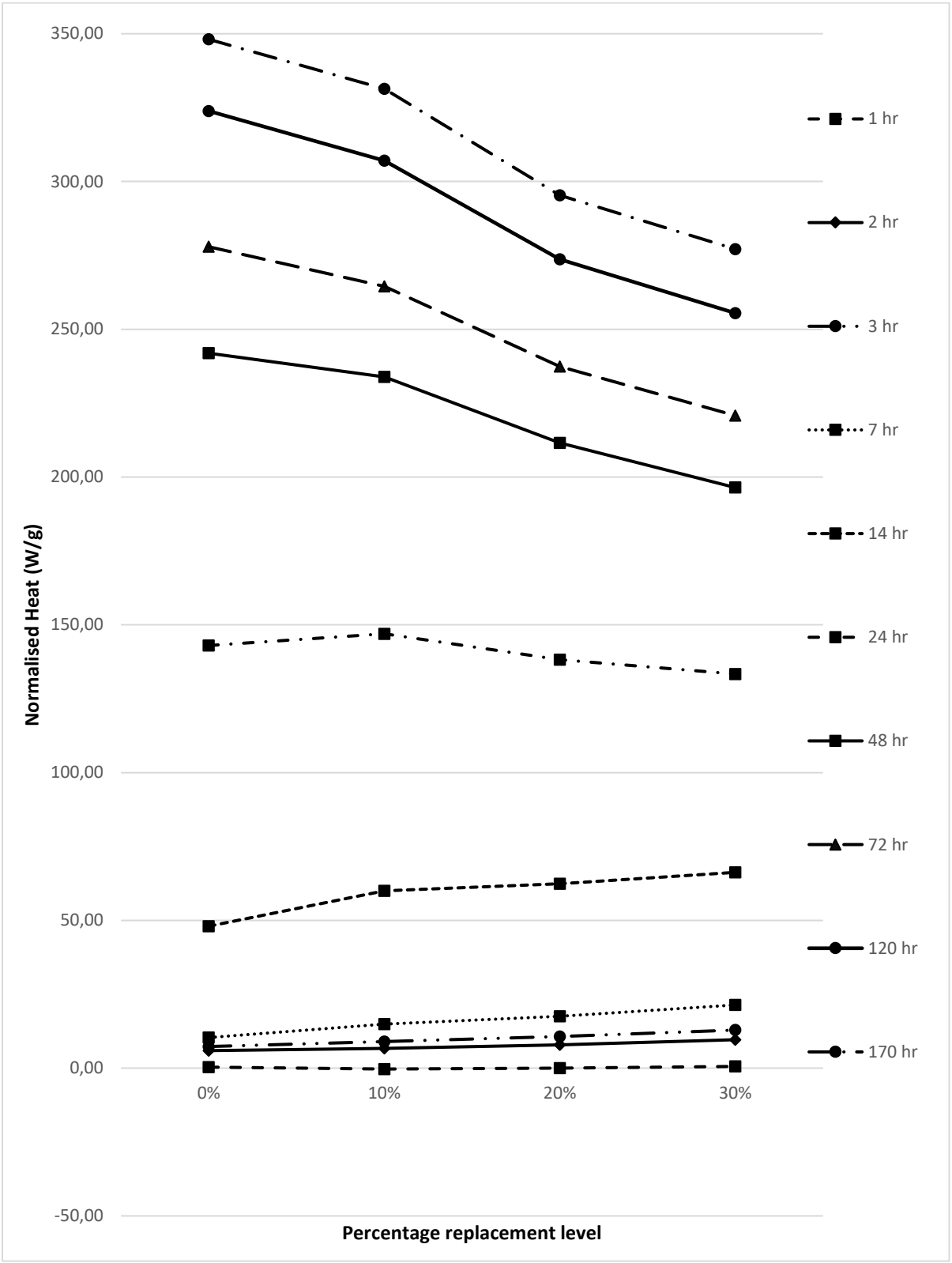

Figure 5.64: Effect of replacement level on heat of hydration for Poz-3

5.3.5 Analysis of replacement level effect on compressive strength

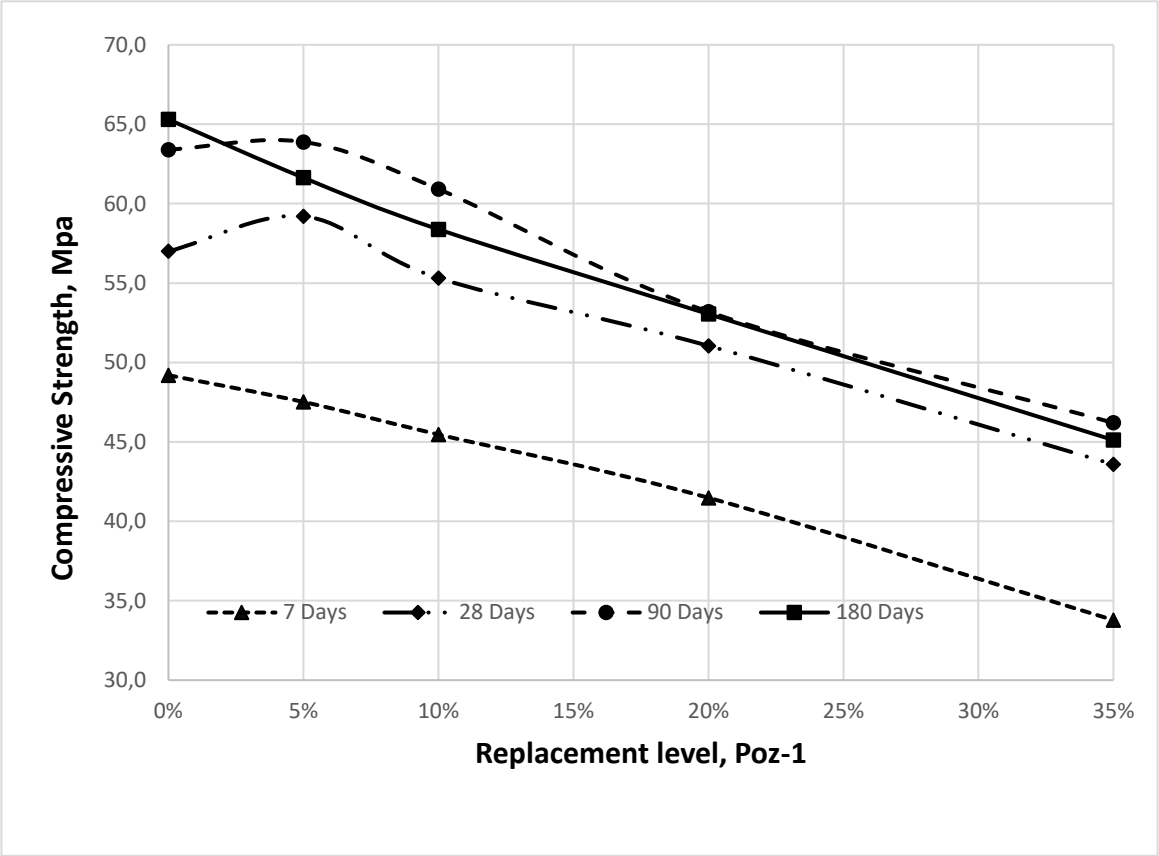

Figure 5.65: Effect of replacement level on compressive strength for Poz-1

Figures 5.65 and 5.66 show the effect of replacement level of test pozzolans on strength development. Partial replacement of cement with test pozzolans led to a general trend of proportional reduction in compressive strength. There is a slight gain in strength with 5% replacement of Portland cement with test pozzolans but this is only sustained up to 90 days. For Poz-1, the 7-day strength results show close to a perfect proportional reduction (a linear relationship) in strength with increase in percentage replacement level of cement with test pozzolans. This linear relationship might indicate a lack of hydration products due to poor pozzolanic performance of the test pozzolan at 7 days. The trend, however, changes indicating some level of pozzolanic reactivity at 28 and 90 days of curing. There is a conversion reaction that appears to peak at 10% replacement level for both samples. The conversion effect is manifested by the compressive strength values at 180 days of curing being less than those at 90 days of curing for blended cements. The exhaustion of hydration reactants in the cement

system after 90 days of curing magnifies the conversion mechanisms leading to lower compressive strength results at 180 days for all the replacement levels.

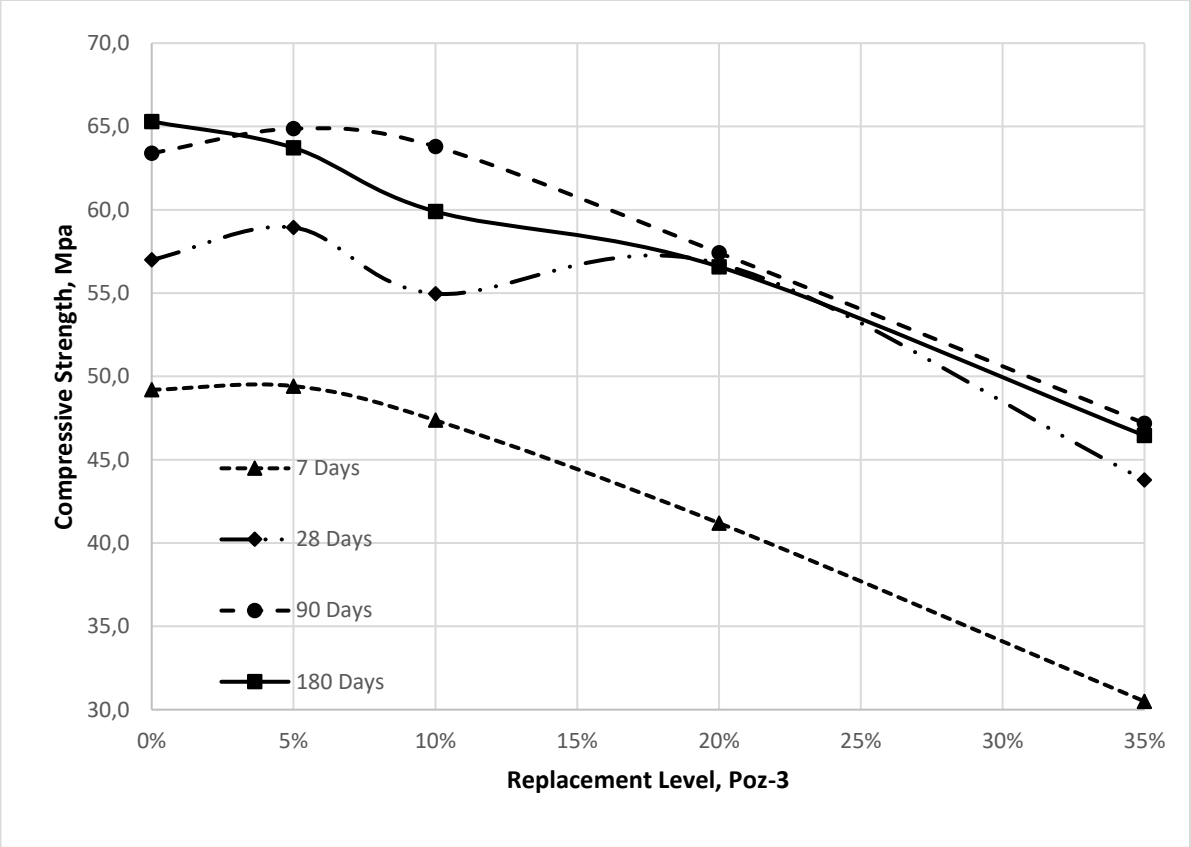

Figure 5.66: Effect of replacement level on compressive strength for Poz-3

5.3.6 The role of compositional factors

It is now known that the filler effect varies with different minerals in SCMs with calcite minerals providing the highest concentration of precipitates as observed by Berodier and Scrivener, 2014 and Oey et al., 2013. The calcite enrichment in both the carbonatite and kamafugites is considered a compositional factor in the effect of the test pozzolans on heat of hydration as discussed in Section 5.2 of this thesis.

The second compositional factor considered in this study is the high alkali content of carbonatites and kamafugites. Kamafugites and carbonatites are ultramafic to mafic rocks with relatively very high content of water soluble alkalis and enrichment in carbonate minerals as explained by the high CaO and LOI values in Table 3.3. Section 5.2 of the current chapter presents the dependence of the hydration acceleration effects

on both alkalis and the carbonate minerals in the test pozzolans. The effect of alkalis is further supported in Ogawa, Uchikawa and Takemoto, 1980. Ogawa, Uchikawa and Takemoto,1980 explains the hydration acceleratory effect of alkalis (Na+, K+ etc) as a deductive consequence of the water-soluble alkalis that accelerate the dissociation of water molecules, which in turn accelerate the dissolution of silica and alumina ions in the system, and the precipitation of hydration products that follows. This same reaction mechanism carries the explanation for early depletion of pozzolanic reactants in the kamafugites and carbonatites. Ogawa, Uchikawa and Takemoto, 1980, observed that alkali enriched pozzolans lost the hydration products precipitate from their particle surfaces, a phenomenon the authors attributed to weak adhesion that gives way to osmotic pressure buildup due to differences in ionic concentrations between the inner and outer layers of the surrounding precipitate. As a consequence, the hydrates layer slips off the surface of the pozzolan particles giving more exposure and leading to more dissolution of alkalis into the system and the resulting dissociation of water molecules and resulting protonic attacks sustaining the acceleration of hydration and pozzolanic reactions.

It is considered in the current work that increase in replacement level would increase the filler effect and alkali content in the system and increase in acceleration of hydration of cement and the dependent pozzolanic reactions. The two mechanisms are more pronounced in the early hydration stages and, as observed in the results on the effect of replacement level of test pozzolans on heat of hydration, explain the increasing trend between heat of hydration and replacement level as observed in Figures 5.63 and 5.64. This increasing trend in heat of hydration with increase in replacement level is reversed after 14 hours from the start of hydration. The reason for this is possibly because the hydration reaction at this stage is diffusion controlled. At 14 hours, the hydration products will have evolved and become thick enough to limit ionic movements. The normal cement hydration and pozzolanic reaction processes dominate after 14 hours and, as a consequence, the cement content in the system determines the energy budget, higher replacement level resulting in less heat of hydration.

The hydration process transitions through two stages, first dissolution and later diffusion. Dissolution mechanisms are controlled by solubility equilibria of the different

ions in the systems and as a consequence, less dependent on particle size within a fineness range. However, diffusion-controlled hydration processes are dependent on particle size, larger particles reacting slower than smaller particles due to moisture movement inhibition caused by hydration products at the surfaces of these particles.

5.4 Chapter summary

In the current chapter, kamafugites and carbonatites are studied for their influence on early age properties of Portland cement, and their pozzolanic reactivity and influence on hydration kinetics and hydration products development. The following conclusions are drawn on the basis of results from the current experimental study.

1. The addition of kamafugites and carbonatites in Portland cement led to a reduction in the setting time, increased water demand, reduced slump flow, and had no measurable influence on soundness property of cement. The reduction in setting time was compositional given that increase in replacement level led to further reduction in setting time. Both calcite and potassic leaning alkalis were hypothesized as the cause of the observed accelerated setting behavior of kamafugites and carbonatites blended cements. Increase in water demand and reduction in slump flow were both attributed to the angular-shaped and rough surfaced particles that led to an increase in their hydrophilicity property.

2. Results show carbonatites and kamafugites, because of their low saturation of silica and alumina phases, to have less pronounced pozzolanic properties. All blended cements showed relative gain in strength to the control (CEM I 52.5 R). The relative gain in strength increased with time up to 28 days indicating either a depletion of reactive aluminosilicates in the kamafugites and carbonatites or conversion of hydrates, except for Poz-2 which shows a parallel trend in compressive strength with the control. The relative gain in strength was not sufficient to fully compensate for the replaced cement content for 7, 28, 56, 90 and 180 days of curing and showed no clear dependence on the silica content in test pozzolans. The strength activity index test, however, pass the carbonatites and kamafugites as viable pozzolanic materials for use in portland cement applications. The results also show a calcite driven conversion effect with strength results of 90 days higher than those of 180 days of

curing. The kamafugites and carbonatites accelerated early heat of hydration and chemical shrinkage.

3. The mechanisms influencing strength development at early stages (7 days) and later stages (180 days of curing) are not dominated by the calico-silicate phases in the test pozzolans. Therefore, the hydration progression and strength development mechanisms in cements blended with Kamafugites and carbonatites cannot be sufficiently appraised on the Si and CaO content in the test pozzolans. The importance of alkalis, MgO and other minerals in the test pozzolans is justified.

4. Heat of hydration results reveal that test pozzolans did not alter early hydration reactions but only had an accelerating effect on the reactions. The results show pozzolanic reactions pronounced after 36 hours from the start of hydration.

5. Chemical shrinkage of portland cement blended with kamafugites and carbonatites showed dependence on reactive silica, CaO, MgO and alkalis, reactive silica dependence proving presence of pozzolanic properties. The trend for reactive silica was similar to that of MgO indicating a possible dependence relationship. Stoichiometrically, a pozzolanic reaction does not consume exta water beyond what is in the CH reaction component and, therefore, is not a contributor to chemical shrinkage in the sense of hydration, but instead results in an increase in volume by 12% of the absolute volume of the reactants. Accordingly, it was observed that chemical shrinkage reduced with increase in reactive silica content of the test pozzolans.

6. Potassic and sodic alkalis in the test kamafugites and carbonatites showed differences in trends indicating differences in their mechanisms of interaction with cement phases, potassic alkalis leading to shrinkage compensating reactions in the cement systems while sodic alkalis trended positive with increase in chemical shrinkage.

7. Addition of SCMs in Portland cement is known to affect early hydration dynamics due to what is known as the filler effect. The chemical interaction between cement compounds and alkalis and other minerals in some pozzolanic materials can have

accelerating effects on hydration rate causing a higher early shrinkage, early heat of hydration and strength development rate. However, the importance of the filler effect is when ions in the paste system have a high mobility and starts to diminish when the cement sets. The observed chemical shrinkage trends with calcite indicated a continued activity between calcite and hydrating cement phases confirming calcite to be part of formed hydration products. Preferential hydration of aluminates to form high density carboaluminates while limiting gypsum to hydrate only to ettringite is hypothesized as the contributor to the observed chemical shrinkage trends.

8. A numerical model for quantification of chemically bound water in a pozzolanic reaction of blended cement pastes is proposed. The equation is a modification based on established TGA models for degree of hydration estimation. The model was used in characterisation of pozzolanic activity of the test pozzolans.

9. Results from applied methods for testing pozzolanic behavior of kamafugites and carbonatites, including the chemical shrinkage test, heat of hydration test, thermogravimetric analysis test (TGA), and strength development test were compared for similarities. While the strength, TGA, heat of hydration and chemical shrinkage registered positive and correlated results, the Fratini test (EN 195-5) failed these materials because of flow of Ca^{2+} ions into the solution from the test pozzolans themselves. The test pozzolans are indicated to have a high water-soluble Ca^{2+} ions which disables the validity of results from the Fratini test. The chemical shrinkage test following dilatometry technique is proposed as a practical test for pozzolanic activity of supplementary cementitious materials in the less developed regions of Africa given the ease and low costs required for the experimental setup.

10. Calcination of kamafugites and carbonatites leads to improved rating on the ASTM C618 minimum composition requirement of 70% for the sum of silica, alumina and iron oxides for a volcanic material to be considered pozzolanic enough for application in portland cement concrete.

11. The addition of kamafugites and carbonatites as natural pozzolans in Portland Cement accelerated setting time, early heat of hydration and increased water demand, all early age properties which were reduced by calcination at 825°C. It is perceived that the

carbon and potassic elements in the test kamafugites and carbonatites are responsible for the hydration accelerating effect observed.

12. Calcination resulted in a 3.4% and 7.6% gain in compressive strength for Poz-1 and Poz-3 respectively at 180 days of hydration. The observed gain in strength as a result of calcination is attributed to increase in the relative density of the test natural pozzolans and not from pozzolanic performance as CH consumption by the test pozzolans is reduced by calcination. The presence of Kaolinite, a secondary mineral that exhibits pozzolanic properties on thermal destabilization, is advanced as the reason for the higher gain in strength observed in Poz-3.

13. Calcination had no detectable effect on the soundness property of Poz-3. However, there was an increase in Le Chaterer's expansion for Poz-1 and Poz-2 though within the range of maximum permissible limits. The presence of relatively large quantities of CaO as a result of calcination of the carbonatite is considered as the cause for increase in expansion due to CaO hydration.

