CHAPTER IV

RESULTS AND DISCUSSION

4.1 Setting Time

4.1.1 Effect of Liquid-to-Binder Ratio on Setting Characteristics

The initial setting time of geopolymer mortars was significantly influenced by the l/b ratio, exhibiting a systematic pattern across the experimental matrix. As illustrated in **Figures 4.1-4.3**, increasing the l/b ratio from 0.3 to 0.5 consistently extended the setting times across all mixture compositions. This phenomenon can be attributed to the dilution effect, where higher liquid content reduces the effective concentration of reactive species in the system, thereby decelerating the geopolymerization reaction kinetics (Chindaprasirt et al., 2007; Deb et al., 2014).

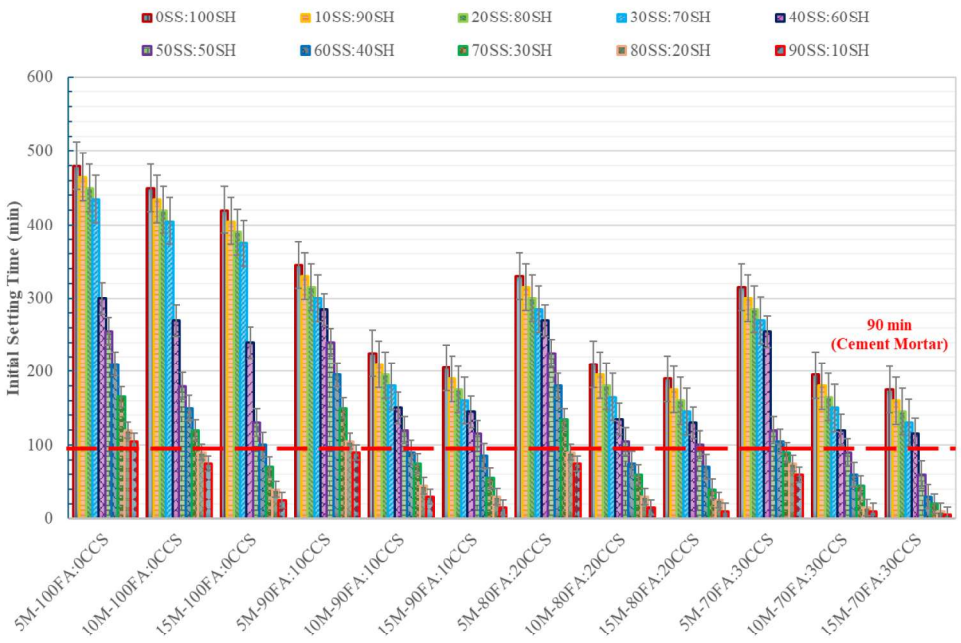


Figure 4.1 Initial setting time of geopolymer mortars with various alkaline solution at l/b=0.3 for different precursors ratios and NaOH concentrations.

At l/b = 0.3 (**Figure 4.1**), the geopolymer mortars demonstrated notably accelerated setting behavior compared to the 90-minute baseline established by the reference cement mortar. This acceleration was particularly pronounced in mixtures with higher sodium silicate-to-sodium hydroxide ratios (SS:SH = 60:40 to 90:10) activated with 15M NaOH concentration. The rapid setting observed under these conditions can be attributed to the enhanced dissolution of aluminosilicate species in the concentrated alkaline environment, facilitating expedited gel formation and subsequent hardening (Fernandez-Jimenez et al., 2006).

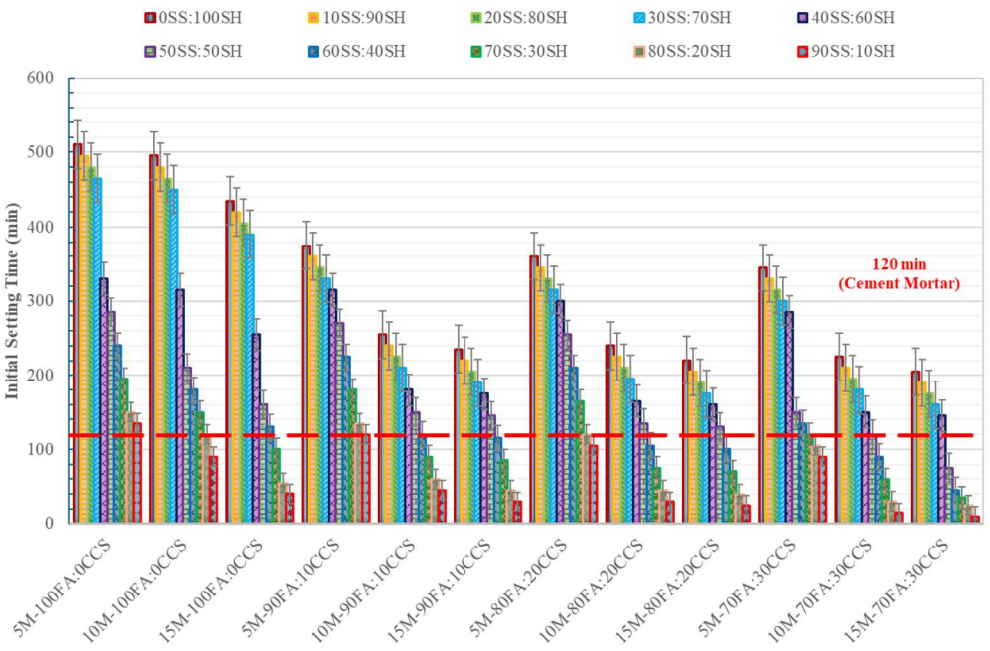


Figure 4.2 Initial setting time of geopolymer mortars with various alkaline solution at l/b=0.4 for different precursors ratios and NaOH concentrations.

As the l/b ratio increased to 0.4 (**Figure 4.2**), a moderate extension of setting times was observed across all mixture compositions, though the general trends regarding the effects of activator composition remained consistent. This intermediate l/b ratio represents an optimal balance between workability and setting characteristics

for most practical applications, aligning with findings reported by Li et al. (2019) and Xie et al. (2020) in their investigations of geopolymer systems.

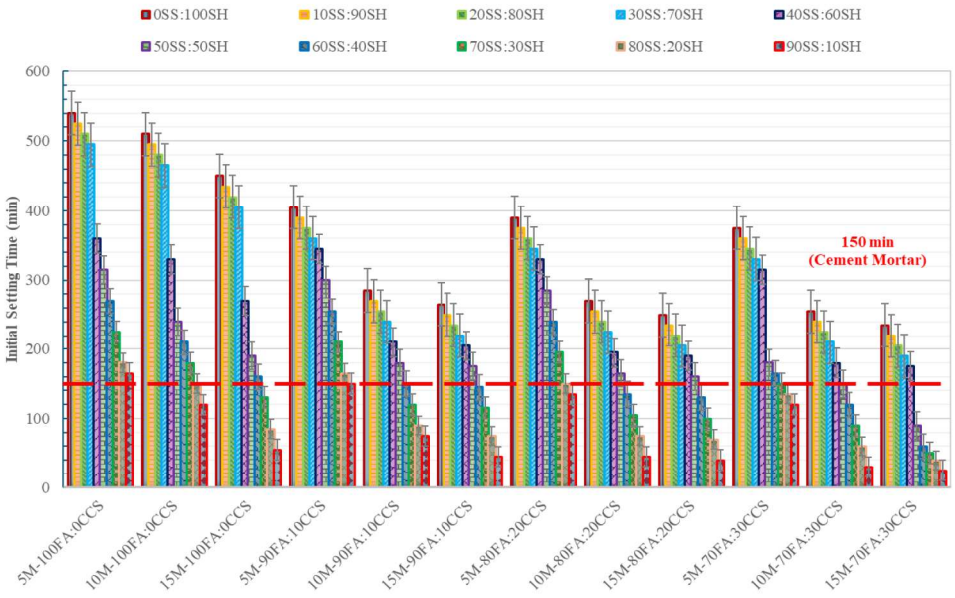


Figure 4.3 Initial setting time of geopolymer mortars with various alkaline solution at l/b=0.5 for different precursors ratios and NaOH concentrations.

