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Review Article

Elucidating Chemo-Mechanical Synthesis and Microstructural Study on the Performance of Partial Cement-Based Concrete Composites Against Sulphate Attack – A Review

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Abstract

The well-known weakness of cement concrete against external/internal sulphate attack and an estimated 7-10% global greenhouse gas emission by the construction industry (mainly contributed by cement manufacturing and supply have encouraged researchers to elucidate the chemical synthesis taking place in the preparation and hydration of cement concrete along with the factors affecting the sustainability of hardened concrete. In this review study, an endeavour has been made to explore the use of Supplementary Cementitious Materials (SCMs) of different hydrocarbon compositions, including organic/ inorganic compounds like pozzolans derived from natural (zeolite/ metakaolin derived from kaolinite), agricultural (rice husk ash, corn cob ash) and industrial fields Pulverised Fly Ash (PFA), Silica Fume (SF) and a renowned cement replacement material, i.e., Ground Granulated Blast Furnace Slag (GGBS),). The partial replacement of 0-30% pozzolans with cement as a binder has been reviewed objectively to achieve economic/ environmental benefits by enhancing strength and durability against dangerous sulphate attacks. The chemo-mechanical synthesis involving SCMs has been explored to understand the formation of additional calcium silicate hydrate C-S-H gel by blending various pozzolans. The research elucidates an improvement in strength up to optimum ratios of 1-15% for different SCMs. However, the strength was observed to reduce beyond a certain % ratio of SCMs blending due to the formation of expansive alkaline silica hydroxide gel, which causes cracking and weak structure. The aviation industry is considered the top emitter of CO_2 (3% of total global emissions), however, the construction industry emits 7-10% of global greenhouse gases, which is nearly three times greater. Therefore, the supportive use of up to 90% SCMs can result in a significant reduction of CO_2 by the construction industry based on the type/ratio of blending SCMs. Microstructural studies using scanning electron microscopy SEM and X-ray Diffraction (XRD) have also been explored. These microstructural studies have further clarified the development of ettringite in concrete after sulphate attack and the beneficial use of pozzolans to a certain extent to prevent the formation/ propagation of ettringite-specific cracks in the micro/ nano-pores of concrete structures. In general, research has shown that the addition of SCMs in concrete results in an increase in strength and superior resistance to sulphate attack.

Keywords: Chemical synthesis; Sulphate attack; Pozzolans-based SCMs; Mechanical properties; Microstructural scanning

Introduction

Technological advancement has enabled engineers to produce masterpieces of construction in diverse geographical/ ecological locations by harnessing nature's power, enabling a comfortable human life but subjecting the environment and infrastructure to different chemical / pollution hazards [1]. The use of lime and natural volcanic pozzolans has been in use since ancient civilisations [2]. The invention of ordinary Portland cement in the 1860s suppresses the use of lime/ pozzolans due to its swift setting time and easy insitu handling [2,3]. Still, it resulted in up to 10% of global CO_2 emissions [4]. The cement concrete was found to be highly vulnerable to the ingress of sulphates and chlorides in marine environments [2-8].

Therefore, the researchers focussed on the formulation of greener alkali activators [9-13] as supplementary cementitious materials SCMs [14] to address cement concrete vulnerabilities [15,16]. The research suggests that using pozzolans in cement concrete as SCMs to specific ratios improves mechanical properties and prevents the ingress of moisture-containing harmful minerals/ chemicals by reducing porosity, permeability and creating defence layers against sulphate internal/ external attacks [8,17-20]. In this paper, a review study has been conducted to explore the beneficial performance of SCMs-based concrete composites under accelerated sulphate attacks.

Review of chemical synthesis in cement hydration and sulphate attack

The chemistry of cement hydration: R.H. Bogue identified the main four ingredients of cement hydration in 1960, which include alite (C_3S tricalcium silicate $3CaO.SiO_2$), belite (C_2A dicalcium silicate $2CaO.SiO_2$), celite (C_3A tricalcium aluminate $3CaO.Al_2O_3$) and felite (C_4AF tetracalcium alumina ferrite $4CaO.Al_2O_3.Fe_2O_3$) [10,21-24]. Alite starts the cement hydration process and is considered the major initial strength-imparting compound, followed by belite, which is considered to impart the latter strength of concrete by the formation of calcium silicate hydrate ($3CaO.2SiO_2.3H_2O$), also known as C-S-H gel (equations 1,2) [10,25,26].

$$2(3CaO.SiO_2)+6H_2O \rightarrow 3CaO.2SiO_2.3H_2O+3Ca(OH)_2+Heat$$

Equation 1

$$2(2CaO.SiO_2)+4H_2O \rightarrow 3CaO.2SiO_2.3H_2O+Ca(OH)_2+Heat$$

Equation 2

The third compound, "celite", contributes to the flash-setting property of cement and does not impart any significant strength to concrete. To prevent flash setting of cement, gypsum ($CaSO_4$) is added to cement, but it reacts with celite and produces hazardous long needle-like crystals of $3CaO.Al_2O_3.CaSO_4.32H_2O$, called ettringite which, is responsible for internal sulphate attack and cracking of hardened cement/ concrete paste, as shown in equation 3 [10,27-33].

$$3CaO.Al_2O_3+3CaSO_4+32H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O$$

Equation 3

However, when gypsum is fully depleted during the reaction, then celite starts to hydrate internally formed ettringite to convert it to a 2.5 times lighter sulphate deficient compound of monosulphate aluminate hydrate ($3CaO.Al_2O_3$. $3CaSO_4.12H_2O$) which cover the cement paste to stop flash setting and reformation of ettringite, thus making concrete a durable material internally as shown in equation 4 [10,29,33,34]. Due to monosulphate aluminate hydrate, the concrete will remain stable in a sulphate-deficient environment. Still, it will reconvert to ettringite-formation when exposed to sulphate-abundance in the form of ingress of sulphate-laden moisture from external sources, also known as external sulphate attack [10,34].

$$3CaO.Al_2O_3+3CaO.Al_2O_3.3CaSO_4.32H_2O\ +22H_2O \rightarrow 3(3CaO.Al_2O_3.3CaSO_4.12H_2O)$$

Equation 4

The fourth compound of cement felite or ferrite is mainly used as a filler material to decrease porosity in the hardened concrete by the formation of ferric aluminate hydrates, which is finally converted to a filler material called garnets (monosulphate ferric aluminium hydrates) as shown in equations 5 and 6 [25,29,33]. The final cement paste contains around 60% C-S-H gel, an estimated 20% ettringite, 15% $Ca(OH)_2$ and 5% voids/ entrapped air [10,29].

$$C_4AF\ +\ Gypsum\ +\ water \rightarrow\ Ettringite\ +\ Ferric\ aluminium\ hydrate\ +\ Lime$$

Equation 5

$$C_4AF\ +\ Ettringite\ +\ Lime\ +Water \rightarrow 3C_4A.F.CaSO_418H+\ Ferric\ aluminium\ hydrate$$