14. Calcination of the carbonatite and kamafugite samples at 825°C effectively decarbonated the test pozzolans. There was no significant effect on other minerals in the test pozzolans. As a result of the decomposition of calcite, the concentration of Augite, a mineral of the pyroxene family, was raised to detectable levels.

15. There is no variation in heat of hydration with fineness for up to 170 hours (7 days) indicating that the specific surface features of the test natural pozzolans, though are considered drivers of the reaction mechanisms running in the early stages of hydration up to 7 days, enable both acceleratory and conversion mechanisms concurrently. This trend was validated by the TGA results of blended cements for up to 7 days of curing.

16. Results show a time dependent variation in heat of hydration which increases with replacement level for the first 14 hours before decreasing. Compressive strength results show dependence on level of replacement and fineness which was pronounced until 90 days, peaking at 28 days. Increase in replacement level resulted in a general reduction in compressive strength.

17. Dependence of compressive strength on fineness is observed to peak at 28 days and ceases in significance at 90 days of curing. Poz-1 showed weak dependence of strength on fineness indicating other reaction mechanisms that are more pronounced than influence of fineness. It is possible that the fineness parameter dominates pozzolanic reactions and its sensitivity is diminished when samples are less pozzolanic. It is possible to characterize pozzolanic performance through varying their fineness levels. The fineness property is sensitive to the pozzolanic reactivity of test pozzolans as revealed in the heat of hydration and compressive strength results.

18. On the effect of replacement level on strength, an increase in percentage replacement of CEM I 52.5R with test pozzolans resulted in reduction in long tern strength. There is a gain in strength above the control sample for a 5% replacement level, however, this gain in strength is lost after 90 days of curing. All other samples blended with test pozzolans gave strength values that were less than those of the control at all ages up to 180 days.

19. There is a reduction in strength between 90 and 180 days of curing for all samples blended with test pozzolans confrirming presence of conversion reactions. The heat of hydration results reveal that the conversion reactions are established in the kamafugites and carbonatites blended portland cement from the start of the hydration reactions with reaction rates dependent on both fineness and replacement levels. Increased fineness resulted in increased rates of conversion reactions. The conversion effect is observed to peak at 10% replacement level and to reduce with increase in replacement level, a condition which promotes use of the test pozzolans in higher volumes. The reduction of cement content seems to influence the extent of reactions that lead to the conversion effect. Compressive strength test results, however, sustain the ASTM C618 and BS 3892 minimum requirement for pozzolanic portland cements indicating that the carbonatites and kamafugites can be gainfully applied in cement production from the resource and energy economy perspectives.

Based on the above conclusions, cements blended with kamafugites and carbonatites as natural pozzolans therefore present interesting perspectives on how paste microstructure and cement durability properties might be influenced. The analysis also

confirms a need for a different approach in characterizing kamafugites and carbonatites as pozzolans in Portland cement. The calcite enriched materials fail on composition requirements stated in established standard specifications. The reaction mechanisms associated with the test carbonatites and kamafugites are acceleratory and more pronounced in the early stages of the hydration reaction. Insights on the possible drivers of these reaction mechanisms, especially the role of calcite and alkalis, are discussed. The first hours of hydration have a fundamental influence on microstructure properties and distribution and, certainly, the accelerating effect would give insights on how presence of carbonatites and kamafugites affect composition and distribution of hydration products in paste microstructure.

CHAPTER 6

THEORETICAL MODELING OF KAMAFUGITES AND CARBONATITES ACTIVITY IN HYDRATING PORTLAND CEMENT

6.1 General

SCMs in Portland cement paste advance modifications that go beyond pozzolanic reactions (Escalante-Garcia, 2003; Ballim and Graham, 2009; Berodier and Scrivener, 2014; Scrivener et al., 2015). Their influences in blended Portland cement systems are therefore not effectively characterized by the pozzolanic activity property. Moreover, existing characterisation methods do not separate the pozzolanic contribution of SCMs from other mechanisms in blended cement that are reported in detail in Chapter 2 of this thesis. The current Chapter presents thermogravimetric analysis based theoretical models that estimate the degree of hydration (α), the degree of pozzolanic activity (β) and the net SCM benefit (λ) of blended Portland cement as characterisation parameters to isolate the different influences kamafugites and carbonatites and other SCMs have on hydrating cement paste. Numerical models advanced by previous authors have been reviewed elsewhere (Chapter 2 of this thesis) and are tested for their effectiveness in predicting degree of hydration of blended Portland cements. New numerical expressions are then proposed to address the gaps established in the previous models. The developed numerical expressions are further applied in analysis of the results presented in Chapter 4 of this thesis to develop prediction models for strength and chemical shrinkage of cements blended with kamafugites and carbonatites. The proposed models based on compositional parameters of hydrating pastes as predictor variables are tested against compressive strength and chemical shrinkage results for validation. Insights into hydration mechanisms of Portland cements that are blended with kamafugites, and carbonatites are advanced. Because the mechanisms of interaction between SCMs and Portland cement go beyond the pozzolanic reaction, the models are advanced as plausible tools in characterizing the total contribution of SCMs in Portland cement systems.

6.2 Quantitative expressions for the degree of hydration (α).

The previous models discussed in Chapter 2, section 2.6, of this thesis guided the current work in setting parameters of the proposed theoretical models. The current work modifies the total inclusion of the dehydroxylation phase in the calculation of the degree of hydration since CH is a residual byproduct of the hydration of the silicate phases as indicated in Equations 6.1 and 6.2.

$C_3S + H_2O \rightarrow C\text{-}S\text{-}H + 3CH$ Equation 6.1

$C_2S + H_2O \rightarrow C\text{-}S\text{-}H + CH$ Equation 6.2

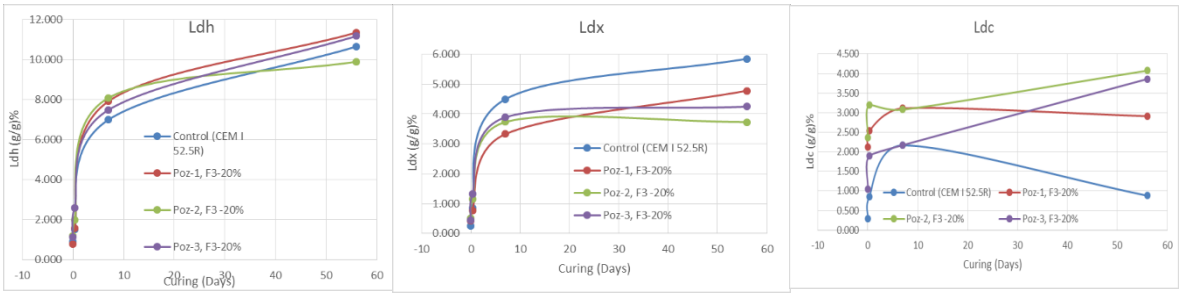

Figure 6.1: Growth of the dehydration (Ldh), dehydroxylation (Ldx) and decarbonation (Ldc) phases for Portland cement blended with kamafugites and carbonatites at 20% replacement level.

It is considered that the CH composition, a derivative of the degree of hydration of the alite and belite phases in cement, has no significant contribution to the important properties of hydrated paste (Mehta and Monteiro, 2001). Therefore, considering the chemically bound water from the dehydroxylation phase as a cumulative contributor to the prediction of the degree of hydration limits the previous models in predicting the different micro and macro properties of hydrating cement paste. Indeed, Figure 6.1 presents results generated from the current study that show inconsistencies in trends between the *Ldh, Ldx* and *Ldc* phases. It is an indication that, even, without regard to their characteristic contribution to the paste strength properties, the different phases cannot be cumulatively combined in a linear trend. The dehydroxylation phase in estimation of degree of hydration should therefore account only for the CH component that contributes to the pozzolanic and hydration reactions. This, therefore, creates a need to isolate the contribution of the pozzolanic

and carbonation reactions and the contribution of Ca^{2+}, alkalis and other reactants in the SCM (the net SCM activity). The contribution here is a quantitative expression that is proposed to estimate the degree of hydration that considers responsiveness to the actual mechanisms governing hydration, chemical shrinkage and strength development of cement pastes.

Accordingly, Papadakis, Antiohos and Tsimas, 2002, advanced a model that predicts compressive strength dependent on the C-S-H phase in a hydrating cement paste following the equation below.

$$f_c = mCSH \qquad \text{Equation 6.3}$$

Where f_c represents the compressive strength, m is a coefficient governed by mix composition properties, and CSH represents the density of C-S-H in a hydrating paste at a given time.

The quantitative expression for the degree of hydration is therefore proposed as follows.

$$\textbf{Degree of hydration } (\propto) = \frac{(Ldh_{cem} + Ldh_a)}{(1-\tau)W_{B\propto}} \qquad \text{Equation 6.4}$$

$$Ldh = Ldh_{cem} + Ldh_a + ((Ldx_{cem} - Ldx_{Poz}) - 0.41(Ldc_t - Ldc_0)) \qquad \text{Equation 6.5}$$

$$\tau = Ldx_{Poz} + 0.41(Ldc_t - Ldc_0) \qquad \text{Equation 6.6}$$

Where Ldh is the mass of chemically bound water attributed to the dehydration phase in the thermal decomposition TGA profile of an SCM blended sample. Ldh_{cem} is the mass of chemically bound water attributed to the dehydration phase of the control sample (plain Portland cement) on the TGA thermal decomposition profile at the same curing time as the SCM blended sample. Ldh_a is the mass component of Ldh that is associated with the non-pozzolanic SCM effects. Ldx_{cem} and Ldx_{Poz} represent the mass loss to dehydroxylation of the control sample (plain Portland cement) and blended sample respectively, the difference accounting for the CH assumed consumed in the pozzolanic and carbonation reactions. Ldc_t and Ldc_0

represent the mass loss to decarbonation (the component of the CH that had been carbonated) for test sample at the test time and at anhydrous state respectively, a quantity that is discounted to give a more accurate estimate of CH consumed in a pozzolanic reaction. $W_{B\propto}$ represents chemically bound water at complete hydration (infinite time) with $\tau W_{B\propto}$ being a correction coefficient to discount chemically bound water due to CH deposited in the paste microstructure that is not consumed in the pozzolanic and hydration reactions.

The parameter Ldh_a characterizes the acceleratory effects of mineral admixtures in Portland cement.

All the input variables, except those of the decarbonation phase, are normalized to cement content.

Since the pozzolanic reaction does not take up water beyond the quantity in the CH part of the reactants, the pozzolanic reaction is not characterized as a hydration reaction and, therefore, bound water due to the pozzolanic reaction is not considered in estimation of degree of hydration. It is however important that we appreciate the equilibrium shift caused by SCMs in blended cement pastes. The consequence of this equilibrium shift is hypothesized to influence hydration progression and is considered within the Ldh_a quantity measured.

6.3 Quantitative expressions for the degree of pozzolanic activity (β).

The silicate phases in plain Portland cement react with water in a hydration reaction to produce C-S-H and CH. The quantity of C-S-H and CH hydration products is dependent on the chemical composition of the cement, degree of hydration and hydration confinement due to depletion of water or a lack of space for deposition of hydration products (Scrivener et al, 2015). When cement is blended with siliceous admixtures, the CH precipitate from the cement hydration reacts with the silica in the mineral admixture to form extra C-S-H hydration products following the pozzolanic equation in Table 5.2, Chapter 5 of this thesis. The pozzolanic equation shows that 3 moles of CH combine with 1 mole of reactive silica in a pozzolan to produce C-S-H. The stoichiometric analysis in Table 5.2, Chapter 5 further shows that, for 1 gram

of CH, 0.54 grams of silica is required for a pozzolanic reaction. Accordingly, the requirement for silica content from the pozzolan can be quantified stoichiometrically from the silicate phases in cement.

Mehta and Monteiro, 2001, give an estimate of 50-60% of C-S-H that result in a deposition of 20-25% CH content by volume in a completely hydrated cement. A conservative figure of 25% has been taken for the purpose of this submission but stoichiometric quantification can be done on specific cement types for quantification of clinker composition and the resulting hydration products. The standards (EN197-1, 2000) present a large range of variability in the chemical composition of ordinary Portland cement and, as such, the volume of hydration products will vary depending on the unique cement composition. The pozzolanic activity should therefore be rated based on the cement type considering that different cements produce different quantities of CH available for pozzolanic reactions.

Considering 25% as the volume of CH hydration products in a unit volume of completely hydrated cement, assuming that all the CH produced in the hydration reaction is available to react with silica, the reactive silica requirement is calculated as follows.

$$\text{CH: Si combination ratio from the pozzolanic equation} = \frac{1}{0.54} = 1.85 \quad \text{Equation 6.7}$$

$$\text{Si requirement for } 25\%\ \text{CH} = \frac{25\%}{1.85} = 13.51\% \quad \text{Equation 6.8}$$

As is demonstrated above (Equations 6.7 and 6.8), the Si requirement in volume is less than the CH content. The 13.51% represents the reactive silica content of a pozzolan that is required to consume all the CH produced by plain Portland cement. The setup for such a possibility can only be achieved if the pozzolan replaces the aggregate part of concrete. However, the ecological and economic interests of using pozzolans in concrete promote its use as an SCM. Replacement of cement with SCMs reduces the amount of clinker compounds responsible for production of the CH hydrate. As a result, the silica content requirement reduces with increase in cement replacement level, a trend that favors pozzolans with low silica content for

application in high volume replacement of cement. Both the trend of change in replacement level and variation of CH content are assumed to be linear trends with a coefficient of proportionality of one.

The Si volumetric quantity presented in Equation 6.8 is the absolute quantity required for exhaustion of the CH produced in a plain Portland cement with a composition that results into 25% volumetric quantity of CH hydrates. This work therefore considered the absolute Si value as the base factor for indexing pozzolanic performance of SCMs (kamafugites, carbonatites and others). The quantitative expression for estimation of the degree of pozzolanic activity is therefore stated as follows (Equation 7.9).

$$\boldsymbol{\beta} = \frac{\mathbf{1.85}\times \boldsymbol{W_{Poz}}}{\boldsymbol{W_{CH\infty}}\times(\mathbf{1}-\boldsymbol{x})} \qquad \text{Equation 6.9}$$

Where β represents the degree of pozzolanic activity, W_{Poz} the mass of chemically bound water of CH consumed in the pozzolanic reaction (Equation 6.10), $W_{CH\infty}$ the mass of chemically bound water of CH at complete hydration for a plain Portland cement sample (reference cement sample), and x the replacement ratio of the test pozzolan, $1 > x > 0$.

$$\boldsymbol{W_{Poz}} = (\boldsymbol{Ldx_{cem}} \times \frac{\propto_{\boldsymbol{poz}}}{\propto_{\boldsymbol{cem}}} - \boldsymbol{Ldx_{Poz}}) - \mathbf{0.41}(\boldsymbol{Ldc_t} - \boldsymbol{Ldc_0}) \qquad \text{Equation 6.10}$$

Where Ldx_{cem} represent the chemically bound water due to the dehydroxylation phase for the reference cement sample, Ldx_{Poz} is chemically bound water due to the dehydroxylation phase of the sample blended with a test SCM, $\frac{\propto_{poz}}{\propto_{cem}}$ is the standardization ratio based on the degree of hydration to adjust for the hydration acceleration due to the presence of SCMs in the blended cement sample. 0.41 is a stoichiometric coefficient for quantification of CH water lost to carbonation, and $(Ldc_t - Ldc_0)$ is the mass due to decarbonation of the carbonate component from the carbonation of CH. Ldc_t is the mass loss due to decarbonation at curing time t while Ldc_0 is mass loss due to decarbonation of the same sample at anhydrous state (before addition of water).

Estimation of chemically bound water in CH for the assumed 25% CH content in a paste at infinity time is guided by the stoichiometric factors presented in EI-Jazairi and lllston, 1977, and the density values presented in Balonis and Glasser, 2009, as follows (Equation 5.11).

$$\boldsymbol{W_{CH\infty}} = \frac{\boldsymbol{CH}\times\mathbf{2.251}}{\mathbf{4.11}} \qquad \text{Equation 6.11}$$

Where CH represents the volumetric content of CH as a percentage of the hydration products at complete hydration of cement, 2.251 the density of CH, and 4.11 a stoichiometric factor for quantification of chemically bound water in a CH mass.

Assumptions made:

1. For the purpose of the theoretical model development, it is assumed that the pozzolanic reaction of the kamafugites and carbonatites is only between its reactive silica component and the CH.

2. That all the CH produced in the hydration of the silicate phases in the Portland cement is available to participate in the pozzolanic reaction.

3. That the pozzolanic reaction does not bond water beyond what is already bonded in the CH component of the reactants (Papadakis, 1999; Escalante-Garcia, 2003).

4. That all the other reactions between the mineral admixtures and cement phases and their hydration products, apart from the pozzolanic reaction, bond water.

The degree of pozzolanic activity (β) is a quantitative expression that considers the cement replacement level, the change in the CH producing phases in cement with a change in replacement levels, and the component of the reactive silica that is needed to react with all the CH produced.

6.4 Quantitative expressions for the net SCM benefit (λ).

The net SCM benefit represents all the modification on the degree of hydration of blended cements. It includes the acceleratory effects of SCMs, reaction

combinations between SCM phases and anhydrous cement phases, and reaction combinations between SCM phases and hydrated cement phases (pozzolanic and other reactions with hydration products). The current work proposes the estimation of the net SCM benefit as a difference between the dehydration phases of the test blended cement and the control plain Portland cement samples as follows (Equation 6.12).

$$\boldsymbol{\lambda} = \frac{\boldsymbol{Ldh_{Poz} - Ldh_{cem}}}{\boldsymbol{Ldh_{cem}}} \times \mathbf{100}\% \qquad \text{Equation 6.12}$$

Where, Ldh_{Poz} is water lost due to dehydration of the SCM admixed sample normalized to cement content.

Assumptions:

1. Carbonates are not a hydrate of blended cement

The effects of equilibrium shift due to consumption of CH by the test pozzolan are captured in the dehydration phase quantification.

6.5 Experimental work

An experimental plan was set up where kamafugites and carbonatites were blended with CEM I 52.5 R to test how their compositional and physical properties affect their performance as SCMs in Portland cement pastes and mortars. The experimental plan focused on quantification of heat of hydration, compressive strength, chemical shrinkage, and chemically bound water characterisation (TGA/DTG) with plain Portland cement (CEM I 52.5 R) as a reference sample. A detailed description of the experimental setup is provided in Chapter 4 of this thesis. A typical TGA/DTG graph for Portland cement is presented in Figure 6.2. The graph shows three main decomposition phases, the dehydration (Ldh), the dehydroxylation (Ldx) and the decarbonation (Ldc) phases (EI-Jazairi and lllston, 1977) following temperature zones of 105°C-400°C, 400°C-600°C, and 600°C-800°C respectively.

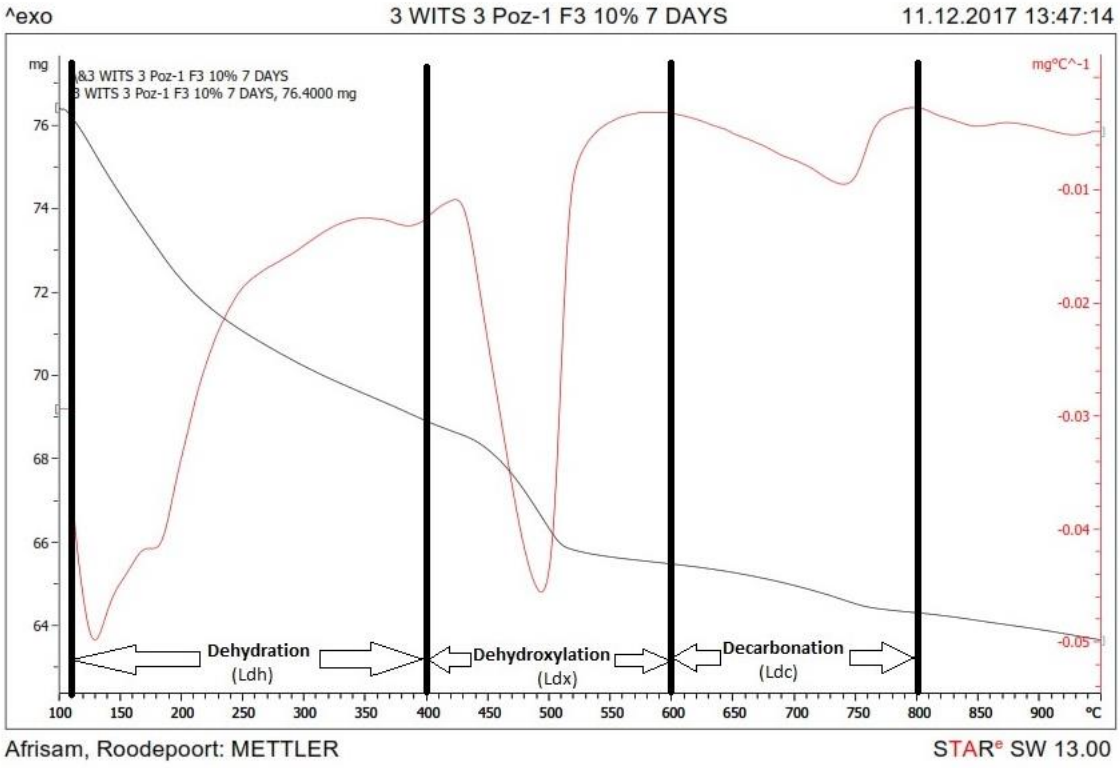

Figure 6.2: Characteristic TGA/DTG graph for a blended cement (CEM I 52.5R with a carbonatite at 10% level of replacement).

