Filler Efficiency Versus Pozzolanic Efficiency: Effects on Hydration Kinetics and Compressive Strength

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ABSTRACT

The efficiency of a quartz-based filler (andesite sand powder) compared to fly ash a pozzolan as a partial replacement for cement has been studied. Both andesite sand powder and fly ash are silica rich material, however, their reactivity and mechanism of reaction by which they influence the properties of cementitious systems are examined. Both andesite sand powder and fly ash were used to partially replace Portland cement at 15% and 30% levels using two w/b ratios of 0.4 and 0.6. The heat of hydration was monitored with an isothermal calorimeter using paste samples while 100 mm concrete cubes were cast to determine the effect on compressive strength. The compressive strength recorded for concrete containing andesite sand powder at 15% content, w/b ratio of 0.4 and 7 days of curing is 63MPa compared to 58MPa for concrete containing fly ash at the same content, w/b ratio and curing age. At 28days of curing, concrete containing fly ash has a strength of 71MPa compared to 70MPa for concrete containing andesite sand powder. The results indicate that the sand being a filler has an early age contribution to strength development with the strength at 7 days being higher than that of fly ash which has a later age contribution to strength development due to its pozzolanic reaction in addition to hydration reaction of Portland cement.

KEYWORDS

Filler
Pozzolan
Andesite Sand Powder
Fly Ash
Hydration Kinetics
Compressive Strength

1. INTRODUCTION

The production of Portland cement is a major contributor to the release of carbon dioxide into the atmosphere and it is said to account for about 8% anthropogenic emissions (Kajaste & Hurme, 2016). There have been several strategies put forward to address the impact of the cement industry on the environment, one important strategy being clinker substitution by supplementary cementitious materials (SCMs) (Scrivener, John, & Gartner, 2018). SCMs in themselves do not possess binding ability but when used with Portland cement in certain proportion can produce desired properties similar to plain Portland cement. This made SCMs viable options to reduce the clinker content of cement. The viability in clinker substitution by SCMs has seen an increase in the research of alternative materials suitable as clinker partial substitute. Different materials have been investigated and used commercially as SCMs ranging from fillers (limestone powder) (Di Salvo Barsi, Marchetti, Trezza, & Irassar, 2020; Rahhal & Talero, 2005), pozzolans (fly ash) (Kara *et al.*, 2020; Nath & Sarker, 2011) and latent hydraulic materials (slag) (Bougara, Lynsdale, & Milestone, 2010; Kocaba, Gallucci, & Scrivener, 2012).

Each category of SCMs namely fillers, pozzolans and latent hydraulic materials has different mechanism of reaction and effectiveness as clinker substitute. Given the differences in reaction mechanism, it is important that new materials be properly characterised and tested for proper identification and classification for use as SCMs. Fillers are often nearly inert and as such influence the properties of cementitious systems by their particle size by acting as nucleation points for the precipitation of the hydration product of Portland cement (Berodier & Scrivener, 2014). In a review on limestone powder use in cement-based materials, Wang *et al.* (2018) noted that the influence of limestone powder on cementitious system properties is associated with dilution, filler nucleation and chemical effects. The filler effect was linked to pore refinement and reduced porosity while the dilution effect was linked to lower hydration peak of tri-calcium silicate and reduced amount of hydration products with a consequential increase in porosity. However, for limestone, the reaction between calcium carbonate and the aluminate present in cement has been reported suggesting a likely reaction and formation of mono and hemi-carboaluminate hydrate (De Weerdt, Kjellsen, Sellevold, & Justnes, 2011). This reaction is peculiar to calcium carbonate-based fillers, however, potential non-carbonate-based fillers being investigated for use as SCMs abounds and their mechanism of reaction need to be ascertained to enhance their utilisation and standardisation.