Equation6

The synthesis of external/ internal sulphate attacks: The formation of monosulphate aluminate hydrates prevents internal sulphate attacks and stops further crack propagation/ instability inside hardened concrete [10,35]. However, when hardened concrete is exposed to solutions containing sodium or magnesium sulphate (Na_2SO_4/ $MgSO_4$) through ingress from external resources [36], this monosulphate aluminium hydrate absorbs SO^-_4. It releases Ca^{++} in the exchange of cations/ anions to reconvert to long needles of ettringite and $CaSO_4$ (gypsum), brucite $Mg(OH)_2$ or NaOH based on the type of sulphate solutions [10,35,37]. The Na_2SO_4 results in expansion, and $MgSO_4$ reduces the strength of the concrete structure [10,37-39]. The cations Mg^{++}/ Na^+ and Ca^{++} exchange with anions SO^-_4 and OH^- exchange. The sulphate ion SO^-_4 from magnesium/ sodium sulphate transfers inwards to form gypsum $CaSO_4$, whereas the OH^- ion from $Ca(OH)_2$ exchanges outward to form brucite $Mg(OH)_2$ or NaOH (equation 7,8) [10,40-45].

$$Ca\left(OH\right)_2+MgSO_4+2H_2O \rightarrow CaSO_4.2H_2O+Mg\left(OH\right)_2$$

Equation 7

$$Ca\left(OH\right)_2+Na_2SO_4+2H_2O \rightarrow CaSO_4.2H_2O+2NaOH$$

Equation 8

The Mg++ exchanges with Ca++ of C-S-H gel and forms magnesium silicate hydrate gel which has no strength and converts the concrete into a 'mushy' material giving a big blow to lose its strength/ hardness (equation 9) [10,46].

$$3CaO.2SiO_2.3H_2O+3MgSO_4+2H_2O \rightarrow 3MgO.2SiO_2.3H_2O+3CaSO_42H$$

Equation 9

The researchers conducted a microstructural and qualitative analysis of OPC paste cubes of 20mmx20mm by placing them in water (reference readings) 0.03 mole/l (0.5% by weight) and 0.35 mole/l (5% by weight) Na_2SO_4 solution for up to 900 days. The cubes were examined for the assessment of surface deterioration and crack propagation on 90,180, 300, 600 and 900 days. The lightly concentrated 0.5% Na_2SO_4 inflicted slight cracking on edges after 180 days, and slight spalling of cubes was observed after 900 days. However, the cubes placed in 5% Na_2SO_4 solution started considerable cracking after 90 days on the edges, which were found to spread to the surface of the cubes after 180 days. The ingress of Na_2SO_4 solution into the inner body of cubes started after 300 days, and considerable peeling and spalling were observed in the cubes due to the formation of gypsum in the veins. After 600 days, significant spalling and peeling of the outer layer was observed due to expansion caused by the development of long ettringite needle crystals inside the outer and inner cores of cubes and the decalcification of C-S-H gel. After 900 days complete outer layer was found to be peeling, cubes started bulging due to expansion/spalling and loss in mass was observed, showing a significant impact of sulphate attack on cement paste cubes as shown in Figure 1; [41]. A reduction of 64% compressive strength (from 70MPa to 25MPa) and 3% mass loss were observed in 5% Na_2SO_4 after 900 days, as shown in Figures 2 & 3; [41].

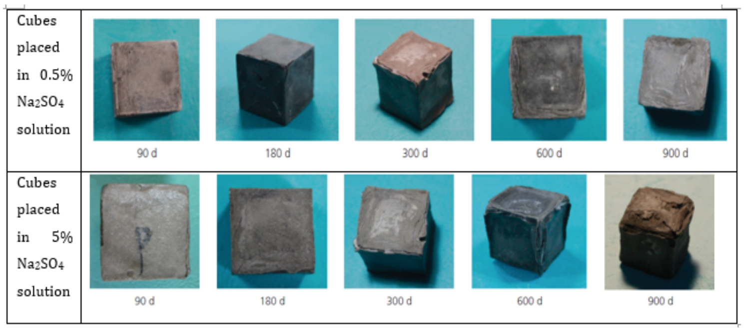


Figure 1: Qualitative Analysis of OPC cubes in 0.5% and 5% Na2SO4 solution after 900 days [41].

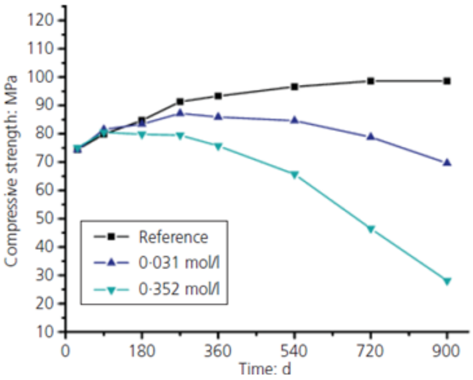


Figure 2: Reduction in compressive strength of OPC cubes in 0.5% and 5% Na2SO4 solution after 900 days [41].

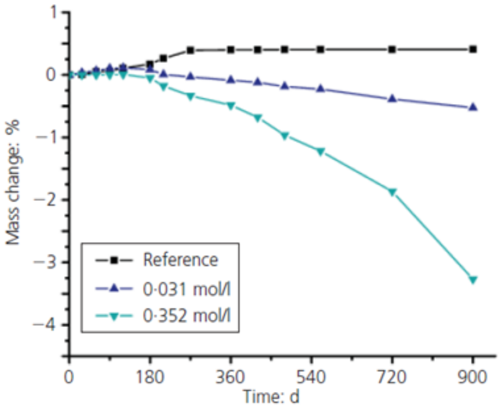
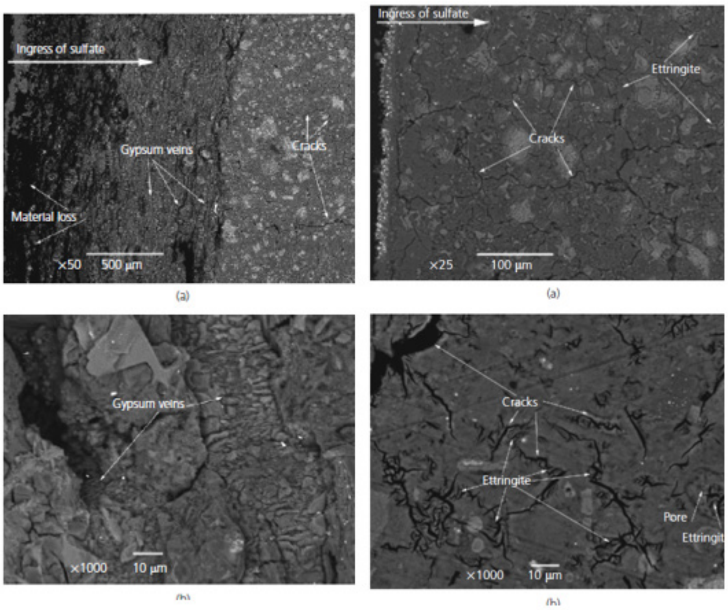


Figure 3: Reduction in the mass of OPC cubes in 0.5% and 5% Na2SO4 solution after 900 days [41].