Further increasing the l/b ratio to 0.5 (**Figure 4.3**) resulted in substantially prolonged setting times, particularly evident in mixtures with lower NaOH concentrations (5M). This extension of setting time at higher l/b ratios can be attributed to two primary mechanisms: (1) the aforementioned dilution effect reducing reaction kinetics, and (2) the increased spatial separation between reactive particles, necessitating longer diffusion pathways for reaction product formation (Provis, 2018).

4.1.2 Influence of Alkaline Activator Composition on Setting Behavior

The composition of the alkaline activator, particularly the SS:SH ratio and NaOH concentration, exhibited profound effects on the setting characteristics of

geopolymer mortars. Higher NaOH concentrations (15M) consistently produced shorter setting times compared to lower molarities (5M and 10M) across all precursor combinations and l/b ratios. This acceleration can be attributed to enhanced dissolution of aluminosilicate species and accelerated geopolymerization in more concentrated alkaline environments (Duxson, Fernández-Jiménez, et al., 2007).

The SS:SH ratio demonstrated a non-linear relationship with setting time, revealing complex interactions within the geopolymerization mechanism. At intermediate SS:SH ratios (40:60 to 70:30), optimum setting times were generally observed, suggesting that a balanced supply of silicate species from the sodium silicate solution and hydroxide ions from NaOH creates favorable conditions for network formation. This observation aligns with the findings of Criado et al. (2007), who identified the critical role of silicate speciation in controlling geopolymerization kinetics.

Interestingly, at very high SS:SH ratios (80:20 to 90:10), a slight retardation in setting was observed, particularly at a lower NaOH concentration (5M). This effect can be attributed to the increased viscosity of the activator solution at high silicate contents, potentially impeding the mobility of reactive species and delaying the formation of three-dimensional networks (Fernández-Jiménez et al., 2005).

4.1.3 Effect of Calcium Carbonate Sludge Incorporation on Setting Dynamics

The incorporation of CCS into the FA system introduced significant modifications to the setting behavior, attributable to the high calcium oxide content (CaO-94.64%) as shown in **Table 2.1**. Across all l/b ratios and activator compositions, increasing the CCS content from 0% to 30% progressively accelerated the setting process, with the effect becoming more pronounced at higher replacement levels.

At 10% CCS replacement, modest reductions in setting time were observed, typically in the range of 10-15% compared to the corresponding 100FA:0CCS formulation. This modest effect suggests that at lower replacement levels, the calcium content remains insufficient to substantially alter the dominant sodium aluminosilicate hydrate (N-A-S-H) gel formation mechanism characteristic of fly ash-based geopolymers (Yip et al., 2008).

As the CCS content increased to 20%, more substantial reductions in setting time became evident, particularly in systems activated with higher NaOH concentrations (15M). This synergistic effect between calcium content and alkaline concentration indicates a cooperative mechanism, where the calcium ions from CCS enhance the dissolution of aluminosilicate species from FA in the highly alkaline environment, promoting accelerated gel formation (Lee & Van Deventer, 2002).

At the maximum CCS replacement level (30%), the most dramatic acceleration of setting was observed, with some formulations achieving initial set in less than 30 minutes when activated with 15M NaOH at l/b = 0.3. This pronounced effect can be attributed to the formation of a sophisticated hybrid binding system containing both N-A-S-H and calcium aluminosilicate hydrate (C-A-S-H) gels. The calcium ions from CCS participate in rapid precipitation reactions, forming calcium-rich phases that accelerate the overall hardening process (García-Lodeiro et al., 2011).

The acceleration effect of CCS was most prominent in systems with lower SS:SH ratios (0:100 to 40:60), suggesting that in these hydroxide-dominated environments, calcium ions can more readily participate in the reaction mechanisms without interference from the complexing effects of silicate species present in sodium silicate solution (Phair & Van Deventer, 2001).

4.1.4 Integration of Setting Time Behavior with Practical Applications

The systematic investigation of setting characteristics across the experimental matrix provides valuable insights for tailoring geopolymer formulations

to specific application requirements. For applications demanding rapid setting, such as emergency repairs or precast elements with high production turnover, formulations incorporating 20-30% CCS activated with 15M NaOH at l/b = 0.3 offer optimal performance, with setting times generally under 45 minutes.

Conversely, for applications requiring extended workability, such as large-scale castings or situations with complex formwork, formulations with lower CCS content (0-10%), activated with 5M or 10M NaOH at l/b = 0.5, provide more manageable setting windows exceeding 90 minutes in most cases.

The observed setting time characteristics also correlate with strength development patterns discussed in subsequent sections, where more rapid setting generally corresponds with enhanced early-age strength but may influence ultimate strength development through densification mechanisms and reaction product distribution. This integrated understanding of setting behavior and mechanical performance enables the strategic design of geopolymer formulations optimized for specific construction applications.

4.2 Compressive Strength Development

The 7-day compressive strength results revealed complex relationships between mixture composition, processing parameters, and mechanical performance. Through systematic evaluation of key variables, this study identified critical factors influencing the development of high strength geopolymer mortars.

4.2.1 Effect of NaOH Molarity on Strength Development

The NaOH concentration significantly influenced compressive strength across all mixture compositions, as illustrated in **Figures 4.4-4.6**. Increasing NaOH molarity from 5M to 15M consistently enhanced mechanical performance, with the effect becoming more pronounced in formulations containing both FA and CCS.

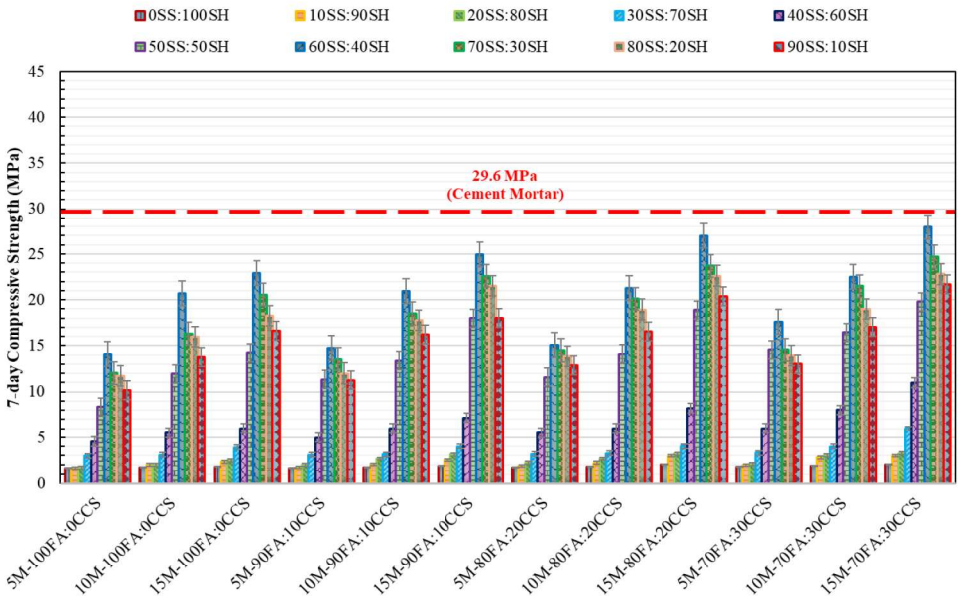


Figure 4.4 7-day compressive strength development of geopolymer mortars with various alkaline solution at l/b=0.3 for different precursors ratios and NaOH concentrations.