Fordham and Smalley, 1985, made a fair attempt at associating cement hydration reactions to the observed DTG peaks, and more recent studies (e.g. Lothenbach and Wieland, 2006; Lothenbach et al., 2008) give more sophisticated details of hydration products responsible for the different peaks observed at different temperatures on a DTG curve (e.g. Figure 2.6). The DTG graph is therefore substantially calibrated for identification of hydration products based on previous works by Fordham and Smalley, 1985, Lothenbach and Wieland, 2006, Lothenbach et al., 2008, and others.

6.6 Results and analysis

The results as generated from the TGA experiments are presented in a graphical form and saved under the file name “TGA data” on the DVD submitted with this thesis. Text data was also generated from the analysis software (STARe Evaluation) for the purpose of estimation of hydration products at different temperature points.

The complete set of text data is also saved on the same DVD and under the file name “TGA dataText”. Typical results are presented in Table 4.14 on page 37 of Chapter 4. The results now presented in Tables 6.1-6.5 are those processed and quantified to show the values of the degree of hydration (α), the degree of pozzolanic activity (β) and the net SCM benefit (λ). The values have been calculated following the proposed quantitative expressions in this study.

6.6.1 Effect of kamafugites and carbonatites on α and β

Table 6.1 shows results for the SCMs (kamafugites and carbonatites) blended with Portland cement at 20% replacement level. The results considered fixed values of CH and w/c at complete hydration at 25% and 0.24, respectively.

The results show the degree of hydration is higher for the blended cements than for the control. The degree of hydration of the control sample at 56 days is calculated to be 48% while that of Poz-1, Poz-2 and Poz-3 at 20% levels of replacement is found to be 65%, 52% and 65% respectively. It is considered that the acceleratory effects of blended cements (Escalante-Garcia, 2003; Ballim and Graham, 2009; Berodier and Scrivener, 2014; Scrivener et al., 2015) give it advantage over the control sample in accumulation of hydration products. The acceleratory effect has been observed in other experimental results and is attributed to mainly the carbonate minerals and the volatile alkalis in the test kamafugites and carbonatites. Moreover, the blended samples provide more space for deposition of hydration products due to the dilution effect they have on cement content (Berodier and Scrivener, 2015). Since cement replacement leaves less clinker per unit volume of a sample, cement particles are more exposed to other reactants for hydration reactions and present minimized confinement for the hydration products. Indeed, works by Berodier and Scrivener, 2015, show the degree of hydration of cement to depend on water filled capillary pores and a higher water to solid ratio to provide a higher degree of hydration. Berodier and Scrivener studied blended cement pastes at 0.4 and 0.6 water to solids ratio. The low values of degree of hydration recorded are considered to be due to the low water to cement ratio (0.35) used in the preparation of the paste samples.

Table 6.1: TGA/DTG results of blended cement at 20% replacement level for the natural sample showing α, β and λ

Test sample and variables	**Curing (Days)**	τ	Water in CH at infinity	Considered chemically bound water at complete hydration	α	β	λ	Non-pozzolanic SCM benefit
Control (CEM I 52.5R)	0	0.003	13.692	0.240	3.866	0.000	0.000	0.000
	0.3	0.011	13.692	0.240	7.388	0.000	0.000	0.000
	7	0.053	13.692	0.240	34.128	0.000	0.000	0.000
	56	0.061	13.692	0.240	48.292	0.000	0.000	0.000
Poz-1, **F3-20%**	0	0.005	13.692	0.240	5.302	-2.876	7.983	10.859
	0.3	0.011	13.692	0.240	9.560	-0.776	29.220	29.997
	7	0.046	13.692	0.240	43.488	19.689	41.465	21.776
	56	0.063	13.692	0.240	65.047	26.697	33.196	6.498
Poz-2, **F3 -20%**	0	0.006	13.692	0.240	7.832	-1.744	61.951	63.695
	0.3	0.018	13.692	0.240	14.424	-2.136	61.762	63.898
	7	0.050	13.692	0.240	46.296	19.383	44.492	25.108
	56	0.054	13.692	0.240	52.247	16.370	16.086	-0.284
Poz-3, **F3-20%**	0	0.005	13.692	0.240	7.208	-1.030	55.121	56.150
	0.3	0.020	13.692	0.240	18.645	2.345	112.124	109.778
	7	0.053	13.692	0.240	44.781	9.825	33.751	23.925
	56	0.065	13.692	0.240	64.899	23.670	31.131	7.461

The results generated in the current study also show a significant value of the degree of hydration for samples at anhydrous state. Topical works report cement reactions with atmospheric elements during storage (Gabrovšeka, Vuk and Kaučiča, 2006). The hygroscopic phases in cement absorb water from the atmosphere causing some initial hydration to take place before mixing.

The results also show the degree of pozzolanic activity to increase with age as is the characteristic of pozzolanic reactions in blended Portland cement pastes. The pozzolanic property is observed to have evolved fully at 7 days for the samples high in carbonates (poz-1 and Poz-2) while Poz-3 starts slowly but overtakes the other pozzolans at 56 days.

The net admixture benefit for the samples blended at 20% replacement level show a decreasing trend with increase in the degree of pozzolanic performance. This trend is emphasized more in the column for non-pozzolanic SCM benefits. The results show the non-pozzolanic reactions associated with the SCMs to have the highest importance at 7 hours (0.3 days) and to reduce for all the samples giving a negative value for Poz-2 at 56 days. Studies on the long term strength development of kamafugites and carbonatites blended Portland cement revealed a reduction in strength gain after 28 days and a trend later that led to degradation of hydration products and a loss of compressive strength. The trend observed in the results in Table 6.1 show this hydration products degradation effect to be governed by the reactions influencing the non-pozzolanic SCM benefits trends.

6.6.2 Effect of calcination of kamafugites and carbonatites on α and β

Table 6.2 presents results of the calcined kamafugites and carbonatites tested at 20% replacement level with Portland cement. Calcination was conducted to remove calcite and volatile alkalis to study their effects on important cement paste properties. Results in Table 4.15 and 4.16 showed calcination to be effective in decarbonating the test pozzolans and in reducing water soluble alkalis. Results presented in Table 6.2 are compared with results in Table 6.1 to show effects of calcination on both the degree of hydration and degree of pozzolanic performance, also shown in Figures 6.3 to 6.8. The results show calcination to have increased the degree of hydration of the samples that are high in calcite content (Poz-1 and Poz-2). It is possible that calcination of the test pozzolans at 850°C leads to formation of elements and compounds that will readily react in water to from extra hydration products, Ca^{2+} ions hypothesized in this case. Poz-2 showed a reduction in the degree of hydration at a later age (56 days). It is considered that the calcination reduces the pozzolanic property of the test kamafugites and carbonatites. Works on calcination of natural pozzolans as an activation method reveal both increase and decrease of the pozzolanic property (Mielenz, Witte and Glantz, 1950; Shi and Day, 2001). Given that Poz-3 is very low in calcite and high in reactive silica, the pozzolanic reactions in Poz-3 are more affected by calcination. This trend is further emphasized in Figures

6.6, 6.7 and 6.8. The Figures 6.6 to 6.8 show calcination to have suppressed the pozzolanic activity of the test kamafugites and carbonatites. The acceleratory effect of calcite was undermined by calcination and, as a consequence, less CH was available in the system to facilitate a higher rate of pozzolanic reaction.

Table 6.2: TGA/DTG results of blended cement at 20% replacement level for the calcined kamafugites and carbonatites

Test sample and variables	**Curing (Days)**	τ	Water in CH at infinity (%)	Considered chemically bound water at complete hydration	α	β	λ	Non-pozzolanic SCM benefit
Control (CEM I 52.5R)	0	0.003	13.692	0.240	3.866	0.000	0.000	0.000
	0.3	0.011	13.692	0.240	7.388	0.000	0.000	0.000
	7	0.053	13.692	0.240	34.128	0.000	0.000	0.000
	56	0.061	13.692	0.240	48.292	0.000	0.000	0.000
Poz-1, **F3-20% Calcined**	0							
	0.3	0.014	13.692	0.240	8.492	-6.490	-1.822	4.668
	7	0.064	13.692	0.240	49.176	1.827	31.194	29.367
	56	0.075	13.692	0.240	66.237	8.939	22.692	13.753
Poz-2, **F3-20% Calcined**	0							
	0.3	0.013	13.692	0.240	7.760	-6.554	-7.851	-1.296
	7	0.059	13.692	0.240	46.294	4.237	30.239	26.002
	56	0.067	13.692	0.240	57.883	5.064	13.643	8.580
Poz-3, **F3-20% Calcined**	0							
	0.3	0.013	13.692	0.240	8.677	-4.738	6.563	11.301
	7	0.058	13.692	0.240	45.262	3.434	28.308	24.874
	56	0.063	13.692	0.240	55.211	6.279	12.233	5.954

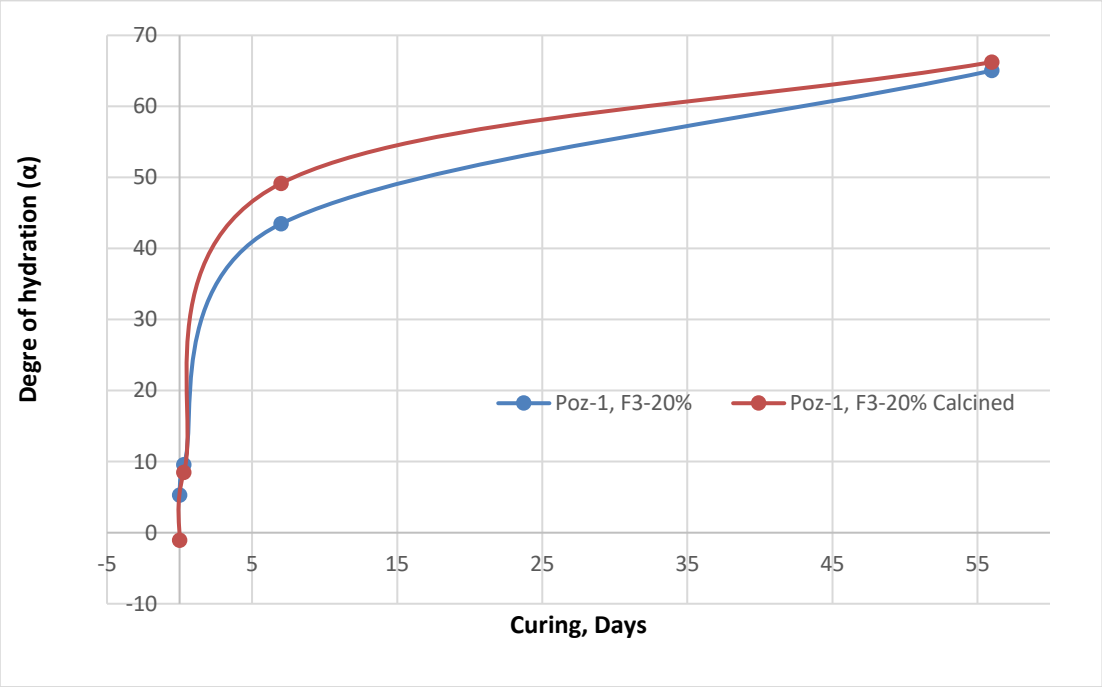

Figure 6.3: Effect of calcination of Poz-1 on the degree of hydration (α)

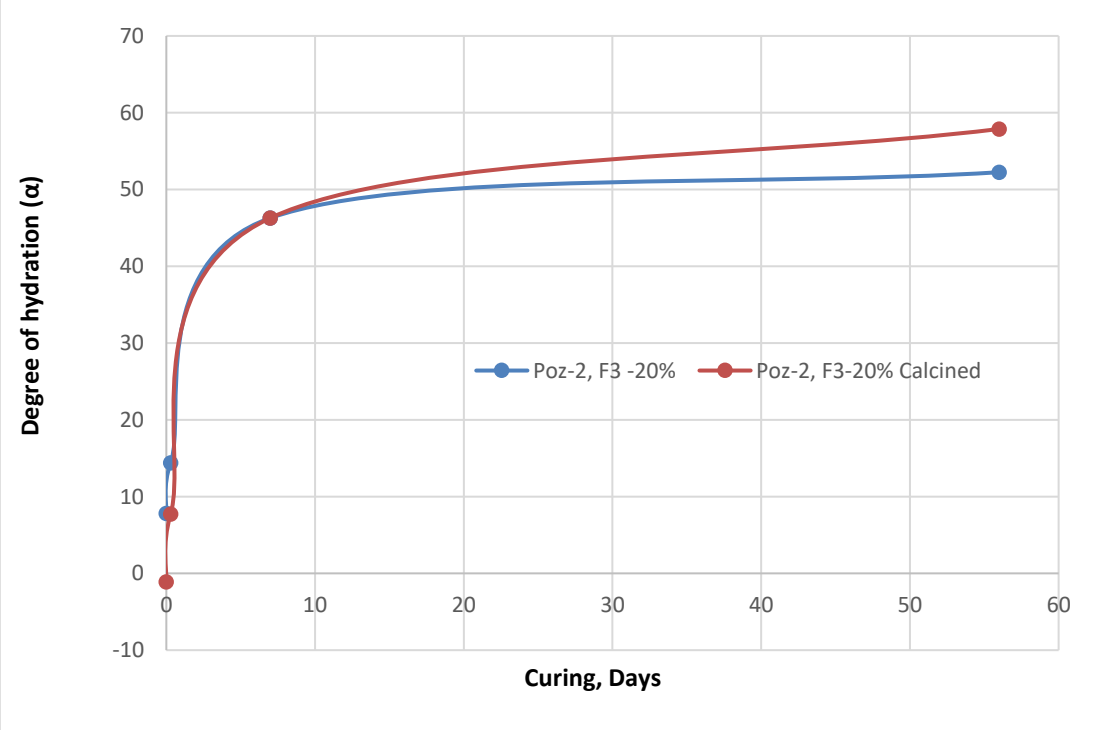

Figure 6.4: Effect of calcination of Poz-2 on the degree of hydration (α)

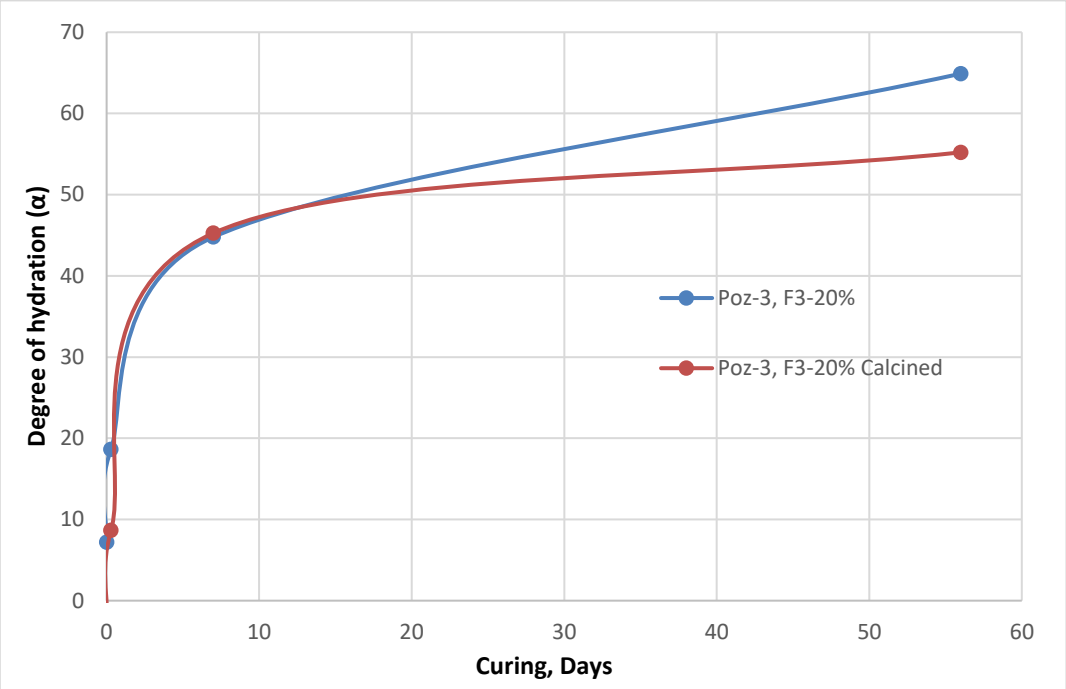

Figure 6.5: Effect of calcination of Poz-3 on the degree of hydration (α)

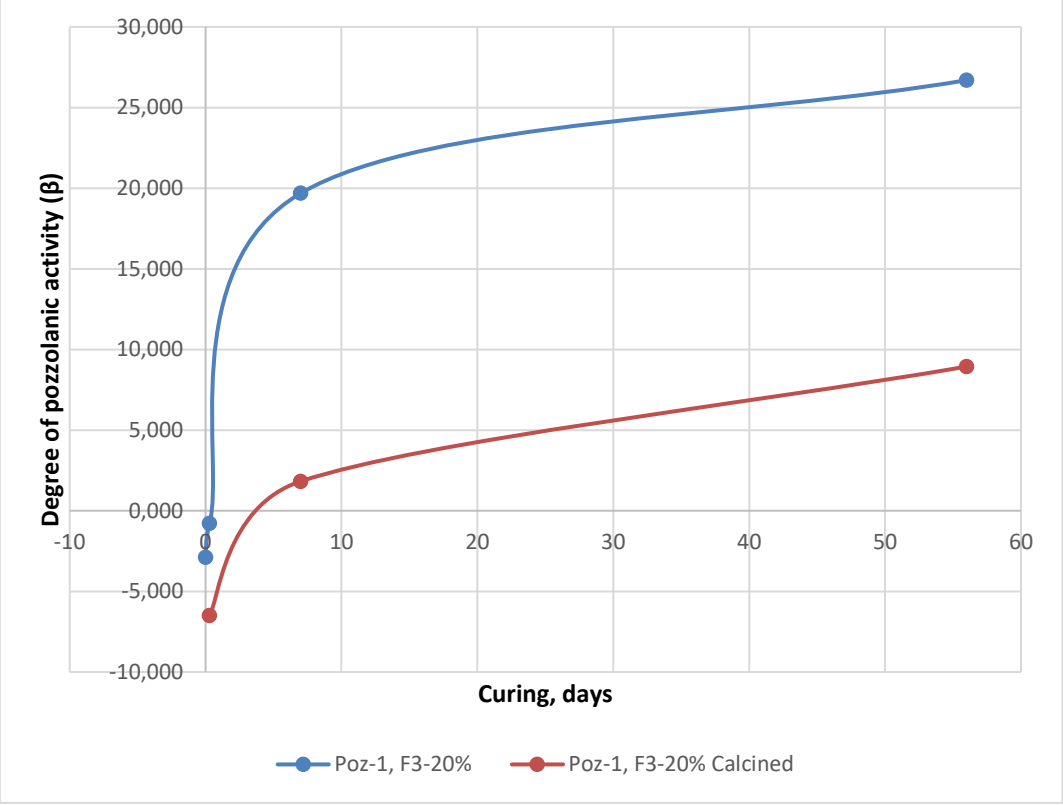

Figure 6.6: Effect of calcination of Poz-1 on the degree of pozzolanic activity (β)