A microstructural analysis was conducted on these cubes to assess the ingress of sulphate solution, propagation of cracks, development of gypsum and ettringite crystals in the cubes and peeling off surface/ loss of mass due to sulphate attack after 900 days. Scanning electron microscopy (SEM) was done after 600 and 900 days on the surface (Figure 4a) and 1mm under the surface (Figure 4b). The sulphate attack has been described as impacting the cubes in four stages. In the first stage, sulphate ions penetrate the surface, react with Ca^{++} and OH^- ions, and form monosulphate. In the second stage, decalcification of C-S-H gel starts and $CaSO_4$ is produced in the veins/cracks. In the third stage, cracks propagate, and gypsum is depleted by converting C-S-H gel into ettringite. In the fourth stage, the sulphate ions keep consuming the Ca^{++} from C-S-H gel and convert it into mushy Na-S-H gel having no strength and ultimately resulting in spalling, peeling, loss of mass and reduction in strength. The concentration of sulphate solution, permeability, period of exposure and cement composition influence the degree of sulphate attack/deterioration [10,41].



Microstructural Analysis of OPC cubes in 5% Na_2SO_4 solution after 600

Microstructural Analysis of OPC cubes in 5% Na_2SO_4 solution after 900 days

Figure 4: Microstructural Analysis of OPC cubes by SEM in 5% Na2SO4 solution after 600 and 900 days [41].

Use of pozzolans as partial SCMs in cement concrete for prevention of sulphate attack: The researchers have been experimentally devising different composites containing cement, lime and waste materials/derivatives from industrial/agricultural and natural resources having an abundance of metals oxides like silica, alumina, ferric oxide etc., making them a good pozzolan at par containing a total of 60% or more pozzolanic material. These materials have got an exhaustive list and generally include pozzolans/cement replacement materials like Ground Granulated Blast Furnace Slag (GGBS), Pulverised Fly Ash (PFA), Silica Fume (SF), Metakaolin (MK), Rice Husk Ash (RHA), Palm Ash (PA), Corn Cob Ash (CCA) and zeolite etc. The silica in these materials reacts with $Ca(OH)_2$ to produce an increased quantity of C-S-H gel, as shown in equation 10 [10,48]. However, an increased quantity of pozzolans results in excess production of alkaline silica hydroxide ($Si(OH)_4$), which remains in pores as an aqueous solution $Si(OH)_4$. It has got swelling properties which produce cracks and result in instead weakening of concrete [10,47-72].

$$2SiO_2 + 3Ca(OH)_2 \rightarrow 3CaO.2SiO_2.3H_2O \text{ Equation 10}$$

Results and Discussion of Different Case Studies/ Microstructural Analysis

Performance of established pozzolans/ cement replacements like GGBS, PFA, SF and MK as binary and ternary SCMs with OPC against sulphate attack

Contemporary research had shown an improvement in the sustainability of concrete when ternary concrete mixes were used in different sulphate solutions compared to binary cement concrete with different pozzolans [10,50,60]. The use of GGBS, PFA, SF and MK in cement concrete is already in practice due to its enhanced environmental benefits. Their use in cement concrete as a partial replacement being a good SCM is an established fact in the construction industry [10,62,65,66].

A detailed experimental study was conducted on the improved sulphate resistance of GGBS blended cement concrete. He blended 60% and 70% GGBS with 40% and 30% OPC along with 2% and 3% $CaSO_4$ and 3% $CaCO_3$ and immersed cubes and prisms in Na_2SO_4 and $MgSO_4$ solutions for six years to observe expansion and reduction in compressive strength. The tests were conducted after 3,7,28 days, and 1,2 and 6 years. The study revealed that 60% GGBS-cement composite with 3% lime and 3% $CaSO_4$ performed the best in all the testing regarding compressive strength and expansion parameters, as shown in Table 1; [70]. The consistent efficacy of GGBS-based cement composite exhibited beneficial impacts against external sulphate attack of concentrated Na_2SO_4 and $MgSO_4$. The presence of lime and $CaSO_4$ provided the Ca++ and SO3- - cations and anions in a chemical reaction which prevented annihilation/ de-calcination of C-S-H gel during the formation of ettringite and gypsum on external sulphate attack by concentrated sulphate solutions. The study shows a beneficial use of GGBS as SCM with lime and $CaSO_4$ for the long-term durability of concrete [70]. OPC cubes were almost wholly disintegrated after five years; 60% of GGBS cubes also impacted more in Na_2SO_4 than in $MgSO_4$. 70% GGBS composite performed the best in both solutions, especially with higher percentages of lime and $CaSO_4$, elucidating that the increased quantity of GGBS performs better in a sulphate environment [70]. The prisms were tested for durability (expansion) in Na_2SO_4 and $MgSO_4$ solutions. The prisms were prepared using composites of OPC with 60% and 70% GGBS with the addition of 2% and 3% $CaSO_4$ and 3% $CaCO_3$. Prisms were immersed in Na_2SO_4 solution for 1 and 3 years, whereas the duration of immersion was extended to 6 years in $MgSO_4$ solution. The promising results exhibited an increased quantity of GGBS up to 70% with higher quantities of $CaSO_4$ and $CaCO_3$ performed better by showing negligible expansion/ surface erosions, followed by 60% GGBS composites as the second-best performer in the sulphate environment. At the same time, control mix prisms comprising only OPC performed the worst by showing considerable surface wear and tear with up to 0.1% expansion in the first nine months of emersion in sulphate solutions. The results reassured that GGBS composites perform better in sulphate attacks by lesser production of ettringite and increased output of C-S-H gel during the hydration process due to pozzolanic reactions, as depicted in Table 1; [10,70].

Table 1: Compressive strength of GGBS composites in water and sulphate solutions [70].

	3-day	7-day	28-day	1-year	2-year	6-year	1-year	2-year	6-year	1-year	2-year	6-year
Portland cement	34	41	53	66	68	69	97	87	0	85	74	28
60% ggbs	17	31	48	65	69	73	106	97	62	95	75	18
70% ggbs	13	28	49	63	66	71	105	89	90	94	77	28
60% ggbs + LS	15	28	45	67	69	76	99	97	84	96	83	41
60% ggbs 2% SO3	19	29	47	68	67	72	97	99	33	94	81	19
60% ggbs 3% SO3	18	32	50	62	69	75	102	99	80	94	88	50