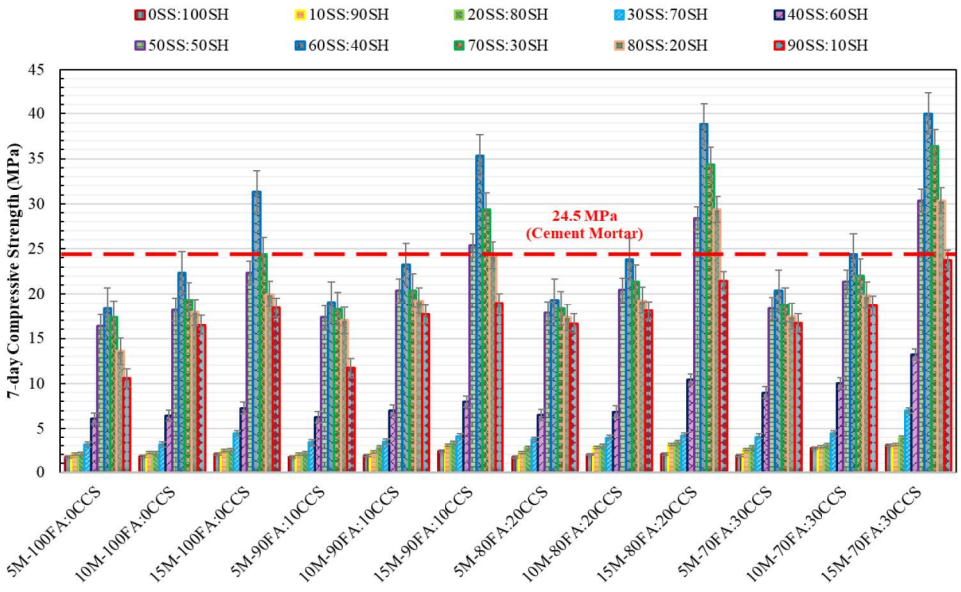


Figure 4.5 7-day compressive strength development of geopolymer mortars with various alkaline solution at l/b=0.4 for different precursors ratios and NaOH concentrations.

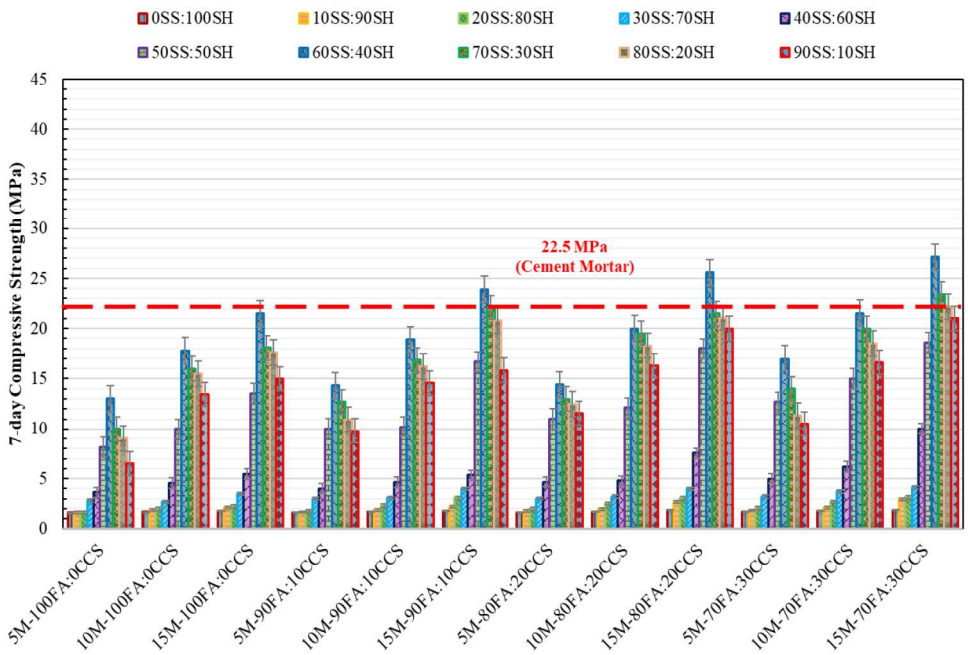


Figure 4.6 7-day compressive strength development of geopolymer mortars with various alkaline solution at l/b=0.5 for different precursors ratios and NaOH concentrations.

At 5M NaOH concentration, most formulations achieved modest strength values ranging from 15-20 MPa, regardless of other mixture parameters. This limited performance can be attributed to insufficient alkalinity for effective dissolution of aluminosilicate species, resulting in incomplete geopolymerization reactions (Kutchko & Kim, 2006). Intermediate NaOH concentration (10M) generated moderate improvements, with typical strength values between 20 25 MPa depending on other formulation variables.

The most substantial strength gains were observed at 15M NaOH concentration, where several formulations exceeded 30 MPa at optimal SS:SH ratios. This enhanced performance stems from comprehensive dissolution of aluminosilicate precursors and accelerated reaction kinetics, leading to the formation of more robust and densely packed geopolymeric networks (Senior & Johnson, 2005). The superior strength at

higher NaOH concentrations demonstrates the critical role of alkalinity in maximizing the reaction potential of aluminosilicate precursors.

4.2.2 Influence of Sodium Silicate-to-Sodium Hydroxide Ratio

The SS:SH ratio emerged as a pivotal parameter influencing strength development. Analysis of **Figures 4.4-4.6** reveals that a SS:SH ratio of 60:40 consistently produced the highest compressive strength across all experimental conditions, regardless of NaOH concentration, FA:CCS ratio, or l/b ratio. This consistent pattern identifies 60:40 as the optimal balance between sodium silicate and sodium hydroxide for maximizing strength development in geopolymer mortars (Fernández-Jiménez & Palomo, 2003).

At lower SS:SH ratios (0:100 to 50:50), insufficient soluble silica limited the formation of silica-rich gel networks, resulting in suboptimal mechanical performance. Conversely, at higher SS:SH ratios (70:30 to 90:10), excessive silicate species potentially impeded precursor dissolution through surface coating effects, leading to strength reduction. The 60:40 ratio represents the ideal balance between silicate species and hydroxide ions, creating favorable conditions for network formation and structural densification (Rostami et al., 2012).

The sensitivity to variations from this optimal 60:40 ratio was most pronounced at higher NaOH concentrations (15M) and in formulations incorporating both FA and CCS. This enhanced sensitivity indicates a sophisticated interplay between silicate speciation, hydroxide concentration, and calcium availability in determining the reaction mechanisms and product formation pathways (Van der Merwe et al., 2014).

4.2.3 Effect of Fly Ash and Calcium Carbonate Sludge Proportions

The incorporation of CCS as a partial replacement for FA significantly altered strength development patterns across the experimental matrix. As evident in **Figures 4.4-4.6**, increasing CCS content from 0% to 30% generally enhanced

compressive strength, particularly when combined with higher NaOH concentrations and the optimal 60SS:40SH ratio.

The strength enhancement with CCS incorporation can be attributed to the formation of a hybrid binding system containing both sodium aluminosilicate hydrate (N-A-S-H) and calcium aluminosilicate hydrate (C-A-S-H) gels (Environment et al., 2018; Provis, 2018). The calcium-rich environment provided by CCS promotes the formation of C-A-S-H phases, which complements the traditional N-A-S-H networks characteristic of FA-based geopolymers. This dual gel formation mechanism creates a more sophisticated binding system with enhanced mechanical properties (Phair & Van Deventer, 2001).

The optimal CCS replacement level appeared to be 20-30%, depending on the NaOH concentration. At this replacement level, formulations typically demonstrated 15-25% higher strength compared to the corresponding 100FA:0CCS reference mixtures. The synergistic effect between FA and CCS was most pronounced at higher NaOH concentrations (15M), indicating that aggressive alkaline conditions facilitate optimal interaction between the precursors (Barcelo et al., 2014).

4.2.4 Comprehensive Analysis of Liquid-to-Binder Ratio Effects

Figure 4.7 presents a comprehensive analysis of how the liquid-to-binder (l/b) ratio affects compressive strength at the optimal SS:SH ratio of 60:40 across various precursor combinations and NaOH concentrations. The relationship between l/b ratio and compressive strength exhibits a consistent parabolic pattern across all mixture compositions, with peak strength occurring at l/b = 0.4 (Duxson, Provis, et al., 2007; Hardjito et al., 2004).

This optimal l/b ratio represents the ideal balance between sufficient liquid content for complete dissolution and reaction of precursors while maintaining adequate particle proximity for effective network formation. For instance, the 15M-70FA:30CCS mixture increased in strength from approximately 18 MPa at l/b = 0.3 to 40 MPa at l/b = 0.4, followed by a decline to about 27 MPa at l/b = 0.5. This substantial

variation (approximately 122% increase from l/b = 0.3 to 0.4) reveals the critical importance of precise l/b ratio control in high-performance geopolymer formulations (Tanya Bakharev, 2005).

