

Activation of Cementless Binder Based on Volcanic ash and Calcium Carbide Residue

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Abstract – This study assessed the performance of a cementless binder comprising volcanic ash (VA) and calcium carbide residue (CCR) with different activation methods. The binder was made of 95% VA and 5% CCR and activated by physical, chemical, thermal, and combinations of the methods. While the physical activation included using CCR of nominal particle size of 45 μm , the chemical activation involved adding 1% NaOH by binder mass to the paste, and thermal activation comprised curing the paste in an oven at 65°C for 24 hours. The performance evaluation was based on flowability, compressive strength, and bulk electrical resistivity. The flowability increased by chemical activation and subsequent physical and chemical activation but decreased with physical activation alone. Meanwhile, all activation methods improved the compressive strength and bulk resistivity. In particular, binders activated by subsequent physical and thermal techniques achieved the highest compressive strength, exceeding 30 MPa at 28 days. In contrast, subsequent chemical and thermal activation produced superior bulk resistivity of 193 $\Omega\cdot\text{m}$ at 28 days compared to other activation techniques. The study illustrated the feasibility of using low-carbon materials to form sustainable cementless binders for different applications in construction.

Keywords: Volcanic ash; Calcium carbide residue; Cementless binder; Flowability; Compressive strength; Bulk resistivity.

1. Introduction

Incorporating alternative materials to Portland cement in cementitious composites has been widely implemented in recent decades. The reduction in the use of Portland cement generally aims at lowering its environmental impacts, including high greenhouse gas emissions, high energy demand, excessive exploitation of natural resources, etc. [1] Indeed, among the plurality of environmental concerns, the CO₂ emissions stands as the most remarkable, as Portland cement contributes to around 5-8% of total emissions worldwide [2]. Nevertheless, partial replacement with alternative materials, such as fly ash and slag, seemed to have only a marginal impact; cement production is continuously rising and would possibly reach 4.4 billion tons in 2050 as per high demand scenario forecasts set by the International Energy Agency (IEA) [3]. Therefore, strategies different than partial substitution should be assessed for more effective reduction in cement and, in turn, carbon emissions alleviation.

Alternatively, replacing Portland cement with other lower-carbon materials in cementitious composites would reduce cement industry emissions. Indeed, Portland cement compromises hydraulic properties, forming hydration products necessary for hardening and gaining strength [4]. On the other hand, cementless binders primarily rely on the pozzolanic reaction between its different components for hardening and strength gain [5]. Through the pozzolanic reaction, pozzolans react with calcium hydroxide [Ca(OH)₂] to form reaction products similar to hydration products, in particular calcium silicate hydrate (C-S-H) [6].

Several factors influence the pozzolanic reaction. Temperature is a pivotal parameter, as elevated temperatures accelerate the reaction rate by providing additional energy for the chemical transformations [7]. The fineness of binders,

referring to the particle size of pozzolans and other components, significantly impacts the reaction's kinetics. Finer particles increase the surface area for interaction, promoting more efficient contact between pozzolan and calcium hydroxide and enhancing reactivity and early strength development [8]. Moreover, adding sodium hydroxide (NaOH) can influence the pozzolanic reaction by increasing the system's alkalinity. Controlled amounts of NaOH can expedite the reaction by fostering a more alkaline environment and, in turn, facilitating the dissolution of silica and alumina from the pozzolan [9].

Volcanic ash (VA) is a pozzolanic material generated by volcanic eruptions [10]. It typically consists of high volumes of silica, aluminum, and iron oxides [11]. Meanwhile, calcium carbide residue (CCR) is an industrial byproduct of acetylene gas production, mainly of calcium oxide [12]. Indeed, both materials are low-carbon, and combining them would possibly create a cementless binder for utilization in various applications in the construction industry. VA was reported to increase the flowability of concrete when replacing cement by up to 20% by mass but decreasing the flowability beyond this replacement level [11]. Also, VA increased the compressive strength of cement mortar when used as cement partial replacement at a 15% substitution rate and extended curing periods [13]. Meanwhile, CCR reduced the flowability of cementless fly ash binder [14]. A different study [12] reported that incorporating CCR as cement replacement at a 5% substitution rate in concrete increased the strength but had the opposite effect at 10%.