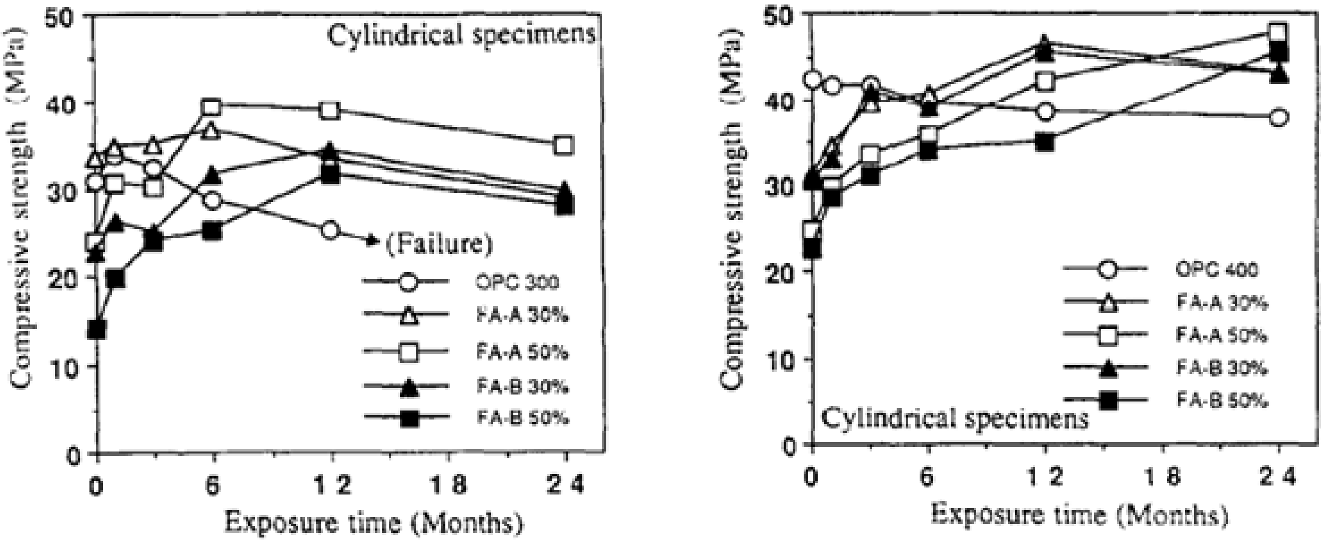


Figure 5: Compressive strength of low/high PFA-based concrete [10,71].

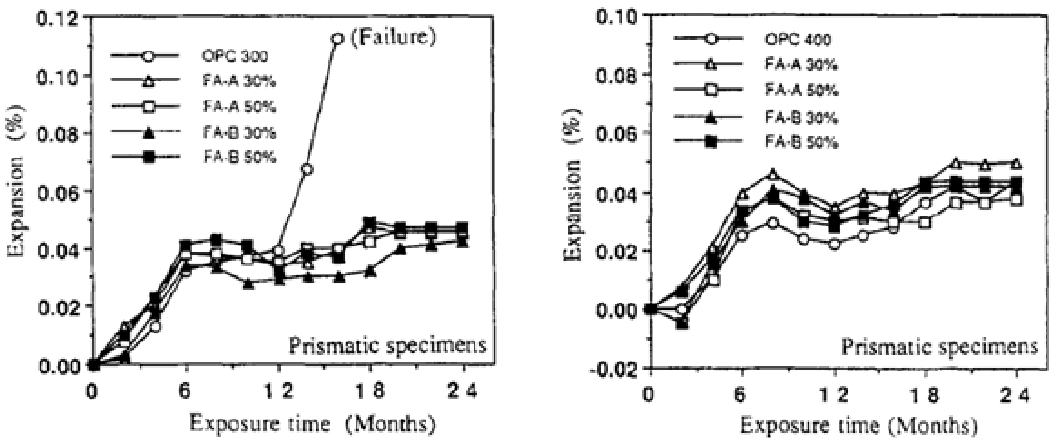


Figure 6: Expansion of low/high PFA-based concrete samples in Na2SO4 solution [10,71].

A sustainability study was conducted on low/ high 30% and 40% PFA composites with 300Kg/m^3 and 400kg/m^3 OPC in 5% Na_2SO_4 solution for 24 months. The study observed that 30% low fly ash with 400kg/m^3 OPC performed better in all compressive strength and expansion testing on cylinders/ prisms, followed by the performance of 30% high PFA with 300kg/m^3. OPC concrete performed the worst and was significantly damaged after ten months of immersion. The pozzolanic reaction of PFA to absorb excessive portlandite and to convert it into C-S-H gel resulted in better performance of PFA composites in the lesser formation of ettringite, whereas a high dosage of PFA resulted in the excess formation of $Si(OH)_4$ which exhibits swelling characteristics resulting into expansion/ cracking/ propagation of sulphate attack. Therefore, it can be elucidated that up to 30% PFA with OPC can provide better durability in the sulphate environment, as shown in Figures 5 & 6; [10,71].

The study of the impact of sulphate attack on binary concrete and ternary concrete using PFA, GGBS, and PFA/GGBS mixes as SCMs with OPC in 5% sodium sulphate, 5% magnesium sulphate and 2.5% sodium/ 2.5% magnesium sulphate solution for 270 days immersion, observed that ternary concrete mixes with up to 30% PFA+GGBS exhibited good performance as compared to individual/ binary composites of OPC with PFA and GGBS [48]. The maximum compressive strength was demonstrated with 5% PFA and 15 % GGBS binary blends, and 3.75% PFA+3.75% GGBS ternary blend. However, the complete replacement of 30 % SCMs also gave some advantages, e.g., good resistance against sulphate attack, less permeability and water absorption compared to the control mix. Still, the disadvantage is a reduction in compressive strength. Visual observations showed the worst degradation with 30% PFA followed by 30% GGBS, whereas the ternary blend of 30% PFA/GGBS showed minimum degradation. The maximum degradation was infused with a mixed solution of 2.5% sodium/ 2.5% magnesium sulphate, followed by 5% magnesium sulphate and 5% sodium sulphate. The sulphate attack by sodium sulphate is characterised by elongation, whereas loss of strength is pronounced more in $MgSO_4$ and Na_2SO_4+$MgSO_4$ [61]. The binary PFA and GGBS mixes with maximum compressive strength exhibited the lowest elongation, whereas the ternary blend showed maximum extension. However, the ternary mixture exhibited higher performance against sulphate attack in 5% magnesium sulphate and 2.5% sodium and 2.5% magnesium sulphate solution (Figure 7). The reduced elongation in SCMs mixes is due to the pozzolans' pore-filling capability, which prevents the formation of secondary ettringite and deep propagation of cracks/ expansion. Mixing SCMs up to 30% reduced alite and celite, resulting in reduced production of portlandite, ettringite and monosulphate aluminates with SO_3, thus reducing the vulnerability of concrete composites against sulphate attacks [48,62].

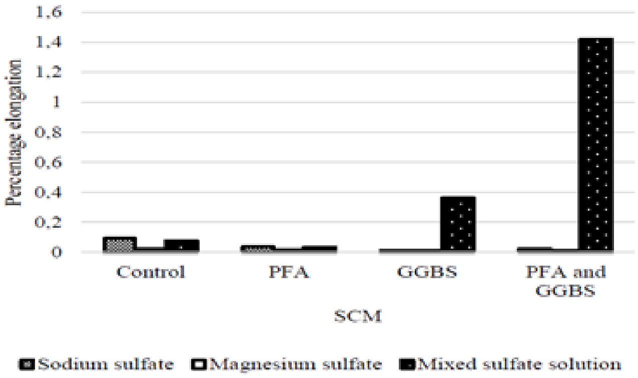
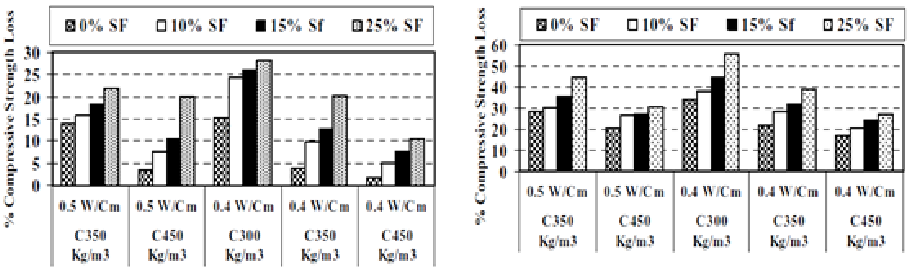


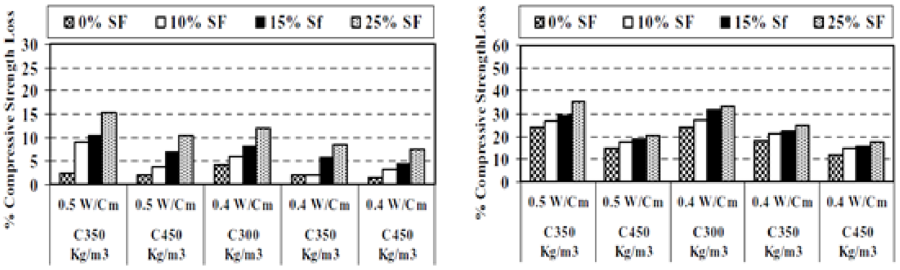
Figure 7: Percentage elongation of mixes with max replacement @ 30% PFA, 30% GGBS and 30% PFA+GGBS [48].

