Fresh and mechanical properties of binary and ternary blended cement binders using Australian calcined clay

Quang Dieu Nguyen[1], Sanket Rawat[1], Paul Thomas[1], Camille Holt[2], Ali Nezhad[2], Kirk Vessalas[1], Arnaud Castel[1]
[1]School of Civil and Environmental Engineering, University of Technology Sydney (UTS), Sydney, NSW 2007, Australia
[2]Boral, 39 Delhi Road, North Ryde, NSW 2113, Australia

Abstract: The concrete industry significantly contributes to CO_2 emissions, with most emissions generated during cement production. Using supplementary cementitious materials (SCMs) to partially replace Portland cement is one of the most effective strategies to reduce the carbon footprint of concrete production while also enhancing the concrete properties. Among promising SCMs, calcined clays have gained remarkable attention due to their abundant availability. In this study, calcined clay was produced using locally available clay sourced in Australia. The fresh and mechanical properties of mortars containing the Australian calcined clay, including the flow and compressive strength of binary and ternary blends have been investigated. The performance of Australian calcined clay mortars was compared to those containing conventional SCMs, including ground granulated blast furnace slag and fly ash. The total cement replacement was up to 50%, reflecting an industry representative standard of targeting low carbon concrete. Furthermore, the compatibility of calcined clay blends with commercial concrete admixtures was assessed based on both the fresh and mechanical properties to demonstrate the feasibility of using calcined clay technology and to support its practical implementation in major Australian infrastructure projects. The fineness, chemical and mineral composition of the Australian calcined clay were analysed to elucidate the performance of the calcined clay binders. The findings from this study provide fundamental insights for selecting appropriate concrete mix design compositions incorporating Australian calcined clay, in compliance with Australian standards and specifications.

Keywords: Australian calcined clay; mortar flow; compressive strength, admixtures.

1. INTRODUCTION

The cement industry is a significant contributor to global greenhouse gas emissions, accounting for approximately 5% of total emissions [1]. This high level of emissions is primarily due to the calcination of limestone and the combustion of fossil fuels in the cement production [2]. As the demand for cement continues to grow, driven by urbanization and infrastructure development, the environmental impact of cement production has become a critical concern. The need to address these environmental impacts has led to increased research and development efforts aimed at finding sustainable alternatives and methods to reduce the carbon footprint of cement production.

Several strategies have been proposed to mitigate the environmental impact of the cement industry [3]. These include the use of supplementary cementitious materials (SCMs), the development of cement-free binders, and the implementation of carbon capture and storage (CCS) technologies [4-6]. Among these options, the use of SCMs is considered the most feasible and immediately implementable solution due to its high technology readiness level. SCMs can partially replace Portland cement in concrete, thereby reducing the overall carbon footprint of cementitious materials. The integration of SCMs into cement production processes not only helps in reducing emissions but also enhances the performance characteristics of the concrete [7, 8].

Fly ash and slag has been widely used in concrete industry as conventional SCMs. However, the availability of fly ash and slag is expected to reduce in the future due to the closure of coal-fired power plants and alternative methods in steel production. Therefore, calcined clay has emerged as a particularly promising candidate [9] to replace conventional SCMs (fly ash and slag) in the future. Calcined clay is commonly produced by the calcination of kaolinite clay [10]. Kaolinite clay is abundant and widely available, making it a sustainable and cost-effective option for reducing the environmental impact of cement production [10]. Additionally, calcined clay has been shown to enhance the mechanical properties and durability of concrete, especially in coastal/chloride environments, further supporting its potential as a primary SCM in the future [11, 12]. The pozzolanic properties of calcined clay contribute to improved strength and durability of concrete, making it an attractive option for various construction applications [13-15].