The use of limestone as a filler in cement production is standardised in some standards like BS EN197-1 which allowed up to 35% content to be interground with Portland cement clinker. In Nigeria, the use of limestone filler in cement production has gradually phased out plain Portland cement in the market space but despite this, the cost of cement has increased in recent times. However, there are other fillers aside limestone which may be used for onsite application and not necessarily interground with Portland cement clinkers at cement plant. These streams of fillers require in-depth investigation to understand their performance and limitation of use with plain Portland cement. Silica-based fillers abound and can be explored based on local availability for reducing the carbon footprint of Portland cement utilisation. It is also necessary to establish the suitability of such materials for use in concrete production given the benefits that can accrue from their use.

Investigation into the use of non-carbonate fillers is growing, Choudhary *et al.* (2016) investigates the effect of rutile, marble dust and crushed hydrated cement seeds on the hydration and compressive strength of mortar. The study reported the effectiveness of marble dust in enhancing compressive strength and the rate of gain of strength while with cement seeds, equivalent strength and hydration rate comparable to plain Portland cement and fly ash blended cement were recorded. In another study, Damineli *et al.* (2021) studied the effect of fillers of six different mineralogy on the compressive strength of mortars. The compressive strength of mortar containing the fillers was reported to be significantly higher at both 7 and 28 days compared to plain Portland cement mortar. Lin *et al.* (2018) studied the effect of quartz powder on some properties of paste including the microstructure. The effect of quartz powder on cement hydration was found to depend on w/b ratio while the use of quartz powder does not impair the compressive strength of paste. Also, Gubio *et al.* (2022)

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investigated the effect of different particle sizes and varying replacement level of quartz powder on the physicochemical properties of Portland limestone cement (PLC). Quartz powder was found to increase the setting times and water demand of PLC paste while the effect on compressive strength of mortar depends on the amount of quartz powder in the mix. Generally, it was found that quartz powder does not significantly impair the compressive strength of mortar. These studies have shown the potential of fillers other than limestone in mortar, but essentially their performance in concrete is also important to their adoption and use at commercial scale.

Andesite sand powder is obtained from crushed andesite rock which is used as aggregates in South Africa, it is one of the several rock minerals available in commercial quantity for construction purposes. Its' utilisation as a filler and partial substitute for plain Portland cement requires further milling of fine particles obtained during crushing. This may add up to the cost but the envisaged contribution to strength and microstructural refinement may offset the cost implication. Fly ash on the other hand, is an industrial by-product from coal based power plant, but this method of producing electricity is said to be the largest source of antropogenic CO_2 (Scrivener *et al.*, 2018). Production of electricity from coal is gradually being phased out and this has a consequence on the availability of fly ash in the future. Therefore, alternative sources of SCMs with suitable properties and similar behaviour to existing streams of SCMs in use in the industry is required both in countries producing fly ash and others where such materials are available.

In this study, the performance of a silica-based filler namely andesite sand powder as partial replacement for Portland cement compared to fly ash, a known pozzolan is investigated in order to understand its reaction mechanism and mode of influence on the properties of cementitious systems. The silica-based filler is considered for onsite application as a partial replacement for plain Portland cement. Usually, the use of fillers has a dilution effect (John, Damineli, Quattrone, & Pileggi, 2018) but any latent reactivity in addition to providing nucleation sites tends to compensate for the dilution effect, yet the nature of the dominant oxide in terms of possessing latent reactivity may be an advantage in the utilisation of fillers.

2. EXPERIMENTAL SET-UP

2.1. Materials

A CEM I 52.5R cement was used in the study as the main binder while fly ash (FA) and andesite sand powder (AS) were used as partial replacement for cement. Fly ash was used as a pozzolan with an amorphous content of 57.5% (determined using XRD) while andesite sand powder was used as a non-reactive filler. The andesite powder was obtained by milling the particles retained from sieving andesite crusher sand through a 300 μm sieve. Information on the chemical composition and particle size analysis of both the sand powder and fly ash compared to plain Portland cement (PC) is presented in Table1, with both materials being silica rich. For the mix proportioning, FA15 depicts a mix containing 15% FA and 85% plain PC, FA30 depicts a mix containing 30% FA and 70% plain PC, AS15 depicts a mix containing 15% andesite sand powder and 85% plain PC while AS30 depicts a mix containing 30% andesite sand powder and 70% plain PC. The replacement levels studied were chosen to reflect the optimum FA content in use in South Africa (30%) and a lower content (15%) to allow for comparison but all within the 35% maximum content of limestone filler allowed in BS EN 197:1.