This study aims to evaluate the performance of a cementless binder comprising VA and CCR with different activation techniques. The studied techniques included physical, chemical, and thermal activation and combinations of these methods. The performance evaluation was based on flowability, compressive strength, and bulk electrical resistivity. This work contributes to the circular economy by recycling VA and CCR while producing sustainable cement-free binders for different construction applications.

2. Materials and Testing

2.1. Materials

Volcanic ash (VA) was used as received and had a specific gravity of 3.05 and D_{50} of 19 μm . The calcium carbide residue (CCR) was received as a slurry and dried in an oven for 24 hours at 105°C. Notably, it was sieved to have a nominal particle size of 45 μm for physical activation. Therefore, the original CCR and sieved CCR had a specific gravity of 2.55 and 2.61 and D_{50} of 24 and 16 μm , respectively. Tap water was also used.

2.2. Activation methods

Three activation methods, used exclusively or synergistically, were performed on the binder as follows:

- Physical (P) by sieving the CCR with a maximum particle size of 45 μm .
- Chemical (C) by adding 1% NaOH by the binder mass to the paste.
- Thermal (T) by curing the samples in an oven at 65°C for 24 hours.
- Subsequent physical and chemical
- Subsequent physical and thermal
- Subsequent chemical and thermal

2.3. Mixture proportions and preparation

A cement-free binder with different proportions of VA and CCR was first evaluated for strength, where the objective was to reach an acceptable compressive strength at 28 days. The studied substitution levels of VA to CCR were 95:5, 90:10, 80:20, and 60:40, with a fixed water-to-binder ratio of 0.45. The preliminary study showed that the binder containing 95% VA and 5% CCR had the highest compressive strength, reaching 19 MPa at 28 days of curing. Therefore, it was selected for the activation stage. Table 1 presents the mixture proportions and activation methods investigated in this study. A total of seven mixes were investigated. The control mix, denoted by "Ctrl," was established for reference. The remaining mixes were denoted by their activation method.

Table 1: Mixture proportions and activation methods of the cementless binder.

Mix ID	Proportions (%)		Water-to-binder	Activation		
	VA	CCR		Physical	Chemical	Thermal
Ctrl	95	5	0.45	-	-	-
P	95	5	0.45	×	-	-
C	95	5	0.45	-	×	-
T	95	5	0.45	-	-	×
P+C	95	5	0.45	×	×	-
P+T	95	5	0.45	×	-	×
C+T	95	5	0.45	-	×	×

The main binder constituents, VA and CCR, were blended first for two minutes in a pan mixer. The water was added gradually after that. The generated paste was subsequently mixed for two minutes. After ensuring consistency, the fresh mix was placed in 50-mm cubic moulds and kept for 24 hours at a room temperature of 21±2°C. Meanwhile, a moist fabric and a plastic sheet were used to cover the samples. Afterward, the specimens were de-moulded and placed in water tanks until the specified testing dates. For chemically activated mixes (C, P+C, and C+T), the NaOH was added as a powder and mixed with the VA and CCR before adding water. The thermally activated mixes (T, P+T, and C+T) were left to harden for 24 hours in lab conditions and then placed in the oven for 24 hours at 65°C.

2.4. Testing program

The flow table measured the flow diameter of the pastes following ASTM C1437 [15]. The compressive strength testing procedures were applied on 50-mm cubic samples and followed ASTM C109 [16]. The strength was evaluated at 7, 28, and 56 days, and the reported value is the average of three specimens. Moreover, the bulk electrical resistivity was determined using an RCON® tester following the procedures of ASTM C1876 [17]. The apparatus measured the impedance, Z , and accordingly, the bulk electrical resistivity was calculated as per Eq. (1):

$$\rho = \frac{A}{L} Z \quad (1)$$

Where ρ is the bulk electrical resistivity in ($\Omega \cdot m$), A is the cross-sectional area of the specimen in (m^2), and L is the length of the specimen in (m). The reported value was the mean of three samples, and the resistivity was evaluated at 7, 28, and 56 days.