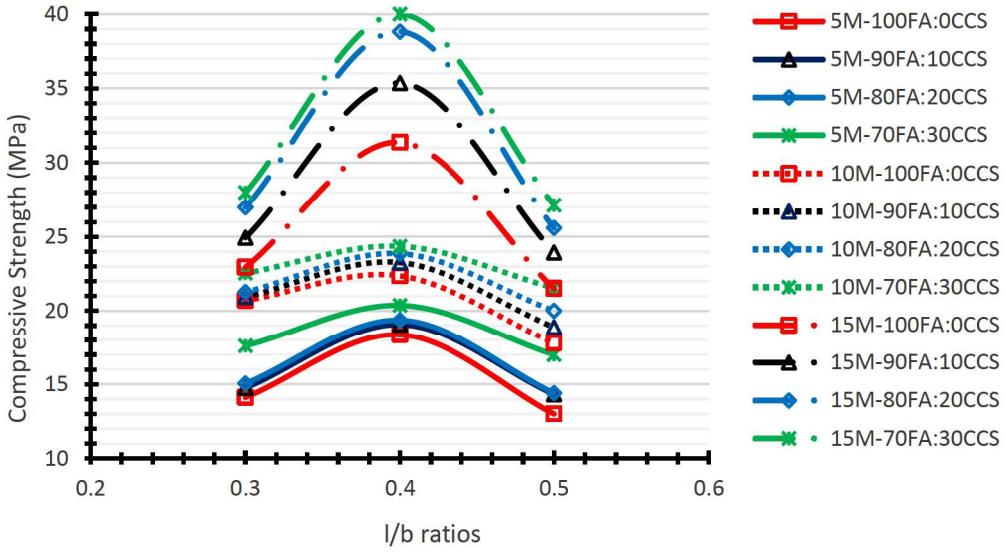


Figure 4.7 Effect of l/b ratio on 7-day compressive strength of geopolymer mortars with 60SS:40SH at different precursors ratios and NaOH concentrations.

The strength reduction observed when increasing the l/b ratio from 0.4 to 0.5 is consistent across all mixtures but more pronounced in 15M NaOH activated systems. This decline in strength (approximately 32-35% for 15M systems) can be attributed to the dilution effect of excess liquid, which creates a more porous microstructure in the hardened matrix and reduces the concentration of reactive species during geopolymerization (Duxson, Provis, et al., 2007).

Similarly, the lower strength observed at l/b = 0.3 compared to l/b = 0.4 indicates insufficient liquid for complete dissolution and reaction of precursors, resulting in incomplete geopolymerization and consequently reduced mechanical performance (Kong & Sanjayan, 2010). This effect is particularly evident in high-strength formulations (15M NaOH with CCS incorporation), suggesting that as performance potential increases, so does the sensitivity to l/b ratio optimization.

4.2.5 Comparison with Conventional Cement Mortar

A critical evaluation criterion for any alternative binder system is its performance relative to conventional cement-based materials. **Figures 4.4-4.6** include benchmark values for conventional cement mortar, providing a direct comparison with the geopolymer formulations across different l/b ratios.

At l/b = 0.4 (**Figure 4.5**), several geopolymer formulations surpassed the reference cement mortar strength of 24.5 MPa. Particularly noteworthy were the 15M NaOH activated mixtures with the optimal 60SS:40SH ratio, where all FA:CCS combinations achieved strengths exceeding the cement benchmark. The 15M-70FA:30CCS formulation demonstrated the most impressive performance, reaching approximately 40 MPa at the optimal parameter combination (i.e., representing a 63% strength enhancement over conventional cement mortar).

Even at l/b = 0.3 and l/b = 0.5 (**Figures 4.4 and 4.5**), select geopolymer formulations with 15M NaOH activation and optimal SS:SH ratio outperformed the reference cement mortar. This consistent superior performance across various l/b ratios demonstrates the robustness of optimized geopolymer systems and their potential as viable alternatives to conventional cement (Kutchko & Kim, 2006).

The 10M NaOH activated geopolymer mortars with 60:40 SS:SH ratio achieved strengths comparable to the cement reference, particularly when incorporating CCS at higher replacement levels. In contrast, the 5M NaOH activated systems generally underperformed relative to conventional cement mortar, indicating that sufficient alkalinity is essential for geopolymer systems to compete with traditional cementitious materials (Škvára et al., 2009).

This benchmarking confirms that properly optimized geopolymer mortars incorporating industrial by-products can match or exceed the mechanical performance of conventional cement-based systems. Given the significant environmental benefits associated with geopolymer production, including substantial reductions in carbon emissions and the valorization of industrial waste streams, these results demonstrate

the practical viability of geopolymer technology as a sustainable alternative to conventional cement in construction applications (Andrew, 2018; Olivier et al., 2017).

It is important to note that the comparison presented here between geopolymer and cement mortar is intended as a practical performance benchmark rather than a rigorous chemical equivalence. The fundamental differences in chemistry between geopolymers (alkalinity, silica modulus, polycondensation) and cement (hydration) make direct comparison inherently limited. A more rigorous comparison would require aligning not only mix proportions but also parameters such as heat release, cumulative reaction degree, and workability under identical curing conditions.

4.2.6 Analysis of Compressive Strength Trends Across Multiple Variables

The relationships between compressive strength and sodium silicate (SS) content across various experimental conditions are systematically illustrated in **Figures 4.8-4.10**, providing deeper insights into the complex interaction of multiple variables in geopolymer systems. They reveal distinctive patterns in how compressive strength responds to sodium silicate content across different formulations. These patterns can be interpreted through the lens of reaction mechanisms and critical threshold effects.

The consistent bell-shaped response curves across **Figures 4.8-4.10** suggest the existence of critical thresholds governing geopolymerization efficiency. At SS contents below approximately 40%, insufficient soluble silicate species limit network formation, resulting in structures dominated by hydroxide-mediated reactions rather than silicate-based polymerization. This "silicate-deficient zone" produces incomplete geopolymerization and consequently reduced mechanical properties (Fernández-Jiménez & Palomo, 2003; Phair & Van Deventer, 2001).

Conversely, at SS contents exceeding approximately 70%, the systems enter a "hydroxide-limited zone" where the high concentration of silicate species without adequate hydroxide ions to catalyze reactions leads to inefficient polymerization and

potentially interference effects. This upper threshold becomes more pronounced at higher NaOH concentrations (**Figure 4.10**), suggesting that excessive silicate species may coat precursor particles and inhibit dissolution when combined with aggressive alkaline conditions (Rostami et al., 2012).

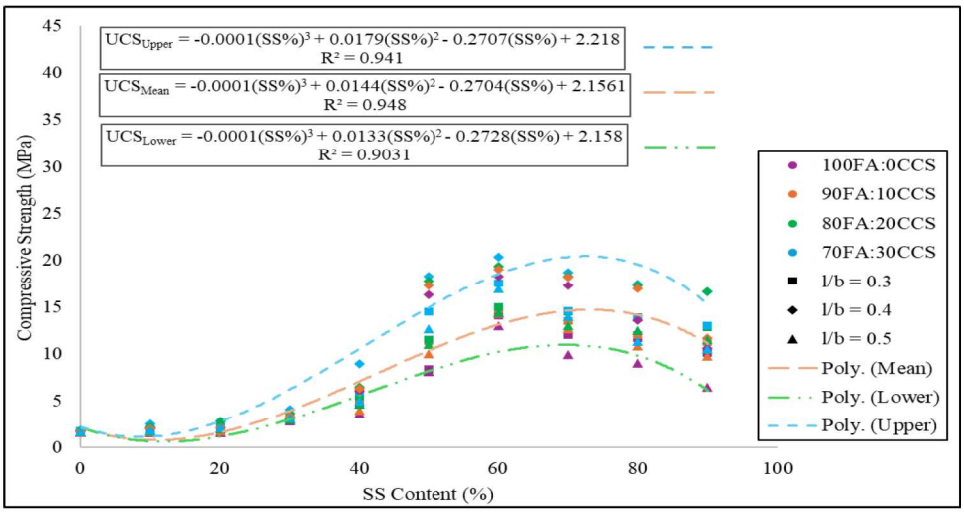


Figure 4.8 Relationship between compressive strength (MPa) and SS content (%) for different alkaline solution with 5M NaOH at different binder ratios and l/b ratios.