2.2. Isothermal Calorimetry

Isothermal calorimeter (ICal 2000H) was used to monitor the heat of hydration of paste containing plain PC and either of fly ash or andesite sand powder. 30g of paste was prepared at a water to powder ratio of 0.4 using deionized water. The deionized water was conditioned at 20°C before adding the powder sample. The paste was mixed in a vial and was placed in the calorimeter in less than 2 minutes from the time deionized water was added to the sample. The experiment was done at an isothermal temperature of 20°C while the data was logged for 48 hours.

2.3. Compressive Strength Determination

For the compressive strength, concrete was prepared at a w/b of 0.4 and 0.6 with 100 mm cubes of concrete cast and demoulded 24 hours after casting. The concrete cubes were cured in water at the ages of 7, 28 and 90 days after casting at ambient temperature, while at each of the ages, cubes were removed from the curing tank and subjected to compressive load until failure via a compression testing machine. The compression machine has a loading rate of 150kN/min. The maximum load sustained by the samples is recorded to estimate the strength of the mix. A total of 72 samples were used for the determination of compressive strength.

Table 1: Chemical composition and particle size analysis of materials

Oxide	CEM 1 52.5R	Fly ash	Andesite sand
CaO	62.57	5.00	7.65
SiO_2	19.57	56.01	54.20
Al_2O_3	4.93	31.74	14.51
Fe_2O_3	2.64	3.31	11.74
MgO	2.06	1.22	4.09
K_2O	0.45	0.77	1.05
MnO	0.37	0.01	0.15
Na_2O	0.00	< 0.01	3.16
TiO_2	0.35	1.59	0.84
P_2O_5	0.10	0.56	0.12
Cr_2O_3	0.03	0.04	0.01
NiO	0.00	0.00	0.02
LOI	3.60	0.81	2.47
D_{10} (μm)	30.11	0.15	1.80
D_{50} (μm)	38.72	1.17	13.70
D_{90} (μm)	225.72	3.37	55.10
Mean size (μm)[a]	95.09	1.38	23.20

Table 2: Mix proportioning for concrete preparation

Mix/ Material	PC (kg/m^3)	FA (kg/m^3)	AS (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)	Stone (kg/m^3)	w/b
FA15	436	77	-	205	582	1126	0.4
FA15	291	51	-	205	725	1126	0.6
FA30	358.75	153.75	-	205	582	1126	0.4
FA30	239	103	-	205	725	1126	0.6
AS15	436	-	77	205	582	1126	0.4
AS15	291	-	51	205	725	1126	0.6
AS30	358.75	-	153.75	205	582	1126	0.4
AS30	239	-	103	205	725	1126	0.6

3. RESULTS AND DISCUSSION

3.1. Heat of Hydration

The heat flow curves of paste containing PC and either fly ash or andesite sand powder are presented in Figures 1 and 2 respectively. The differences in the heat flow pattern of both materials become distinguishable at the acceleration phase which succeeds the induction phase. The heat flow pattern of andesite sand powder is similar to that of plain Portland cement which shows that the finer particle size than plain Portland cement was able to compensate for the reduced cement content. In a previous study, Berodier & Scrivener (2014) reported that quartz powder enhanced the rate of reaction of Portland cement with a higher main heat peak and steeper slope at the acceleration phase. A similar effect was also observed in the study by Kumar *et al.* (2017) for quartz powder. The enhanced or similar rate of reaction is attributed to the filler effect of the materials which is consequent of their particle size and surface area provided with the surface acting as nucleation points for the C-S-H. For fly ash, the rate of hydration is slightly lower than that of Portland cement showing that fly ash has an effect on the acceleration phase of cement hydration. A slightly lower heat peak and delayed evolution of the acceleration peak was observed in the study of Deschner *et al.* (2012) for fly ash, an effect associated to the low calcium ions concentration in the pore solution due to the reaction of the aluminate phase present in fly ash. The slight shoulder on the deceleration for both materials is associated with aluminate reaction (Berodier & Scrivener, 2014). The shoulder relates to depletion of calcium sulfate associated with second aluminate reaction with a likely formation of ettringite (Deschner *et al.*, 2012).

