EISSN: 2707-0425

East African Journal of Science, Technology and Innovation, Vol. 3 (2): March 2022

This article is licensed under a Creative Commons license, Attribution 4.0 International
(CC BY SA 4.0)

Hydration and compressive strength of Portland cement blended with kamafugites and carbonatites: Effect of Physical Properties

[1*]BUREGYEYA A., [1]NWAUBANI S

[1]School of Civil and Environmental Engineering, University of the Witwatersrand, Johannesburg, South Africa

***Corresponding Author**: apollo.buregyeya@mak.ac.ug

Abstract

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. The current study sought to characterise their physical and chemical properties and compare them with those of published works on natural pozzolans. Two samples, a carbonatite and a kamafugite, from the Toro-Ankole geological region of East Africa are investigated for their effect on specific properties of pastes and mortars when used as natural pozzolans in Portland cement. The volcanic tuffs milled to three fineness levels and blended with Portland cement at 0%, 5%, 10%, 20% and 35% replacement levels are tested for effects on hydration and compressive strength. Results show a time dependent variation in heat of hydration which increases for the first 14 hours before decreasing. The variation seems dependent on level of replacement. 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. A compressive strength conversion process that peaks at 10% replacement level is observed in all blended samples leading to compressive strength results at 180 days being lower than those at 90 days of curing. 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.

Keywords: *Alkalis, carbonatites, compressive strength, filler effect, heat of hydration, Kamafugites, natural pozzolan*

Received:	27/09/21
Accepted:	28/02/22
Published:	31/03/22

Cite as: *Buregyeya and Nwaubani, (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 3(2).*

Introduction

Kamafugites and carbonatites are materials of volcanic origin whose primary composition consists of carbonate minerals and potassic alkalis. Their high content of carbonates results in silica undersaturation and, consequently, advances interest in their applicability and performance as pozzolanic materials in Portland cement concrete. A pozzolan is a non-cementitious inorganic material with sufficient aluminosilicates in its composition that can react with portlandite or lime in hydrating Portland cement systems to form reaction products with binding properties that are similar to those of hydrated cement (ASTM C618, 2005). Pozzolans, when used as partial substitutes in Portland cement, present benefits of long-term strength, improved cement paste microstructure and, as a result, more durable, low cost and sustainable concrete (Blanco *et al.,* 2006; Mehta and Monteiro, 2006; Schneider, 2011; Taylor, 1997).

Pozzolans are classified primarily based on their source, either natural or artificial (Snellings *et al.,* 2012; Taylor, 1997). The natural pozzolan classification considers natural materials of volcanic origin that require minimal processing to be used as mineral additions in cement while artificial pozzolans are industrial byproducts, mainly waste materials generated as a result of industrial processes (e.g. Fly ash (FA) from coal burning in thermal power plants, ground granulated blast furnace slag (ggbs) from production of pig iron, and silica fume (SF) as a waste extract from silicon metal or its alloys) and thermal activation of natural materials (e.g. calcined clay). Because of process controls at the time of production, artificial pozzolans are more predictable in their performance and are preferred to natural pozzolans (Snellings et al 2012). Availability of artificial pozzolans is limited to industrialized regions of the world leaving less industrialized regions to a limited option of using natural pozzolans (Blanco *et al.,* 2006). Indeed, Schmidt *et al.,* 2018, advance natural pozzolans as the most feasible choice of SCMs for sub-Sahara Africa (SSA). Kamafugites and carbonatites, being materials of volcanic origin, fall in the natural pozzolan classification. They are the primary source of pozzolans used in production of pozzolanic cements in Western Uganda.

Works on natural pozzolans 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 also on the relief gained in improving the sustainability functions of Portland cement concrete. 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; Caputo *et al.,* 2008; Luke, 2007; Martinez-Ramirez *et al.*, 2006; Mertens *et al.,* 2009; Pourkhorshidi *et al.,* 2010; Shannag and Turanli *et al.,* 2004; Snellings *et al.,* 2010; Uzal *et al.,* 2010 Yeginobali, 1995). 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 published about their performance as mineral admixtures in Portland cement concrete.

Previous studies on kamafugites and carbonatites show the test pozzolans to accelerate hydration, reduce setting time and accelerate strength development, all effects contrasting with the general trends of natural pozzolans and attributed mainly to the presence of the carbonate minerals and potassic alkalis (Buregyeya *et al.,* 2018a). These studies on pozzolanic performance fixed the replacement level of test pozzolans to 20% and evaluated the role of the carbonate minerals through calcination at 850°C. The current work addresses the role of variation in fineness and replacement levels of the test pozzolans on heat of hydration and compressive strength development. Both the heat of hydration and compressive strength development have been used as proxy indicators of hydration progression of blended cement samples and the observed trends are a guide to further research questions leading to microstructure characterization of hydration progression.