In recent years, the investigation and production of calcined clay has commenced in various regions around the world [16], including Australia [17]. The use of calcined clay in Australia is particularly noteworthy due to the country's commitment to sustainable practices and reducing carbon emissions. Additionally, kaolinite clay is abundant in the topsoils and subsoils in Australia [18]. However, the performance of calcined clay combined with fly ash or slag in ternary blends and different admixtures have not been addressed. The paper aims to present the fresh and hardened properties of binary and ternary blended cement binders using Australian calcined clay produced by the Calix renewably powered electric calcination technology [19] through a SmartCrete CRC project with Boral, Transport for NSW, Calix and University of Technology Sydney (UTS). Mortar flow and compressive strength up to 90 days were investigated in this study. By investigating the fresh and mechanical performance of these blended binders, this study seeks to contribute to the growing body of knowledge on demonstrating the feasibility and validating the performance of Australian calcined clay as a SCM and to promote its adoption in the Australian cement industry.

2. MATERIALS, MIX DESIGNS AND EXPERIMENTAL PROGRAM

2.1 Materials

The binder used in this study includes general purpose (GP) cement, calcined clay, fly ash and ground granulated blast furnace slag (GGBFS). GP cement, fly ash and GGBFS (branded as Environment®), supplied by Boral, complies with Australian Standards AS 3972, AS 3582.1 and AS 3582.2 respectively. The calcined clay was produced by the renewably powered electric calcination technology at Calix. The raw clay was supplied by Boral after a preliminary study to meet the target kaolinite content. The kaolinite content in the Australian raw clay prior to calcination was 48.6 ± 0.77%, measured by thermogravimetric analysis (TGA). The particle size distribution of GP cement, calcined clays, fly ash and GGBFS, measured using the dry laser diffraction method, are shown in Figure 1. The fine aggregate was river sand with water absorption of 1.1%.

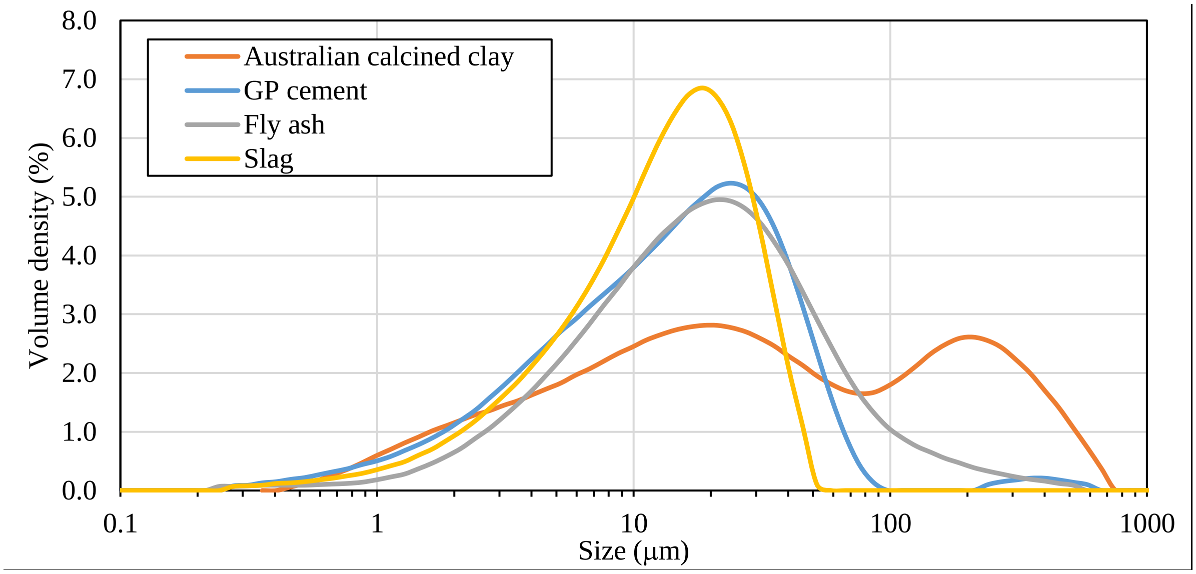

Figure 1. Particle size distribution of binders

2.2 Mortar mix design

The mortar mix composition including total binder content, water-binder ratio and sand content complied with Australian standard AS 2350.12. Table 1 shows the mortar mix proportions to fabricate three mortar prisms (40 × 40 × 160 mm).

