#### **Review Article**

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# Durability and microstructure analysis of concrete made with volcanic ash: A review (Part II)

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**Abstract:** Concrete is the most frequently employed man-made material in modern building construction. Nevertheless, the serviceability of concrete structures has been significantly reduced owing to a variety of durability issues, especially when serving in a non-ideal environment and exposed to internal/external attacks such as chloride penetration, carbonation, sulfate, and so on. Several scholars have performed numerous studies on the strength and microstructure features of volcanic ash (VA) concrete and have discovered encouraging findings. However, since the information is spread, readers find it difficult to evaluate the benefits of VA-based concrete, limiting its applicability. As a result, a detailed study is required that offers the reader an easy approach and highlights all essential facts. The goal of this article (Part II) is to conduct a compressive review of the physical and chemical aspects of VA and its impact on concrete durability and microstructure properties. The findings demonstrate that VA considerably improves concrete durability owing to pozzolanic reaction and micro-filling voids in concrete materials. Cost-benefit analysis shows that 10% utilization of VA as cement decreased the overall cost by 30%. The assessment also notes a research gap that must be filled before VA may be utilized in practice.

**Keywords:** volcanic ash, concrete, durability, heat of hydration, scanning electronic microscopy

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#### 1 Introduction

Concrete is a material that is frequently used in building and acts as the basis for all building and civil engineering developments globally [1-5]. The primary components of concrete (cement) have varying environmental consequences depending on the type and quantity of cement used. Since concrete is used in such large quantities around the world, there are numerous concerns regarding its prolonged-period capability [3,6]. Building manufacturing has played an important role in urbanization and industrialization in past decades. The building division counts for about 40% of worldwide energy use and 30% of total natural resource depletion. Furthermore, these building businesses are responsible for 40% of CO<sub>2</sub> emissions and around 30% of waste production. The production process of this hydraulic cement is responsible for around 7-9% of worldwide CO2 emissions [7].

Carbon dioxide emissions from cement plants represent approximately greater than 5% of global CO2 discharges [8]. Cementitious materials may be utilized to minimize CO2 releases by replacing cement with alternative cementitious materials [9-11]. A range of industrial wastes could be used in concrete for a variety of reasons [12]. Various investigations on creating concrete utilizing supplementary ingredients to reduce the cost and shortage of conventional materials have been conducted [13]. Increasing solid waste production has made environmental disposal a serious issue due to concerns about garbage's possibly dangerous social and environmental influences. Recycling waste materials is one way for addressing these issues [14–16]. The construction industry has a large capacity to cover various industrial wastes provided that they are properly assessed before even being employed as building materials.

The construction industry must integrate sustainability to maintain ecological integrity, control waste products, improve air quality, and safeguard the environment [17,18]. Serious obstacles, such as waste generation and natural resource depletion, influence industrial productivity [12,19,20]. Manufacturing waste collects over the period, causing major

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destruction to both the ecosystem and people's health world-wide [3,14,21]. The quantity of waste, related dumping expenses, and eco-friendly impact may be decreased by developing efficient reusing options [22–24]. Natural resource conservation and economic advantages are two more possible results of such an excellent approach [25]. Economic efficiency may be achieved by employing quarry waste as a possible alternative for sand and as a by-product of stone grinders [26]. To solve this complex challenge, researchers have begun to investigate potential alternative materials (waste products) to natural aggregates and binding materials such as ash silica fume (SF) [27], fly ash (FA) [28], waste glass [29], sea sand [30], plastic waste [31], and iron–copper tailings [32].

Recycling waste has a lot of ecological benefits, although its properties are sometimes lower than those of natural aggregates. This raises the issue of establishing an appropriate replacement ratio to minimize harmful replacement effects and improve mortar characteristics [33]. Density, absorption reduction, enhanced resilience, ductility, impact resistance, and so on are all advantages of incorporating waste into concrete as filler or fibers. In addition to the aforementioned improvements, changes in the kind of substitution and unfavorable effects, such as increased or decreased compressive capacity or durability, may be observed [34,35]. Experiments were conducted to assess the performance of concrete. It was revealed that ultrafine concrete had greater early compressive capacity (3 days), reduced penetrability, and longer durability than standard concrete [36].