3. Results

3.1. Flowability

The flowability of the cementless binder activated by different activation techniques is illustrated in Fig. 1. The control binder (i.e., no activation) had a flowability of 180 mm. Using physical activation caused a slight decrease in the flowability of the binder. This was expected due to the higher surface area provided by the sieved CCR, increasing the water demand and, in turn, decreasing flowability. Meanwhile, using chemical activation increased the flowability of the binder to reach 195 mm. Adding 1% NaOH increased the pH of the binder, affecting its viscosity and increasing its flow. When using subsequent physical and chemical activation, the flowability slightly increased, indicating that adding 1% NaOH counteracted the effect of the increased fineness of the sieved CCR.

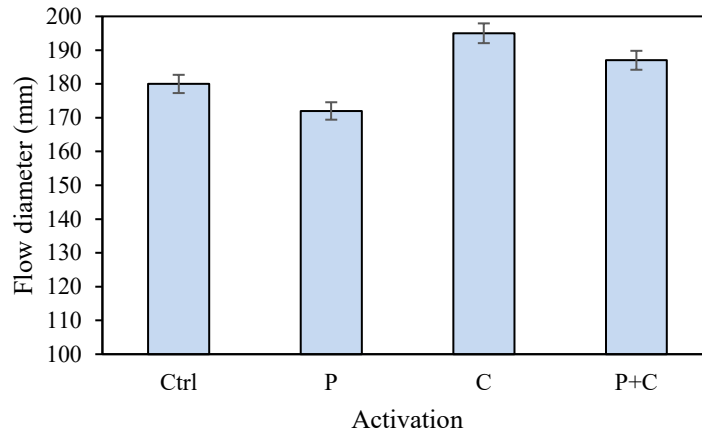


Fig. 1: Flowability of the cementless binder for different activation methods.

3.2. Compressive strength

The compressive strength of the cementless binder for the different activation methods is depicted in Fig. 2. The compressive strength was tested at curing ages of 7, 28, and 56 days. At 7 days of curing, the compressive strength ranged between 7.4 and 16.8 MPa. While the control mix had the lowest strength, subsequent physical and thermal activation had the highest. Indeed, all activation methods improved the strength. Using physical activation increased the strength to reach 9.4 MPa. The increase in strength could be explained by the higher surface area of the sieved CCR, providing more reaction sites with the VA and activating the pore-filling effect [18]. Chemical activation resulted in a strength higher than the control mix by around 35%. Adding 1% NaOH by binder mass enhanced the pozzolanic reaction between VA and CCR, producing more reaction products and, consequently, higher strength. Meanwhile, thermal activation triggered a 66% increase in 7-day compressive strength. The reaction between VA and CCR accelerated as the cementless binder was subjected to elevated temperatures, causing a refined pore structure and higher strength [19].

The combined activation of the cementless binder caused higher improvement in the 7-day compressive strength. Subsequent physical and chemical activation raised the compressive strength to 14.2 MPa at 7 days, which is higher by 96% compared with the control mix and at least 40% in comparison with any of the two activation techniques. Combined physical and thermal activation achieved the highest 7-day compressive strength of 16.8 MPa, corresponding to a 127% improvement compared to the control mix and at least 37% with any of the two activation methods. Similarly, the binder subjected to subsequent chemical and thermal activation had a strength of 15.1 MPa, 104% higher than the control binder and at least 23% higher than chemical or thermal activation alone. Similar results were reported earlier in the literature using chemical, physical, or thermal activation techniques on cement-free binders containing fly ash and CCR [20].