Table 1. Mortar mix compositions

Total binder (g)	River sand in SSD condition (g)	Water (g)	Water-binder ratio
450	1350	225	0.5

In this study, the primary focus was on varying the proportion of CC (as shown in Table 2) to assess its effect in various blended systems. Three reference mixes were included: Ref 1, which was composed of 100% cement; Ref 2, a 50:50 blend of cement and GGBFS; and Ref 3, which consisted of 70% cement and 30% fly ash. These reference mixes served as a baseline for comparison with the CC mixes. The calcined clay was utilised to fabricate the binary and ternary blends as presented in Table 2.

Table 3. Binder compositions considered in this study

Mix ID	Details
Ref 1 (100 GP)	100% Cement
Ref 2 (50 GP + 50 GGBFS)	50% Cement + 50% Slag
Ref 3 (70 GP – 30 FA)	70% Cement + 30% Fly ash
50 GP – 35 GGBFS – 15 CC	50% Cement + 35% Slag + 15% Calcined clay
50 GP – 25 GGBFS – 25 CC	50% Cement + 25% Slag + 25% Calcined clay
50 GP – 15 GGBFS – 35 CC	50% Cement + 15% Slag + 35% Calcined clay
50 GP – 50 CC	50% Cement + 50% Calcined clay
70 GP – 30 CC	70% Cement + 30% Calcined clay
70 GP – 15 CC – 15 FA	70% Cement + 15% Fly ash + 15% Calcined clay
70 GP – 20 CC – 20 FA	70% Cement + 20% Fly ash + 20% Calcined clay

2.3 Experimental program

The mortar flow and flow retention test were conducted according to Australian Standard AS 2350.18. Mortar prisms (40 × 40 × 160 mm) were fabricated following AS 2350.12 to measure the mortar compressive strength up to 90 days. At least two strength measurements were carried out in each testing day with the loading rate of 2.4 kN/s according to AS 2350.11.

3. RESULTS AND DISCUSSION

3.1 Mortar flow without water reducing admixtures

Figure 2 presents the flow of different mortar mixes including the reference mixes and blends with CC. It can be observed that the reference mixes, both with and without supplementary cementitious materials (SCMs), showed similar flow values of approximately 92-95 mm. However, the flow value significantly decreased as the CC content increased, likely due to its higher fineness and early pozzolanic activity. This reduction is consistent with previous studies of calcined clay [20, 21]. When GGBFS was replaced with CC, the flow value decreased from 92 mm to 75 mm at 15% replacement, 67 mm at 25% replacement, and 34 mm at 50% replacement. Similarly, for Ref 3 mixes, the flow value dropped from 92 mm to 71 mm with 15% replacement of fly ash and 52 mm with 30% replacement. This suggests that the addition of CC will require water-reducing admixtures to achieve the necessary flow for field trials