Numerous academics have investigated the usage of volcanic ash (VA) in mixed cement. VA decreased compressive capability during the early phases however a little improvement was seen at a later age (90 days). The combined replacement of VA and recycled concrete aggregate (RCA), on the other hand, resulted in a substantial improvement. VA has been studied as a partial cement replacement at 0, 5, 7.5, 10, 12.5, 15, and 20% amounts. The results revealed that using VA as a cement alternative increased compressive strength [37]. Furthermore, utilizing low VA percent extends the lifespan of the concrete by forming materials that are more resistant to saltwater attack [38], carbonation, and chloride ion infiltration [39]. According to mechanical and microstructural properties, the cement replacement by VA of 10-30% offered the highest benefit [40]. According to the study, the normal consistency for VA improved by 9.79% when the VA fraction was increased from 0 to 25% [41]. VA-extended pozzolanic activity is responsible for the fine VA's greater later-age strength [42]. Strength reduced as VA percentages increased and when the VA content was above 40%, it decreased significantly. When the VA content was increased by more than 40%, the compressive strength of VA-based self-compacting concrete declined dramatically. VA may be utilized up to 50% to make VA-based concrete with a compressive strength higher than 15 MPa [43]. According to one study, VA increases compressive strength by causing a response that results in the formation of calcium silicate hydrate (CSH). The interaction between free  $\text{Ca}(\text{OH})_2$  and VA during cement hydration results in a more impermeable mix due to careful control of the porous structure [44]. As a consequence, the compressive strength of concretes containing VA is comparable to reference concrete after long-term curing [45].

Brief literature shows that VA can be used in concrete production. Many scholars have carried out many studies on the strength, durability, temperature, and microstructure features of VA concrete and have discovered encouraging findings. However, since the information is spread, readers find it difficult to evaluate the benefits of VA-based concrete, limiting its applicability. Therefore, a review study is required that offers the reader an easy approach and highlights all essential facts. This study's goal (Part II) is to collect all essential data on durability and microstructure study. The main aspects of this review are the following: (a) the general background of VA, (b) the physical and chemical properties of VA, (c) the impact of VA on concrete durability, (d) the impact of VA on the microstructure, and (e) the cost benefits, and finally, a conclusion. Furthermore, the assessment also detects the research gap that requires more analysis. Figure 1 shows an overview of the different sections of this review.

# 2 Physical and chemical properties

The physical characteristics of VA utilized in concrete are shown in Table 1. VA absorbs 0.41% more water than average [46]. The density of VA is 2,450 kg/m³ [40], greater than the density of cement (1,440 kg/m³) but similar to the density of fine aggregate (1,450–2,000 kg/m³). Tomoyose et al. [47] categorize different physical qualities for various uses as building materials that aim to fully utilize the material. For this categorization, an air table is utilized as equipment, as shown in Figure 2.

Figure 3 shows a representation of a scanning electron microscope (SEM) image of VA. The particle nature of VA may be investigated using a variety of microscopic techniques, including SEM. In addition to this, it was observed that the particle shape of the VA particles is angular, and the surface of the VA particles has a rough texture. Because of the sharp shape and the surface irregularity, the internal resistance between the different components of the concrete was increased, which had a negative impact on the flow.

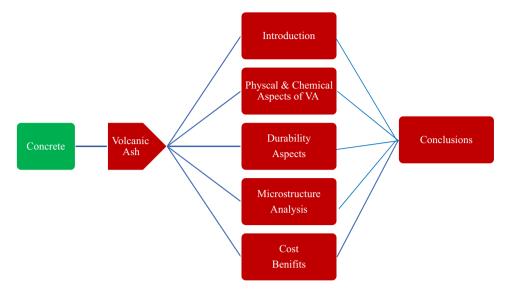


Figure 1: Sections of the review.

Table 1: Physical properties of VA

Reference	[46]	[40]	[48]	[49]
Strength activity index (%)	_	87	_	68.48
Water absorption (%)	0.41	_	_	_
Fineness (m <sup>2</sup> /kg)	_	396	_	396
Moisture content (%)	_	_	_	0.89
Bulk density (kg/m³)	2,450	_	_	_
Specific gravity	_	_	1.98	_
Air content (%)	_	6.5	_	_
Consistency (%)	_	23.4	_	_

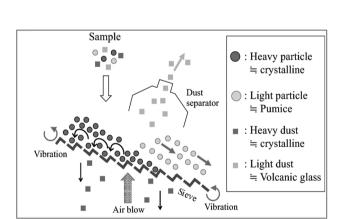


Figure 2: Air table for classification of particles [47].

The chemistry of the source magma determines the chemical structure of VA. Compared to mineral crystals, VA has typically more silica but less non-silica material. Figure 4 shows the X-ray diffraction pattern of the VA sample. It was discovered that SiO<sub>2</sub> may be found in VA in both crystalline and amorphous forms. Additionally, Table 2 displays the chemical makeup of VA. The material may be considered as a pozzolanic material when the sum of chemicals like silica, calcium, alumina, magnesia, or iron is greater than 70%, according to ASTM [50]. The total sum of silica, calcium, alumina, magnesia, and iron present in VA is greater than 70%. Thus, VA is a reliable pozzolanic material that may be used in concrete as a cement alternative.

# 3 Durability

#### 3.1 Density

Concrete durability qualities are heavily affected by its density. The denser concrete often has better strength

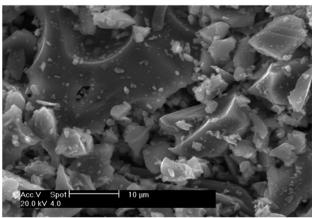


Figure 3: SEM of VA particles [45].