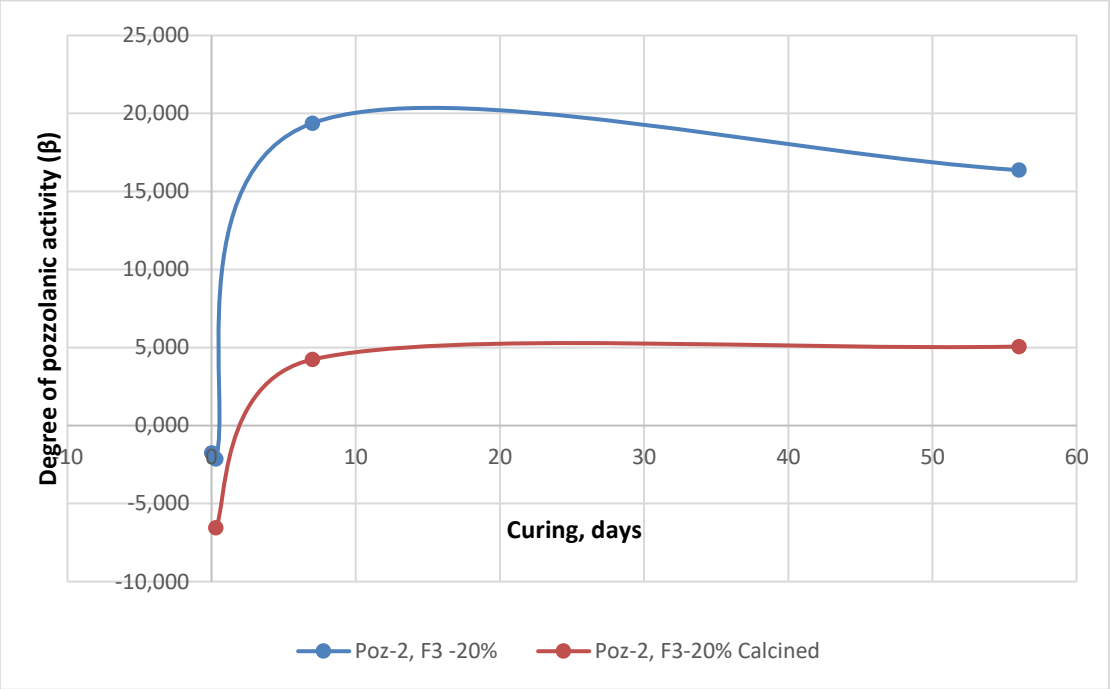

Figure 6.7: Effect of calcination of Poz-2 on the degree of pozzolanic activity (β)

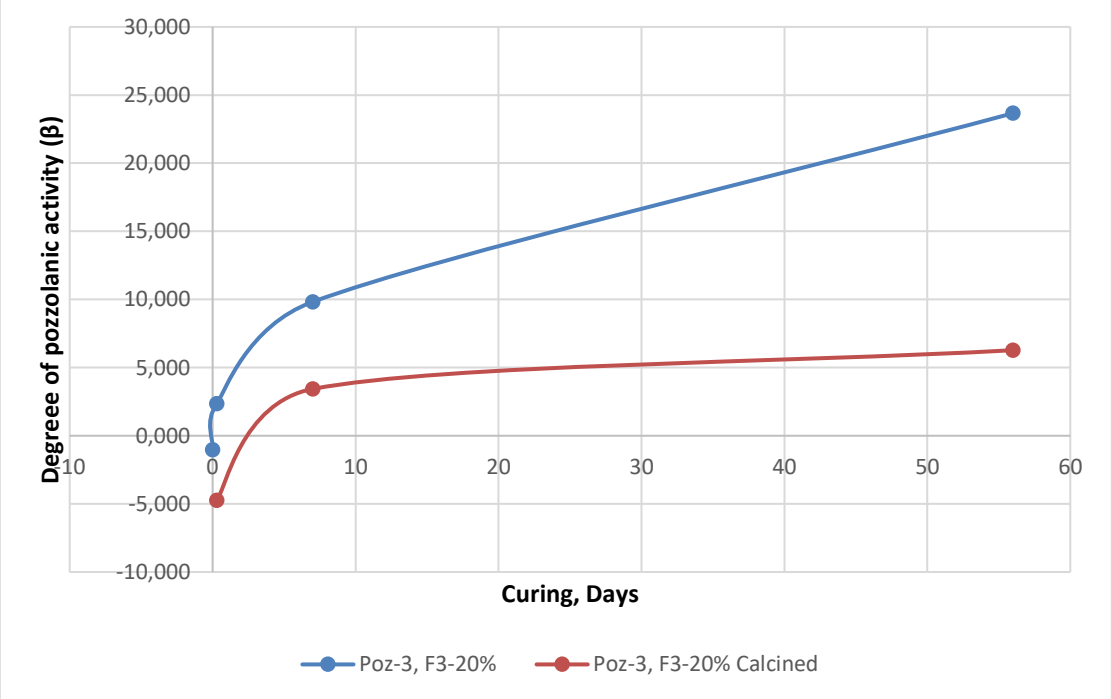

Figure 6.8: Effect of calcination of Poz-3 on the degree of pozzolanic activity (β)

The results show the non-pozzolanic reactions associated with the calcined kamafugites and carbonatites to have the highest importance at 7 days unlike the

natural samples that showed the highest value at 7 hours after the start of hydration. The net SCM benefits reduce for all the samples but are sustained at higher values for all the calcined samples indicating that calcination weakens the reaction mechanisms responsible for long term loss in compressive strength observed in the natural (uncalcined) samples.

6.6.3 Effect of replacement level of kamafugites and carbonatites on α and β

Table 6.3: TGA/DTG results of blended cement at 10% replacement level for the natural (not calcined) sample

Test sample and variables	**Curing (Days)**	τ	Water in CH at infinity (%)	Considered chemically bound water at complete hydration	α	β	λ	Non-pozzolanic SCM benefit
Control (CEM I 52.5R)	0	0.003	13.692	0.240	3.866	0.000	0.000	0.000
	0.3	0.011	13.692	0.240	7.388	0.000	0.000	0.000
	7	0.053	13.692	0.240	34.128	0.000	0.000	0.000
	56	0.061	13.692	0.240	48.292	0.000	0.000	0.000
Poz-1, **F3-10%**	0	0.004	13.692	0.240	4.959	-0.834	14.189	15.023
	0.3	0.015	13.692	0.240	13.549	0.929	67.725	66.796
	7	0.053	13.692	0.240	50.414	20.240	52.436	32.196
	56	0.058	13.692	0.240	49.489	2.669	5.395	2.726
Poz-2, **F3-10%**	0	0.005	13.692	0.240	4.522	-2.669	-7.247	-4.577
	56	0.058	13.692	0.240	51.519	6.670	9.922	3.252
Poz-3, **F3-10%**	0							
	0.3	0.012	13.692	0.240	9.638	-1.571	25.911	27.482
	7	0.056	13.692	0.240	45.398	5.985	31.562	25.576
	56	0.061	13.692	0.240	55.316	8.748	14.564	5.816

Table 6.3 presents results of samples blended at 10% replacement level while Table 6.4 presents results of 30% replacement level. The results are analyzed together with results of Table 6.1 (sample at 20% replacement level) to evaluate the effect of replacement level on both the degree of hydration and degree of pozzolanic performance of samples blended with test kamafugites and carbonatites. The results show the degree of hydration, the degree of pozzolanic performance and the net SCM benefit to increase with increase in replacement level. The results also show

the hydration products degradation reactions to increase with increase in replacement level with net SCM benefits of Poz-1 and Poz-2 going into negatives while that of Poz-3 reduced to 0.7% at 30% cement replacement level.

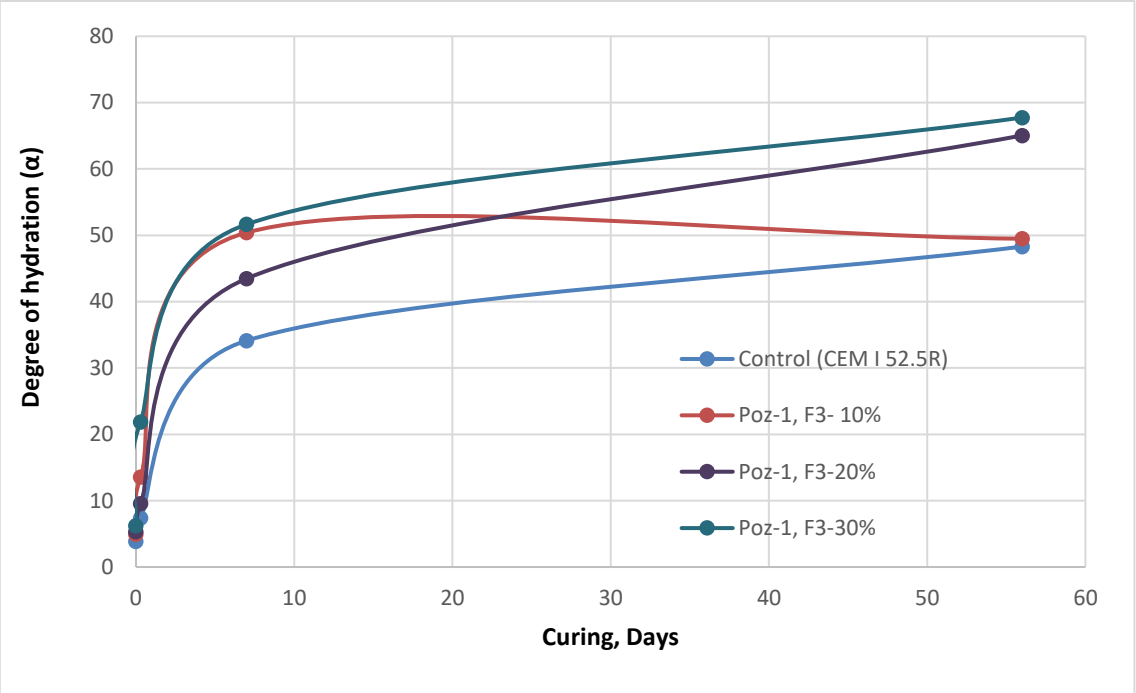

Figure 6.9: Effect of replacement level on the degree of hydration (α) for Poz-1

Table 6.4: TGA/DTG results of blended cement at 30% replacement level for the natural (uncalcined) kamafugites and carbonatites

Test sample and variables	**Curing (Days)**	τ	Water in CH at infinity (%)	Considered chemically bound water at complete hydration (w/c)	α	β	λ	Non-pozzolanic SCM benefit
Control (CEM I 52.5R)	0	0.003	13.692	0.240	3.866	0.000	0.000	0.000
	0.3	0.011	13.692	0.240	7.388	0.000	0.000	0.000
	7	0.053	13.692	0.240	34.128	0.000	0.000	0.000
	56	0.061	13.692	0.240	48.292	0.000	0.000	0.000
Poz-1, **F3-30%**	0	0.007	13.692	0.240	6.243	-4.755	17.005	21.760
	0.3	0.024	13.692	0.240	21.860	1.422	131.892	130.470
	7	0.052	13.692	0.240	51.658	30.412	57.498	27.086
	56	0.060	13.692	0.240	67.749	43.257	42.540	-0.717
Poz-2, **F3-30%**	56	0.056	13.692	0.240	64.309	42.559	38.861	-3.699
Poz-3, **F3-30%**	0							
	0.3	0.019	13.692	0.240	17.296	2.322	100.575	98.253
	7	0.052	13.692	0.240	50.878	29.567	55.908	26.342
	56	0.062	13.692	0.240	69.849	43.714	44.461	0.747

Table 6.5: TGA/DTG results of blended cement at 20% replacement level for the natural sample at F1 level of fineness. Fineness level F 1 and its values are defined in chapter 4 of this thesis.

Test sample and variables	**Curing (Days)**	τ	Water in CH at infinity (%)	Considered chemically bound water at complete hydration	α	β	λ	Non-pozzolanic Admixture benefit
Control (CEM I 52.5R)	0	0.003	13.692	0.240	3.866	0.000	0.000	0.000
	0.3	0.011	13.692	0.240	7.388	0.000	0.000	0.000
	7	0.053	13.692	0.240	34.128	0.000	0.000	0.000
	56	0.061	13.692	0.240	48.292	0.000	0.000	0.000
Poz-1, **F1-20%**	0	0.005	13.692	0.240	5.302	-2.876	7.983	10.859
	0.3	0.012	13.692	0.240	10.993	1.390	49.113	47.723
	7	0.052	13.692	0.240	48.302	20.017	47.414	27.397
	56	0.058	13.692	0.240	60.092	25.433	28.377	2.944
Poz-3, **F1-20%**	0	0.005	13.692	0.240	7.208	-1.030	55.121	56.150
	0.3	0.016	13.692	0.240	14.849	1.588	79.976	78.388
	7	0.056	13.692	0.240	47.908	12.897	40.237	27.340
	56	0.058	13.692	0.240	56.219	16.500	19.512	3.012

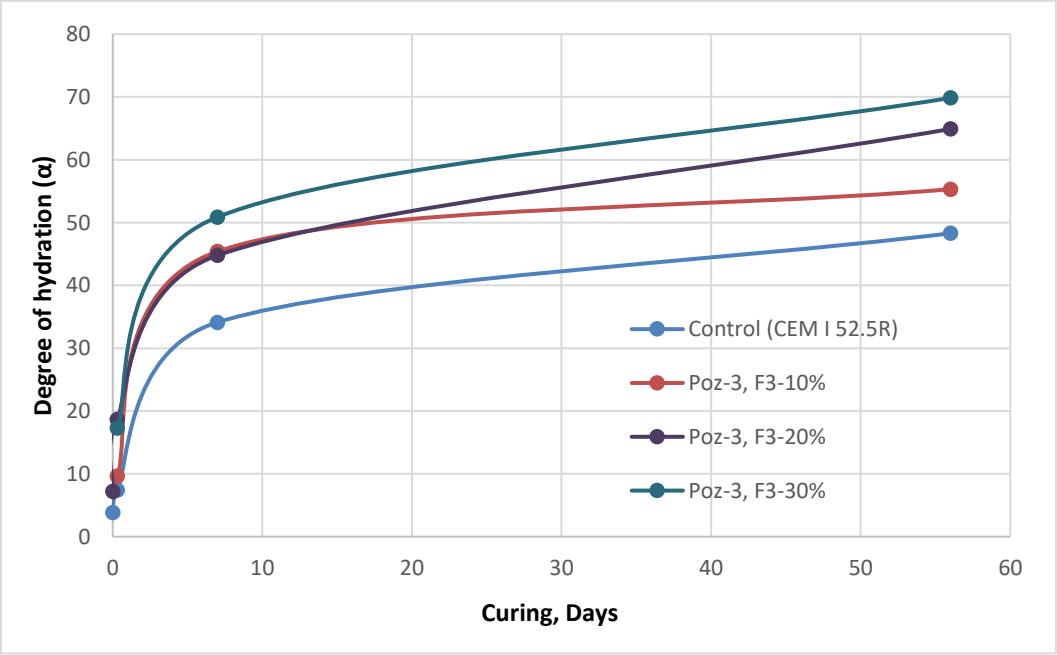

Figure 6.10: Effect of replacement level on the degree of hydration (α) for Poz-3

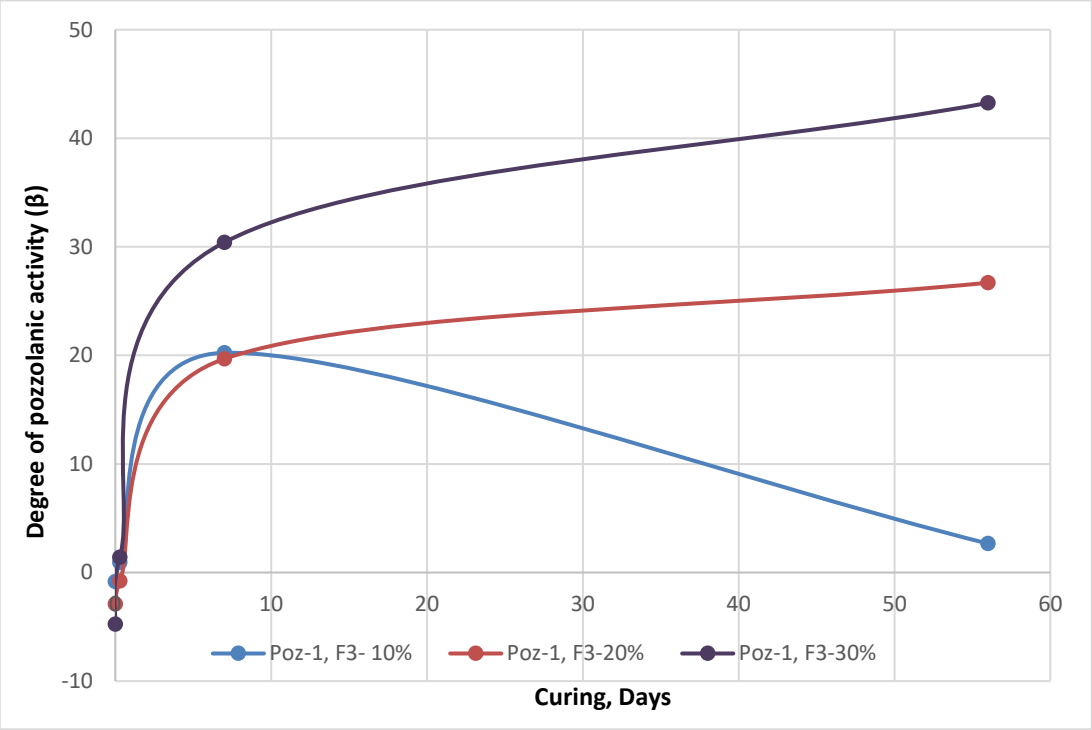

Figure 6.11: Effect of replacement level on the degree of pozzolanic activity (β) for Poz-1

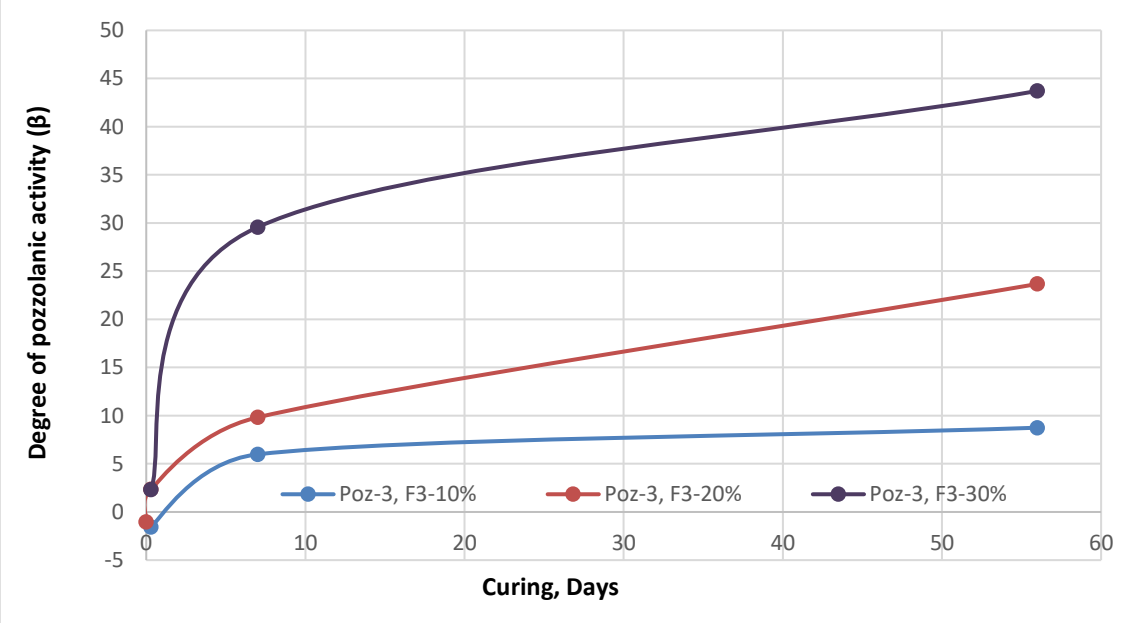

Figure 6.12: Effect of replacement level on the degree of pozzolanic activity (β) for Poz-3

The trend on replacement level agrees with the previous results on heat of hydration and chemical shrinkage reported in Chapter 6 of this thesis. The acceleratory effect of the blended samples is compositional and both calcite and water-soluble alkalis are advanced as being responsible for the unique acceleratory effect of pastes blended with kamafugites and carbonatites.