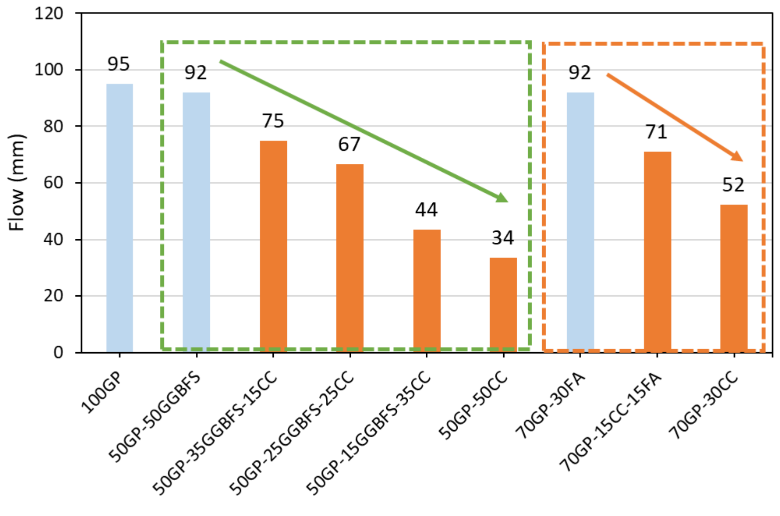

Figure 2. Flow of mortar mixes without water reducing admixtures

3.2 Effect of water reducing admixtures

Considering the lower flow values observed in mixes containing CC, the effects of water reducers were investigated to determine if the desired flow could be achieved using these admixtures. Seven different water-reducing admixtures were used for this assessment as listed in Table 3. Six of these admixtures are commonly available and used in Australia, while HRWR-O is not currently available in Australia. This high-range water reducer is specifically formulated for CC blends and is accessible in European regions for this application and was included in the study to compare its performance with the admixtures available in Australia. Mix 70GP-30CC was selected as the base mix, and the dosage of each admixture was adjusted to achieve the target flow of 105 ± 5 mm.

Table 3. Water reducing admixtures used in this study

Admixture name	Type
MFWR	Multi-functional water reducer (MFWR)
WR	Water reducer (WR) - based on modified polycarboxylates
AMRWR	Advanced Mid-Range water reducer (AMRWR) - true neutral set
NCAA	Non-chloride accelerator admixture (NCAA) - based on modified copolymer technology
MRWR	Mid-Range Water Reducer (MRWR)
HRWR	High Range Water Reducer (HRWR) - based on modified polycarboxylates
HRWR-O	High Range Water Reducer (from overseas source)

Figure 3 details the dosage required for each admixture to achieve the target flow of 105 ± 5 mm. The target flow was achieved for each admixture trials, although the dosages varied significantly. For HRWR-O, which is specifically formulated for CC, 507 ml was needed per 100 kg of binder to reach the target flow. Interestingly, this dosage was nearly same as that required for HRWR, which needed 509 ml per 100 kg of binder. This suggests that current high range water reducer based on modified polycarboxylates can effectively improve the workability of calcined clay mixes. Other normal or mid-range water reducers also performed well in achieving similar flow.