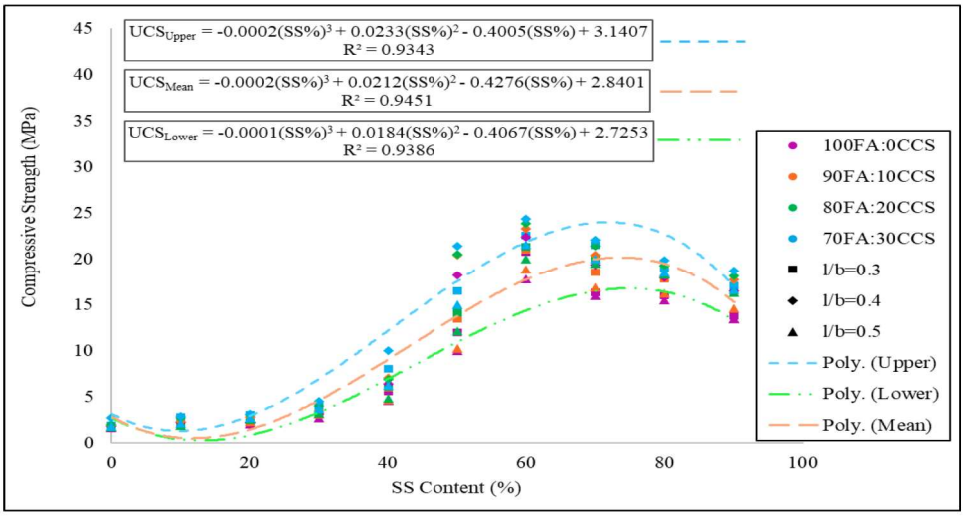


Figure 4.9 Relationship between compressive strength (MPa) and SS content (%) for different alkaline solution with 10M NaOH at different binder ratios and l/b ratios.

The data consistently identify an "optimum zone" between approximately 50:50 and 70:30 SS:SH ratios where balanced dissolution and polymerization mechanisms operate synergistically. Within this range, sufficient hydroxide ions facilitate effective precursor dissolution while adequate silicate species enable robust network formation (Škvára et al., 2009).

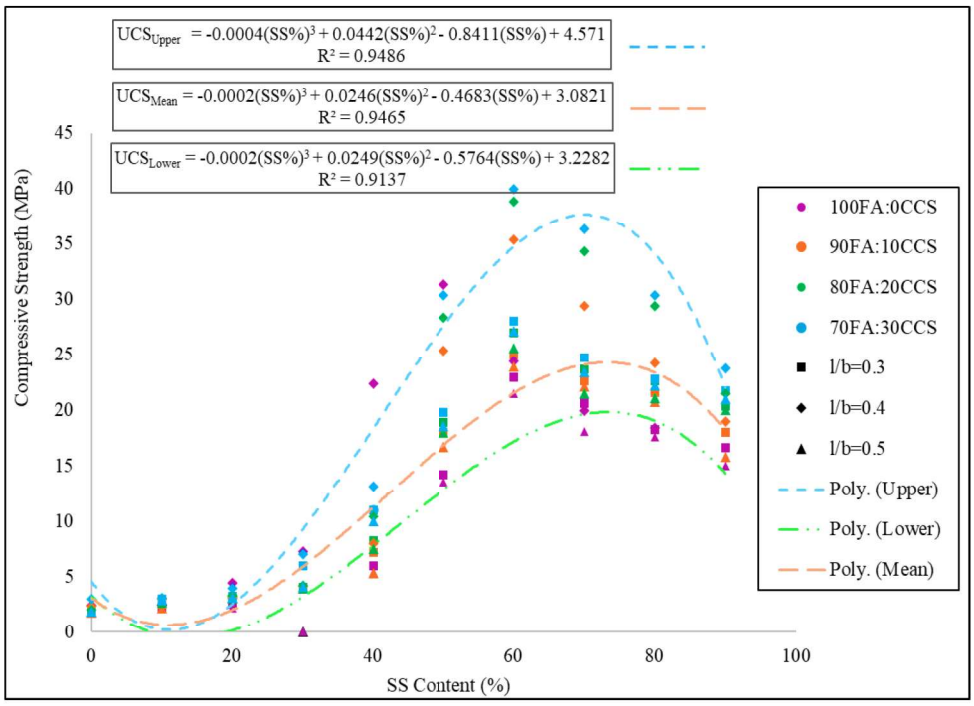


Figure 4.10 Relationship between compressive strength (MPa) and SS content (%) for different alkaline solution with 15M NaOH at different binder ratios and l/b ratios.

Notably, this optimum zone shifts slightly depending on other parameters. At higher NaOH concentrations (**Figure 4.10**), the optimum narrows and shifts toward lower SS content (50:50 to 60:40), likely because the increased hydroxide concentration enhances silicate species formation from precursor dissolution, reducing the need for additional silicate from the activator (Environment et al., 2018).

The presence of CCS also modulates the optimum zone, with higher CCS contents generally performing better at slightly lower SS content ranges. This shift can

be attributed to calcium's ability to modify silicate speciation and create additional reaction pathways through C-A-S-H gel formation, reducing dependence on silicate species from the activator solution (Provis, 2018; Van der Merwe et al., 2014).

Figure 4.11 provides a comprehensive comparative analysis of compressive strength development in 5M and 15M NaOH systems across various SS ratios, FA proportions, and l/b ratios. This multivariable comparison reveals several significant trends that illuminate the fundamental geopolymerization mechanisms under different activation conditions.

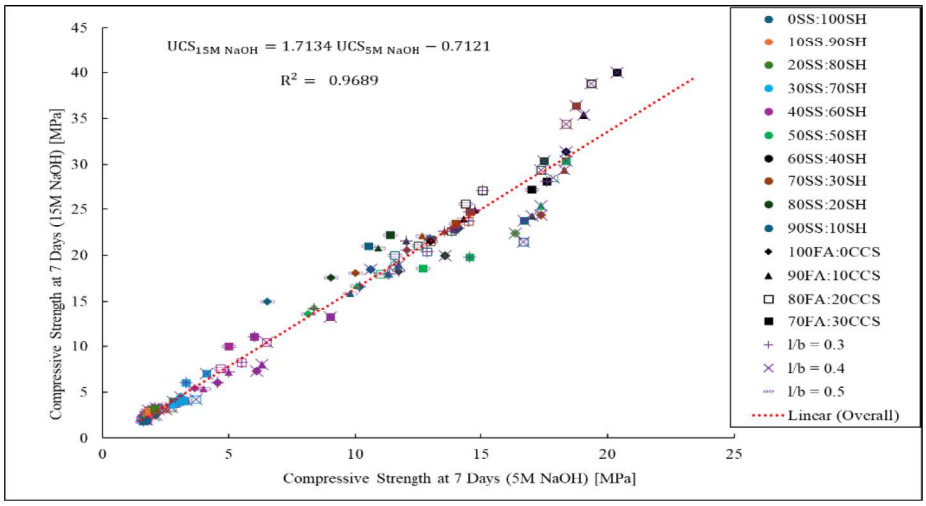


Figure 4. 11 Relationship between 7-day compressive strength of various FA: CCS geopolymer mortars at 5M and 15M NaOH concentrations at different SS:SH and l/b ratios.

The strength difference between 5M and 15M systems is consistently substantial, with 15M systems demonstrating 40-100% higher strength values depending on other formulation parameters. This enhancement is most pronounced at intermediate SS contents (40-60%) and in formulations incorporating higher CCS proportions, suggesting a synergistic effect between high alkalinity and calcium availability, consistent with observations by García-Lodeiro et al. (2011). The enhanced dissolution of aluminosilicate species under more aggressive alkaline conditions

creates a more reactive environment for Ca^{2+} incorporation into the developing gel structure.

The influence of l/b ratio is particularly evident in 15M systems, where the optimal l/b ratio of 0.4 consistently produces superior performance compared to either 0.3 or 0.5. The sensitivity to l/b ratio variation is more pronounced in high-alkalinity systems, indicating that as reaction kinetics accelerate under more aggressive alkaline conditions, the balance between reactant concentration and mobility becomes increasingly critical, as demonstrated by Zhang et al. (2023).