Materials and Methods

Two test pozzolans, a carbonatite (Poz-1) and a kamafugite (Poz-3), were sourced from tuffs located in the Toro-Ankole geological region of the East Africa Rift System. Percentage oxide composition of the test pozzolans is presented in Table 4 below. The kamafugite composition is ultrapotassic and enriched with relatively high content of carbonate minerals while the carbonatite composition is silica undersaturated and composed of predominantly carbonate minerals (Buregyeya *et al.*, 2018b). The cement used in this study was of type CEM 1(52.5R) sourced from Afrisam (South Africa) (Pty) Ltd at their Rooderport cement plant. For preparation of mortar prisms in compressive strength tests, standard sand meeting the EN 196-1 requirements was used.

The experimental plan for heat of hydration studies is presented in Table 1 while that of compressive strength is presented in Table 2. In studying the effect of fineness on heat of hydration and compressive strength development, all experiments were conducted at a fixed replacement level of 20% test pozzolan for the different levels of fineness. The effect of fineness on heat of hydration was observed for 170 hours (7days) while that on compressive strength run up to 180 days.

Table 1. *Experimental plan 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 *SC1*			0.4g	3.6 g	4.0 g
	20%	0.8g *SC2*	0.8g *SC3*	0.8g *SC4*	0.8g	0.8g	0.8g	3.2 g	4.0 g
	30%			1.2g *SC5*			1.2g	2.8 g	4.0 g
Control sample CEM1(52.5R)		4.0 grams *SC6*			4.0 grams			0 g	4.0 g

F1: Fineness after milling for 20 minutes; F2: Fineness after milling for 30 minutes; F3: Fineness after milling for 40 minutes; F-C: Fineness of the control sample. SC1: Loading configuration for channel 1 in an 8-channel isothermal conduction calorimeter

To improve on reaction sensitivity of the test pozzolans, the effect of replacement level on heat of hydration and strength development was evaluated by considering only samples with the highest level of fineness, F3. Test pozzolans blended in Portland cement (CEM I 52.5R) at 5%, 10%, 20% and 35% replacement levels were tested against the control in both paste and mortar states.

Fineness of test pozzolans:

To establish the role of fineness (mechanical activation) and particle size distribution of the test pozzolans on the rate of hydration and strength development of blended cement, each of the test pozzolans were milled to three (3) fineness levels, F1 representing a 20 minutes period of milling, F2 representing a 30 minutes period of milling, and F3 representing a 40 minutes period of milling for fixed quantities of the kamafugites and carbonatites. The fineness properties are presented in Table 3. Fineness characterisation was done following laser diffraction instrumental techniques using a Melvin mastersizer 2000 particle size analyzer. Samples milled to different fineness levels using a lab scale ball mill were kept in an oven at 105°C until constant mass and then used in determination of fineness parameters. The fineness parameters are presented in Table 3.

Heat of hydration experiments: An 8-channel isothermal calorimeter (TAM Air, TA instruments, USA) was used in the study of the effect of fineness and replacement level of test pozzolans on heat of hydration. The calorimeter was accessed at the Afrisam (South Africa) (Pty) Ltd center for product excellency laboratories, Rooderport. Glass ampules loaded with samples prepared following the mix designs presented in Table 1 were loaded into a calorimeter before adding water to the samples. Water was introduced after thermal stabilization of the samples inside the calorimeter in order to observe all the heat of hydration stages pre-induction and post induction. Buregyeya *et al.,* (2017a) reports kamafugites and carbonatites to have no alteration in the form of the standard trend of cement hydration other than for the acceleration effect. The experiments run for 7 days (170 hours) and the results recorded are normalized for cementitious materials content.

Compressive strength of mortar prisms: *For* compressive strength testing, mortar prisms of 40x40x160mm standard size were cast according to EN 196-1(2005) standard using a standard mould and mix proportions presented in table 2. The standard presents a combination ratio of 1:3 for cement to sand and a water binder ratio of 0.5. Samples due for testing were removed from curing water and tested within 10 minutes for compressive strength at a load rate of 2500 N/s.

Table 2. Experimental design for compressive strength tests: Effect of fineness and replacement level 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 Pozzolan	427.50	22.50	1350	225
10%	F3	Test Pozzolan	405.00	45.00	1350	225
20%	F1, F2, F3	Test Pozzolan	360.00	90.00	1350	225
35%	F3	Test Pozzolan	292.50	157.50	1350	225

Results

Properties of the test pozzolans

The fineness parameters presented in Table 3 are ranked F1, F2 and F3 depending on the level of fineness, F1 being the lowest. 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 (0.1) value of the test pozzolans in relation to the control sample. The chemical composition and physical properties are as reported in Table 4 and in Buregyeya et al. (2018b). Poz-1 has a very high content of CaO (25%) which is responsible for its silica undersaturation. Poz-3 is silica saturated 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 (Buregyeya *et al.,* 2018a). Poz-3 has higher values of water-soluble alkalis than Poz-1.