The 28-day compressive strength ranged between 19.0 and 27.4 MPa, while the strength at 56 days ranged from 25.0 to 31.2 MPa. For all VA-CCR pastes, the strength increased with time. Also, the pattern of change was identical between different curing ages. The total increase in strength between 7 and 28-56 days of curing for physical, chemical, and thermal activation reached 121-185, 122-175, and 102-141%, respectively. Meanwhile, a total increase in strength of 89-111%, 63-86%, and 74-104% was experienced for mixes subjected to subsequent physical and chemical, physical and thermal, and chemical and thermal, respectively, between 7 and 28-56 days. The increase in strength with time could be explained by the pozzolanic reaction taking place during the curing periods. Additionally, the strength development rate was higher for single activation methods. This could be interpreted as a more rapid increase in strength at an early curing age when using two different activation techniques.

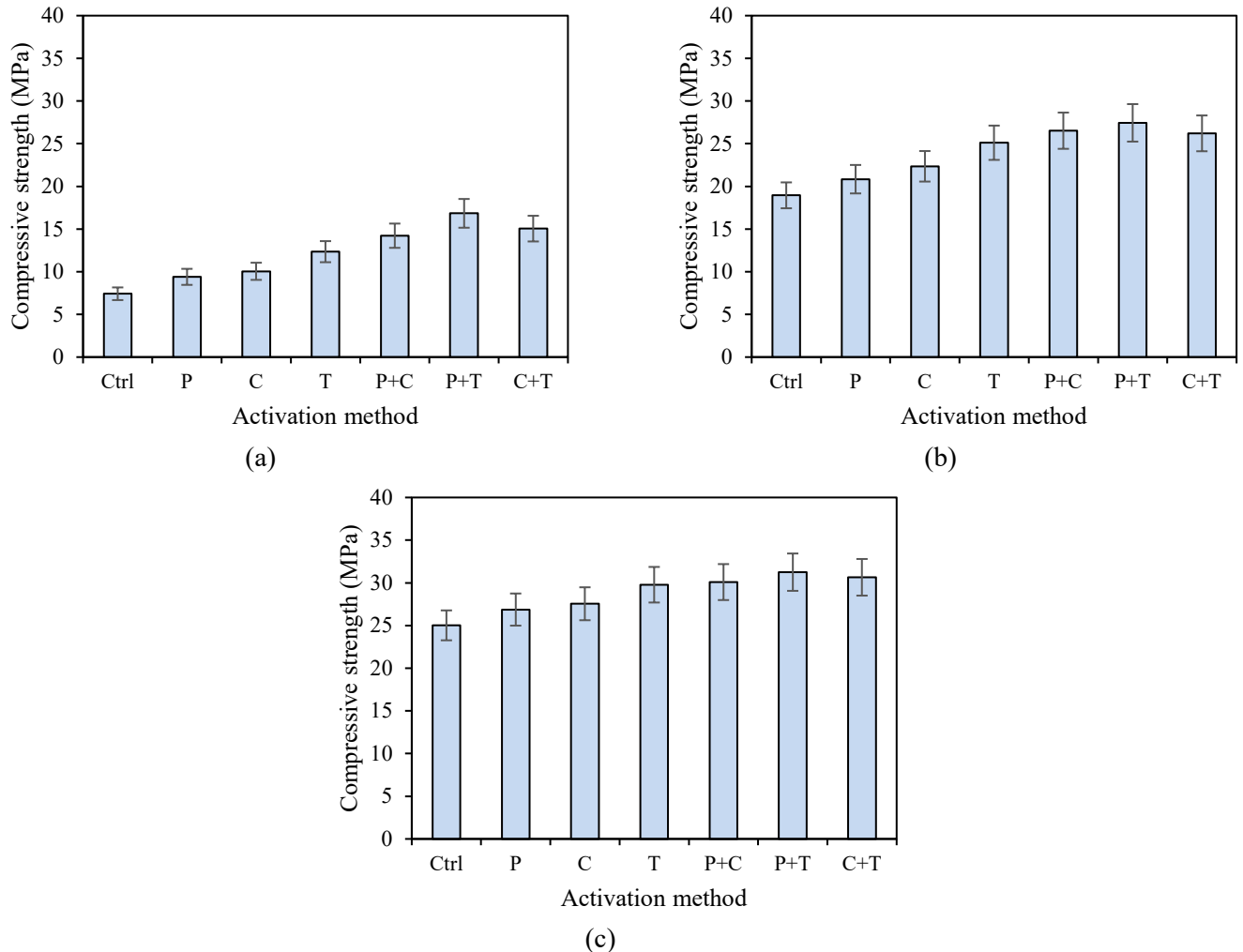


Fig. 2: Compressive strength of the cementless binder for different activation methods at (a) 7-day, (b) 28-day, and (c) 56-day curing periods.