Figure 3 shows the total heat output of FA and AS at each replacement level compared to plain PC. Both materials at each replacement level have a lower total heat than plain PC and this is seen as a dilution effect resulting from reduced plain PC content in the paste. This further implies that either FA or AS can reduce the heat output associated with PC thereby reducing the chance of early cracking in cementitious systems.

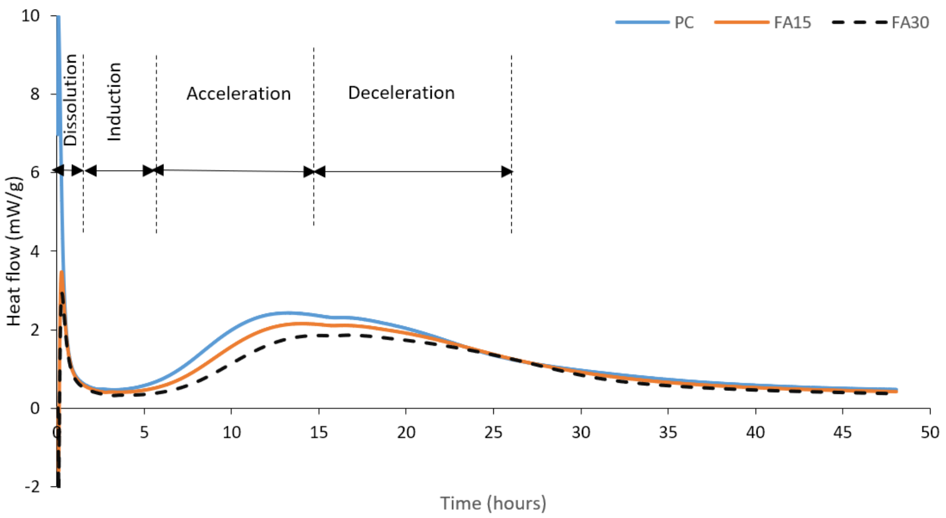

Figure 1: Heat flow curve of fly ash at different percentage replacement level

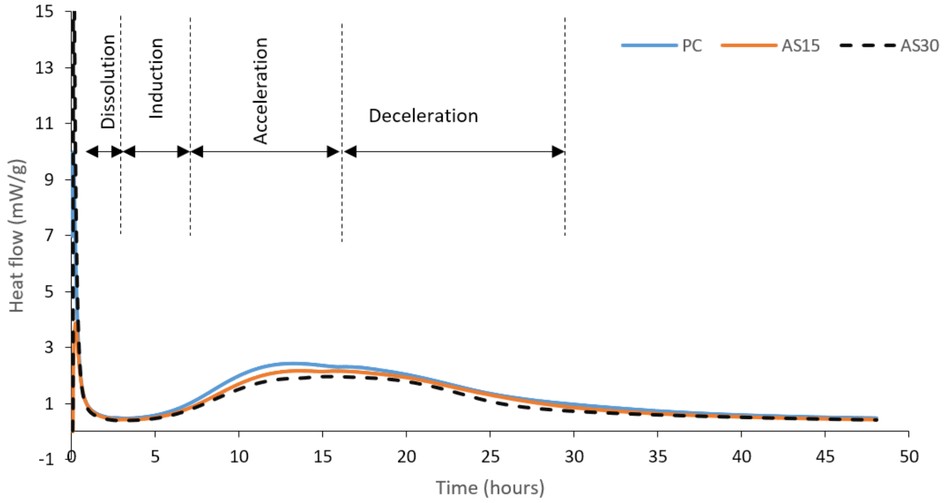

Figure 2: Heat flow curve of andesite sand powder at different percentage replacement level