Table 3. Fineness parameters for test pozzolans, Poz-1 and Poz-3

Sample name		**Specific surface area (m²/g)**	**d(0.1) (µm)**	**d(0.5) (µm)**	**d(0.9) (µm)**
Control		1.75	1.422	12.533	32.070
Poz-1	**F1**	1.22	2.380	48.320	158.386
	F2	1.63	1.374	22.467	115.496
	F3	2.18	0.848	14.695	99.808
Poz-3	**F1**	1.46	1.484	39.712	188.151
	F2	1.79	1.077	26.155	186.670
	F3	2.10	0.852	21.898	178.719

Effect of fineness of test pozzolans on heat of hydration

The effect of fineness of carbonatites and kamafugites on the heat of hydration progression is shown in Figure 1 for Poz-1 and Figure 2 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.

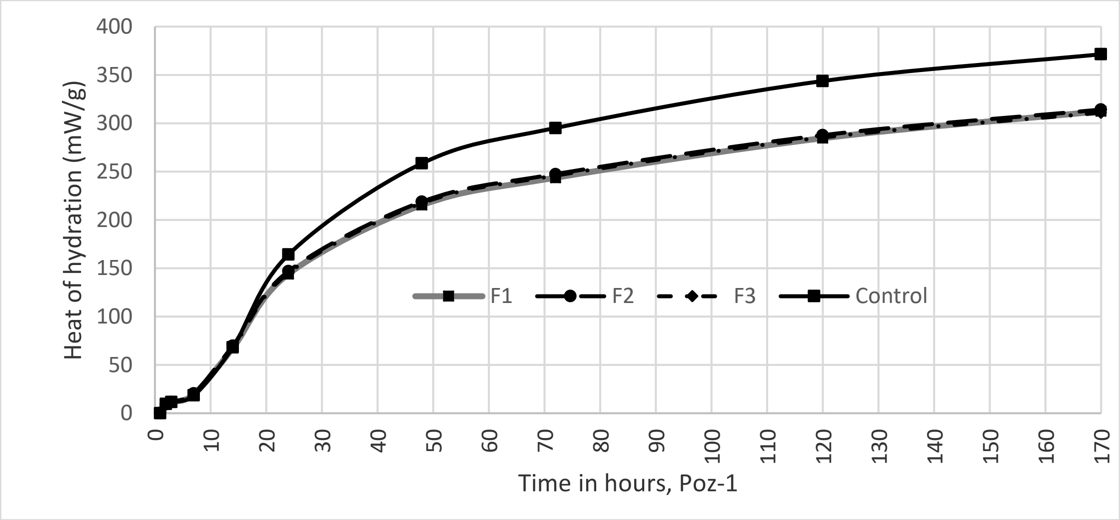

Figure 1. Effect of fineness on heat of hydration for Poz-1

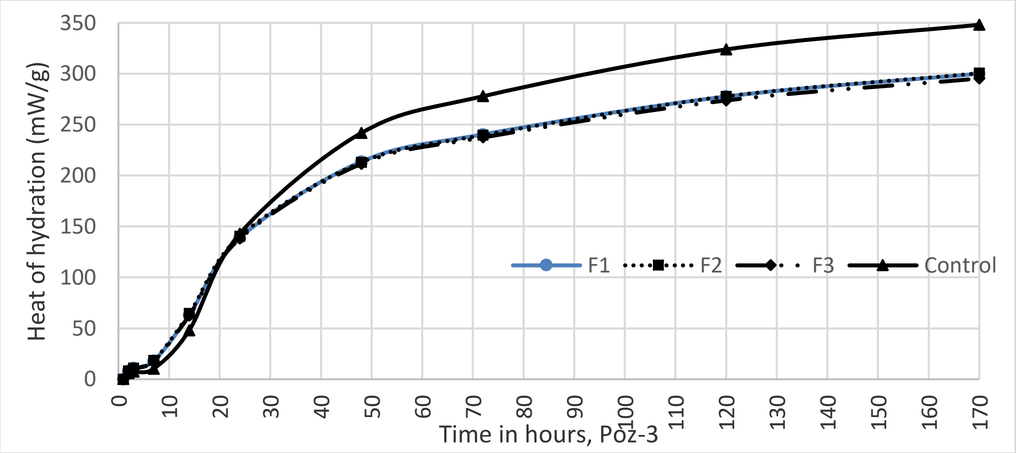

Figure 2. Effect of fineness on heat of hydration for Poz-3

Effect of fineness of test pozzolans on compressive strength development

Figures 3 and 4 present 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 reduces 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 authors attribute 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.