An experimental study on the impact of blending silica fume with cement concrete to improve sulphate resistance, elucidated the use of 0 % (control mix), 10%, 15% and 25% SF with class I and class V cement (350kg/m^3 and 450kg/m^3) with 0.4 and 0.5w/c ratios. It was elucidated that 10% SF used with OPC 450kg/m^3 and 0.4w/c ratios exhibited the best performance when subjected to a concentrated sulphate attack of 5% $MgSO_4$ for 224 and 700 days, as shown in Figure 8; [69]. The research on existing literature supports the use of pozzolans in cement concrete and geopolymer concrete for enhancement of mechanical properties and resistance of composites against sulphate attack due to absorption of portlandite, production of more C-S-H gel and filling of voids to prevent the propagation of cracks and formation of ettringite as discussed in the section above.



2-a Compressive strength after 224 days, Type I Cement

2-b Compressive strength after 700 days, Type I cement



2-c Compressive strength after 224 days, Type V Cement

2-dCompressive strength after 700 days, Type V Cement

Figure 8: Compressive strength loss after sulphate attack of 224 and 700 days [69].

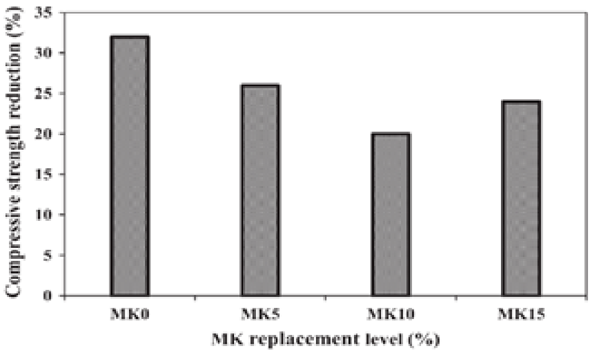


Figure 9: Reduction in compressive strength after 15 weeks of immersion in 5% MgSO4 solution [51].

Metakaolin (MK) can be used as a pozzolan in partial cement replacement to develop a concrete composite. The researchers observed that an optimum value of 10% MK in OPC exhibited higher resistance against sulphate and chloride attacks [51]. Use of 10-15% MK exhibited up to 15% reduction in emission of CO_2 [59], and 5% use of MK improved compressive strength by 10%. The compressive strength was reduced with increased use of metakaolin up to 10% and 15% MK; water absorption was observed maximum in the control mix with 0% MK and minimum in MK10%. The durability testing after 15 weeks of immersion in 5% $MgSO_4$ solution exhibited a maximum reduction in compressive strength in control samples (MK 0%), whereas 10% MK performed the best with minimum reduction in strength and minimum water absorption in sulphate solution (Figure 9 & 10); [51]. The microstructural investigation using SEM (Figure 8) supported the findings by showing improvement in the pore structure due to pozzolanic filler capability and reduction in the formation of ettringite, thaumasite, gypsum and brucite (resultant products due to sulphate attack) in MK10% mix as compared to MK 0% [51].

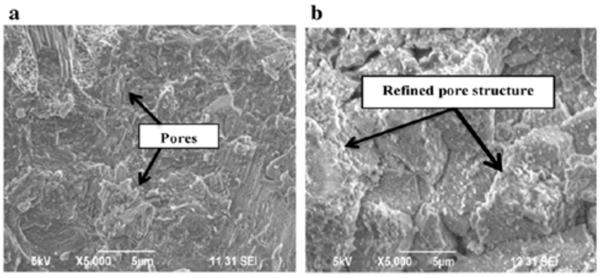


Figure 10: SEM images showing improvement in pore structure due to MK10% (b) filler capability [51].

Applications of agriculture-based pozzolans like RHA and CCA

A study on the use of rice husk ash (RHA) as an agricultural pozzolanic material, elucidated the blending of 0-20% RHA with OPC as SCM and observed an increase of 25-36% in compressive strength and split tensile strength with 15% RHA at 7, 28 and 56 days of curing (Figure 11); [49]. RHA was found to be a feasible alternative pozzolan and filled the pores befittingly to reduce permeability. The rapid chloride permeability tests were performed and exhibited that RHA reduces porosity, thus exhibiting reduced chloride permeability [85]. The increase in strength was attributed to more formation of C-S-H gel due to pozzolanic reaction in cement concrete composites [49]. The microstructural analysis of RHA mixes by SEM was carried out and explained the formation of dense C-S-H gel and improvement in the void filling, with the use of up to 15% RHA in concrete composites; however, due to the formation of $Si(OH)_4$ (because of excess SiO_2 and its hydration with portlandite in aqueous solution in pozzolanic material). C-S-H gel was observed to reduce/thin out beyond 15% use of RHA, as is evident by lower strength and decreased permeability observed with 20% use of RHA (Figure 12); [49].

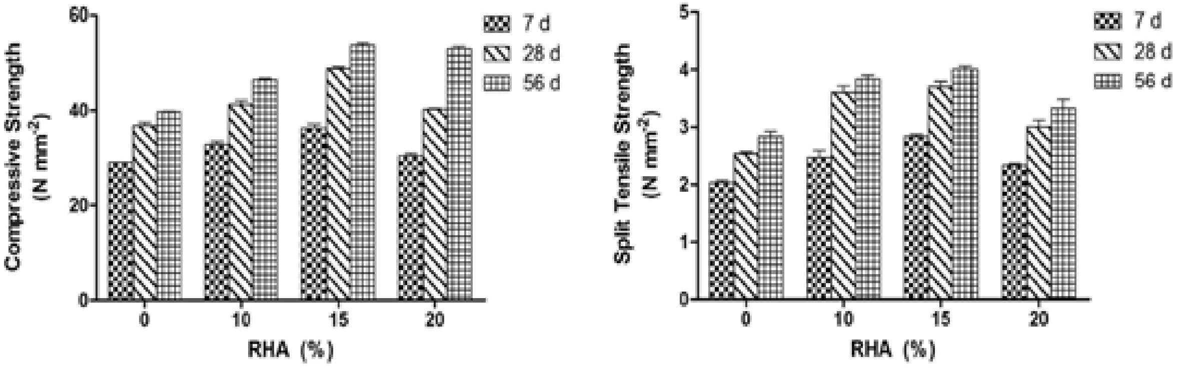


Figure 11: Compressive/ split tensile strength of 0-20% RHA [49].