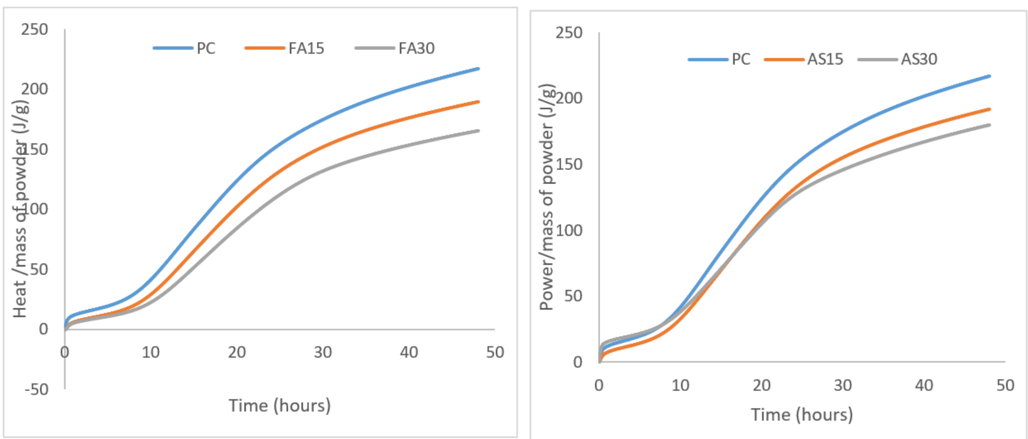

Figure 3: Total heat output

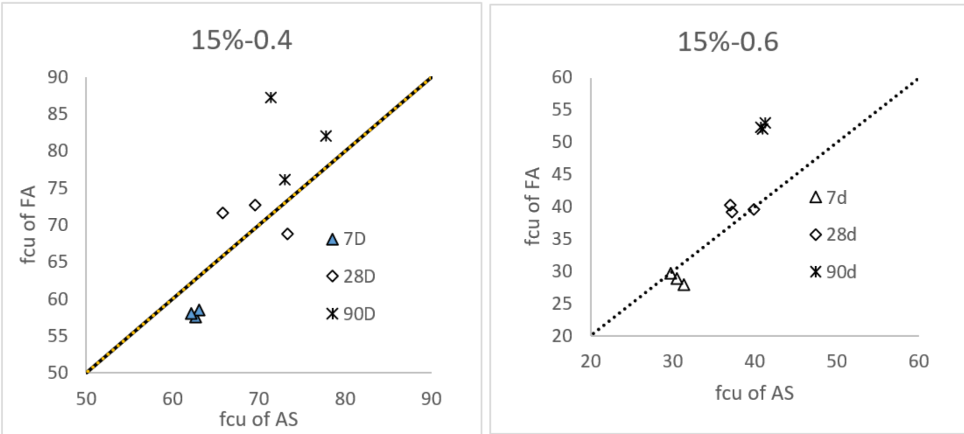

Figure 4: Comparison of the compressive strength of fly ash and andesite sand powder at 15% replacement level

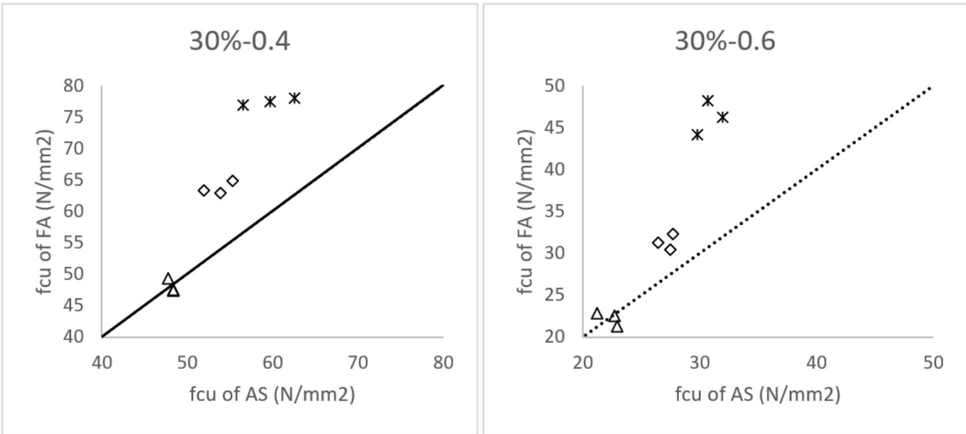

Figure 5: Comparison of the compressive strength of fly ash and andesite sand powder at 30% replacement level