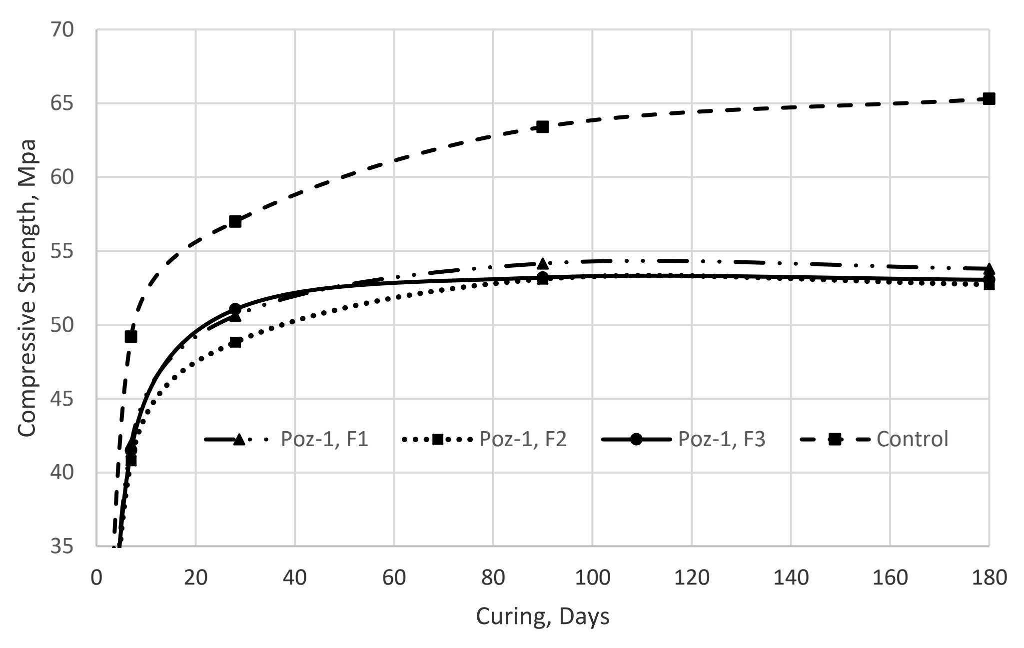

Figure 3. Effect of fineness on compressive strength development for Poz-1

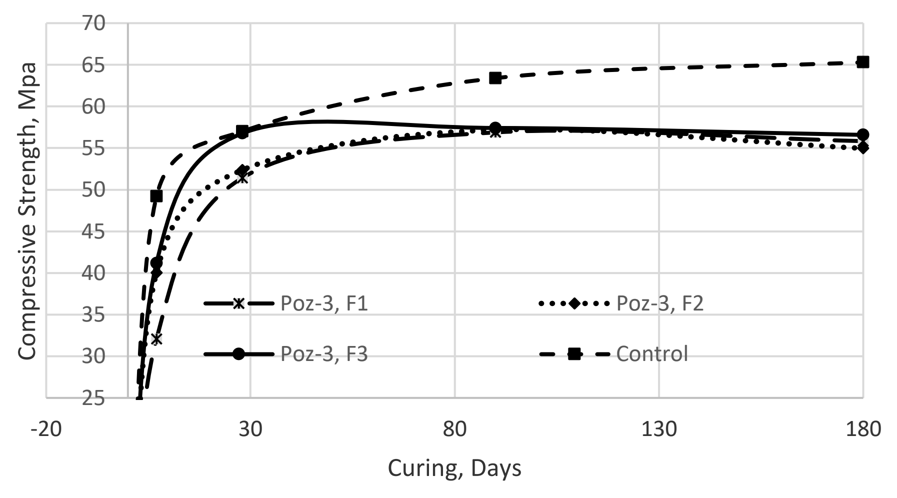

Figure 4. Effect of fineness on compressive strength development for Poz-3

Effect of replacement level of test pozzolans on heat of hydration

Referring to Figures 5 and 6, a time dependent influence of replacement level on heat of hydration is observed. 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 hour data which indicates that the earlier reaction mechanisms are suppressed completely after 120 hours.