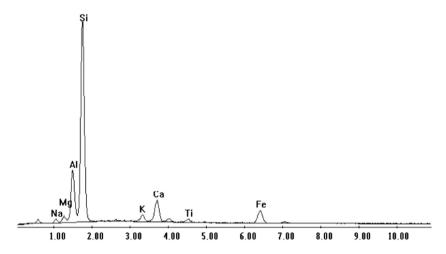


Figure 4: X-ray spectroscopy [45].

Table 2: Chemical composition of VA

Reference	[45]	[43]	[51]	[40]	[52]
SiO <sub>2</sub>	57.76	59.5	21.4	38.89	62.30
$Al_2O_3$	14.56	17.5	5.7	13.0	7.60
Fe <sub>2</sub> O <sub>3</sub>	11.0	7.1	3.5	12.41	4.20
MgO	2.44	2.6	2.1	6.16	_
CaO	8.27	6.1	64.1	9.09	62.30
Na <sub>2</sub> O	2.41	3.8	0.5	3.12	0.10
K <sub>2</sub> O	2.14	2.0	_	1.31	0.19

and fewer voids and porosity. Concrete becomes less permeable to water and soluble substances. As a result, water absorption or penetration of chemicals will be reduced, and this form of concrete will survive a longer lifespan. Figure 5 depicts the dry density of the various concrete series evaluated after 28 curing days. All the VA-containing series had somewhat greater densities than the reference concrete. Because of the VA's filler function, its particles fill the pores of the material, releasing trapped water and enhancing the density and compactness of the concrete. The materials utilized as cement substitutes, according to Silva et al. [53], have a restricted filler capacity. Once this limit is reached, the concrete density tends to decrease.

According to Memon et al. the addition of bentonite clay caused a decrease in density, and the higher the proportion of bentonite, the lesser the density. It can be attributed to the fact that density is related to specific gravity. Because ordinary Portland cement (OPC) has greater specific gravity than bentonite, the reference blend has a higher density than the bentonite combination [54]. Previously, the use of wood ash was related to a drop in density [55], and this decline occurs more severely at higher substitute concentrations. This drop is caused by ash's

lower specific gravity when linked to OPC [56]. According to Ibrahim, the presence of SF and FA in concrete does not considerably influence the density while the glass powder has a reducing reason for the density [57]. The author studied the impact of bagasse ash substitution for cement in concrete construction ranging from 10 to 50%. The results reveal that as the bagasse ash replacement percentages increased, the concrete became more porous, as demonstrated by a drop in density and increased water absorption [58]. The specific gravity of VA is 1.98 [48], which is less than the specific gravity of cement. The replacement of low specific gravity material (VA) with high specific gravity material results in a lower overall density of composites.

#### 3.2 Porosity

Concrete is a porous material that has air/water permeability features, which have a significant impact on not

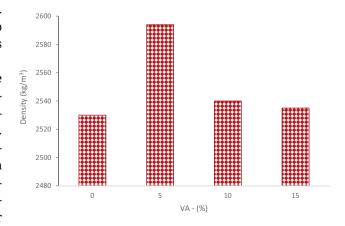


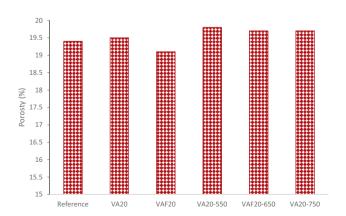
Figure 5: Density of concrete made with VA [45].

just strength but also durability. Typically, degrading chemicals that might cause steel corrosion, such as chloride ions and carbon dioxide, infiltrate concrete through pores or their connection [59]. According to one research, extremely comparable patterns in water absorption and apparent porosity were identified across all mortars, as illustrated in Figure 6. For example, 20% VA porosity values increased somewhat when linked to the blank blend; however, 20% ultra-fine VA porosity values decreased when linked to both the blank blend and 20% VA. It is because of the smaller particle sizes, which would result in superior packing and filling abilities as well as increased pozzolanic activity. Once again, heat treatment had a detrimental influence on porosity in mortars containing heat-treated VA. The findings suggest that heated-treated VA mortars had greater values than untreated VA mortars or reference mix mortars. Poon et al. [60] discovered that replacing cement with FA enhances porosity while it decreases the average pore size in pastes aged 28 and 56 days. The addition of up to 5% SF to the cement did not appreciably modify the pore size distribution or permeability of either the blank blend or the FA blend. However, introducing FA and shale ash (SA) into the mortars had a considerable impact on interfacial porosity. Chindaprasirt et al. [61] also found that the fineness and replacement of FA had a substantial influence on the permeability and pore size of the blended cement paste. The usage of FA instead of Portland cement enhanced porosity.