3.3. Bulk electrical resistivity

The bulk electrical resistivity of the cementless binder at different activation methods is presented in Fig. 3. The bulk electrical resistivity was measured at 7, 28, and 56 days. The control mix had the lowest 7-day bulk resistivity at 14.7 $\Omega\cdot\text{m}$. In contrast, the highest resistivity was recorded for the binder subjected to chemical and thermal activation at 97.7 $\Omega\cdot\text{m}$. Comparing individual activation techniques to the control binder, a slight increase of 12% was experienced for binders containing sieved CCR (i.e., physical activation). The higher surface area of sieved CCR improved the packing density, leaving less space for the conductive medium [18]. Meanwhile, chemical activation increased the 7-day bulk resistivity by 87%, mainly owing to the change in the chemical composition of the pore structure due to the addition of 1% NaOH by the binder mass. Similarly, thermal activation enhanced the bulk resistivity by around 116% compared to the control mix at 7 days. This could be explained by high-temperature curing that refined the pore size distribution of the binder.

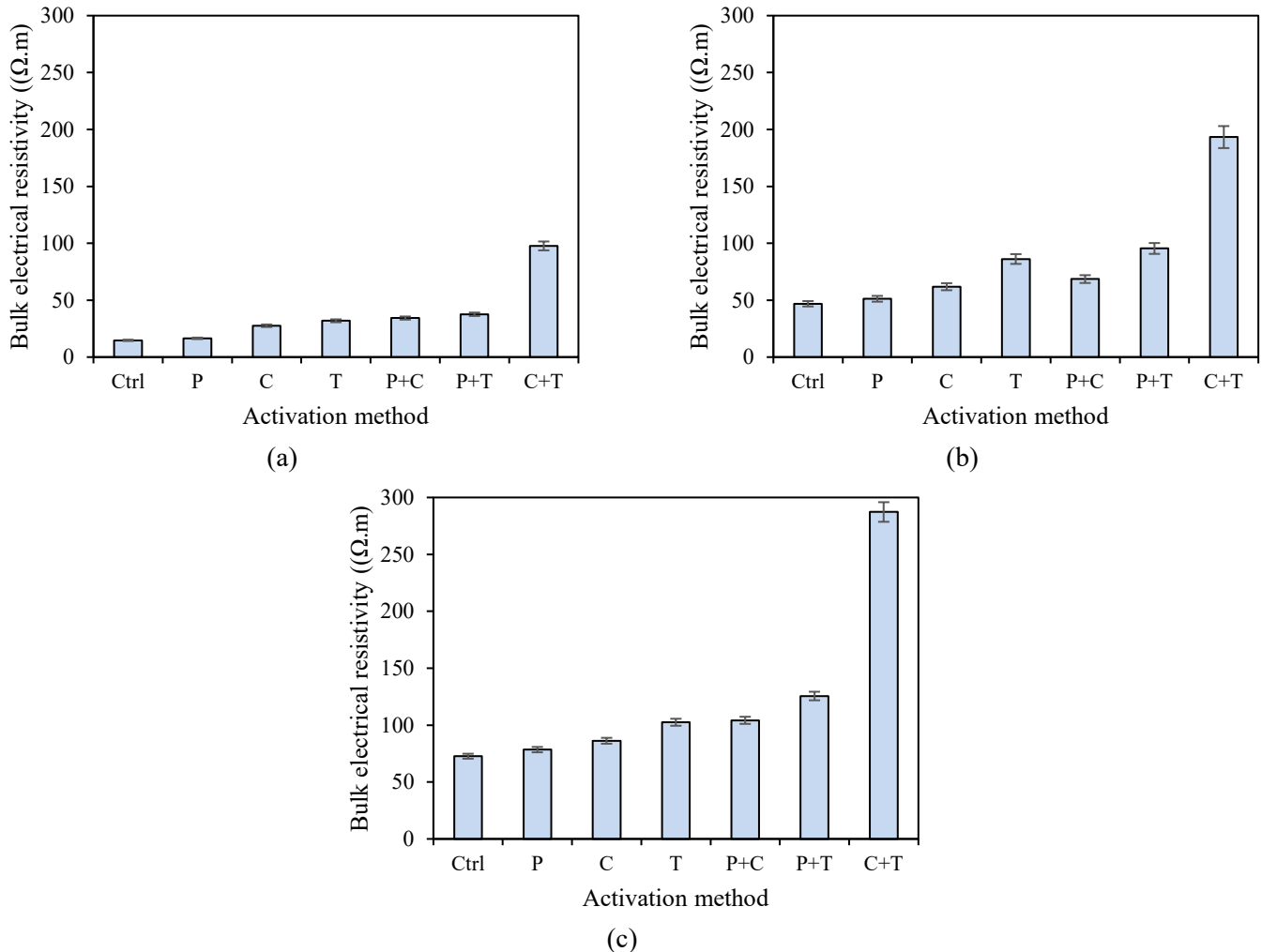


Fig. 3: Electrical bulk resistivity of the cementless binder for different activation methods at (a) 7-day, (b) 28-day, and (c) 56-day curing periods.

The combined activation of the cementless binder caused further improvement in the bulk resistivity at 7 days. Combining chemical and physical activation triggered a 136% increase in resistivity compared to the control mix and at least a 25% increase compared with any activation methods alone. Subsequently, physical and thermal activation resulted in a 155% improvement compared with the control mix and at least an 18% increase compared with the counterpart individual activations. Meanwhile, subsequent chemical and thermal activation led to a significant increase in resistivity, particularly an improvement of 564%, compared with the control mix. Also, this combined activation improved the resistivity by 207% when compared with individual chemical or thermal activation techniques.