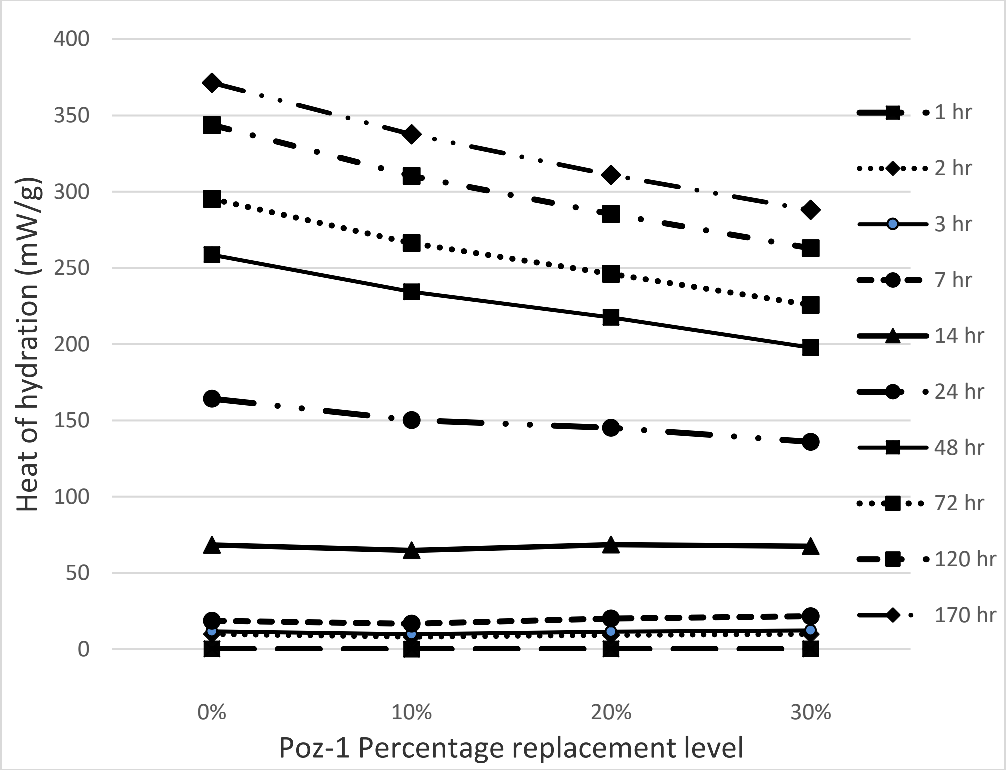

Figure 5. Effect of replacement level on heat of hydration for Poz-1

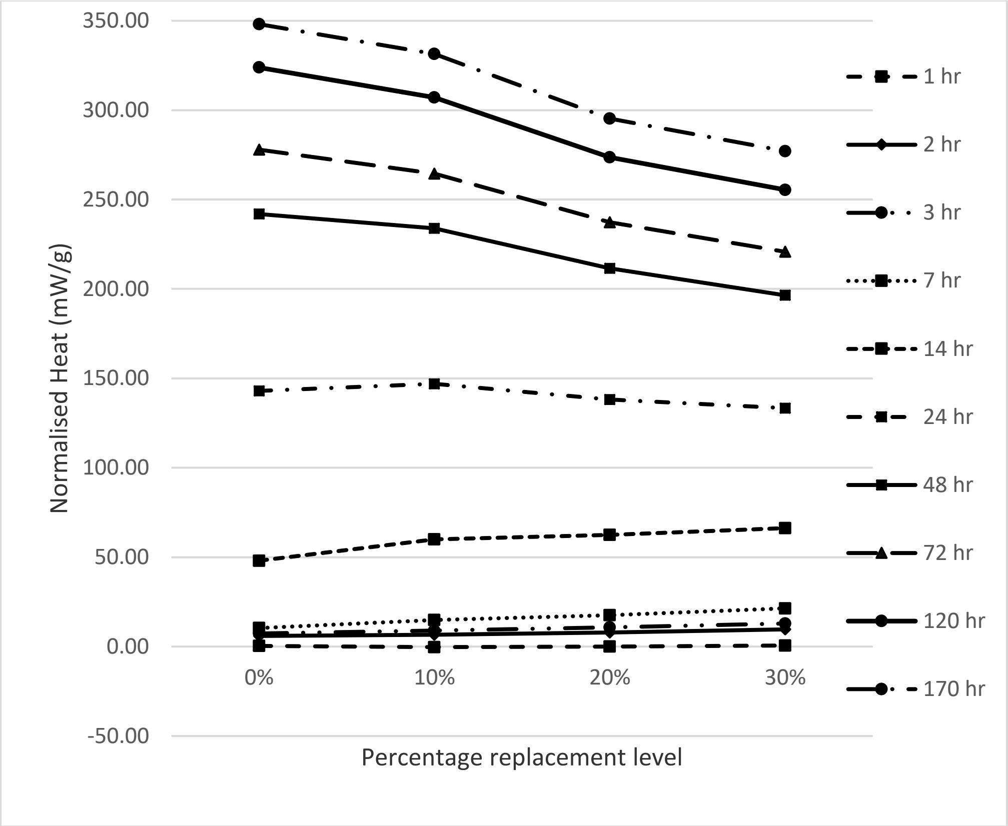

Figure 6. Effect of replacement level on heat of hydration for Poz-3

Effect of replacement level of test pozzolans on compressive strength

Figures 7 and 8 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.