#### 3.3 Water absorption

Water absorption is an important indicator of concrete durability. Water absorption reduction may significantly enhance the long-term concrete performance under harsh service situations [57]. Figure 7 depicts the addition of varying concentrations (0, 5, 10, 15, 20, and 25%) of VA to the mortar mixture. The absorption of mortar decreases with the addition of VA. This implies that the substitution of VA decreases the size of the paste hole due to the filler's action of VA, which seals the space. The chemical interaction between natural pozzolans (NPs) and CH in the hydrated paste utilizing lime leading to more CSH gel that increased the adhesive properties of the paste, causing a much denser structure and lower water absorption of concrete. Second, since the particle size of pozzolanic materials is lower than that of OPC, it may provide a more dense mass by packing cavities, resulting in less water absorption [62,63]. Ahmad et al. found that bentonite clay replacements lowered water absorption by up to 30% [64]. Also, clay has a higher Young's modulus, i.e., 200 GPa [65], which makes concrete more stiff. Furthermore, based on the study, cementitious materials lowered water absorption owing to micro packing, which enhanced concrete density, causing less water absorption. However, higher dosages of pozzolanic materials resulted in an increase in water absorption due to a shortage of workability, which enhanced compaction energy leading to permeable concrete, which finally increased water absorption [66].

According to the findings, mortars having up to 20% ash exhibited worse total permeability and water absorption at 3–7 days than the reference sample. This is because the geopolymer structure was enhanced due to a large number of reaction products [68]. The modified mortars have low porosity, which might indicate that the concrete is absorbing less water. Amorphous CSH gels may have packed the blend pores, resulting in a dense microstructure. As a consequence, the CSH concentrations are greater and the quantity of non-hydrated cement is smaller [69]. According to Du and Tan, raising the replacement amount of glass powder to 60% reduces the water absorption in





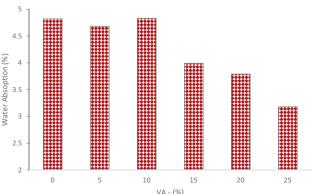


Figure 7: Water absorption [67].

concrete [70]. According to Jain et al., glass powder lowers the concrete porosity by up to 16.41%, which is less than the reference concrete [71].

#### 3.4 Shrinkage

Drying shrinkage is a critical feature of cementitious composites that affect their durability, shrinkage is caused by the loss of capillary water in the hardened cement mixture, which causes contraction and fracture development inside the concrete. Figure 8 depicts the fluctuation of shrinkage in concrete with various amounts of VA. Concrete shrinkage was somewhat greater as compared to the reference sample (0% VA). The shrinkage varied with the time of curing of concrete. Nevertheless, the pace of growth was faster in the first six weeks. The 12-week shrinkage with 5, 10, 15, and 20% VA was about 516, 508, 502, and 488 macro strains, correspondingly, compared to approximately 471 macro strains in normal concrete. Even though the shrinkage of 5 and 10% VA was more than that of 15 and 20% VA, the total shrinkage in concrete was greater than that of conventional concrete (0% VA) during 12 weeks of curing. For any mix, the greatest shrinkage did not more than 600 macro strains. Gopalan and Haque [72] discovered similar results in FA concrete. However, Samarin and Ryan [73] demonstrated that when assessed to control OPC concrete, excellent-grade Australian FAs usually result in less shrinkage. A researcher performs shrinkage tests on concrete mixes with VA substituting 0-25%. The results show that the shrinking of 10 and 15% of VA mortars was greater than that of 20 and 25%. It implies that the presence of VA in cement reduces shrinkage [41]. The collective pozzolanic reaction and mineral additive micro filler increased the binding characteristics and density, resulting in less dry shrinkage of concrete [63]. According to Bheel et al., reducing the cement concentration in pastes reduces the shrinkage of the mortar [74]. Furthermore, the study discovered that the pozzolan reduced the heat of hydration, avoiding speedy evaporation of moisture from the concrete surface and reducing the creation of shrinkage fractures [1]. According to Wang et al. cement containing 8% SF has outstanding properties such as strong early strength, low hydration heat, and low shrinkage [75].

According to Ghafari et al. when used as an SF substitute, ground granulated blast furnace slag may minimize autogenous shrinkage because of its bigger grain size when compared to SF, resulting in larger pore size and hence lower capillary action [76]. However, when utilized instead of cement, the smaller grain size of the slag has been demonstrated to promote shrinkage [77]. According to Termkhajornkit et al., non-hydrated FA may inhibit autogenous shrinkage by serving as a constraint [78]. In contrast, Tazawa and Miryazawa [79] discovered that extremely fine FA may cause plastic shrinkage cracking through both pore size reduction and pozzolanic reaction. Given that pozzolanic materials may affect the competing process of capillary action and stiffness, more work is needed to understand the effect of pozzolanic materials at a variety of binder (cement and SF) replacement ratios.