6.6.4 Effect of fineness of kamafugites and carbonatites on α and β

Table 6.5 presents results of the test pozzolans at a different fineness level. Fineness level F1 and its values are defined in Chapter 3 of this thesis, under the particle size analysis subsection. The experiment was designed to evaluate the effect of fineness on the degree of hydration (α) and the degree of pozzolanic performance (β) of the kamafugites and carbonatites. The analysis of results is presented in figures 6.13 to 6.16. The results show fineness to play a significant role at a later stage of hydration (56 days) for all the test samples, Poz-3 taking more prominence for both the degree of hydration and degree of pozzolanic performance. The influence of fineness on the degree of hydration and degree of pozzolanic performance seems to correlate with reactive silica content at 56 days indicating that the fineness parameter supports pozzolanic reactions which dominate the hydration reactions at a later age (after 28 days). The observed inverse relationship between fineness and degree of hydration and degree of pozzolanic performance at earlier stages of hydration is a confirmation that the SCMs have retarding reactions/conversion reactions that are more prominent at the early stages of hydration. These hydration products conversion reactions are enhanced by the fineness property leading to reduction in the degree of hydration and degree of pozzolanic performance of the blended samples in the early stages of hydration. This observation is also reflected in the strength, chemical shrinkage and heat of hydration results that showed the samples with a higher fineness level to trail those with lower fineness levels at the early stages of hydration.

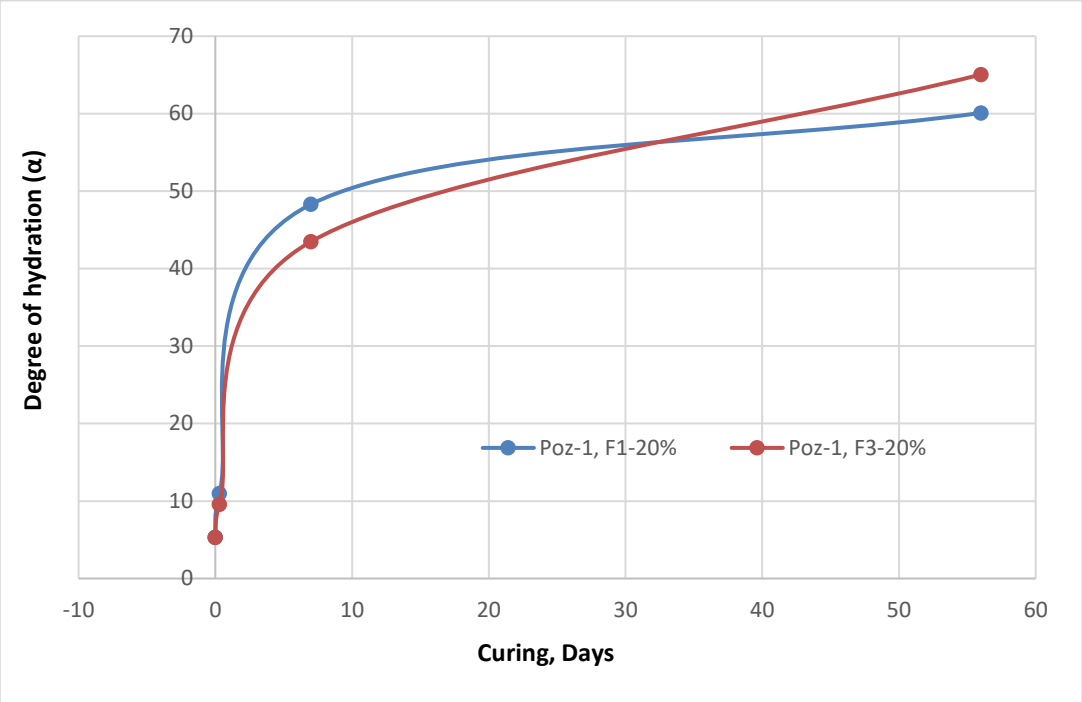

Figure 6.13: Effect of fineness of the test pozzolans on the degree of hydration (α) for Poz-1

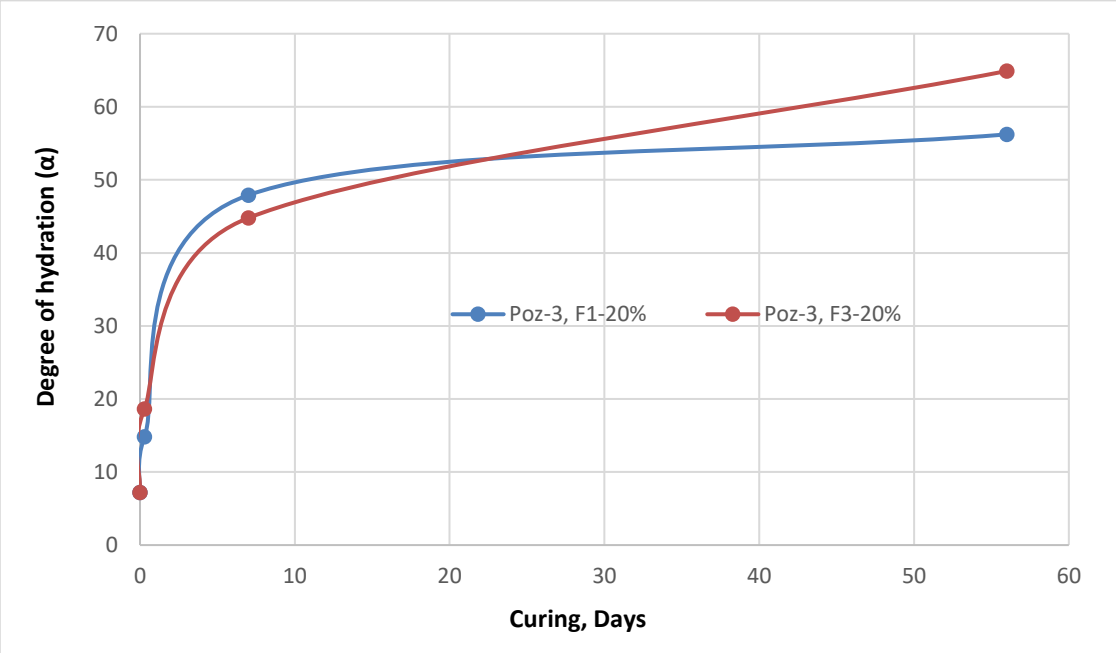

Figure 6.14: Effect of fineness of the test pozzolans on the degree of hydration (α) for Poz-3

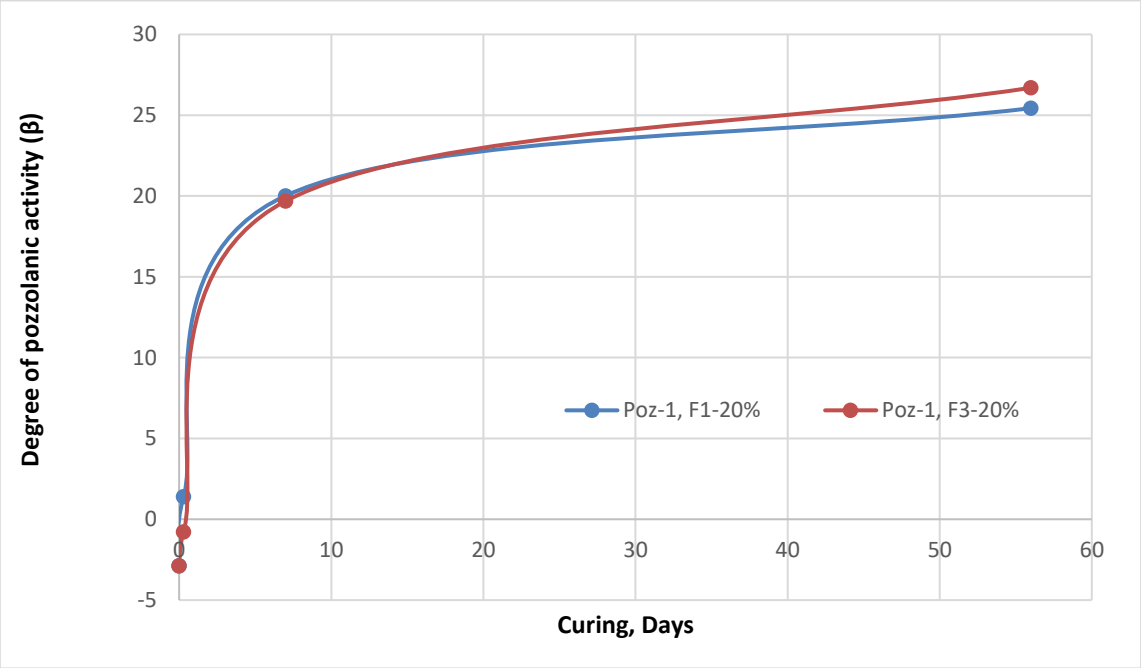

Figure 6.15: Effect of fineness of the test pozzolans on the degree of pozzolanic performance (β) for Poz-1

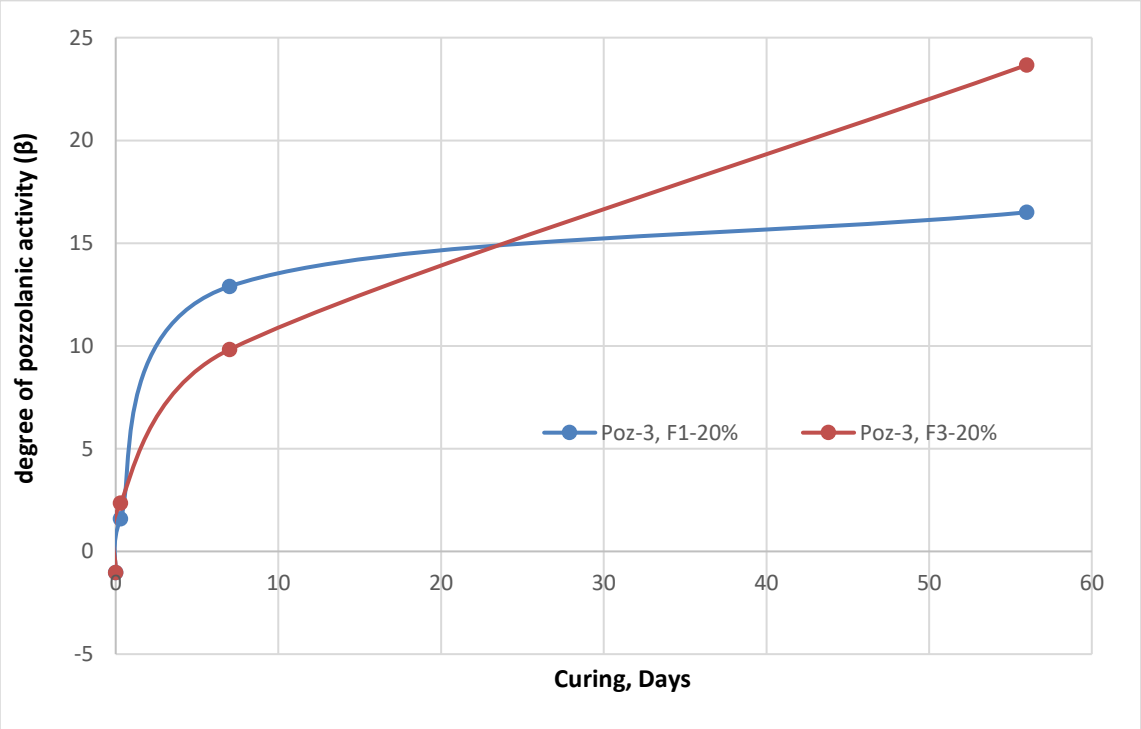

Figure 6.16: Effect of fineness of the test pozzolans on the degree of pozzolanic performance (β) for Poz-3

5.6.5 Estimation of the initial carbonate content in blended pastes.

Table 6.6: Experimental and calculated values of calcite in the different test kamafugites and carbonatites

Sample Name	Level of replacement	Experimental Values	Calculated Values
CEM I 52.5R Anhydrous		0.296	
Poz-1 Anhydrous		9.499	
Poz-2 Anhydrous		9.770	
Poz-3 Anhydrous		4.501	
Poz-1	0%	0.296	0.296
	10%	1.256	1.246
	20%	2.121	2.196
	30%	3.085	3.146
Poz-2	0%	0.296	0.296
	10%	1.294	1.273
	20%	2.370	2.250
	30%		3.227
Poz-3	0%	0.296	0.296
	10%		0.746
	20%	1.052	1.196
	30%		1.646

Both the quantitative expressions for the degree of hydration (α) and the degree of pozzolanic performance (β) require establishment of the carbonate content of samples at anhydrous state. This section tests the possibility of theoretically estimating calcite content of blended cements at anhydrous state. The ability to theoretically quantify calcite at anhydrous stage enables a saving in experimental time and in checking the reliability of the test results. Experimental data was generated on blended test samples for their calcite content. The data was used in assessing the reliability of quantified results generated using linear mathematical relationships. Based on the composition of calcite in the primary materials of the blend, a linear mathematical relationship that considers the percentage compositions of the constituent primary materials is applied as a simple tool to estimate the composition of calcite at anhydrous state of the different samples. Both the experimental data and calculated values are presented in Table 6.6. The results are further plotted for correlation as shown in Figures 6.18 and 6.19. The considered

results for Poz-1 and Poz-2 gave a strong correlation with a very high coefficients of determination (0.999).

The observations confirmed that the calcite content at anhydrous state for blended cements can be quantified based on the calcite content of the primary materials used in formulation of blends. The observation is important in data prediction where the anhydrous data is not processed due to access constraints in the experimental processes.

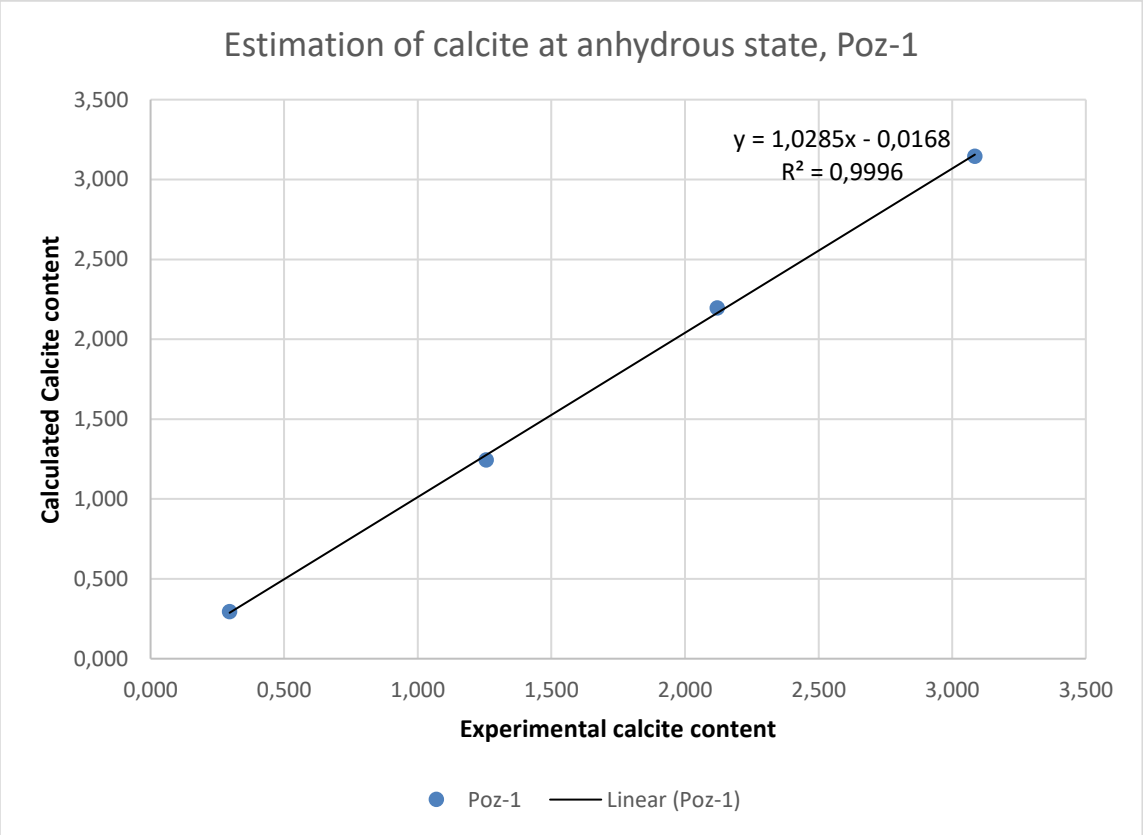

Figure 6.17: Correlation of calculated calcite content data with experimental data for Poz-1.

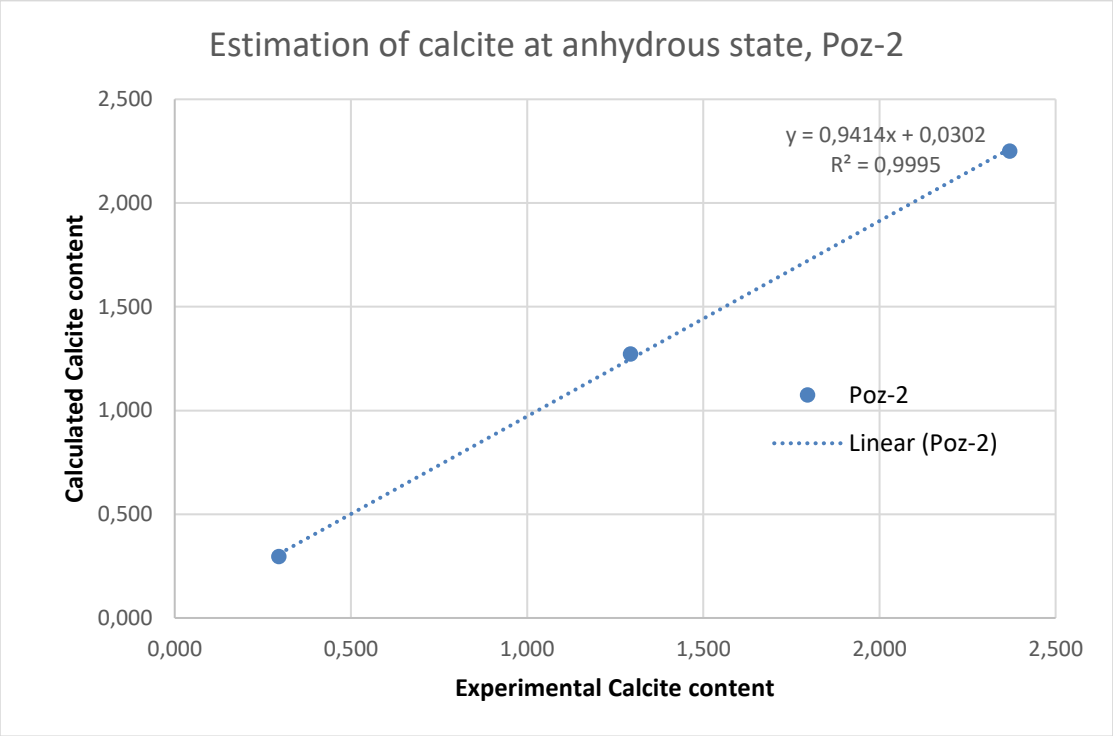

Figure 6.18: Correlation of calculated calcite content data with experimental data for Poz-2.

6.7 Comparison of model results with other properties of cement pastes

6.7.1 Correlation between chemical shrinkage and degree of hydration data for the raw kamafugites and carbonatites

The results of chemical shrinkage presented in Chapter 4 of this thesis and plotted against the degree of hydration results considered all the data points for the blended paste samples at 20% replacement level and the control sample. From the results in Figure 6.19, a model exists taking the following form.

$$y = Ax + B \qquad \text{Equation 6.13}$$

Where x and y are, respectively, the chemical shrinkage and degree of hydration results, A is a scale factor (correction coefficient) and B the intercept.