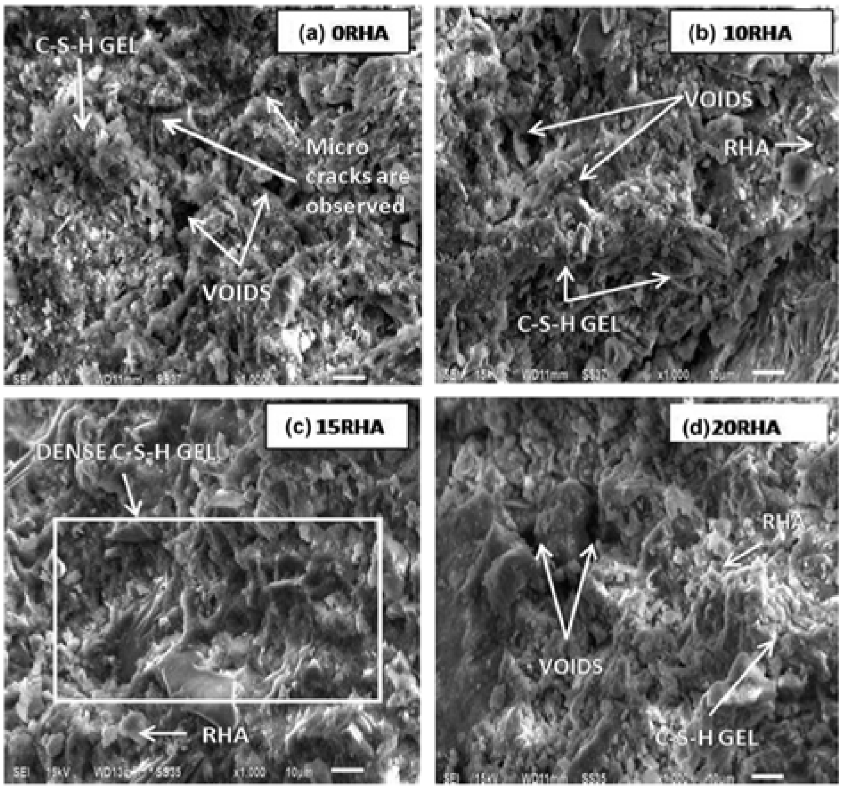


Figure 12: Microstructural analysis of RHA mixes by SEM (a) 0% RHA, (b) 10% RHA, (c) 15% RHA, (d) 20% RHA. Thedensest formation of C-S-H gel was observed with 15% RHA (c) [49].

The researchers used Corn Cob Ash (CCA) as SCM in cement concrete using 0-30% replacement and suggested 7.5% as an optimum value for better compressive strength (Table 2); [50]. The cubes from the control mix (0% CCA) and 7.5% were immersed in 5% NA_2SO_4, 5% $MgSO_4$ and 2.5%Na_2SO_4+2.5%$MgSO_4$ solutions for 270 days. It was observed that the use of CCA exhibited good performance versus the control mix against all sulphate attacks in all three solutions because of the pozzolanic reaction of CCA in concrete hydration by reacting with excess $Ca(OH)_{2,}$ and forming more C-S-H gel, reduction of secondary ettringite and behaving as filler material to reduce the porosity of CCA blended concrete composite [50]. The 7.5% CCA blended mix exhibited reduced elongation in 5% NA_2SO_4 and 2.5% Na_2SO_4+2.5% $MgSO_4$ solutions compared to the control mix. However, the control mix performed better in the $MgSO_4$ solution than the 7.5% CCA mix. It exhibited lesser elongation because the control has more compressive strength than CCA mixes [50]. The strength deterioration factors were calculated for these samples using the formulae SDF = ((fcw' – fcs')/fcw') x 100 (where fcw' is the compressive strength of control specimen cubes and fcs' is the compressive strength of sulphate immersed specimen cubes.). The control was observed to be the least impacted by sodium sulphate due to its higher compressive strength, but 7.5% CCA blended composite performed better in 5% $MgSO_4$ and 2.5% Na_2SO_4+2.5% $MgSO_{4,}$ concluding that the use of CCA up to 7.5% is a feasible option against sulphate attacks as shown in Figure 13; [50].

Table 2: Compressive strength of 0, 5, 7.5, 10, 15, 20, 25, and 30% CCA blended cement composites [50].

Curing Age (days)	Compressive strength at percentage replacement (N/mm^2)							
	Control	5%	7.50%	10%	15%	20%	25%	30%
7	56.2	42.0	42.3	32.1	28.1	19.2	16.2	15.3
28	61.6	49.0	51.3	37.9	34.3	23.5	18.9	19.3
56	67.6	51.8	54.4	43.1	38.3	25.9	23.0	22.0
91	71.3	55.9	63.5	47.8	41.5	29.8	24.0	23.5

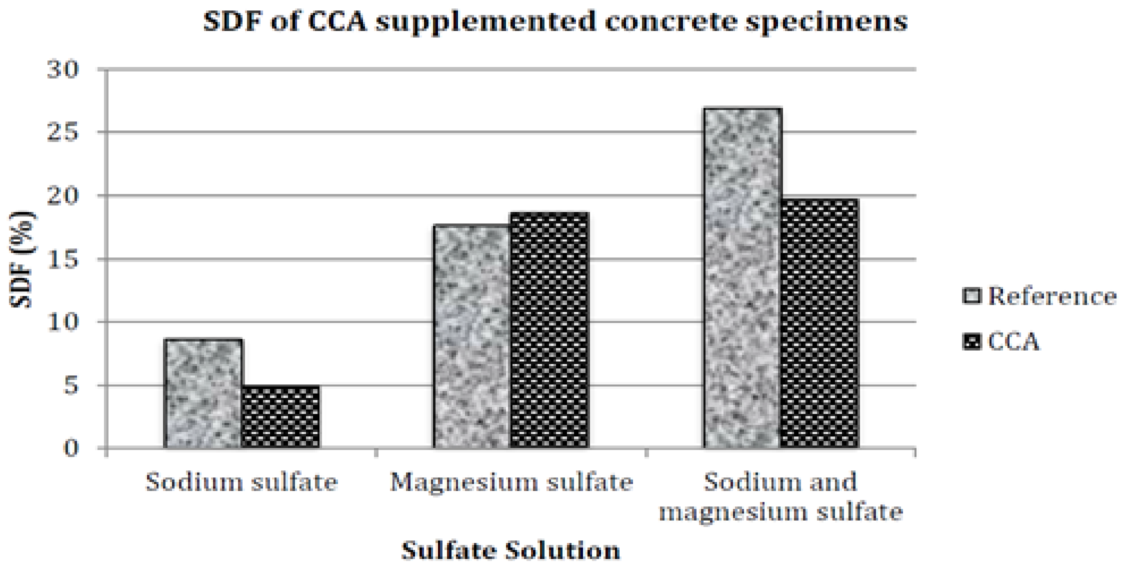


Figure 13: SDF of 0% and 7.5% CCA blended cement composites immersed in 5% Na_2SO_4, 5% MgSO4 and 2.5% Na_2SO_4+2.5% $MgSO_4$ solutions after nine months [50].