#### 3.5 Rapid chloride penetration (RCP)

Infiltration of chloride may cause reinforced concrete structures to degrade. As a consequence, chloride penetration is

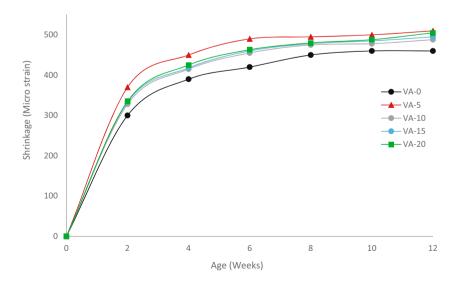


Figure 8: Fluctuation of shrinkage in concrete with various amounts of VA [46].

an important component in determining how long the concrete will endure. The important condition for the long-term durability of structures prone to reinforcing corrosion is the capacity to maintain the permeability as low as possible. The chloride penetration of reference blends containing 0% VA was minimal, ranging between 1,100 and 1,405 C as shown in Figure 9. It shows that VA might increase concrete penetrability by changing big holes into tiny pores and minimizing microcracking in the transition region. When pozzolanic VA was added to regular Portland cement concretes, there was a considerable decline in the permeability and average pore diameter. This impact was connected to the refinement of VAC pore architecture as the amount of VA increased [80]. As concrete ages increased, the pozzolanic interaction between VA and CH occurs at a slow rate, resulting in dense concrete. The decrease in porosity with age offers the advantage of increasing long-term corrosion protection [81]. Concrete containing a 20% replacement of stone dust exhibited less RCP than the blank blend, according to study. Because stone dust particles are rougher than sand particles, they fill the gaps among ingredients. There are fewer holes in concrete, its density increases, and the voids are filled with stone dust [82].

According to Çelik et al. increasing the percentages of FA and SF in concrete mixes reduced the fast chloride permeability and water absorption values of concrete in 180 days. At 180 days, concrete mixes made with FA had extremely poor chloride penetration resistance. At 180 days, the concrete with 45% FA had the lowest chloride permeability resistance (345 C) [83]. According to Tomoyose et al., using VA at a replacement ratio of 20% offers enough

resistance to chloride ion penetration while also being successful in lowering the quantity of Portland cement used [47]. According to Sahoo et al., the quantity of charge delivered steadily decreases as the SF or rice husk ash percentage increases. In addition, when the curing age increases, the ion penetrability decreases. It can be because the mix becomes denser as the curing time increases. Furthermore, the pozzolanic interaction results in the production of the CSH gel, which increases the durability of the concrete [84].

#### 3.6 Carbonation depth

Carbonation is one of the extremely significant challenges affecting reinforced concrete's long-term durability [85]. Pozzolan may be utilized in concrete to improve sustainability and lower the carbon footprint of the concrete industry. However, certain unfavorable misconceptions concerning their carbonation challenges are impeding their widespread use [86]. Lowering the water to cement (w/c)from 0.65 to 0.52 caused a considerable drop in the carbonation depth while expanding the number of pozzolanas in the blend led to increases in the carbonation depth. As shown in Figure 10, employing up to 10% NP, either VA or SA, does not influence the carbonation of the blends. Nevertheless, raising the cementitious material concentration over this limit (10%) caused a substantial rise in the carbonation intensity. The depth of carbonation reported when using NP was greater than when using SA at the same alternative concentration (30%) of plain concrete by the cementitious

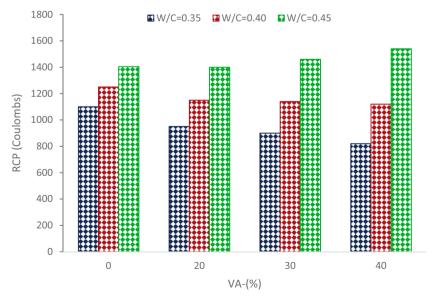


Figure 9: Rapid chloride ion penetration [43].

material and for both *w/c* proportions. SA appears to be a supplementary reactive particle to VA. The system may produce more hydrate products (CSH) because of the SA's relative responsiveness and grain size, which serves to fill the open pores, polish the larger capillary pores, and disconnect the pore network.

Furthermore, the powder's filling capacity may diminish CO<sub>2</sub> permeability and penetration. According to Ahmad et al., although the addition of SF increased the carbonation intensity, it was far less than the cover width generally given over reinforcing steel, ruling out the potential of corrosion [87]. Generally, the use of cementitious materials such as VA and SA might substantially enhance the pore structure and particle packing by filling the spaces among the ingredients; being reactive materials, they reduce chloride transport and other hazardous substance infiltration. Nonetheless, penetrability to chloride ions is inextricably connected to the blend design specifications and matrix microstructure, particularly the microporous network properties. The greater the penetrability and chloride dispersion quantity, the greater the volume of coarser and linked pores.

#### 3.7 Resistance to sulfate

Naseer et al. [88] studied two Pakistani VAs, VA1 (calcined) and VA2 (as is), which were mixed into mortar. The comparative loss of compressive capacity detected when cement samples containing VA were submerged in 2 and 5% sodium sulfate mixtures for up to 28 days was used to assess the sample resistance to sulfate attack. To guarantee that the sample obtained adequate strength before being attacked by sulfates, they were treated in potable water for 7 days earlier to immersion in the sulfate solution. Every week, the solution was changed to maintain a consistent concentration. The results show that the compressive capacity loss was larger in the 5% sodium sulfate solution than in the 2% sulfate medium. In the presence of 2% sulfate, there was a small or no sulfate attack on the cement sample including VA. Because of their excellent sulfate resistance, these mortars might be utilized in places where a sulfate attack is likely. The partial substitution of cement with FA is known to be useful in increasing the resistance to sulfate damage [89].