3.2. Compressive Strength

Figures 4 and 5 give the correlation between the compressive strength of fly ash and andesite sand powder at 15% and 30% replacement levels respectively. The replacement levels were chosen to reflect the optimum FA content conventionally in use in South Africa which is 30% and a lower content than the optimum that falls within the range of limestone filler content recommended by BS EN 197:1-2000. The compressive strength for the sand powder at both replacement levels is mostly higher at 7 days of curing than that of the fly ash as the strength values falls below the line of equality on Figures 4 and 5. This is seen as an early age contribution to strength development by the filler consequent of the physical presence and finer particle sizes. The particles of the filler being finer than those of plain Portland cement provide extra surfaces for the nucleation of hydration products which subsequently modifies the pore structure leading to enhanced strength (Lothenbach, Scrivener, & Hooton, 2011). Berodier and Scrivener (2014) reported the presence of nuclei of ettringite and calcium hydroxide on the surface of quartz which is attributed to heterogeneous nucleation of hydrates on the surface. Generally, for supplementary cementitious materials, the dominance of the filler effect at early ages has been noted resulting in increased and sometimes faster reaction of plain Portland cement (Lothenbach *et al.*, 2011).

The influence of fly ash on strength development is notable at 28 days at which time the strength is higher than those of andesite sand powder as the strength values lies higher above the line of equality on Figures 4 and 5. The mechanism of the enhanced strength is attributed to reactivity of fly ash which contributes to its pozzolanic reaction which is a time dependent function as well as filler effect due to finer particles. It is worth noting that the fly ash particles were finer than those of the sand powder, while the amorphous content as determined by XRD (Figure 6) is 57.5%. Fly ash being reactive is expected to react with the calcium hydroxide produced by the hydration reaction of Portland cement to produce more C-S-H leading to enhanced strength as a result of refined pore structure. It could be seen that the pozzolanic effect contributes significantly to strength development at later ages compared to andesite sand powder. For instance, the strength of concrete containing 15% and 30% fly ash is 82MPa and 77 MPa respectively at w/b ratio of 0.4 compared to 74MPa and 60MPa for concrete containing andesite sand powder at the same replacement level and for 90 days of curing. Also, at w/b ratio of 0.6, the corresponding strength is 52MPa and 46MPa for concrete containing fly ash while for concrete containing andesite sand powder, the strength is 41MPa and 31MPa at 15% and 30% replacement level respectively. Little contribution of pozzolanic reaction to strength development at ages up to 7 days was also reported for silica fume while a significant improvement in strength was noted between 7 and 28 days which is a combined effect of cement hydration and pozzolanic reaction (Detwiler & Mehta, 1989).

3.3. Statistical Analysis of compressive strength data

The result of the Analysis of variance presented in Table 3 shows that there is a significant difference in the strength data across the mixes and curing ages at 95% confidence level. This is reflective of the differences in the percentage replacement levels and w/b ratios studied. The difference in compressive strength data at each of the curing ages is expected and it is attributed to the hydration reaction of Portland cement and the additional pozzolanic reaction in mixes containing fly ash as well as the differences in w/b ratio. With the increase in curing age, comes the increase in compressive strength and the variation in the strength values recorded at each of the curing ages. This is responsible for the significant difference within groups of mixes and curing age as well as the interaction between the groups.