Use of natural pozzolan like zeolite

Zeolite is used effectively in the cement industry to reduce CO_2 gas emissions in developed countries. Zeolite is found naturally in volcanic and sedimentary rocks and contains hydrated aluminosilicates of alkali/ alkaline metal cations [63]. These cations react swiftly with portlandite to form dense C-S-H gel. The three-dimensional molecular structure of zeolite makes it a suitable filler to decrease porosity and create a defence against sulphate/chloride attack [52]. The researchers conducted an experimental study on the durability properties of concrete containing 0, 15% and 30% zeolites as SCM with OPC. The use of zeolite exhibited improvement in concrete's mechanical and micro-structural properties. Although the compressive strength remained lower than the control mix, later curing ages showed a reduced gap in strength achievement due to a slow pozzolanic reaction [52]. The water absorption, porosity, dry shrinkage and corrosion rate were improved using the increased quantity of zeolite [52]. However, enhanced resistance against sulphate attack was observed with increased zeolite use versus the control mix (Figure 14 & 15); [52]. Using up to 30% of zeolite can decrease CO_2 emissions by 30% while giving compatible structural outputs at par with OPC. However, a 15% replacement ratio produces the optimum blended composite [52]. Considering its environmental benefits and the improvements in mechanical properties of the zeolite-cement composite, it can be recommended as a suitable pozzolanic SCM [52].

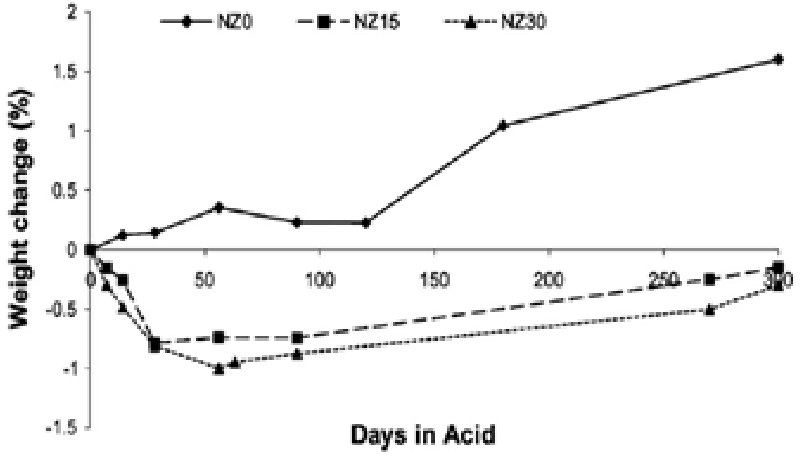


Figure 14: Weight changes in 0%, 15%, and 30% zeolite mixes after immersion in H_2SO_4 for 300 days [52].

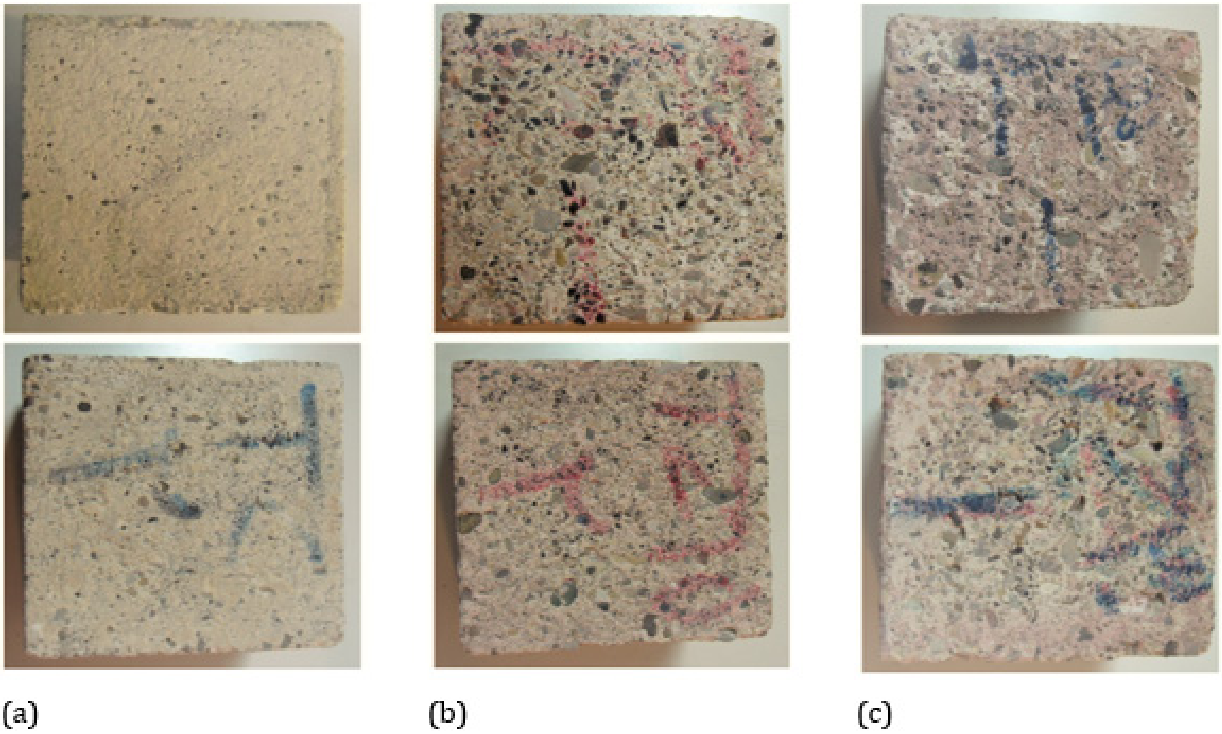


Figure 15: Comparison of surface degradation in 0% (a), 15% (b), and 30% (c) zeolite mixes [52].

Application of SF, PFA and GGBS in geopolymer-based concrete for better sulphate resistance

The use of SF, PFA and GGBS in manufacturing geopolymer-based concrete is already in practice due to their enhanced environmental benefits. Their use as total cement replacement to produce geopolymer concrete is explained in Figure 16; [67], where industrial/ agricultural/ natural pozzolans are mixed with an alkali activator with normal sand and aggregates to produce geopolymer concrete [67].

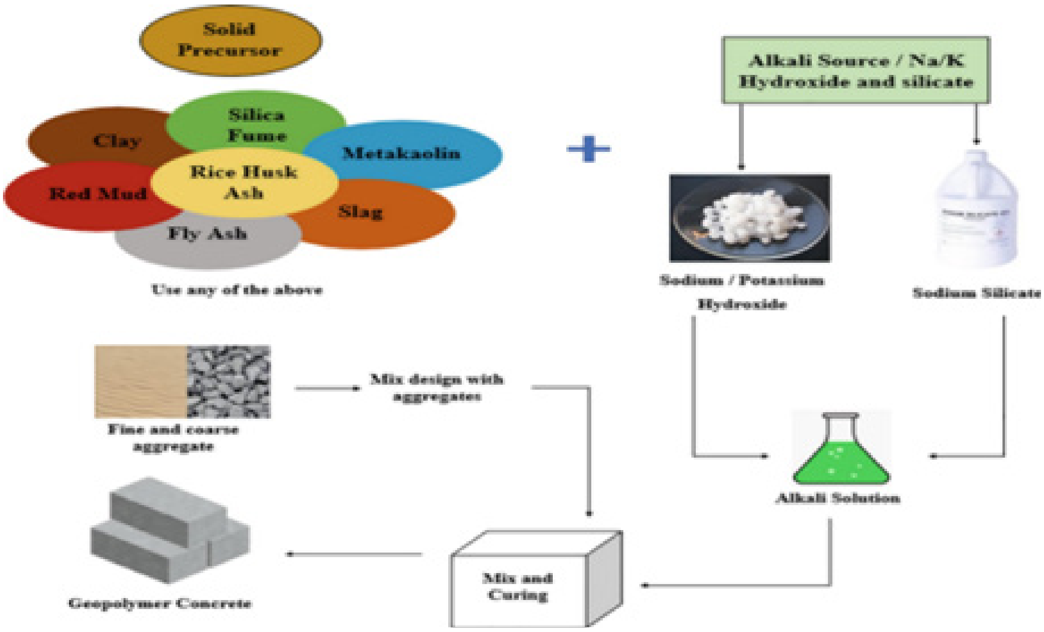


Figure 16: Manufacturing process of geopolymer concrete [67].