The enhancement effect of CCS incorporation is magnified at higher NaOH concentrations, with 70FA:30CCS formulation showing the most substantial performance improvement in 15M systems compared to their 5M counterparts. This observation suggests that the calcium-rich environment provided by CCS can be more effectively leveraged under highly alkaline conditions, leading to more sophisticated hybrid binding systems incorporating both N-A-S-H and C-A-S-H gels, as described by Hanifa et al. (2025) and Yang et al. (2024).

These comprehensive analyses of compressive strength trends across multiple variables provide valuable insights for optimizing geopolymer formulations for specific strength requirements and processing conditions. The identified patterns demonstrate the complex interplay between alkaline activation parameters, precursor characteristics, and mixing proportions in determining the ultimate mechanical performance of geopolymer mortars.

4.3 Microstructural Analysis

4.3.1 SEM Analysis

The microstructural evolution of geopolymer mortars with varying NaOH concentrations and precursor compositions was systematically investigated using SEM analysis. **Figure 4.12** presents SEM micrographs of specimens with different NaOH

concentrations (5M, 10M, and 15M) and precursor ratios (100FA:0CCS and 70FA:30CCS) at the optimal liquid-to-binder ratio of 0.4.

In the 100FA:0CCS system activated with 5M NaOH **(Figure 4.12a**), the microstructure exhibits partially reacted fly ash particles embedded in a relatively loose matrix. The geopolymeric gel formation was incomplete, with visible boundaries between particles and gel phases, indicating limited dissolution of aluminosilicate species under low alkaline conditions. This microstructural observation corresponded directly with the modest compressive strength values (15-20 MPa) as reported in compressive strength test results.

As the NaOH concentration increased to 10M (**Figure 4.12b**), a notable densification of the microstructure was observed, with increased gel formation and reduced interparticle porosity. Partially reacted fly ash spheres remained visible but showed signs of surface etching and dissolution, indicating more effective alkaline activation. The enhanced gel formation creates stronger particle-matrix interfaces, explaining the moderate increase in compressive strength (20-25 MPa) observed in these systems.

At 15M NaOH concentration (**Figure 4.12c**), the pure fly ash system demonstrated substantially improved microstructural characteristics with extensive gel formation. Most fly ash particles show advanced dissolution, with reaction products filling interparticle spaces and creating a more homogeneous matrix. This densified microstructure provides the structural foundation for the enhanced compressive strength (25-31 MPa) recorded in these high-alkali formulations, as detailed in compressive strength test results.

The progressive microstructural refinement with increasing NaOH concentration aligns with the reaction mechanisms proposed by Duxson, Provis, et al. (2007), where higher alkalinity enhances the dissolution of aluminosilicate species, leading to more extensive N-A-S-H gel formation and consequently improved mechanical properties.

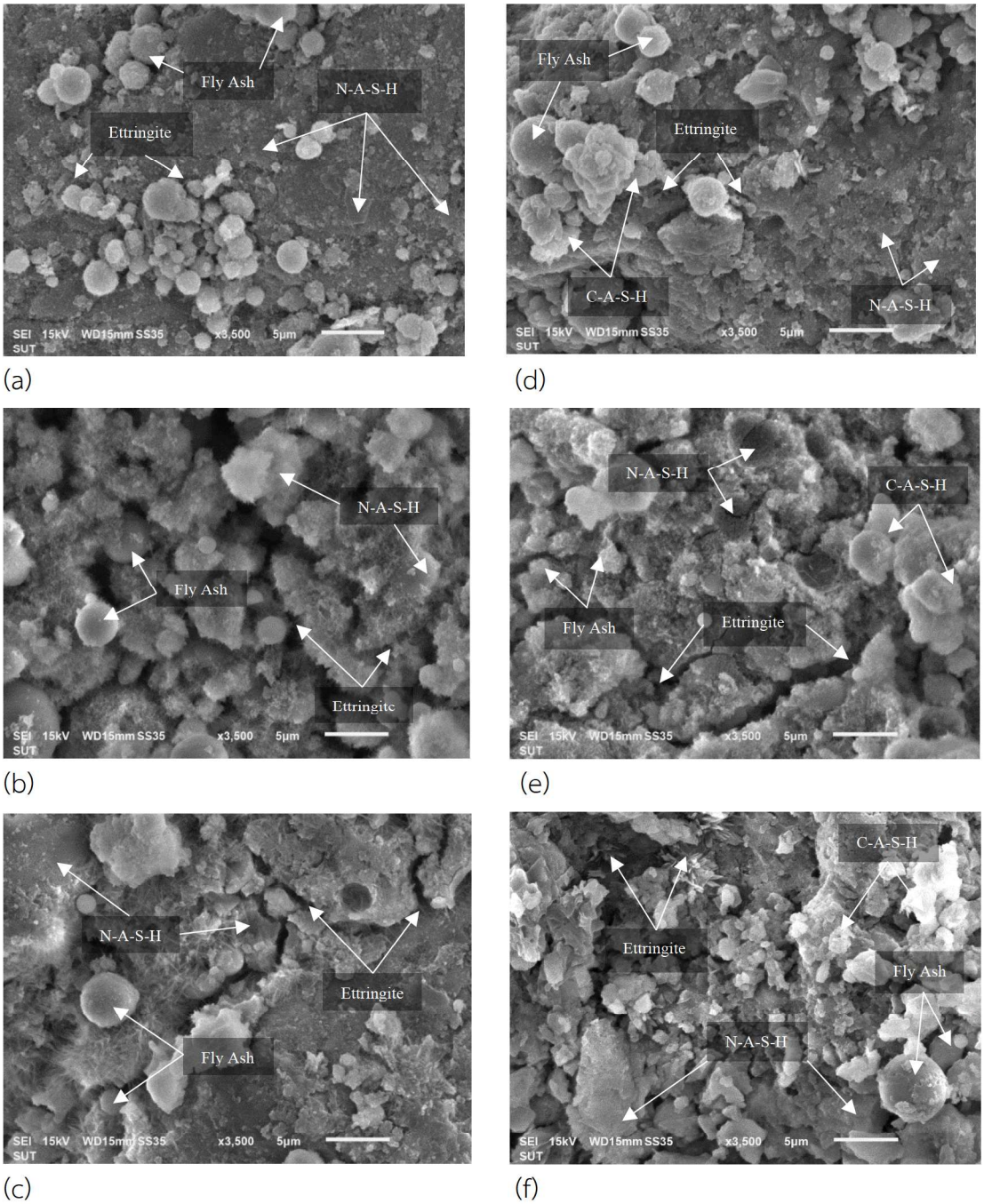


Figure 4.12 Scanning electron microscope images of (a) 5M-100FA:0CCS (b) 10M-100FA:0CCS (c) 15M-100FA:0CCS (d) 5M-70FA:30CCS (e) 10M-70FA:30CCS (f) 15M-70FA:30CCS at l/b ratio of 0.4.

The incorporation of 30%CCS replacement of FA introduces significant microstructural modifications across all NaOH concentrations. At 5M NaOH (**Figure 4.12d**), the 70FA:30CCS system exhibited a more compact microstructure compared to its pure fly ash counterpart, with visible calcium-rich reaction products filling interstitial spaces. The microstructure remains somewhat heterogeneous, with distinct regions of varying morphology, revealing the simultaneous formation of different gel types, likely N-A-S-H and C-A-S-H phases as reported by García-Lodeiro et al. (2011).

When activated with 10M NaOH (**Figure 4.12e**), the 70FA:30CCS system demonstrated enhanced microstructural integration, with reaction products effectively binding particle clusters into a more cohesive matrix. The improved interfacial transition zones between particles and binding phases corresponded to the increased compressive strength observed in these formulations.

The most significant microstructural refinement was observed in the 15M NaOH activated 70FA:30CCS system (**Figure 4.12f**), which exhibited remarkably dense geopolymeric gels. The microstructure shows characteristics of advanced geopolymerization, with extensive reaction product formation creating a sophisticated binding network. The formation of this hybrid binding system, containing both N-A-S-H and C-A-S-H gels as suggested by Hanifa et al. (2025) provides the microstructural foundation for the exceptional compressive strength (approximately 40 MPa) recorded in these formulations.