Table 3: Summary of Analysis of variance of compressive strength data

Source of Variation	SS	df	MS	F	P-value	F crit
Sample	18355.63	7	2622.233	719.7213	2.46E-46	2.207436
Curing age	3817.415	2	1908.707	523.8808	2.49E-33	3.190727
Interaction	729.8715	14	52.13368	14.30907	1.28E-12	1.903653
Within	174.8832	48	3.6434			
Total	23077.8	71				

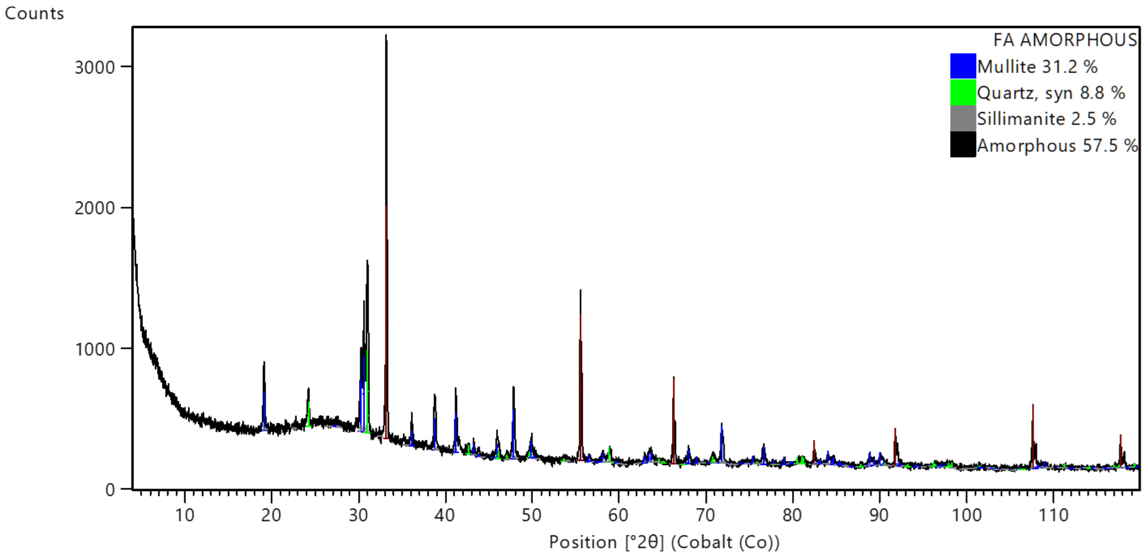

Figure 6: XRD diffractogram for the phase quantificaation of FA

4. CONCLUSION

The efficiency of andesite sand powder as a filler and the efficiency of fly ash as a pozzolan has been studied with the following conclusions drawn:

i. The sand powder is inert with its mechanism of influencing strength being mainly physical due to finer particle size than plain PC. Being a filler, the finer particle size was able to compensate for the dilution effect of reduced PC content as the heat flow curve at the two replacement levels studied is similar to that of plain PC.
ii. When compared to fly ash, the filler effect of the sand powder which contributed to strength development is pronounced at early age.
iii. For fly ash, the pozzolanic effect was more significant to strength development at later ages compensating for the dilution effect of reduced plain PC content and increased w/c ratio.
iv. Both materials have lower total heat of hydration than plain PC with an indication that they could reduce the risk or shrinkage cracking at early ages in cementitious system compared to plain PC.
v. Andesite sand powder may be used as a partial replacement for cement with effect on heat of hydration and compressive strength comparable to fly ash a known pozzolanic material.

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REFERENCES

Berodier, E., & Scrivener, K. (2014). Understanding the filler effect on the nucleation and growth of C-S-H. Journal of the American Ceramic Society, 97(12), 3764–3773.

Bougara, A., Lynsdale, C., & Milestone, N. B. (2010). Reactivity and performance of blastfurnace slags of differing origin. Cement and Concrete Composites, 32(4), 319–324. https://doi.org/10.1016/j.cemconcomp.2009.12.002

Choudhary, A., Shah, V., & Bishnoi, S. (2016). Effect of low cost fillers on cement hydration. Construction and Building Materials, 124, 533–543. https://doi.org/10.1016/j.conbuildmat.2016.07.088

Damineli, B. L., Pileggi, R. G., Lagerblad, B., & John, V. M. (2021). Effects of filler mineralogy on the compressive strength of cementitious mortars. Construction and Building Materials, 299(March). https://doi.org/10.1016/j.conbuildmat.2021.124363

De Weerdt, K., Kjellsen, K. O., Sellevold, E., & Justnes, H. (2011). Synergy between fly ash and limestone powder in ternary cements. Cement and Concrete Composites, 33(1), 30–38.