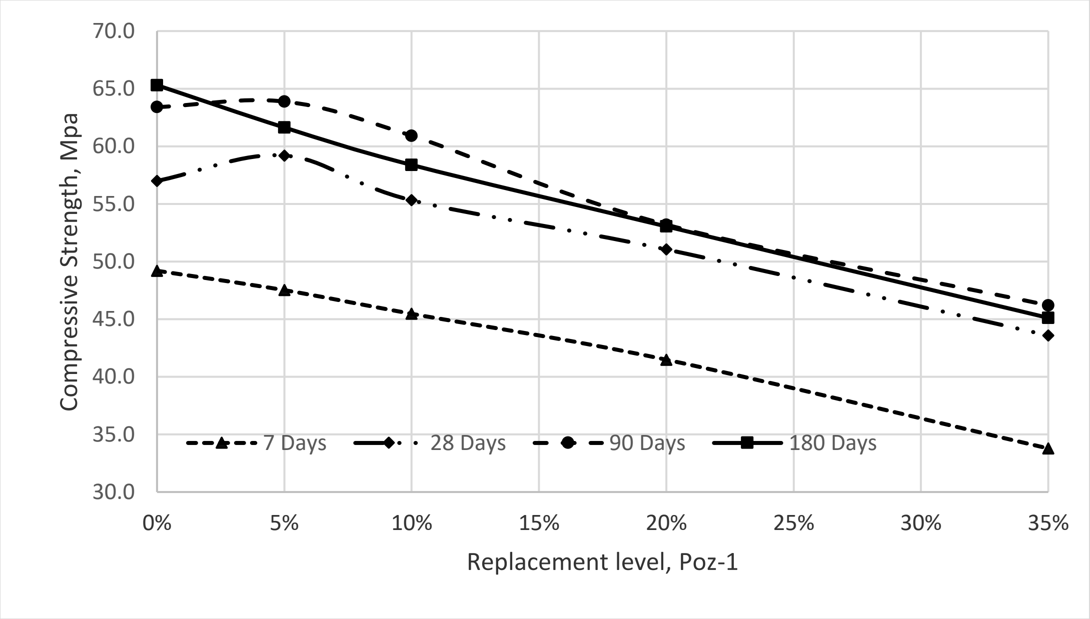

Figure 7. Effect of replacement level on compressive strength development for Poz-1

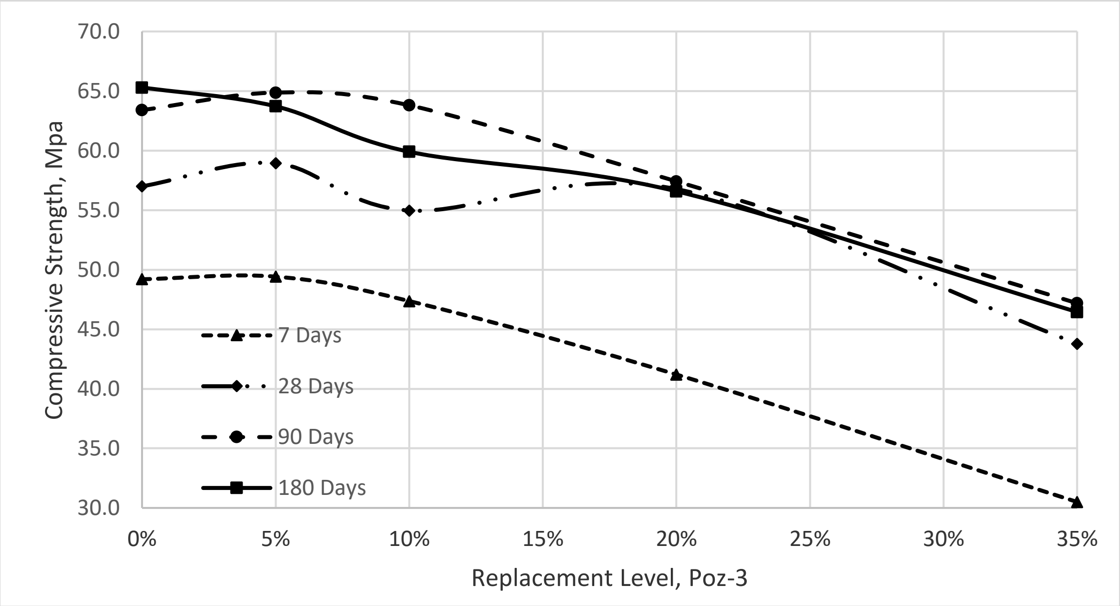

Figure 8. Effect of replacement level on compressive strength development for Poz-3

Discussion

Physical properties 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 fixed 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) showed variations in their properties as presented in Table 3. Though the variations in the specific surface area parameters are distinct for comparative studies, the d10 values for F3 are nearly similar. Also, the particle size spread between d10 and d90 is much wider in comparison with the cement control sample. This is possibly due to the predominantly 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 *et al.,* 2004 on 3 Turkish natural pozzolans which reposts dependence of particle size parameters on the level of hardness of the natural pozzolan materials. The closeness of the d10 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.