The SEM observations further validate the proposed mechanisms for CCS incorporation effects, where calcium ions from CCS participate in the formation of C-A-S-H gels in addition to N-A-S-H gels typical of fly ash-based geopolymers. This dual gel formation creates a more sophisticated binding system with enhanced mechanical properties.

4.3.2 XRD Analysis

XRD analysis was conducted to investigate the crystalline phases and mineralogical transformations in geopolymer mortars with varying NaOH concentrations and precursor compositions. **Figure 4.13** presents the XRD patterns for 100FA:0CCS and 70FA:30CCS specimens with different NaOH molarities (5M, 10M, and 15M) at the optimal liquid-to-binder (l/b) ratio of 0.4.

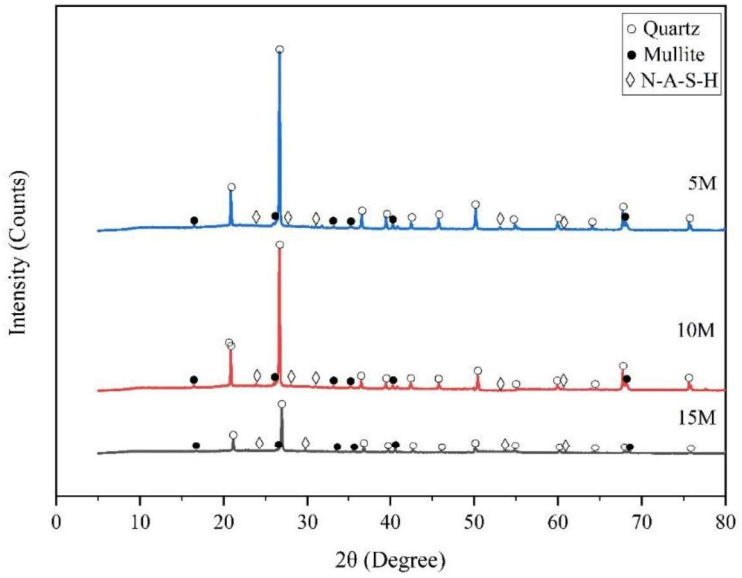
The XRD patterns of 100FA:0CCS specimens (**Figure 4.13a**) reveal several characteristic crystalline phases across all NaOH concentrations. Primary crystalline phases include quartz (SiO_2) identified by characteristic peaks at approximately 2θ = 26.6° and 20.8°, and mullite ($Al_6Si_2O_{13}$) indicated by peaks at approximately 2θ = 16.4°, 25.9°, and 33.2°. These phases represent the crystalline components of the original fly ash that remain largely unreacted during the geopolymerization process, as similarly observed by Criado et al. (2016).

A prominent broad hump observed between 20° and 35° 2θ indicates the formation of amorphous geopolymeric gel, primarily N-A-S-H. The intensity and breadth of this amorphous hump increase with higher NaOH concentrations, indicating more extensive dissolution of aluminosilicate species and subsequent formation of amorphous reaction products. This observation aligns with the SEM findings, where higher NaOH concentrations resulted in more advanced geopolymerization and densified microstructures.

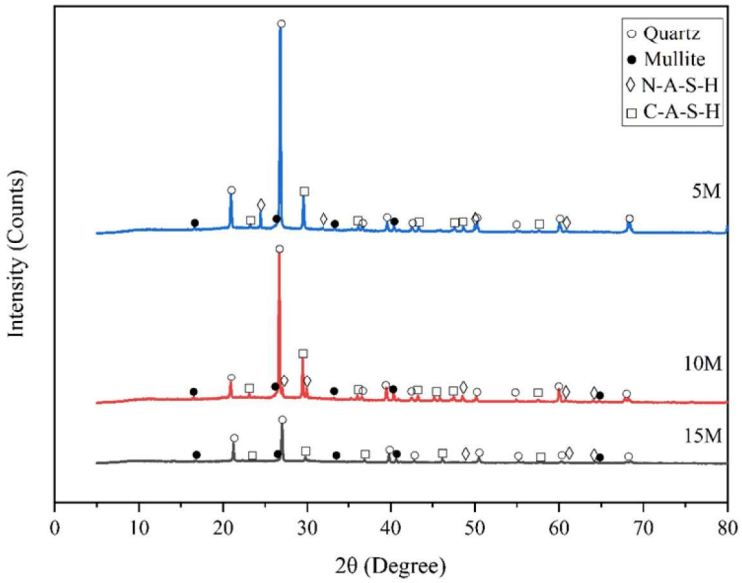
The relative intensity of crystalline peaks, particularly quartz and mullite, illustrated slight but progressive reduction with increasing NaOH concentration. This reduction indicated partial dissolution of the crystalline phases under more aggressive alkaline conditions, contributing additional reactive species to the geopolymerization process. These findings supported the mechanical performance trends, where higher NaOH concentrations consistently produced enhanced compressive strength.

The XRD patterns of 70FA:30CCS specimens (**Figure 4.13b**) exhibit notable differences compared to the pure fly ash systems, reflecting the influence of calcium incorporation on reaction product formation. While the primary crystalline phases

(quartz and mullite) from the original fly ash remain present, their relative intensities appear diminished compared to the 100FA:0CCS systems, revealing enhanced dissolution in the calcium-rich environment.



(a)



(b)

Figure 4.13 X-ray diffraction patterns of (a) 100FA:0CCS and (b) 70FA:30CCS with different molarities of NaOH at l/b ratio of 0.4.

Additional peaks corresponding to calcium-bearing phases can be observed in the 70FA:30CCS patterns. These include potential C-S-H and C-A-S-H phases, which were characteristic of systems containing both calcium and aluminosilicate sources. The formation of these calcium-bearing phases aligns with the proposed hybrid binding mechanism, where calcium ions from CCS participate in reaction pathways parallel to traditional geopolymerization.

The amorphous hump between 20° and 35° 2θ in the 70FA:30CCS patterns appears broader and potentially incorporates multiple overlapping amorphous phases compared to the 100FA:0CCS systems. This broader amorphous feature likely represented the coexistence of N-A-S-H and C-A-S-H gels, as suggested by García-Lodeiro et al. (2011) in their investigation of compatibility between these gel types.

The influence of NaOH concentration on mineralogical composition is evident in both precursor systems. Higher NaOH molarity (15M) consistently results in more pronounced amorphous characteristics and reduced crystallinity compared to lower molarities (5M and 10M). This trend indicates more extensive dissolution of precursor materials and formation of reaction products under more aggressive alkaline conditions, supporting microstructural observations.

The most significant mineralogical transformations were observed in the 15M-70FA:30CCS specimen, which exhibited the most pronounced amorphous features and the least distinct crystalline peaks. This enhanced transformation aligns with the exceptional mechanical performance of this formulation, which achieved the highest compressive strength (approximately 40 MPa) among all tested compositions.

These findings validated the optimization strategies developed through the systematic parameter evaluation and provided mineralogical evidence for the microstructural characteristics observed in the SEM analysis. The XRD results confirmed that optimal performance was achieved when reaction conditions facilitated extensive amorphous gel formation while maintaining appropriate phase compatibility between N-A-S-H and C-A-S-H gels in hybrid systems.

It is noted that the presence of quartz sand in the mortar samples may contribute to dominant crystalline peaks, potentially masking signals from amorphous or weak crystalline geopolymer gel phases. Future mineralogical analysis should be performed on paste samples to minimize aggregate interference and improve the detection of reaction products.

4.4 Machine Learning Model Performance and Analysis

The comparative analysis of machine learning algorithms revealed substantial differences in predictive capability for geopolymer strength estimation. XGBoost demonstrated superior performance with an exceptional R^2 value of 0.998 (on a scale of 0 to 1), indicating it explained nearly all variance in the compressive strength data. This was complemented by the lowest error metrics (MSE=0.142, RMSE=0.377 MPa), representing predictions within approximately 0.4 MPa of actual strength values across the entire range of experimental results.

CatBoost achieved the second-best performance (R^2=0.992, MSE=0.620, RMSE=0.787 MPa), maintaining strong predictive power while showing moderately higher error values. Both gradient boosting algorithms substantially outperformed traditional approaches, with SVM (R^2=0.946, MSE=4.045, RMSE=2.011 MPa) and AdaBoost (R^2=0.929, MSE=5.198, RMSE=2.280 MPa) exhibiting considerably higher prediction errors.