Lv et al. investigated the function of extra cementitious materials such as FA, slag (granulated blast furnace slag [GBFS]), and SF in cement mortar's long-term resistance to external sulfate attack (ESA) at room temperature. For 36 months, the cement sample was submerged in a 5% sodium sulfate solution at 20°C. According to the findings, the

number of degradation products and pore features were the two most important elements influencing sulfate resistance. The pore properties were more influential on longterm sulfate resistance than the number of degradation effects. After 36 months of ESA exposure, FA retained remarkable sulfate resistance. SF was more sulfate resistant than FA because it favored overall permeability and the fraction of non-toxic pores over portlandite elimination through the pozzolanic interaction. The substitution of GBFS, on the other hand, exacerbated the degradation process and resulted in the poorest sulfate opposition since the overall permeability and proportion of harmless pores changed dramatically [90]. The research concluded that the inclusion of 20% NP improved the sulfate resistance, with the strength loss decreasing by 62% owing to the substitution of cement with 20% NP. In addition, when 5% SF was added to the concrete blends, the strength drop was decreased by 94% [87].

### 4 Microstructure analysis

#### 4.1 Heat of hydration

The influence of VA concentration on the hydration process was evaluated using an isothermal calorimeter, and the thermal curve produced for several mixtures is demonstrated in Figure 11. The thermal curve depicts the many phases of hydration, including the beginning hydration phase, the inactive phase, and the primary hydration peak, as well as expedited aluminate hydration. According to the heat of the hydration curve, the heat development is greatest after 9 h for all blends. A quantitative investigation was performed to determine the heat of hydration of various mixtures. The overall heat of hydration (in kJ/kg) was 50.60, 47.55, 45.48, 39.00, and 34.96 for reference, 10% VA mix, 20% VA mix, 30% VA mix, and 40% VA mix respectively. These findings demonstrated that as the proportion of VA increased, the total heat of hydration dropped, suggesting significant retardation in hydration owing to the substitution of VA, which is supported by the presented data [91]. This feature might be employed in mass concreting to prevent cracking in concrete by lowering the heat of hydration. Figure 11 depicts the % decrease in the heat of hydration for various mixtures. It has been shown that replacing OPC with 40% VA reduces the heat of hydration by more than 30%.

According to Ukrainczyk et al. [92], the addition of ash causes a lag in the time required for the blend to set and a smaller reaction rate obtained at later times (11, 15, 16, and

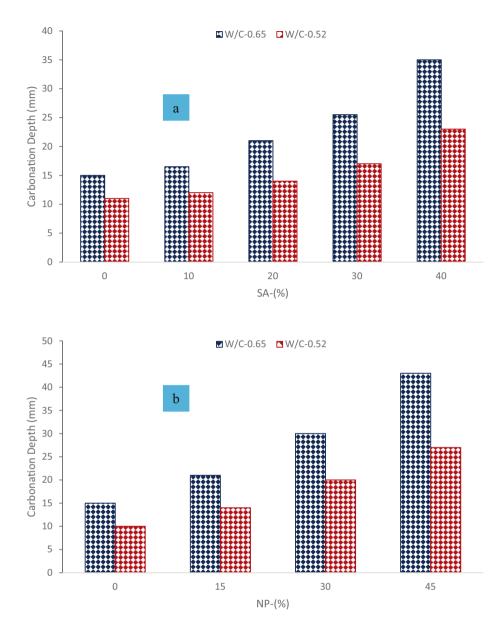


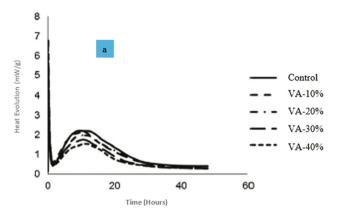
Figure 10: Influence of carbonation depth with (a) SA and (b) NP [39].

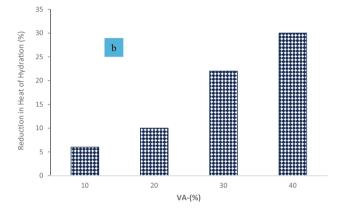
17 h), and a considerable interruption in cement hydration. Due to the slowing of the hydration processes, the final heat created after 45 h was lowered by -6, -13, and -25% of the reference blend with substitution of 10, 20, and 30% ash, respectively. The CaO and MgO hydration processes as well as larnite and aluminate periods are accountable for the significant hydration heat production found in ash hydration alone. According to Sonebi et al., mortars containing 6% metakaolin had higher microfractures and shrinkage. When materials with powerful pozzolanic capacity, such as metakaolin and SF, react with hydrated CH, the hydration rate rises, adding to the heat-releasing effect of the pozzolanic reactivity [93]. The higher hydration rate reduces concrete durability, particularly due to shrinkage

and the formation of microscopic cracks. According to Ambroise et al. [94], the greater temperature rises of metakaolin mixed samples associated with pure OPC-based samples are due to the faster influence of metakaolin on cement hydration.