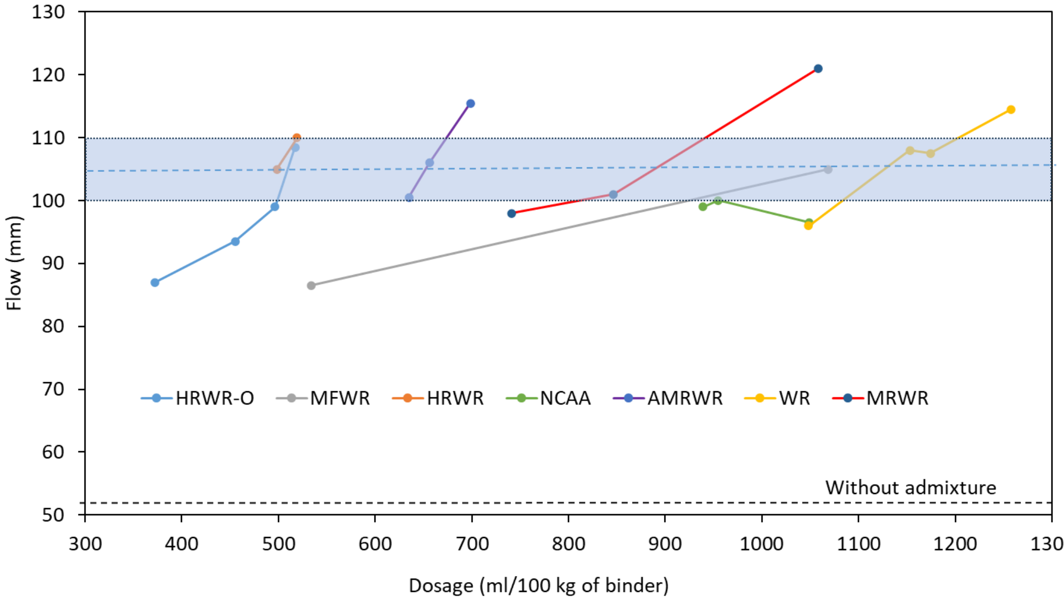

Figure 3. Effect of different admixtures on flow behaviour of 70GP-30CC

Once the required dosage for 70GP-30CC was defined for all the admixtures, the dosages for the reference mixes and ternary blends were also measured for comparison. Three types of admixtures were chosen including HRWR, MFWR, and WR. Figure 4 illustrates the dosages needed for both the reference mixes and the CC blend mixes. It is evident that the dosages required for the binary CC blends are significantly higher, irrespective of the type of water reducer used. Additionally, it was observed that the dosages for mixes containing SCMs (both fly ash and GGBFS) were comparatively lower than those needed for the 100% cement mix. The FA-CC ternary blends, 70GP-15FA-15CC and 60GP-20FA-20CC, required substantially lower dosages than the binary blend. Notably, the dosage of WR was significantly reduced and fell within the recommended range. For the 70GP-30CC binary blend, the initial dosage was 1164 ml per 100 kg of binder. This dosage dropped by 56% for 50GP-25GGBFS-25CC, 73% for 60GP-20FA-20CC, and 78% for 70GP-15FA-15CC. A similar pattern was observed with AMRWR, where the dosage reductions compared to the binary blend were 42% for 50GP-25GGBFS- 25CC and 67% for both 60GP-20FA-20CC and 70GP-15FA-15CC. HRWR also demonstrated reductions in dosage compared to the CC binary blend.

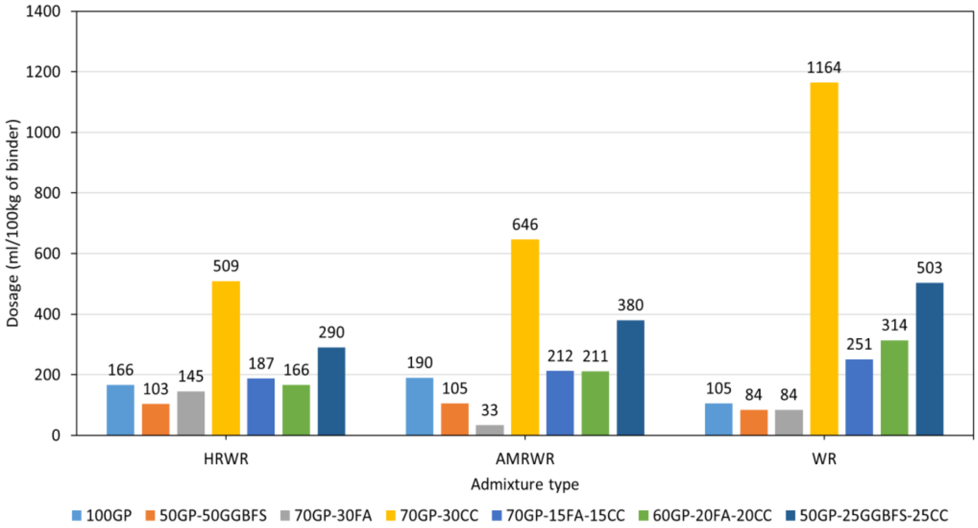

Figure 4. Comparison of different admixture dosage to achieve target flow of 105±5 mm

3.3 Compressive strength

Figure 5 presents the mortar strength development of binary calcined clay mixes together with three references mixes: 100% cement, 50% cement with 50% GGBFS, and 70% cement with 30% fly ash. Calcined clay binary blends were produced using HRWR-O and HRWR to achieve the flow of 105 ± 5 mm. The reference mix with 100% cement (Ref 1 – 100GP) showed the highest compressive strength up to 7 days, highlighting the early strength development of cement. Calcined clay binary blends exhibited similar 28-day compressive strength to 100% GP cement mix. The Ref – 3 with 30% fly ash showed the lowest compressive strength at 28 days.