Given its superior performance metrics, XGBoost was selected for further interpretability analysis using SHAP. The XGBoost model demonstrated exceptional predictive capability for geopolymer strength estimation as evidenced by **Figure 4.14**. The scatter plot reveals a remarkably strong linear relationship between actual and predicted compressive strength values spanning the entire experimental range (2-40 MPa). The fitted regression line ($y = 0.9971x + 0.0306$) exhibits a slope approaching unity and a negligible y-intercept, confirming the model's extraordinary accuracy across all strength levels.

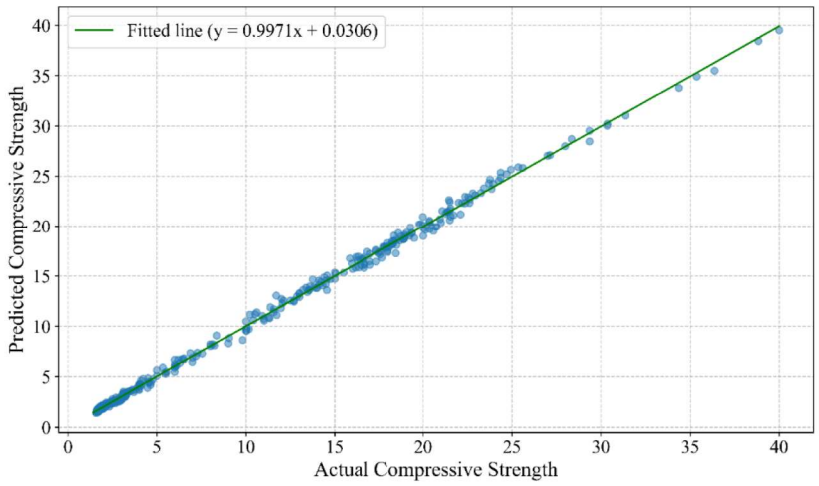
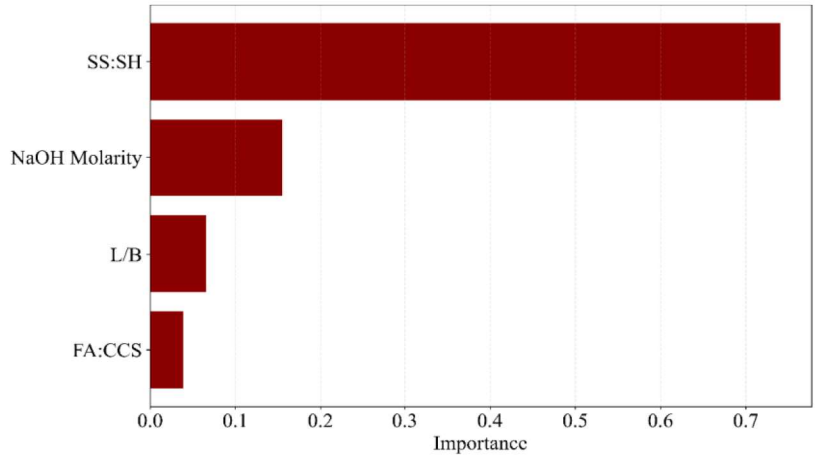


Figure 4.14 A relationship between actual and predicted compressive strength based on machine learning models.

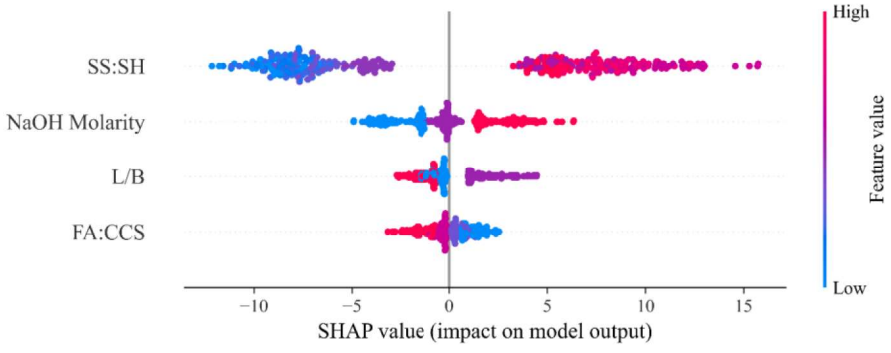
The XGBoost-SHAP analysis presented in **Figure 4.15** provides critical insights into the relative importance and specific impacts of compositional parameters on geopolymer strength development. **Figure 4.15a** clearly establishes a hierarchical ranking of parameters that influence compressive strength prediction. The SS:SH ratio emerged as the most influential parameter with a normalized importance value of approximately 0.7 (on a scale of 0 to 1), significantly higher than all other parameters. NaOH molarity ranks second in importance (approximately 0.15), showing moderate influence on strength predictions but significantly less than the SS:SH ratio. l/b ratio and FA ratio show substantially lower importance values (approximately 0.05 each), suggesting these traditionally emphasized mix design parameters exert less influence than activator composition in determining final strength properties.

The SS:SH ratio's predominant influence stems from its critical role in regulating silicate network formation during geopolymerization, fundamentally shaping the molecular architecture of binding gels. This parameter directly controls the availability of soluble silica species necessary for forming the three-dimensional aluminosilicate framework that provides structural integrity to the hardened material. The precise

balance between silicate and hydroxide ions determines reaction pathway efficiency, network connectivity, and ultimate mechanical properties. NaOH molarity emerges as the secondary influence by governing precursor dissolution kinetics and subsequent gel formation. The hydroxide concentration dictates the rate at which aluminosilicate species are released from raw materials into the reaction medium, while also affecting pH-dependent condensation reactions that form the geopolymer backbone. Optimized molarity ensures efficient precursor activation without disrupting critical polymerization processes.



(a)



(b)

Figure 4.15 XGBoost-SHAP analysis: (a) Features importance ranking, (b) Features impact on the model output (compressive strength).

Figure 4.15b expands on the importance ranking by revealing how specific values of each parameter positively or negatively impact strength predictions. SS:SH ratio displays a distinct pattern where higher values (represented by red points, generally SS:SH ratios above 60:40) predominantly appear on the positive side of the SHAP value axis, indicating that increased sodium silicate proportions generally enhance compressive strength. Lower SS values (blue points, SS:SH ratios below 40:60) consistently show negative impacts, suggesting insufficient soluble silicate undermines strength development.

NaOH molarity exhibits a more complex non-linear relationship. Moderate molarity values (purple points, particularly in the 10-12M range) tend to contribute positively to strength predictions, while both very low concentrations (below 7M, blue points) and very high concentrations (above 13M, red points) often show negative impacts. This supports the existence of an optimal alkalinity range for geopolymerization.

l/b ratio demonstrates a clear inverse relationship with strength, where lower l/b values (blue points, particularly ratios below 0.4) consistently show positive contributions to the predicted strength, while higher values (red points, ratios above 0.45) exhibit negative impacts. This confirms the detrimental effect of excessive liquid content on mechanical properties. FA ratio shows a more nuanced distribution where certain specific ratios (particularly in the 70:30 to 80:20 FA:CCS range) exhibit stronger positive contributions than others, suggesting optimal replacement levels rather than a simple linear trend.

These SHAP analysis findings reveal that activator composition parameters (particularly SS:SH ratio) exert significantly greater influence on geopolymer strength development than precursor proportions or water content. This insight challenges conventional mix design approaches that often prioritize solid precursor ratios and suggests that optimizing the alkaline activator should be the primary focus for enhancing geopolymer performance. For practical implementation, this indicates that

practitioners should first establish the optimal SS:SH ratio (around 60:40) and NaOH concentration (10-12M) before fine-tuning precursor ratios and water content. The non-linear relationships identified between specific parameter values and strength impacts further highlight the complexity of geopolymer systems and demonstrate the value of machine learning approaches in capturing these intricate interactions.

It is of interest to note that the machine learning models developed in this study are based on a focused dataset of 45 mix designs. While this represents comprehensive coverage of the parameter space investigated, model predictions outside the studied ranges should be approached with caution. The models are most reliable for interpolation within the investigated parameter ranges rather than extrapolation beyond them.