The electrical bulk resistivity at 28 and 56 days ranged from 46.8-193.3 and 72.7-287.3 $\Omega.m$. Due to the pozzolanic reaction during the curing periods, the microstructure was densified, and the bulk resistivity consequently increased with time. The increase of bulk resistivity reached 375, 213, and 222% between 7 and 56 days for physical, chemical, and thermal activation methods, respectively. Meanwhile, a total increase in resistivity of 203, 234, and 195% was observed for mixes having subsequent physical and chemical, physical and thermal, and chemical and thermal, respectively, between 7 and 56 days.

4. Conclusion

This study aimed to assess the influence of different activation methods on the properties of a cementless binder comprising volcanic ash (VA) and calcium carbide residue (CCR). Physical, chemical, and thermal activation methods, through sieving the CCR, adding 1% NaOH by the binder mass, and subjecting the binder to 65°C for 24 hours in an oven, oven, respectively, were assessed. Also, combinations of these activation methods were evaluated. The investigated properties included flowability, compressive strength, and bulk electrical resistivity. The following outcomes were observed:

- Chemical activation increased the flowability of the cementless binder compared with the control mix, while physical activation decreased it. Combined chemical and physical activation caused a slight increase in the flowability.
- Using any individual or combined activation triggered an improvement in the compressive strength at 7, 28, and 56 days. Strength increased with time due to the pozzolanic reaction. The highest improvement was recorded for subsequent physical and thermal activation, reaching 31.3 MPa at 56 days.
- The electrical bulk resistivity was optimum for chemical and thermal activation, reaching 287.3 $\Omega\cdot\text{m}$ at 56 days.

The cementless binder developed in this study offers a plurality of characteristics, including a lower carbon footprint and adequate performance for different applications in the construction industry.

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