#### 4.2 **SEM**

The SEM images of a concrete specimen including VA and recycled materials are shown in Figure 12. It shows the differences in behavior between old and modern cement hydration matrices. When advancing from ITZ to cement in the case of old cement paste, a permeable morphology





**Figure 11:** (a) Heat evaluation and (b) reduction in the heat of hydration [49].

was seen. However, a much heavier and smaller amount of porous morphology was noted in the fresh paste.

Figure 13a depicts the microstructure prepared with a 30% substitution of cement with VA (30%), and Figure 13b depicts the microstructure of a concrete specimen including RCA with cement (30%), VA (30%), and ground granulated blast-furnace slag (GGBS) (30%) as the binder. In SVA30,

VA particle were extensively scattered with no uniformly distributed cementitious blend. When linked to typical conventional concrete and SCC specimens, a weak and permeable interfacial transition zone (ITZ) was also observed. According to Rong et al., increasing the proportion of pozzolanic elements results in a denser mix, particularly in the ITZ. However, above 10% metakaolin inclusion leads to cracks (14% metakaolin replacement), which negatively affects concrete performance [96]. Similarly, the impact of the interlocking structure of the sand particle was reduced as the gaps in the calcareous sand were packed with calcium carbonate [97]. As a consequence of the pozzolanic activity and metakaolin filling cavities, the structure becomes denser, which improves mechanical and durability properties. A larger dosage of metakaolin, on the other hand, has negative consequences owing to an absence of fluidity, which generates additional cavities in blends. Homogeneous distribution of aggregates was observed with somewhat porous cement matrices in the case of a mix comprising 30% VA, GGBS, and RCA (Figure 13b). Denser ITZs were detected in comparison to loosely attached ITZs reported in another specimen with RCA. This may have enabled the GGBS-containing mortar to penetrate the holes to a particular depth, resulting in stronger connections [98]. The increase in strength properties of concrete specimens including VA and GGBS, as shown above, is consistent with the heavier microstructure of concrete in the ternary blend.

# 4.3 Fourier-transform infrared spectroscopy (FTIR)

Figure 14 depicts that spectroscopy lines are seen in identical locations but at varying intensities in all paste samples. This is mainly related to the development of the CSH

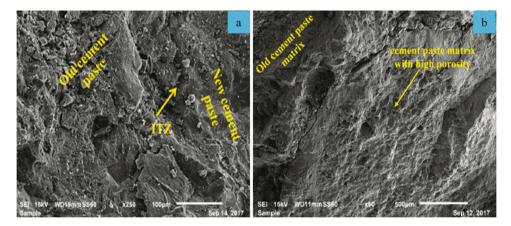


Figure 12: SEM images of the concrete specimen: (a) 0% VA + 30% RCA and (b) 30% VA + 30% RCA [95].

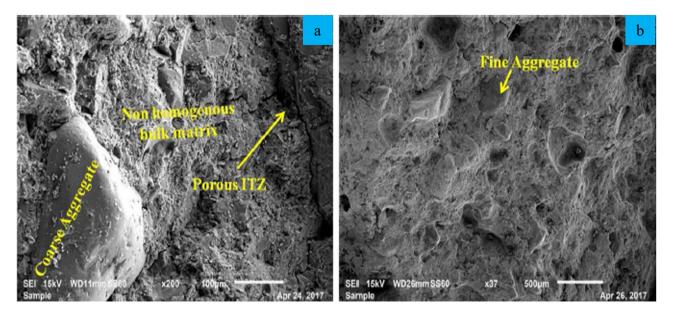


Figure 13: Microstructure of a concrete specimen: (a) 30% VA and (b) 30% VA + 30% RCA + GGBS [95].

and CH stages. Si-O connections in the CSH stage create peaks between 900 and 1,100 cm<sup>-1</sup> [99]. The FTIR spectra depict that the Si-O line in VAF has a higher relative intensity than the other binary mixtures and the blank blend. In VAF specimens, the Si-O line is strong and evolves to a superior wavelength (992 cm<sup>-1</sup>), suggesting considerable Si polymerization and, finally, the greatest number of high-density CSH gel. The creation of compact C-S-H stages produces densification of the micro and concentrate configuration, causing better strength. Furthermore, when compared to the blank blend, the VA blend demonstrated a little raise in the concentration of Si-O bands (984 cm<sup>-1</sup>), showing that VA has a lower pozzolanic reactivity than VAF. In heat-treated VA, the concentration of the Si-O band reduced, suggesting inadequate pozzolanic action,

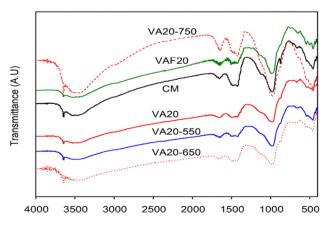


Figure 14: FTIR analysis [42].

which starts the growth of less compact CSH stages and, eventually, weakens required qualities.