Deschner, F., Winnefeld, F., Lothenbach, B., Seufert, S., Schwesig, P., Dittrich, S., … Neubauer, J. (2012). Hydration of Portland cement with high replacement by siliceous fly ash. Cement and Concrete Research, 42(10), 1389–1400. https://doi.org/10.1016/j.cemconres.2012.06.009

Detwiler, R. J., & Mehta, P. K. (1989). Chemical and physical effects of silica fume on the mechanical behaviour of concrete. ACI Materials Journal, 86(6), 609–614.

Di Salvo Barsi, A., Marchetti, G., Trezza, M. A., & Irassar, E. F. (2020). Carbonate rocks as fillers in blended cements: Physical and mechanical properties. Construction and Building Materials, 248, 118697. https://doi.org/10.1016/j.conbuildmat.2020.118697

Gubio, K. B., Ismail, M. M., & Olu, O. O. (2022). Effect Of Quartz Particle Size and Cement Replacement on Portland Limestone

Cement properties. Journal of Building Material Science, 4(2), 16–25. https://doi.org/10.30564/jbms.v4i2.5091

John, V. M., Damineli, B. L., Quattrone, M., & Pileggi, R. G. (2018). Fillers in cementitious materials — Experience, recent advances and future potential. Cement and Concrete Research, 114(September 2017), 65–78.

Kajaste, R., & Hurme, M. (2016). Cement industry greenhouse gas emissions - Management options and abatement cost. Journal of Cleaner Production, 112, 4041–4052.

Kara, P., Maeijer, D., Craeye, B., Snellings, R., Kazemi-kamyab, H., Loots, M., … Nuyts, G. (2020). Effect of ultra-fine fly ash on concrete performance and durability. Construction and Building Materials, 263, 120493. https://doi.org/10.1016/j.conbuildmat.2020.120493

Kocaba, V., Gallucci, E., & Scrivener, K. L. (2012). Methods for determination of degree of reaction of slag in blended cement pastes. Cement and Concrete Research, 42(3), 511–525.

Kumar, A., Oey, T., Falzone, G., Huang, J., Bauchy, M., Balonis, M., … Neithalath, N. (2017). The filler effect: The influence of filler content and type on the hydration rate of tricalcium silicate. Journal of the American Ceramic Society, 100(7), 3316–3328.

Lin, R. S., Wang, X. Y., & Zhang, G. Y. (2018). Effects of quartz powder on the microstructure and key properties of cement paste. Sustainability (Switzerland), 10(10). https://doi.org/10.3390/su10103369

Lothenbach, B., Scrivener, K., & Hooton, R. D. (2011). Supplementary cementitious materials. Cement and Concrete Research, 41, 1244–1256.

Nath, P., & Sarker, P. (2011). Effect of Fly Ash on the Durability Properties of High Strength Concrete. Procedia Engineering, 14, 1149–1156. https://doi.org/10.1016/j.proeng.2011.07.144

Rahhal, V., & Talero, R. (2005). Early hydration of portland cement with crystalline mineral additions. Cement and Concrete Research, 35(7), 1285–1291.

Scrivener, K. L., John, V. M., & Gartner, E. M. (2018). Eco-efficient cements: Potential economically viable solutions for a low-CO2 cement-based materials industry. Cement and Concrete Research, 114, 2–26. https://doi.org/10.1016/j.cemconres.2018.03.015

Wang, D., Shi, C., Farzadnia, N., Shi, Z., Jia, H., & Ou, Z. (2018). A review on use of limestone powder in cement-based materials: Mechanism, hydration and microstructures. *Construction and Building Materials*, *181*, 659–672.