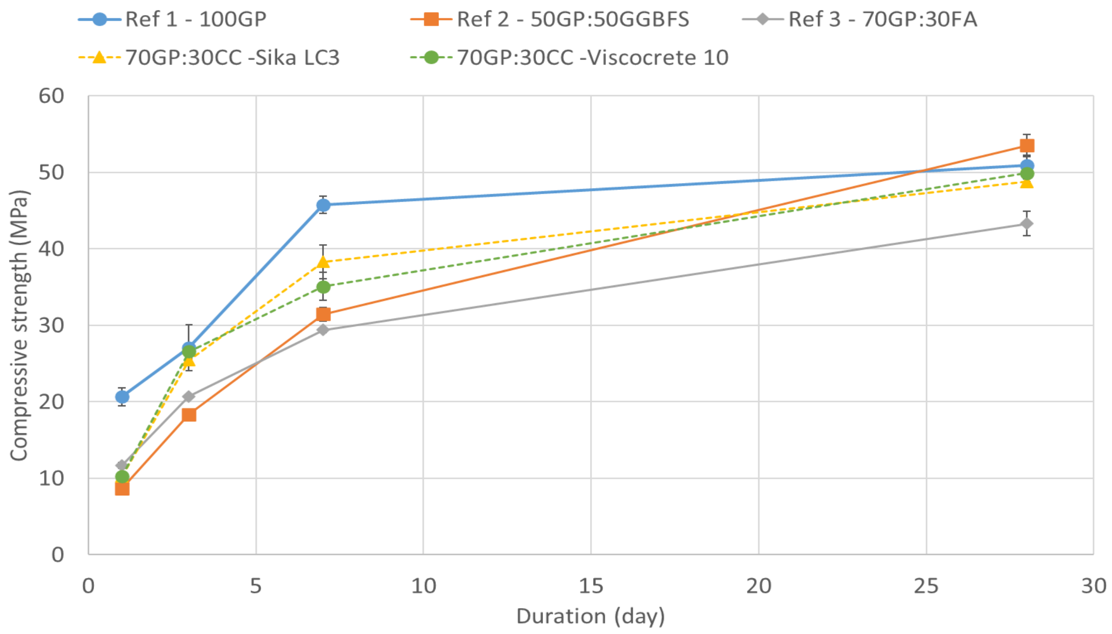

Figure 5. Compressive strength of calcined clay binary blends and reference mixes

Figure 6 compares the compressive strength of three ternary blends using HRWR and WR with Ref 1 containing 100% GP cement. The 70GP:15FA:15CC and 50GP:25GGBFS:25CC mixes demonstrated comparable 28-day strengths, both higher than the 28-day strength of 60GP:20FA:20CC. This highlights the beneficial effect of GGBFS in enhancing the compressive strength of ternary blends, despite its high 50% replacement rate. Compared to Ref 1 (100% GP cement), the Australian calcined clay binary and ternary blends met the requirements for at least Grade 2 strength index (greater than 75%), as per Australian Standard AS 3582.4. Furthermore, the binary blend (70GP:30CC in Fig. 5) and the ternary blend containing GGBFS (50GP:25GGBFS:25CC) achieved a strength index exceeding 85%, meeting the criteria for Grade 1 Manufactured Pozzolans.