Jiang et al. studied the thermogravimetry properties of the metakaolin-based paste after 28 days [100]. The study traces for metakaolin-CH paste as a function of temperature show four distinct zones of apparent mass damage, each with its distinct peak. The initial peak, which appears at 90°C, is caused by the desorption of CSH gel and stratlingite (C<sub>2</sub>ASH<sub>8</sub>) physiosorbed and interlayer water particles [101]. The next dehydrating peak at 165°C relates to the attaching of C<sub>2</sub>ASH<sub>8</sub>. The third peak at 215°C is due to lattice dihydroxylation and the cessation of C<sub>2</sub>ASH<sub>8</sub> [102]. The fourth peak at 670°C is initiated by calcium disintegration [103].

According to Hughes et al., the highest point at 3,645 cm<sup>-1</sup> reveals the presence of available OH classes, confirming the presence of portlandite [104]. In the control sample, the highest point at 3,645 cm<sup>-1</sup> is wider and more noticeable. This peak decreased for the binary mixtures, demonstrating pozzolanic activity of the VA through Ca(OH)2. The portlandite peak is relatively tiny for VA, notably in the VAF specimen, when linked to the other combined mix, which exhibits stronger reactivity of VA, causing the formation of a more refined microstructure and hence superior strength properties.

#### Cost benefits

Two Pakistani VA, namely VA1 (calcined) and VA2 (as is), were studied in detail as a partial alternative for conventional OPC in mortar cubes, concrete cylinders, and concrete beams. A cost study was performed for a two-room elementary school with a veranda [88]. Cement was largely replaced by pozzolan by weight in all forms of reinforced concrete, plain concrete, and mortar blend. It was discovered that replacing 40% VA lowered the OPC price by 30.4% and strength by 35%. For VA1, for example, the entire price of the school was reduced by 16.8%. Therefore, it is possible to infer that partial substitution of OPC with VA may cause a significant reduction in the cost provided the compressive capacity drop is bearable, i.e., no more than 17.2 MPa at 28 days for standard construction. The research was conducted on the economics of bacterial SF concrete [105]. The benefit/cost ratio of SF concrete decreased as the SF amount increased. In contrast to the reference blend, SF concrete with 10% SF displayed the greatest advantage in terms of improvement in properties and the highest benefit/ cost ratio. According to Panesar et al., using pozzolanic elements in concrete may increase concrete durability, lengthen service time, and cause fewer energy, releases, and costs linked with structural preservation and restoration throughout the structure's planned service life. Furthermore, even the greatest distance that FA can be delivered for concrete including FA provides ecological and financial advantages over concrete without the presence of FA [106]. It can be concluded that VA decreased the concrete cost considerably compared to other pozzolanic materials. However, it slightly decreased the concrete strength. Furthermore, there are no studies showing a detailed relationship between the cost and concrete strength with the substitution of VA.

#### 6 Conclusions

This review study provides a thorough examination of the durability and microstructure analysis characteristics of concrete utilizing VA. The following are the findings of the study:

- The shape of VA particles is angular and of rough surface texture, which causes a decrease in concrete flowability.
- The durability of concrete improved considerably with the replacement of cement with VA due to pozzolanic activity and micro fillings. The collective effect of the pozzolanic reaction and micro filling of VA increased the durability aspects of concrete. However, a higher dose of VA adversely affects durability due to the absence of flowability. Different researchers recommend distinct ideal dose changes on the source of VA. However, the typical optimum dose of VA ranges from 10 to 30%.
- The peaks of the heat of hydration declined with the replacement of cement with VA due to the pozzolanic reaction, which continues gradually.

- FTIR analysis showed the presence of a substantial quantity of dense CSH gel due to the pozzolanic reaction of VA producing a dense pore structure.
- The review also concludes that with substitution of VA as a binder in concrete declined the price of construction. Based on the analysis, a 10% substitution of VA instead of cement results in a decrease in the cost of construction by about 30%.

Although VA could be used in concrete either as a filler or binder, however, fewer researchers consider VA in their research to compared it with other with other materials such as FA, etc. Additionally, most researchers focus on strength properties while limited data are accessible on long-term durabilities such as acid resistance, creep, alkalisilica, and freeze—thaw effects. Consequently, this study proposes detailed analyses of durability (acid resistance, creep, alkali-silica, and freeze—thaw effects) with the substitution of VA. Additionally, some studies claimed that the performance of concrete decreased with VA. However, the particle size mainly affects the performance of concrete but researchers focus on it. The review also recommends a detailed study on VA with varying particle sizes as well as a detailed study on concrete's cost—benefit analysis with the substitution of VA.

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