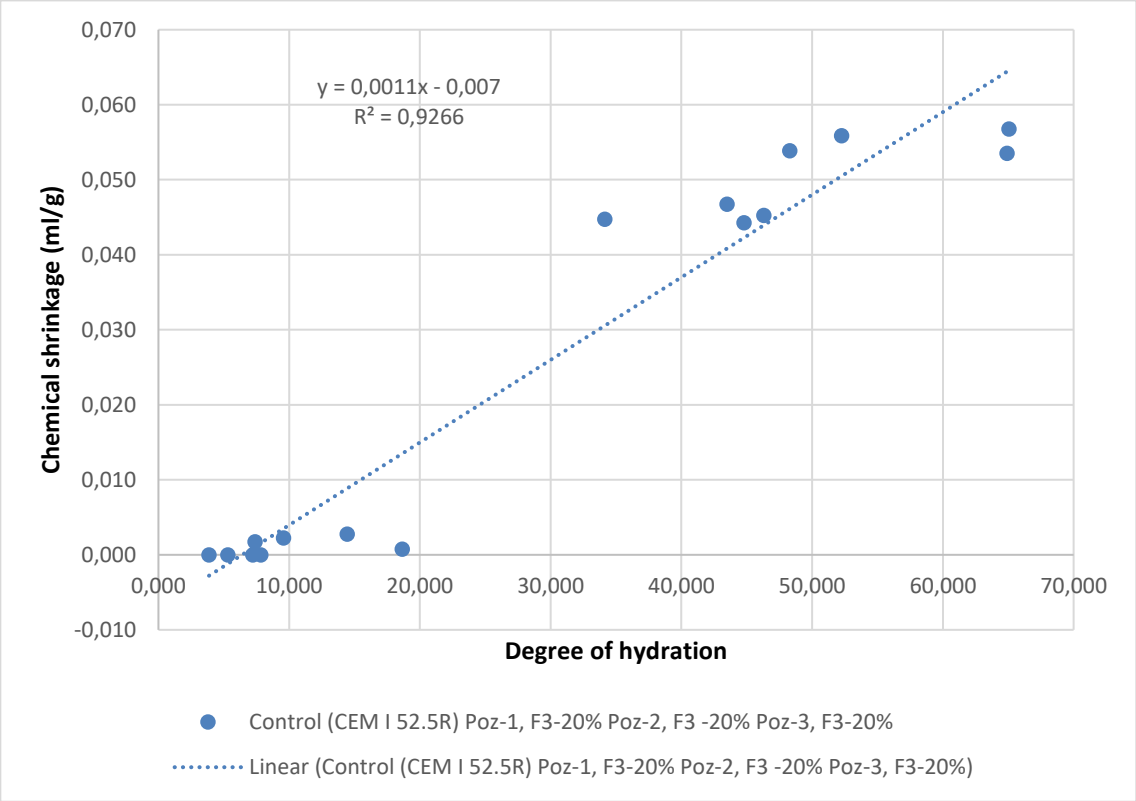

Figure 6.19: Relationship between the chemical shrinkage and the degree of hydration of raw test pozzolans

Theoretically, both chemical shrinkage and degree of hydration should be zero at the start of the experiment but, as observed in actual results, hydration processes in cement start at the time the cement is exposed to the atmosphere and before the addition of water. Moreover, rapid changes in the initial stages of hydration of cement would cause a slight offset in the correlation model and reduce the coefficient of determination. The correlation results are sensitive to the initial hydration processes that are reflected in the degree of hydration values presented in Table 6.1. The analysis shows a strong relationship between the chemical shrinkage and the degree of hydration with a coefficient of determination of 0.93.

6.7.2 Correlation between compressive strength and degree of hydration data for the raw kamafugites and carbonatites

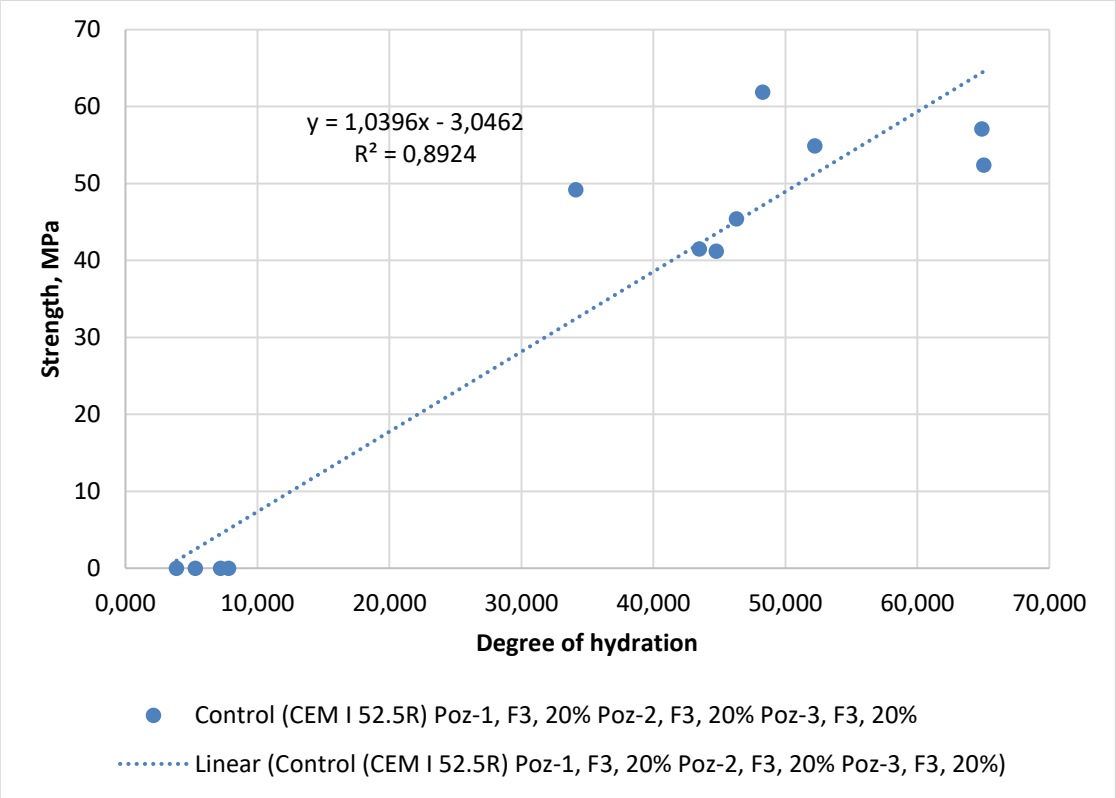

Figure 6.20: Relationship between the compressive strength and the degree of hydration of raw test pozzolans

Results comparison between compressive strength and the degree of hydration (Figure 6.20) advance a linear correlation with a strong coefficient of determination (R^2=0.89). The relationship assumes a form like that observed in Equation 6.13. The established relationship can be used to predict strength from the degree of hydration results.

6.7.3 Correlation between compressive strength and degree of pozzolanic performance for the raw kamafugites and carbonatites

Figure 6.21 presents a correlation relationship between compressive strength and the degree of pozzolanic performance. A dependence relationship exists between the strength parameters and the degree of pozzolanic performance with a coefficient of determination of 0.89. The trend equation serves as a good model for prediction

of the strength property of hydrating cement pastes that are blended with pozzolanic SCMs. The pozzolanic activity is confirmed by the observed trend.

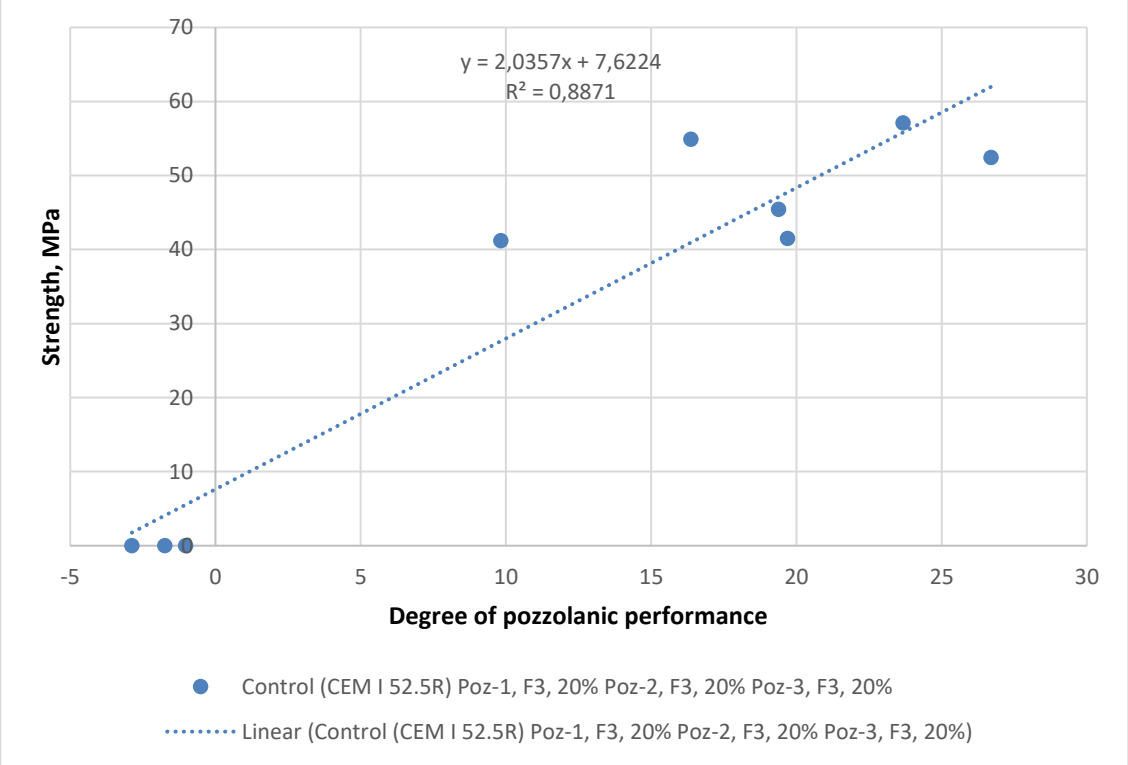

Figure 6.21: Relationship between the compressive strength and the degree of pozzolanic activity for the raw test pozzolans

6.7.4 Correlation between chemical shrinkage and degree of hydration data for the calcined kamafugites and carbonatites

Chemical shrinkage values of paste samples made with calcined kamafugites and carbonatites are compared against the degree of hydration values from the TGA results. The correlation analysis is presented in Figure 6.22. The results show a slight improvement in the fitting of the correlation line with a better R^2 value (0.936) compared to that of the natural kamafugites and carbonatites (R^2=0.926).

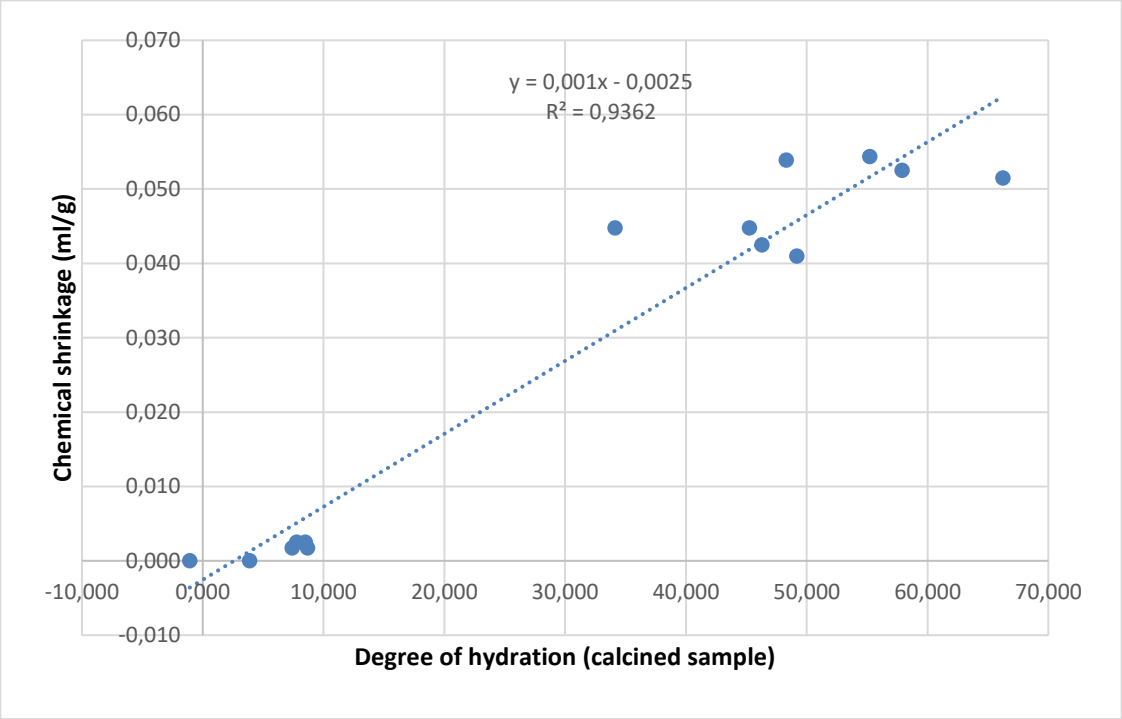

Figure 6.22: Relationship between the chemical shrinkage and the degree of hydration for the calcined test pozzolans

6.7.5 Correlation between chemical shrinkage and degree of pozzolanic performance data for the calcined kamafugites and carbonatites

Like the results discussed in previous sections, a linear trend is observed in Figure 6.23 between chemical shrinkage and the degree of pozzolanic performance for the calcined samples. It is observed in Chapter 5 of this thesis and in the application of the theoretical models in assessing the effect of calcination on pozzolanic performance of kamafugites and carbonatites that calcination reduces the pozzolanic performance property of the kamafugites and carbonatites. Consequently, the observed trend between the chemical shrinkage and the degree of hydration results presents a slightly lesser R^2 value (0.864) than the trend established in the pastes made from raw samples (R^2=0.887).

The analysis presented above establishes that the degree of hydration and the degree of pozzolanic performance properties have a dominant linear influence on the strength and chemical shrinkage properties of cement pastes blended with kamafugites and carbonatites.

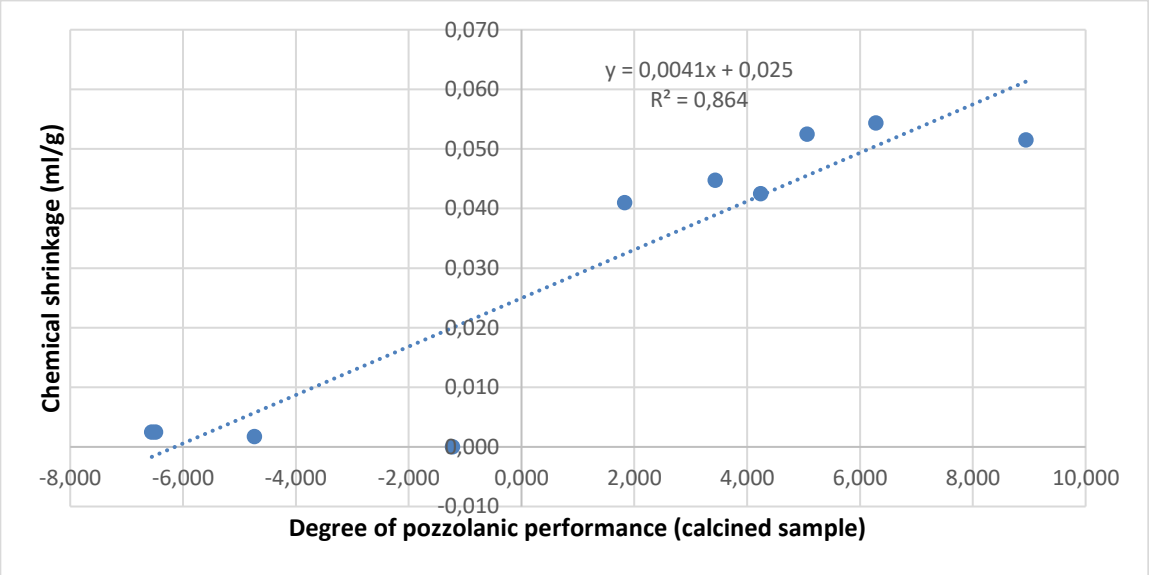

Figure 6.23: Relationship between the chemical shrinkage and the degree of pozzolanic activity for the calcined test pozzolans

6.8 Application of the models on historical data

Monteagudo et al (2014) presents TGA data on Portland cement blended with blast furnace slag (BFS), fly ash (FA) and silica fume (SF) at two different levels for each test pozzolan. The data presents a reference sample as a plain Portland cement (CEM I 42.5N) but an analysis shows the data to be very high in calcite and can therefore not be considered as a plain Portland cement. Important to note, the formulation of the models proposed in the current thesis can correct for the carbonate anomalies if data for the anhydrous sample is acquired. Monteagudo did not provide text data on the anhydrous samples and, therefore, the initial values for the correction of the calcite content in the samples was assumed to be the lowest Ldc (decarbonation) reading of the control sample. The calcite replacement level was assumed at 15% considering the high carbonate content reported in the results of the control sample. The current study further assumed that the test pozzolans do not contain calcite in their composition. Monteagudo's results were normalised to cement content and are presented in Table 6.7. The results for the degree of hydration (α), including the values generated by applying previous models by Bhatty, 1985, Pane and Hansen, 2005, and Monteagudo et al., 2014, are considered as presented in Monteagudo et al., 2014. The results presented in Monteagudo et al., 2014, and their

analysis using the proposed model in the current study are presented in Table 6.8. Table 6.8 also shows analysis results for the degree of pozzolanic performance (β) and the net SCM benefit (λ) results as calculated following the numerical expressions proposed in this thesis.

Table 6.7: TGA results from Monteagudo et al., 2014 all normalized to cement content

Test sample and variables	**Curing (Days)**	Ldh (g/g)%	Ldx (g/g)%	Ldc (g/g)%
P/OPC	7	9.570	2.713	5.513
	28	11.160	2.753	5.266
	90	11.772	3.215	5.149
P/20% BFS	7	11.769	3.154	5.951
	28	13.219	3.333	5.535
	90	15.122	3.570	5.306
P/35% BFS	7	13.615	3.444	5.097
	28	16.605	3.766	5.113
	90	18.302	4.182	5.141
P/20% FA	7	10.626	3.111	5.640
	28	12.278	3.269	5.411
	90	13.624	3.368	5.343
P/35% FA	7	11.785	3.439	5.190
	28	13.100	3.669	5.166
	90	15.108	3.868	5.159
P/6% SF	7	10.835	2.863	6.097
	28	11.579	2.812	5.473
	90	12.585	2.795	4.845
P/10% SF	7	11.738	2.818	6.398
	28	12.846	2.673	5.785
	90	13.702	2.455	5.361

The results as presented in Monteagudo et al., 2014, were normalised for cement content to facilitate for the application of the proposed quantitative expressions. The results show disagreements in the degree of hydration values, the Bhatty model giving lower values followed by the Pane and Hansen's model and then the Monteagudo model. As observed in the current reporting, the three models consider the contributions of a residue phase, the dehydroxylation phase, as a cumulative

contributor to the degree of hydration giving it a scale factor of one. This distorts the data and demands a higher level of standardisation of the control cement sample which is not practical for application of the method universally.

Table 6.8: Analyzed TGA results from Monteagudo et al., 2014, that compare the degree of hydration values from previous models, and values of the proposed model resulting from the current study

Test sample and variables	**Curing (Days)**	Bhatty α	Pane-Hansen α	Monteagudo α	Proposed α	Proposed β	Proposed λ	Non-pozzolanic SCM benefit
P/OPC	7	60.60	69.44	84.55	49.05	-2.37	0.00	2.372
	28	66.96	72.85	93.72	56.52	-0.76	0.00	0.759
	90	71.25	78.57	99.89	59.62	0.00	0.00	0.000
P/20% BFS	7	59.91	75.63	84.73	63.68	0.78	22.97	22.185
	28	64.63	79.55	91.60	70.89	-0.77	18.45	19.220
	90	71.38	84.99	101.44	79.06	12.49	28.46	15.974
P/35% BFS	7	54.91	71.99	77.84	72.70	11.90	42.26	30.360
	28	63.90	81.70	90.95	89.65	12.23	48.80	36.568
	90	69.68	87.45	99.40	98.56	22.56	55.47	32.903
P/20% FA	7	55.43	76.05	84.07	56.91	-3.27	11.03	14.298
	28	61.07	81.63	92.91	65.45	-3.75	10.02	13.774
	90	65.77	85.93	100.27	70.35	6.87	15.73	8.857
P/35% FA	7	50.10	76.00	83.95	63.61	1.24	23.14	21.899
	28	54.24	80.86	91.14	71.36	-3.98	17.38	21.362
	90	60.21	87.14	101.49	80.39	9.20	28.34	19.137
P/6% SF	7	64.08	96.87	94.17	57.63	-1.28	13.22	14.498
	28	65.71	95.51	96.65	59.45	-0.98	3.76	4.738
	90	68.52	95.96	100.90	60.64	11.92	6.91	-5.009
P/10% SF	7	65.52	96.94	93.82	62.65	2.15	22.65	20.503
	28	68.09	96.61	97.61	65.79	4.30	15.11	10.815
	90	69.75	96.15	100.06	65.53	15.76	16.39	0.631

6.8.1 The Bhatty model results

It is reported that the degree of hydration of cements blended with SCMs, whether pozzolanic or not, will be higher than that of the plain Portland cement (Berodier and Scrivener, 2015). This is due to both the acceleratory effects of the mineral

admixtures but also because more space and pore water is available for the hydrates to precipitate without confinement pressure. This implies that cement particles with more space to deposit hydration products and excess supply of water will achieve a higher degree of hydration. Blending cement with pozzolanic and other mineral admixtures provide this extra space and facilitates a higher degree of hydration. This is not the case for the Bhatty model as the degree of hydration values of blended samples is lower than that of the control.