Effect of fineness on heat of hydration: It is anticipated that, considering the acceleratory role the filler effect (explained in next section) has on hydration progression of blended cements (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. Considering that 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 in this study. The author takes the assumption in explaining the observed results 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. 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.

Effect of fineness on compressive strength: The reaction mechanisms advanced to influence hydration of pozzolan blended cements are the filler effect and the pozzolanic reactions (Berodier and Scrivener 2014; Oey *et al.,* 2013; Scrivener *et al.,* 2015). 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 (SCM) provide surfaces as nucleation sites for precipitation and growth of cement hydration products. Ogawa *et al.,* (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% (Buregyeya *et al.,* 2018). Other than the filler effect that explains early hydration processes (first 3 days), it 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.

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 (Buregyeya *et al.*, 2017).

Table 4. Chemical analysis and physical properties of kamafugites and carbonatitic lavas

Chemical composition (%)	**Poz-1**	**Poz-3**	**CEM I (52.5R)**
LOI	13.57	10.43	0.09
SiO_2	35.88	57.5	20.33
Al_2O_3	9.41	8.83	4.41
Fe_2O_3	14.09	8.13	2.53
CaO	25	8.47	65.19
MgO	5.49	7.05	1.8
K_2O	1.09	4.77	0.48
Na_2O	1.71	0.32	0.09
P_2O_5	2.84	1.07	0.08
TiO_2	2.39	2.75	0.41
Mn_2O_3	0.44	0.16	0.1
Cr_2O_3	0.02	0.03	0.01
V_2O_5	0.05	0.05	0.01
XRF Total	98.4	99.15	95.42
SO_3 %	0.07	0.01	2.6
Reactive SiO_2	18.8	26.6	
Reactive CaO	8.4	5	
Sum of acidic oxides	59.38	74.46	
Soluble K+	48	105	
Soluble Na+	6	8	
Soluble Mg+	737	875	
PH	9.09	9.15	
Relative density	2.75	2.38	3.14

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 4. The authors, in their previous work (Buregyeya *et al.,* 2018a), has shown 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 *et al.,* 1980. Ogawa *et al.,* 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 *et al.,* 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 and 6. 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.

Conclusion

The observed spread in particle size distribution of the test pozzolans is due to their heterogeneous mineral composition, which preferentially sets different rates of particle disintegration based on their levels of hardness. This same mechanism might be the reason why both Poz-1 and Poz-3 have d10 values that are nearly similar. Poz-1, a carbonatite, appears to have a distribution of softer minerals than Poz-3, a kamafugite.

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 are not the driver of the reaction mechanisms running in the early stages of hydration up to 7 days for the fineness range tested.

Heat of hydration increased with increase in replacement levels of the test pozzolans for the first 14 hours agreeing with the accelerating effect of the test pozzolans reported in Buregyeya et al 2018b. The filler effect and high alkali content are advanced as the cause of the early trend. Starting after 14 hours of curing, a reduction in heat of hydration is observed with increase in replacement level. This trend stabilizes at 120 hours of curing indicating pacification of accelerating reactants in the test pozzolans at 120 hours.

Dependence of compressive strength on fineness is observed to 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.

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.

There is a reduction in strength between 90 and 180 days of curing for all samples blended with test pozzolans. 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.

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.

Acknowledgement

The experimental work was conducted by the main author as a student at University of the Witwatersrand under a fellowship provided by the National Research Foundation (NRF), a government agency of the Republic of South Africa. The corresponding author wishes to recognize the support provided by his research supervisor, Prof. Yunus Ballim. Also, to the lab technicians working at Afrisam (South Africa) (Pty) Ltd centre for products excellence laboratory at their Rooderport plant Motlatso Lebidi and Bakang Morole.

References

Berodier, E., and Scrivener, K. 2014. “Understanding the Filler Effect on the Nucleation and Growth of C-S-H.” J. Am. Ceram. Soc., Vol. 97, pp. 3764– 3773. DOI:10.1111/jace.13177

Blanco Varela, M.T., Martinez Ramirez, S., Erena, I., Gener, M., Carmona, P. 2006. “Characterisation and pozzolanicity of Zeolitic rocks from two Cuban deposits.” Applied Clay Sciences 33 pp. 149 - 159, Elsevier.