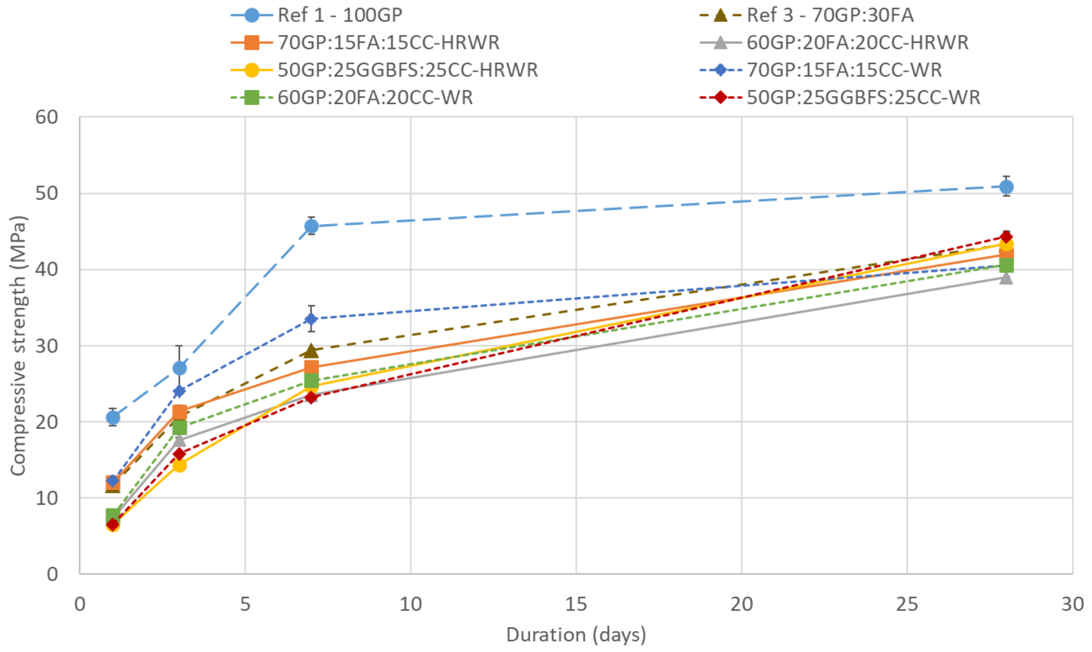

Figure 6. Compressive strength of calcined clay ternary blends.

4. CONCLUSION

This study investigated the fresh and hardened properties of mortar using Australian calcined clay. The performance of Australian calcined clay mortars was compared to those containing conventional SCMs, including GGBFS and FA. The required mortar flow of 105 ± 5 mm for calcined clay binary and ternary blends could be achieved by using water reducer admixtures including: multi-functional water reducer (MFWR), advanced mid-range water reducer (AMRWR) - true neutral set, and high range water reducer (HRWR) - based on modified polycarboxylates. The dosages required for the calcined clay blends are significantly higher than GGBFS or fly ash, irrespective of the type of water reducer used.

Calcined clay binary blends using Australian calcined clay and water reducer admixtures exhibited similar 28-day compressive strength to that of 100% GP cement mix, higher than the reference mix with 30% fly ash. The calcined clay ternary blends 70GP:15FA:15CC and 50GP:25GGBFS:25CC mixes demonstrated comparable 28-day strengths, both higher than the 28-day strength of 60GP:20FA:20CC. This highlights the beneficial effect of GGBFS in enhancing the compressive strength of calcined clay ternary blends, despite its high 50% replacement rate. The Australian calcined clay binary and ternary blends met the requirements for at least Grade 2 strength index (greater than 75%), as per Australian Standard AS 3582.4. Furthermore, the 30% calcined clay binary blend (70GP:30CC) and the ternary blend containing GGBFS (50GP:25GGBFS:25CC) achieved a strength index exceeding 85%, meeting the criteria for Grade 1 Manufactured Pozzolans.

5. ACKNOWLEDGEMENT

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