6.8.2 The Pane and Hansen model results

The Pane and Hansen model erroneously considers carbonates as non-evaporable water. As a consequence, the model values are higher. Pane and Hansen used a w/c ratio of 0.35 which is similar to what was used in the current study. The trends in results should therefore be similar but, as observed in Table 6.8, the effects of erroneously considering carbonate phases as chemically bound water becomes significant and changes the trend when the level of replacement of cement is increased to 35%.

6.8.3 The Monteagudo model results

Monteagudo reported very high values for the degree of hydration with some samples showing values in excess of 100% at 90 days of curing. It is observed that the water to solids ratio is an important parameter in determining the degree of hydration. It is considered that cement hydrates expand to occupy space more than twice its original volume (Neville, 2002). Berodier and Scrivener, 2015, used two levels of mixing water at 0.4 and 0.6 and the results stress the importance of pore water spaces to the degree of hydration of cement. The water to solids ratio applied by Monteagudo limits the possibility of the cement pastes to achieve the quantified degree of hydration.

6.8.4 Degree of hydration values with the proposed model

The model presents lower degree of hydration values for the control sample. It is considered that the w/c value of 0.35 applied in the current study limits the amount of cement particles that can hydrate to fill the available water pores. As a result, lower

w/c mixes result in lower values of degree of hydration. This hypothesis is limited to cement pastes. The behaviour of cement paste in the presence of aggregates in concrete is different. The model can present consistent and relatable values for the degree of hydration. The degree of hydration increases with increase in cement replacement levels. The degree of hydration is also dependent on the type of mineral admixture used, BFS ranking better than FA for the testing period. The proposed model for estimation of the degree of hydration is therefore a more dependable model and is responsive to the mechanisms that govern the development of important properties in hydrating cement pastes.

6.8.5 Degree of pozzolanic activity values with the proposed model.

The results of the degree of pozzolanic activity advanced by the proposed model are presented in Table 6.8. The results show BFS to show the highest degree of pozzolanic performance followed by SF and FA trailing. The degree of pozzolanic performance increases with increase in replacement level due to an increase in reactive silica content with increase in replacement level. The trend observed is a confirmation that the proposed quantitative expressions for calculation of the degree of pozzolanic activity are valid.

6.8.6 The net SCM benefit with the proposed model.

The quantitative expressions for the net SCM benefit consider both the pozzolanic and other admixture influences in a blended cement paste. As a consequence, the value of the degree of total mineral admixture activity must be higher than that of the degree of pozzolanic activity if the non-pozzolanic processes are contributing to the improvement of the paste properties. Table 6.8 shows the net SCM benefit values for the different samples tested. Table 6.8 also presents a column that shows the total SCM values less the pozzolanic activity contribution. The results show that BFS has more contribution to non-pozzolanic products than FA. The non-pozzolanic admixture benefits for SF are highest at 7 days of curing and become negligible at 90 days of curing. This is probably because SF is very reactive and it’s pozzolanic reactants are depleted fast. The non-pozzolanic SCM benefits increase with

replacement level. The non-pozzolanic SCM benefits are also pronounced more at the early stages of hydration.

6.9 Chapter summary

In the current chapter, quantitative expressions for estimation of the degree of hydration, the degree of pozzolanic performance and the net SCM benefit are proposed. The quantitative expressions have been applied in the analysis of both the data generated in the current study and data from published literature. The observed trends from the analysis are validated by literature and specific trends established for the test materials studied in the current work using different tools of analysis. The quantitative expressions have also been compared with the different paste properties important for paste performance characterisation. Correlations have been established which calibrate the quantitative expressions as useful models for prediction of the different paste properties studied in the current work. The following conclusions can be made.

1. The quantitative expressions for the degree of hydration (α), the degree of pozzolanic activity (β) and the net SCM benefit (λ) are valid tools for characterisation of SCMs in Portland cement concrete. The models were verified by comparison of their results with the strength and chemical shrinkage results generated in the current study. The models were also applied on results from published works and advanced plausible interpretations. The proposed models offer a robust package of information that enables adaptive use of different mineral admixtures and clinker properties. The models are therefore not limited to only kamafugites and carbonatites but can characterize other mineral admixtures as demonstrated in the current chapter.

2. The application of the degree of hydration (α), the degree of pozzolanic activity (β) and the net SCM benefit (λ) analysis tools revealed the kamafugites to exhibit both pozzolanic and hydration products degradation reaction mechanisms. The conversion mechanisms undo the strength benefits of pozzolanic reactions in influencing the total admixture benefit. A positive net SCM benefit shows that the

admixture adds value to the hydration products beyond the pozzolanic reactions while a value less than the pozzolanic contribution indicates a loss on hydration products due to probably hydration products degradation effects. The quantitative expressions proposed do have the capacity to separate the different important variables.

3. Blended samples presented higher degrees of hydration than the control. The degree of hydration for blended samples increased with increase in replacement level. The role of extra reactive silica in bonding with the CH precipitates from cement hydration and the acceleratory effects of mineral admixtures are advanced as compositional factors responsible for the observed increase in the degree of hydration.

4. Calcination increased the degree of hydration but reduced the degree of pozzolanic activity of blended cements. Calcination at 850 °C appears to activate elements and minerals of kamafugites and carbonatites to contribute in the hydration reactions leading to an increase in the volume of hydrates in the dehydration zone. The acceleratory effects associated with calcite and volatile alkalis accelerate the rate of deposition of CH phases in the raw pozzolans which accelerates pozzolanic performance in the raw pozzolans. Calcination diminishes these effects.

5. The fineness property of the kamafugites and carbonatites confirm on two main reaction mechanisms in the hydrating pastes, pozzolanic and hydration products degradation reactions. Fineness is observed to have an inverse relationship for the early age results and a direct relationship for the 56 days result for both the degree of hydration and degree of pozzolanic activity. The results compare well with the strength results and confirm the prominence of retardation/degradation reactions at early stages of hydration which benefit from the fineness property at that stage. The later stage reactions are dominated by the pozzolanic reactions leading to a linear relationship with fineness of test pozzolans.

6. It is demonstrated that a substantial amount of CH phases is exposed to carbonation in the testing process. This implies that quantification of non-evaporable water in the

dehydroxylation phase must consider carbonation of the CH precipitate. Accordingly, TGA pozzolanic activity characterisation that focuses only on the dehydroxylation phase advances a higher value of CH than is consumed in a pozzolanic reactions. The proposed models are able to correct for this trend.

7. It is further argued that the CH composition is a derivative of the degree of hydration of the alite and belite phases in cement and has no significant contribution to the important properties of hydrated paste. Furthermore, considering the chemically bound water from the dehydroxylation phase as a cumulative contributor to the prediction of the degree of hydration limits the previous models in characterizing the different micro and macro properties of hydrating cement paste.

CHAPTER 7

GENERAL CONCLUSIONS

7.1 General

Kamafugites and carbonatites studied in this thesis are currently applied in the production of pozzolanic cements in Uganda. They are currently the only feasible source of SCMs in the less industrialized sub Saharan Africa region that lacks the well-studied and generally accepted SCMs of industrial origin. There was a lack of published research on their performance as mineral admixtures in Portland cement concrete. For this reason, their application in structural engineering works was limited to only structures that are of low importance to the public. This meant that the ecological and economic benefits of blended cements were missed in the sub-Saharan Africa region that has a critical infrastructure deficit. The main aim of the current thesis was to characterize the compositional properties of kamafugites and carbonatites and how these properties affect hydration progression, hydration products, strength development and other properties of blended cement pastes. The studies were conducted using both standard test methods and instrumental techniques that included XRD, XRF, TGA, isothermal calorimetry and dilatometry. Theoretical models for quantification of the degree of hydration (α), the degree of pozzolanic activity (β) and the net admixture benefit (λ) for cements blended with SCMs were developed and tested using generated data from the current study and also data from published works. The models developed based on TGA results recognize the importance of different reaction mechanisms and were developed to separate the three defined mechanisms, hydration, pozzolanic, and net admixture benefit, for a more robust characterisation of SCMs in portland cement. Applying the characterisation tools stated above and the subsequent analysis of results generated, several observations and conclusions have been made.

The current chapter therefore presents general observations and conclusions drawn from the different sections of this thesis. Both physical and compositional characteristics of kamafugites and carbonatites were studied for their effect on cement hydration kinetics, hydration products assemblage, strength

development and fresh properties of Portland cement and the discussions in the different chapters of this thesis inform the conclusions presented in the current chapter. The report also presents suggestions on future research in relation to compositional and physical characteristics of kamafugites and carbonatites and their effect on hydration and microstructure when blended with Portland cement. Where necessary, proposals have been made on the appropriate tools of analysis for the suggested research areas.

7.2 Observations and Conclusions

- The kamafugites and carbonatites are polymineralic volcanic materials. The minerals present highly varying levels of hardness, a condition that led to particle size driven segregation of minerals during milling. Calcite, a mineral that ranks low on the Mohs' relative hardness scale, dominated the finer part (d_{10}) of the bulk sample on milling, a consideration that gave it a dominant role in influencing reactivity of the test natural pozzolans.

- Both crystalline and amorphous phases exist in the test kamafugites and carbonatites. The particles are fairly irregular, angular and with rough textures that reveal inclusions of amorphous phases in crystalline particles.

- Although cement manufacturers in Uganda consider kamafugites and carbonatites as natural pozzolans, the materials are nonresponsive to the minimum chemical composition, volatile compounds (LOI) and reactive silica content required for natural pozzolans under ASTM C618 and EN 197-1. There is no standard that addresses the calcite-aluminosilicate-alkalis parallel reaction mechanisms, yet all these mechanisms are reported independently to influence cement performance.

- The addition of kamafugites and carbonatites in Portland cement led to a reduction in the setting time, increased water demand, reduced slump flow, and had no measurable influence on soundness property of cement. The reduction in setting time was compositional given that increase in replacement level led to further reduction in setting time. Both calcite and potassic leaning alkalis were hypothesized as the cause of the observed accelerated setting behavior

of kamafugites and carbonatites blended cements. Increase in water demand and reduction in slump flow were both attributed to the angular-shaped and rough surfaced particles that led to an increase in their hydrophilicity property.

- Carbonatites and kamafugites, because of their low saturation of silica and alumina phases, have less pronounced pozzolanic properties. All blended cements showed relative gain in strength to the control (CEM I 52.5 R). The relative gain in strength increased with time up to 28 days indicating either a depletion of reactive aluminosilicates in the kamafugites and carbonatites or hydration products conversion by parallel reaction mechanisms, except for Poz-2 which shows a parallel trend in compressive strength with the control. The relative gain in strength was not sufficient to fully compensate for the replaced cement content for 7, 28, 56, 90 and 180 days of curing and showed no clear dependence on the silica content in test pozzolans. The strength activity index test, however, pass the carbonatites and kamafugites as viable pozzolanic materials for use in portland cement applications. The results also show a calcite and alkalis driven loss of strength over time with strength results of 90 days higher than those of 180 days of curing. The strength conversion reactions are established in Kamafugites and Carbonatites blended Portland cement from the start of hydration and their reaction rates are dependent on both the level of replacement and fineness of the test pozzolans. While increase in fineness increased the strength conversion effect, increase in replacement level showed a non-linear relationship with the conversion effect peaking at 10% level of replacement and reducing with increase in replacement level.

- The mechanisms influencing strength development at early stages (7 days) and later stages (180 days of curing) are not dominated by the calico-silicate phases in the test pozzolans. Therefore, the hydration progression and strength development mechanisms in cements blended with Kamafugites and carbonatites cannot be sufficiently appraised on the Si and CaO content in the test pozzolans. The importance of alkalis, MgO and other minerals in the test pozzolans is justified.

- The kamafugites and carbonatites accelerated early heat of hydration. Heat of hydration results reveal that test pozzolans did not alter early hydration

reactions but only had an accelerating effect. The results show pozzolanic reactions were pronounced after 36 hours from the start of hydration.

- Chemical shrinkage of Portland cement blended with kamafugites and carbonatites showed dependence on reactive silica, CaO, MgO and alkalis, reactive silica dependence proving presence of pozzolanic properties. The trend for reactive silica was similar to that of MgO indicating a possible dependence relationship with MgO. Stoichiometrically, a pozzolanic reaction does not consume exta water beyond what is in the CH reaction component and, therefore, is not a contributor to chemical shrinkage in the sense of hydration, but instead results in an increase in volume by 12% of the absolute volume of the reactants. Observed increase in chemical shrinkage in mineral admixed portland cements is due to pronounced non-pozzolanic reaction mechanisms associated with the filler effect and other hydration mechanisms between the hydrating cement and mineral admixture. Accordingly, it was observed that chemical shrinkage reduced with increase in reactive silica content of the test pozzolans.

- Potassic and sodic alkalis in the test kamafugites and carbonatites showed differences in trends indicating differences in their mechanisms of interaction with cement phases, potassic alkalis leading to shrinkage compensating reactions in the cement systems while sodic alkalis trended positive with increase in chemical shrinkage.

- Addition of mineral admixtures in Portland cement is known to affect early hydration dynamics due to what is known as the filler effect. The chemical interaction between cement compounds and alkalis and other minerals in some pozzolanic materials can have accelerating effects on hydration rate causing a higher early shrinkage, early heat of hydration and strength development rate. However, the importance of the filler effect is when ions in the paste system have a high mobility and starts to diminish when the cement sets. The observed chemical shrinkage trends with calcite indicated a continued activity between calcite and hydrating cement phases confirming calcite to be part of formed hydration products. A time dependent preferential hydration of aluminates to form high density carboaluminates while limiting gypsum to hydrate only to

ettringite is advanced as the contributor to the observed chemical shrinkage trends. The trend was further supported by the TGA studies.

- Mathematical expressions for quantification of chemically bound water in hydration and pozzolanic reactions of blended cement pastes are presented. The equations are variations based on established TGA models for degree of hydration, degree of pozzolanic activity and degree of total mineral admixture estimation. The mathematical expressions were used in characterisation of pozzolanic and non-pozzolanic interactions between the test pozzolans and hydrating portland cement. The expressions are presented in Tables 7.1-3.

Table 7.1: Mathematical expressions for estimation of the degree of hydration of blended cements

Parameter	Mathematical expression
Degree of hydration ($\propto$)	$\propto = \frac{(Ldh_{cem} + Ldh_a)}{(1-\tau)W_{B\propto}}$, $Ldh = Ldh_{cem} + Ldh_a + ((Ldx_{cem} - Ldx_{Poz}) - 0.41(Ldc_t - Ldc_0))$, $\tau = (Ldx_{Poz} + 0.41(Ldc_t - Ldc_0))$

Where Ldh is the mass of chemically bound water attributed to the dehydration phase in the thermal decomposition TGA profile of a test blended sample. Ldh_{cem} is the mass of chemically bound water attributed to the dehydration phase of the control sample (plain Portland cement) on the TGA thermal decomposition profile at the same curing time as the test blended sample. Ldh_a is the mass component of Ldh that is associated with the non-pozzolanic admixture effects. Ldx_{cem} and Ldx_{Poz} represent the mass loss to dehydroxylation of the control sample (plain portland cement) and test sample respectively. Ldc_t and Ldc_0 represent the mass loss to decarbonation for test sample at the test time and at anhydrous state respectively. $W_{B\propto}$ represents chemically bound water at complete hydration (infinite time) with $\tau W_{B\propto}$ being a correction coefficient to discount chemically bound water due to CH deposited in the paste microstructure that is not consumed in the pozzolanic and hydration reactions.

The parameter Ldh_a characterizes the acceleratory effects of mineral admixtures in Portland cement.

All the input variables, except those of the decarbonation phase, are normalized to cement content.

Since the pozzolanic reaction does not take up water beyond the quantity in the CH part of the reactants, the pozzolanic reaction is not characterized as a hydration reaction and, as a consequence, bound water due to the pozzolanic reaction is not considered in estimation of degree of hydration. It is however important that we appreciate the equilibrium shift caused by mineral admixtures in blended cement pastes. The consequence of this equilibrium shift is hypothesized to influence hydration progression and is considered within the Ldh_a quantity measured.

Table 7.2**:** Mathematical expressions for estimation of the degree of pozzolanic activity of blended cements

Parameter	Mathematical expression
Degree of pozzolanic activity (β)	$\beta = \frac{1.85 \times W_{Poz}}{W_{CH\infty} \times (1-x)}$, $W_{Poz} = (Ldx_{cem} \times \frac{\propto_{poz}}{\propto_{cem}} - Ldx_{Poz}) - 0.41(Ldc_t - Ldc_0)$, $W_{CH\infty} = \frac{CH \times 2.251}{4.11}$.

Where β represents the degree of pozzolanic activity, W_{Poz} the mass of chemically bound water of CH consumed in the pozzolanic reaction (Equation 7.10), $W_{CH\infty}$ the mass of chemically bound water to CH at complete hydration for a plain portland cement sample, and x the replacement ratio of the test pozzolan, $1 > x > 0$.

Ldx_{cem} represent the chemically bound water due to the dehydroxylation phase for the reference cement sample, Ldx_{Poz} is chemically bound water due to the dehydroxylation phase of the sample blended with a test pozzolan, $\frac{\propto_{poz}}{\propto_{cem}}$ is the standardization ratio based on the degree of hydration to adjust for the hydration

acceleration due to the presence of mineral admixtures in the blended cement sample. 0.41 is a stoichiometric coefficient for quantification of CH water lost to carbonation, and $(Ldc_t - Ldc_0)$ is the mass due to decarbonation of the carbonate component from the carbonation of CH. Ldc_t is the mass loss due to decarbonation at curing time t while Ldc_0 is mass loss due to decarbonation of the same sample at anhydrous state (before addition of water).

CH represents the volumetric content of CH as a percentage of the hydration products at complete hydration of cement, 2.251 the density of CH, and 4.11 a stoichiometric factor for quantification of chemically bound water in a CH mass.

Table 7.3: Mathematical expressions for estimation of the net admixture benefit of blended cements

Parameter	Mathematical expression
Degree of total mineral admixture activity (β)	$\lambda = \frac{Ldh_{Poz} - Ldh_{cem}}{Ldh_{cem}} \times 100\%.$

Where, Ldh_{Poz} is water lost due to dehydration of the mineral admixed sample normalized to cement content.

- The quantitative expressions for the degree of hydration (α), the degree of pozzolanic activity (β) and the degree of total admixture activity (λ) are valid tools for characterisation of SCMs in portland cement concrete. The models were verified by comparison of their results with the strength and chemical shrinkage results generated in the current study. The models were also applied on results from published works and advanced plausible interpretations. The proposed models offer a robust package of information that enables adaptive use of different mineral admixtures and clinker properties. The model is therefore not limited to only kamafugites and carbonatites but can characterize other mineral admixtures as demonstrated in the current chapter.

- The application of the degree of hydration (α), the degree of pozzolanic activity (β) and the degree of total mineral admixture activity (λ) analysis tools revealed the kamafugites to exhibit both pozzolanic and strength conversion reaction

mechanisms. The strength conversion mechanisms undo the strength gains from pozzolanic reactions to negatively influence the total admixture benefit. A positive total admixture benefit shows that the admixture adds value to the hydration products beyond the pozzolanic reactions while a value less than the pozzolanic contribution indicates a loss on hydration products due to strength conversion effects. The quantitative expressions proposed do have the capacity to separate the different important variables.