Buregyeya A., Ballim Y., Nwaubani S., Kerali A.G., Otieno M. 2018a, “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., Nwaubani S., Schmidt W., Kerali A. G., & Bagampadde U., 2018b., "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

Burris, L. E., and Juenger, M. C. G. 2016. "Milling as a pretreatment method for increasing the reactivity of natural zeolites for use as supplementary cementitious materials." Cement and Concrete Composites, Vol. 65, pp 163-170, DOI: http://dx.doi.org/10.1016/j.cemconcomp.2015.09.008

Caputo D., Liguori B., Colella C. 2008. "Some advances in understanding the pozzolanic activity of zeolites: The effect of zeolites structure." Cement & Concrete composites, Vol. 30, pp. 455-462

Celik K., Jackson M. D., Mancio M., Meral C., Emwas A.-H., Mehta P.K., Monteiro P.J.M. 2014. "High-volume natural volcanic pozzolan and limestone powder as partial replacements for Portland cement in self-compacting and sustainable concrete." Cement & Concrete Composites Vol. 45, pp. 136–147

Luke K. 2007. "The effect of natural zeolites on the composition of cement pore fluids at early ages." 12th International Congress on the Chemistry of Cement (ICCC), Montreal, Canada.

Martinez-Ramirez S., Blanco-Varela M. T., Erena I., Gener M. 2006. "Pozzolanic reactivity of zeolitic rocks from two different Cuban deposits: Characterization of reaction products." Applied Clay Science, Vol. 32, pp. 40-52.

Mehta, P. K. 1981. "Studies on blended Portland cements containing Santorin earth." Cement and Concrete Research., Vol. 11, pp. 507-518

Mehta P. K., Monteiro P. J. M. 2006. "Concrete microstructure, properties, and materials." Berkeley: McGraw-Hill.

Mertens G., Snellings R., Van Balen K., Bicer-Simsir B., Verlooy P., Elsen J. 2009. "Pozzolanic reactions of common natural zeolites with lime and parameters affecting their reactivity." Cement and Concrete Research Vol. 39 pp 233-240.

Oey, T., Kumar, A., Bullard, J. W., Neithalath, N., Sant, G. 2013. "The Filler Effect: The Influence of Filler Content and Surface Area on Cementitious Reaction Rates." Journal of the American Ceramic Society, 96: 1978–1990. doi: 10.1111/jace.12264

Ogawa, K., Uchikawa, H., and Takemoto, K. 1980. "The mechanism of the hydration in the system C3S-pozzolana." Cement and Concrete Research, Vol. 10, pp. 683-696

Pourkhorshidi A. R., Najimi M., Parhizkar T., Jafarpour F., Hillemeier B. 2010. "Applicability of the standard specifications of ASTM C618 for evaluation of natural pozzolans." Cement & Concrete Composites, Vol. 32, pp. 794-800

Schmidt, W., Msinjili, N. S., and Kühne, H. C., (2018), "Materials and technology solutions to tackle the challenges in daily concrete construction for housing and infrastructure in sub-Saharan Africa", African Journal of Science, Technology, Innovation and Development, Taylor & Francis online, https://doi.org/10.1080/20421338.2017.1380582

Schneider, M., Romer M., Tschudin M., Bolio H. 2011. "Sustainable cement production-present and future." Cem Concr Res, 41, 642-650

Scrivener, K. L., Juilland, P., and Monteiro, P. J. M. 2015. "Advances in understanding hydration of Portland cement." Cement and Concrete Research, Vol. 78, Part A, pp. 38-56. https://doi.org/10.1016/j.cemconres.2015.05.025

Shannag, M., J., and Yeginobali, A. 1995. "Properties of pastes, mortars and concretes containing natural pozzolans." Cement and Concrete Research, Vol. 25, No.3, pp. 647-657

Snellings R., Mertens G., Cizer O., Elsen J. 2010. "Early age hydration and pozzolanic reaction in natural zeolite blended cements: Reaction kinetics and products by in situ synchrotron X-ray powder diffraction." Cement and Concrete Research, Vol. 40, Issue 12, pp. 1704-1713

Snellings R., Mertens G., and Elsen J. 2012. "Reviews in Mineralogy and Geochemistry: Supplementary Cementitious Materials." Applied Mineralogy of Cement & Concrete, Vol. 74. Pp. 211-278, Mineralogical Society of America

Taylor H. F. W. 1997. "Cement chemistry." 2nd ed. Thomas Telford Publishing, London

Turanli, L., Uzal, B., Bektas, F. 2004. "Effect of materials characteristics on the properties of blended cements containing high volumes of natural pozzolans." Cement and Concrete Research, Vol. 34, pp. 2277–2282

Turanli L., Uzal B., Bektas F. 2005. "Effect of large amounts of natural pozzolan addition on properties of blended cements." Cement and concrete research, Vol. 35, pp.1106-1111

Uzal B., Turanli L., Yucel H., Goncuoglu M. C., Culfaz A. 2010. "Pozzolanic activity of clinoptilolite: A comparative study with silica fume, fly ash and a non-zeolitic natural pozzolan." Cement and Concrete Research, Vol. 40, pp. 398-404

Stoppa F., and Schiazza M. 2013. "An overview of monogenetic carbonatitic magmatism from Uganda, Italy, China and Spain: Volcanologic and geochemical features." Journal of South American Earth Sciences, Vol. 41, pp. 140-159