A study was conducted on geopolymer concrete containing 100% PFA, 50% PFA+50% GGBS and 100% GGBS. The research found that 100% GGBS geopolymer concrete performed at par with OPC concrete. The study exhibited 57.6MPa compressive strength on 28 days, followed by 50% PFA+50% GGBS composite achieving 52.5MPa strength, and 100% PFA geopolymer provided the least compressive strength of 11 MPA as shown in Figure 17; [68]. The sulphate resistance studies were conducted by immersing geopolymer concrete cubes in 3% H_2SO_4 for 28 days. The maximum loss in weight and compressive strength post-acid attack was observed in 100% PFA composite by 5.6% and 33.6%, respectively. Whereas 100% GGBS geopolymer composite performed the best with the least weight and compressive strength reduction by 1.5% and 11%, respectively, as shown in Table 3. The GGBS-based geopolymers exhibited a par performance with OPC concrete because GGBS is considered a suitable/complete cement replacement [68].

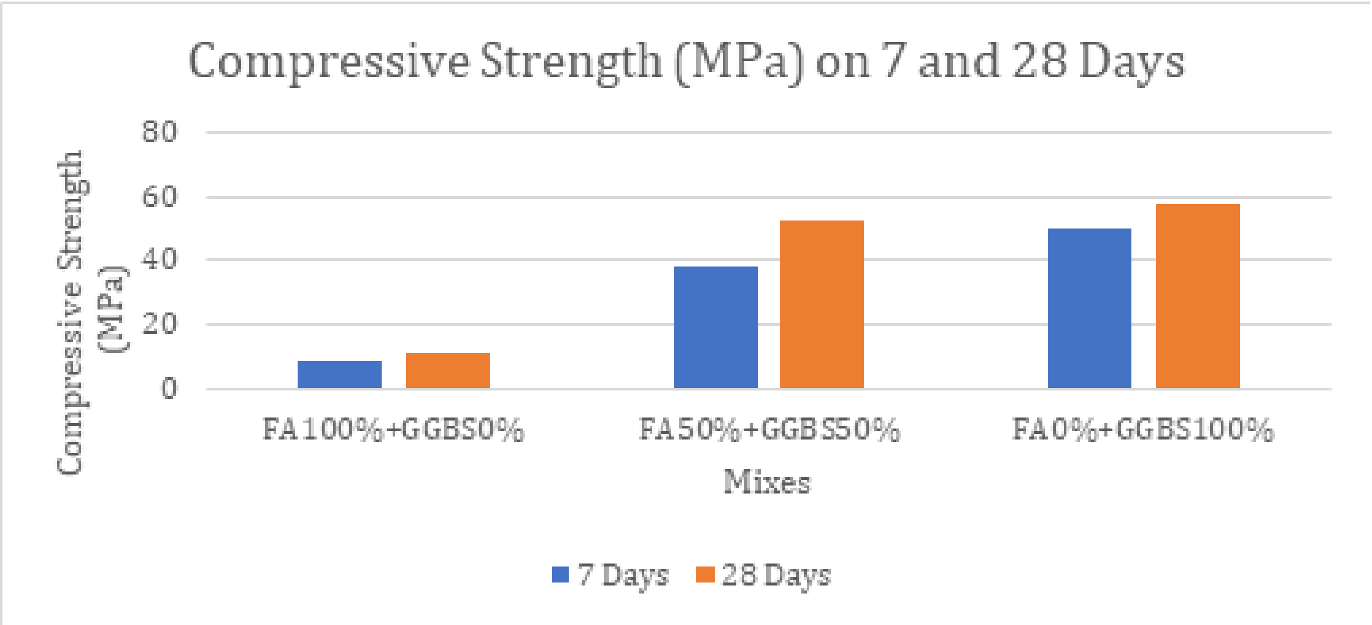


Figure 17: Compressive strength (MPa) 7 and 28 days [68].

Table 3: Comparison of loss in weight and compressive strength of geopolymer concrete composites after the acid attack [68].

Property		Composite Types		
		FA100- GGBS0	FA50- GGBS50	FA0- GGBS100
Weight (kg)	Initial	7.3	7.73	8.09
	After aid attack	6.89	7.55	7.97
Loss of weight (%)	5.62	2.33	1.48	
Compressive strength (Mpa)	Initial	11.08	52.5	57.6
	After aid attack	7.35	44.61	51.24
Loss of compressive strength (%)		33.66	15.03	11.04

Conclusion

Based on the detailed literature review and study of different experimental works, this paper suggests the following conclusions:

1) The evolution and improvement of construction materials is a continuous process, and more avenues are required to explore to produce environmentally friendly, cost-effective, and robust materials.

2) Cement is the most used construction material and produces around a ton of CO_2 per ton of cement during manufacturing which results in the industry emitting up to 10% of global CO_2 emissions.

3) The hydration of cement involves the production of the two most pronounced compounds, i.e., $Ca(OH)_2$ and C-S-H gel. The C-S-H gel is responsible for the strength of concrete and is produced by the hydration of C_3S, C_2S and pozzolans. Portlandite is responsible for an anti-corrosion alkaline environment. Still, it causes a reduction in strength by reacting with reactive metal cations on sulphate attack and converts to gypsum and brucite.

4) The internal sulphate attack is caused by gypsum and ettringite, produced during the hydration of cement. The external attack is severe and occurs over an extended period by absorption of sulphate solutions from the atmosphere and soil water, converts monosulphate aluminate hydrates into ettringite and causes expansion and cracks leading to ultimate failure.

5) The concentration of sulphate solution, permeability, period of exposure and cement composition influence the degree of sulphate attack/ deterioration.

6) The water-cement (w/c) ratio of more than 0.45 makes the concrete susceptible to external sulphate attack. In contrast, a w/c ratio of 0.35 and less is found to be the least vulnerable to external sulphate attack even after decades of exposure.

7) Using pozzolans as SCMs is considered beneficial in reducing CO_2 emissions and improving strength by producing more C-S-H gel on the chemical reaction of silicates and portlandite.

8) The use of high sulphate cement and blending of various pozzolanic materials improve the sustainability of cement concrete composites against sulphate attacks.

9) The microstructural studies using SEM and XRD support the use of pozzolanic composites to improve pore structures and the formation of lesser ettringite during sulphate attack.

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