- Blended samples presented higher degrees of hydration than the control. The degree of hydration for blended samples increased with increase in replacement level. The role of extra reactive silica in bonding with the CH precipitates from cement hydration and the acceleratory effects of mineral admixtures are advanced as compositional factors responsible for the observed increase in the degree of hydration.
- Calcination increased the degree of hydration but reduced the degree of pozzolanic activity of blended cements. Calcination at 850 °C activates elements and minerals of kamafugites and carbonatites to contribute in the hydration reactions leading to an increase in the volume of hydrates in the dehydration zone. The acceleratory effects associated with calcite and volatile alkalis accelerate the rate of deposition of CH phases in the hydrating cement which accelerates pozzolanic performance in the raw pozzolans. Calcination diminishes these effects.
- The fineness property of the kamafugites and carbonatites confirm on two main reaction mechanisms in the hydrating pastes, pozzolanic and strength conversion reactions. Fineness is observed to have an inverse relationship for the early age results and a direct relationship for the 56 days result for both the degree of hydration and degree of pozzolanic activity. The results compare well with the strength results and confirm the prominence of strength conversion reactions at early stages of hydration which benefit from the fineness property at that stage. The later stage reactions are dominated by the pozzolanic reactions leading to a linear relationship with fineness of test pozzolans.

- It is demonstrated that a substantial amount of CH is exposed to carbonation in the testing process. This implies that quantification of non-evaporable water in

the dehydroxylation phase must consider carbonation of the CH products. Accordingly, TGA pozzolanic activity characterisation that focuses only on the dehydroxylation phase of the TGA profile advances a higher value of CH than is consumed in a pozzolanic reactions. The proposed models can correct for this trend.

- It is further argued that the CH composition is a derivative of the degree of hydration of the alite and belite phases in cement and has no significant contribution to the important properties of hydrated paste. That, considering the chemically bound water from the dehydroxylation phase as a cumulative contributor to the prediction of the degree of hydration limits the previous models in predicting the different micro and macro properties of hydrating cement paste.

- Results from applied methods for testing pozzolanic behavior of kamafugites and carbonatites, including the chemical shrinkage test, heat of hydration test, thermogravimetric analysis test (TGA), and strength development test were compared for similarities. While the strength, TGA, heat of hydration and chemical shrinkage registered positive and correlated results, the Fratini test (EN 195-5) failed these materials because of flow of Ca^{2+} ions into the solution from the test pozzolans themselves. The test pozzolans are indicated to have a high water-soluble Ca^{2+} ions which disables the validity of results from the Fratini test. The chemical shrinkage test following dilatometry technique is proposed as a practical test for pozzolanic activity of supplementary cementitious materials in the less developed regions of Africa given the ease and low costs required for the experimental setup.

CHAPTER 8

RECOMMENDATIONS FOR FUTURE RESEARCH

- The current study revealed kamafugites and carbonatites to significantly influence the early age hydration kinetics and hydration products assemblage of blended Portland cement. The early age hydration kinetics are known to influence the important properties of fresh concrete (workability, setting and paste microstructure), which will in turn directly impact on the strength and durability properties of hardened concrete. Cements blended with carbonate bearing natural pozzolans therefore present interesting perspectives on how paste microstructure composition and durability performance properties might develop.
- Future research should investigate high volume replacement of Portland cement with kamafugites and carbonatites. Properties of concrete such as water demand, strength development, microstructure and hydration products assemblage are known to depend on physical properties of pozzolans, specifically fineness and replacement levels. The current study limited replacement level to 35% and no experimental work focusing on high volume replacement of cement with the test pozzolans has been published. Characterization of variation of natural pozzolan content in the cement mix as a function of workability as measured by slump flow is a subject of study under high volume displacement of cement with kamafugites and carbonatitic lavas.
- The role of the CO_3^{2-} ions, Mg^{2+} ions and potassic alkalis from kamafugites and carbonatites in hydration kinetics and paste microstructure development need further investigation. The current study established strong linear relationships with high coefficients of determination (R^2>95%) between reactive CaO, water-soluble Mg^{2+} ions and alkalis with chemical shrinkage. Future research should characterize the reaction mechanisms and final hydration products formed.
- The current study established a strength conversion effect that was driven by the carbonates and alkali compounds in kamafugites and carbonatites. A negative trend observed between strength development and reactive CaO and water soluble potassic alkalis led to a conclusion that the two compounds drive the

conversion effect. The actual reaction mechanisms between cement hydration products and the carbonate and alkali compounds that resulted in the conversion effect should be defined. Long term performance of kamafugites and carbonatites as SCMs in Portland cement concrete is recommended for future research.

- Blended Portland cements present a more complex and dynamic process of hydration with the cement phases reacting to produce CH while the pozzolanic mechanism consumes the precipitated CH at rates that are controlled by the physico-chemical properties of both the cement and the mineral admixture. Moreover, carbonation as a chemical process that too consumes the CH in the system. Measurement of CH content in the dihydroxylation phase must therefore be sensitive to all possible chemical reactions that can influence CH generation, deposition and fixation. The hydration rate of the alite and belite phases in cement (A), the accelerating effect due to the presence of the SCMs (B), the consumption of the CH phase by the pozzolanic reaction (C), and consumption of CH in a carbonation reaction (D), these are reaction mechanisms requiring quantification in the dihydroxylation phase of TGA. The quantification will improve on the accuracy of characterisation methods for mineral admixtures based on measurement of the degree of hydration (α), the degree of pozzolanic activity (β) and the net admixture benefit (λ) proposed in this thesis.

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APPENDICES

Appendix 1: Consistencies in chemical composition between milled and raw samples

	PPC Customer Services - Uganda Pozzolan - Wits PhD Samples
Analysis Request Form No.:	**7382**
Project number	**GLS-CHEM-10-3-2015-19**
Report Reference No.:	**T150372**
Date:	**10-Jul-15**

Sample ID	**Sample Reference**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**Mn_2O_3**	**TiO_2**	**CaO**	**MgO**	**P_2O_5**	**SO_3**	**K_2O**	**Na_2O**	**LOI**	**Total**	**Reactive SiO_2**	**Reactive CaO**
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
GLS15MAR00461	Poz-1 Original	31.9	8.40	11.9	0.39	1.99	21.4	4.98	2.14	0.11	0.92	1.38	13.7	99.2	18.8	8.40
GLS15MAR00465	Poz-1 Milled	31.9	8.25	12.3	0.39	2.10	21.1	4.88	2.27	0.07	0.98	1.33	13.7	99.2	18.8	9.25
GLS15MAR00462	Poz-2 Original	35.3	7.47	10.5	0.24	2.80	16.5	5.52	1.49	0.07	2.35	0.81	16.2	99.2	23.3	1.81
GLS15MAR00466	Poz-2 Milled	35.6	7.53	10.3	0.23	2.76	16.3	5.47	1.48	0.01	2.37	0.80	16.4	99.2	22.4	3.89
GLS15MAR00463	Poz-3 Original	49.9	7.52	7.41	0.16	2.47	8.12	6.25	0.88	0.01	4.06	0.19	12.2	99.2	26.6	5.00
GLS15MAR00467	Poz-3 Milled	51.1	7.50	7.44	0.15	2.51	8.09	6.16	0.93	0.01	4.13	0.08	11.1	99.2	27.6	3.45

0.0 Means not detected by X-Ray at this level and does not imply zero %

Appendix 2: Mortar strength results with their statistical tests

Curing	7 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	49.6	49.2	47.6	48.5	50.4	49.6	0.97929	**49.2**	100
Control 2 Fly Ash 20%	38.9	39.6	39.1	40.3	38.9	40.5	0.70922	**39.6**	80
Poz-1-5%F3	47.5	46.0	48.1	48.7	46.9	47.9	0.95586	**47.5**	97
Poz-1-10%F3	44.9	46.2	44.4	46.8	44.9	45.6	0.90701	**45.5**	93
poz-1-20%F3	41.6	41.6	41.7	41.7	41.2	41.1	0.26394	**41.5**	84
Poz-1-35%F3	33.9	34.1	33.5	34.0	33.4	33.8	0.27869	**33.8**	69
Poz-1-20%F1	42.0	42.7	42.0	41.3	42.7	41.0	0.70071	**42.0**	85
poz-1-20%F2	41.8	40.6	40.0	41.7	40.7	40.0	0.79246	**40.8**	83
Poz-1-20%F40 Calcined 850^{o}C	43.3	43.2	43.9	44.6	42.3	43.9	0.78655	43.5333	89

Curing	28 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	57.0	57.1	58.5	56.6	55.4	57.4	1.0139	**57.0**	100
Control 2 Fly Ash 20%	54.2	55.4	54	54.4	54.7	52.7	0.89592	54.2	95
Poz-1-5%F3	59.1	59.5	58.8	58.4	59.9	59.5	0.54406	**59.2**	104
Poz-1-10%F3	54.7	55.7	54.9	55.9	55.3	55.4	0.45789	**55.3**	97
poz-1-20%F3	51.9	51.2	50.3	50.7	50.6	51.6	0.62209	**51.1**	90
Poz-1-35%F3	43.5	43.6	44.5	43.2	43.5	43.2	0.47924	**43.6**	76
Poz-1-20%F1	49.3	50.6	51.4	51.8	49.7	50.9	0.96626	**50.6**	89
poz-1-20%F2	49.8	48.0	49.9	49.0	48.5	47.7	0.91524	**48.8**	86
Poz-1-20%F3 Calcined 850^{o}C	48.1	49.5	51.1	49.6	49.9	49.6	0.95847	49.6333	87.076

Curing	90 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	62.3	59.8	61.6	64.4	65.0	67.3	2.68998	**63.4**	100
Poz-1-5%F3	63.1	62.9	63.8	65.7	63.9	63.9	0.98877	**63.9**	101
Poz-1-10%F3	61.3	59.2	61.6	60.1	59.8	63.5	1.55874	**60.9**	96
poz-1-20%F3	52.7	53.2	52.8	51.4	54.7	54.4	1.21161	**53.2**	84
Poz-1-35%F3	46.3	47.0	47.3	46.2	45.5	44.9	0.89889	**46.2**	73
Poz-1-20%F1	54.9	53.5	54.6	53.7	53.9	54.3	0.54314	**54.2**	85
poz-1-20%F2	53.8	52.3	54.7	52.6	52.5	52.7	0.94446	**53.1**	84

Curing	180 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	65.4	65.4	65.1	65.6	65.4	64.8	0.28577	**65.3**	100
Control 2 Fly Ash 20%	72	71.8	71.4	72.5	73	72.1	0.55737	72.1	110
Poz-1-5%F3	61.3	63.8	63.7	61.3	59.7	60.0	1.76597	**61.6**	94
Poz-1-10%F3	59.8	58.2	56.2	58.3	60.5	57.3	1.57913	**58.4**	89
poz-1-20%F3	52.6	52.0	53.6	52.9	54.2	53.0	0.76877	**53.1**	81
Poz-1-35%F3	45.3	44.9	45.5	46.1	44.4	44.5	0.64627	**45.1**	69
Poz-1-20%F1	52.3	52.7	55.0	54.2	53.4	55.2	1.19833	**53.8**	82
poz-1-20%F2	52.1	54.3	52.0	54.4	52.1	51.5	1.27227	**52.7**	81
Poz-1-20%F3 Calcined 850^{o}C	54.3	56.2	54.7	53.9	55.7	54.7	0.86814	54.9	84

Curing	7 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	49.6	49.2	47.6	48.5	50.4	49.6	0.97929	**49.2**	100
Control 2 Fly Ash 20%	38.9	39.6	39.1	40.3	38.9	40.5	0.70922	**39.6**	80
Poz-2-5%F3	47.8	49.1	47.6	48.6	49.9	49.4	0.90701	**48.7**	99
Poz-2-10%F3	46.8	46.7	47.0	46.3	46.5	46.9	0.26077	**46.7**	95
Poz-2-20%F3	44.2	45.6	45.6	45.1	46.1	45.6	0.6532	**45.4**	92
Poz-2-35%F3	34.7	36.2	35.7	36.9	36.1	36.0	0.72296	**35.9**	73
Poz-2-20%F1	43.5	44.3	44.2	44.1	44.1	43.0	0.50859	**43.9**	89
Poz-2-20%F2	42.0	39.8	41.7	41.4	40.9	40.5	0.8167	**41.1**	84
Poz-2-20%F3 Calcined 850^{o}C	42.8	43.3	42.7	43.1	42.7	42.9	0.24014	**42.9**	87

Curing	28 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	57.0	57.1	58.5	56.6	55.4	57.4	1.0139	**57.0**	100
Control 2 Fly Ash 20%	54.2	55.4	54	54.4	54.7	52.7	0.89592	54.2	95
Poz-2-5%F3	56.0	54.4	57.4	56.2	55.6	56.1	0.97108	**56.0**	98
Poz-2-10%F3	55.9	54.0	54.3	54.7	55.4	55.0	0.70261	**54.9**	96
Poz-2-20%F3	53.4	52.9	51.5	51.8	52.3	52.1	0.70616	**52.3**	92
Poz-2-35%F3	46.1	47.7	46.1	47.2	46.9	46.2	0.67231	**46.7**	82
Poz-2-20%F1	51.8	51.8	52.4	51.4	52.1	52.8	0.49699	**52.1**	91
Poz-2-20%F2	51.0	53.5	52.8	51.5	52.5	52.2	0.90056	**52.3**	92
Poz-2-20%F3 Calcined 850^{o}C	54.9	53.9	52.8	52	53.3	53.5	0.98387	53.4	94

Curing	90 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	62.3	59.8	61.6	64.4	65.0	67.3	2.68998	**63.4**	100
Poz-2-5%F3	63.0	61.8	65.7	61.3	66.5	60.0	2.5634	**63.1**	99
Poz-2-10%F3	64.4	66.3	60.9	63.9	61.5	59.0	2.67033	**62.7**	99
Poz-2-20%F3	55.7	56.3	55.4	56.2	56.5	56.7	0.49261	**56.1**	89
Poz-2-35%F3	52.7	52.2	51.1	52.9	46.1	50.3	2.54434	**50.9**	80
Poz-2-20%F1	57.3	56.8	55.5	54.6	57.4	58.2	1.33666	**56.6**	89
Poz-2-20%F2	62.7	60.9	61.7	61.7	60.7	62.0	0.73326	**61.6**	97

Curing	180 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	65.2	64.3	65.9	65.8	65.3	65.2	0.57067	**65.3**	100
Control 2 Fly Ash 20%	72	71.8	71.4	72.5	73	72.1	0.55737	72.1	110
Poz-2-5%F3	61.3	64.8	62.6	61.6	61.0	62.5	1.38275	**62.3**	95
Poz-2-10%F3	60.2	60.3	61.1	60.6	60.6	59.1	0.67355	**60.3**	92
Poz-2-20%F3	58.1	58.5	59.2	57.0	57.6	58.3	0.75741	**58.1**	89
Poz-2-35%F3	50.6	51.2	51.4	54.0	51.4	53.3	1.34226	**52.0**	80
Poz-2-20%F1	58.1	57.9	59.0	59.2	56.7	59.1	0.96885	**58.3**	89
Poz-2-20%F2	56.5	56.5	58.5	54.8	58.3	56.2	1.3914	**56.8**	87
Poz-2-20%F3 Calcined 850^{o}C	58.6	58.5	59.4	61.3	60.5	56.5	1.68839	59.1	91

Curing	7 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	49.6	49.2	47.6	48.5	50.4	49.6	0.98	**49.2**	100
Fly Ash 20% Control	38.9	39.6	39.1	40.3	38.9	40.5	0.71	**39.6**	80
Poz-3-5%F3	49.1	49.1	50.0	49.2	48.9	50.2	0.54	**49.4**	101
Poz-3-10%F3	46.8	46.5	47.3	47.0	47.8	48.8	0.83	**47.4**	96
Poz-3-20%F3	40.5	41.0	41.9	41.4	40.7	41.7	0.56	**41.2**	84
Poz-3-35%F3	29.3	30.6	30.9	31.2	30.0	31.0	0.72	**30.5**	62
Poz-3-20%F1	31.9	31.9	32.7	31.1	32.8	32.1	0.62	**32.1**	65
poz-3-20%F2	39.4	39.4	40.4	39.2	41.2	40.6	0.81	**40.0**	81
Poz-3-20%F3 Calcined 850^{o}C	41.8	42.4	41.1	41.6	42.1	42.9	0.63	42.0	85

Curing	28 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	57.0	57.1	58.5	56.6	55.4	57.4	1.01	**57.0**	100
Fly Ash 20% Control	54.2	55.4	54	54.4	54.7	52.7	0.9	54.2	95
Poz-3-5%F3	59.6	58.7	57.4	59.6	59.7	58.6	0.89	**58.9**	103
Poz-3-10%F3	56.4	55.4	55.6	55.2	53.6	53.6	1.13	**55.0**	96
Poz-3-20%F3	56.5	57.2	56.9	58.2	55.7	56.1	0.88	**56.8**	100
Poz-3-35%F3	44.9	43.7	43.2	44.2	43.4	43.3	0.66	**43.8**	77
Poz-3-20%F1	51.3	51.6	51.9	51.6	51.5	50.6	0.44	**51.4**	90
poz-3-20%F2	52.1	52.8	52.5	52.7	51.3	52.8	0.59	**52.4**	92
Poz-3-20%F3 Calcined 850^{o}C	54.2	55.1	54.2	55.8	55.6	54.9	0.68	55.0	96

Curing	90 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	62.3	59.8	61.6	64.4	65.0	67.3	2.69	**63.4**	100
Poz-3-5%F3	66.5	64.6	64.2	66.6	64.6	62.7	1.48	**64.9**	102
Poz-3-10%F3	64.6	64.9	63.2	63.5	64.4	62.2	1.02	**63.8**	101
Poz-3-20%F3	56.7	57.7	57.9	57.7	56.1	58.4	0.85	**57.4**	91
Poz-3-35%F3	45.4	48.4	46.8	47.6	47.9	47.0	1.05	**47.2**	74
Poz-3-20%F1	56.1	57.6	56.7	58.4	56.7	55.8	0.97	**56.9**	90
poz-3-20%F2	56.9	57.8	57.3	57.9	56.1	57.1	0.66	**57.2**	90

Curing	180 DAYS CURING								SAI
Sample No	Compresive strength readings						SD	**Mean**	
Control 1 CEM I 52.5R	65.2	64.3	65.9	65.8	65.3	65.2	0.57	**65.3**	100
Fly Ash 20% Control	72	71.8	71.4	72.5	73	72.1	0.56	72.1	110
Poz-3-5% F3	66.7	60.3	66.5	62.8	62.0	64.0	2.54	**63.7**	98
Poz-3-10% F3	57.8	59.4	59.9	60.9	60.2	61.2	1.22	**59.9**	92
Poz-3-20%F3	55.4	55.7	56.6	55.9	58.3	57.6	1.15	**56.6**	87
Poz-3-35%F3	46.8	46.3	46.1	45.5	46.5	47.5	0.67	**46.5**	71
Poz-3-20%F1	56.7	57.1	55.6	56.8	54.2	54.6	1.23	**55.8**	86
poz-3-20%F2	54.1	54.6	55.5	54.4	54.3	56.9	1.07	**55.0**	84
Poz-3-20%F3 Calcined 850^{o}C	61.1	60.8	60.6	60.2	61.7	60.8	0.5	60.9	93

Appendix 3: Heat of Hydration results

Isothermal calorimetry results are saved on the DVD submitted together with this thesis. The results present type of test pozzolan, fineness and replacement levels as variables.

Appendix 4: Chemical Shrinkage Results

Curing (Days)	Control 1: Andesite	Control 2: Fly Ash	Poz-1	Poz-2	Poz-3	Poz-1 Calcined	Poz-2 Calcined	Poz-3 Calcined
0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.0018	0.0020	0.0023	0.0028	0.0008	0.0025	0.0025	0.0018
1	0.0255	0.0263	0.0270	0.0265	0.0240	0.0253	0.0263	0.0268
2	0.0318	0.0328	0.0338	0.0328	0.0298	0.0303	0.0323	0.0330
3	0.0365	0.0380	0.0385	0.0373	0.0348	0.0345	0.0363	0.0378
7	0.0448	0.0460	0.0468	0.0453	0.0443	0.0410	0.0425	0.0448
14	0.0490	0.0510	0.0510	0.0500	0.0480	0.0455	0.0468	0.0493
21	0.0505	0.0553	0.0525	0.0515	0.0498	0.0470	0.0483	0.0508
28	0.0520	0.0553	0.0545	0.0530	0.0515	0.0490	0.0500	0.0523
90	0.0558	0.0613	0.0590	0.0588	0.0555	0.0540	0.0550	0.0565
180	0.0583	0.0645	0.0628	0.0655	0.0580	0.0580	0.0585	0.0593

Appendix 5: TGA/DTG Results

Thermogravimetric analysis results are saved on the DVD submitted together with this thesis. The results present type of test pozzolan, fineness and replacement levels as variables