CHAPTER III

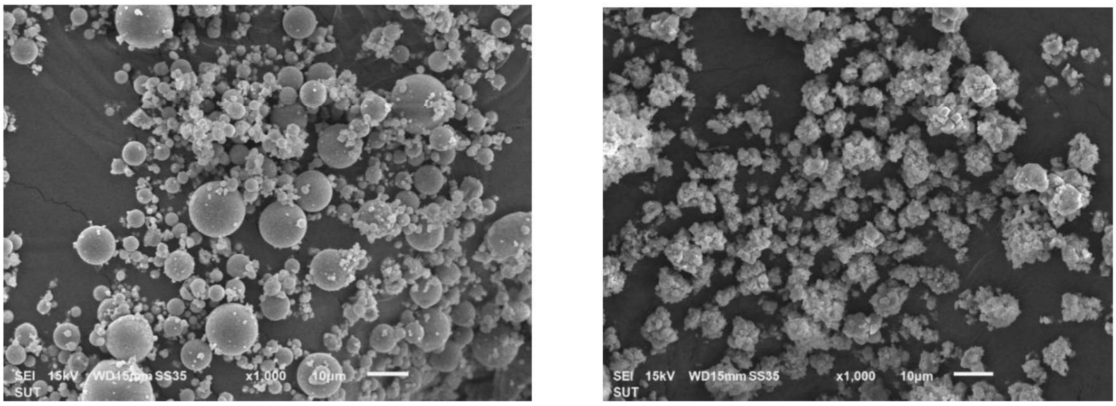
RESERCH METHODOLOGY

3.1 Materials

3.1.1 Precursor Materials

This study investigated calcium carbonate sludge (CCS) as a potential alternative precursor to partially replace conventional fly ash (FA) in geopolymer systems. The FA used in this study was obtained from Mae Moh Power Plant, Lampang Province, Thailand, which is a lignite coal-fired power plant. The FA was collected from electrostatic precipitators and classified as Class C fly ash according to ASTM C618 due to its high calcium content (CaO: 28.72%). The CCS was collected as a by-product from a sugar refinery plant in Nakhon Ratchasima, Thailand. This CCS was generated during the sugarcane juice clarification process, where lime ($Ca(OH)_2$) was added to remove impurities through precipitation. The CCS was air-dried for 3 days, followed by oven-drying at 105°C for 24 hours to remove residual moisture. The morphological characteristics of both materials were examined using scanning electron microscopy (SEM) as shown in **Figure 3.1**. FA displayed the smooth and spherical particle characteristic typical of coal combustion by-products (**Figure 3.1a**); a morphology that typically facilities reactivity due to high surface area and enhanced dissolution kinetics. In contrast, CCS exhibited irregular and agglomerated particles with rough surface textures (**Figure 3.1b**), reflecting its origin as a precipitated waste material from sugar processing.

X-ray diffraction (XRD) analysis provided critical insights into the crystalline composition of both precursors. The FA pattern (**Figure 3.2a**) revealed primary crystalline phases of quartz, mullite, and hematite, with a pronounced amorphous hump between 20° and 30° at 2θ, indicating substantial reactive aluminosilicate content essential for geopolymerization. The CCS diffractogram (**Figure 3.2b**) showed strong peaks for calcium oxide with minor quartz and alumina phase, indicating its potential role as a calcium-enriching additive rather than a direct aluminosilicate source.

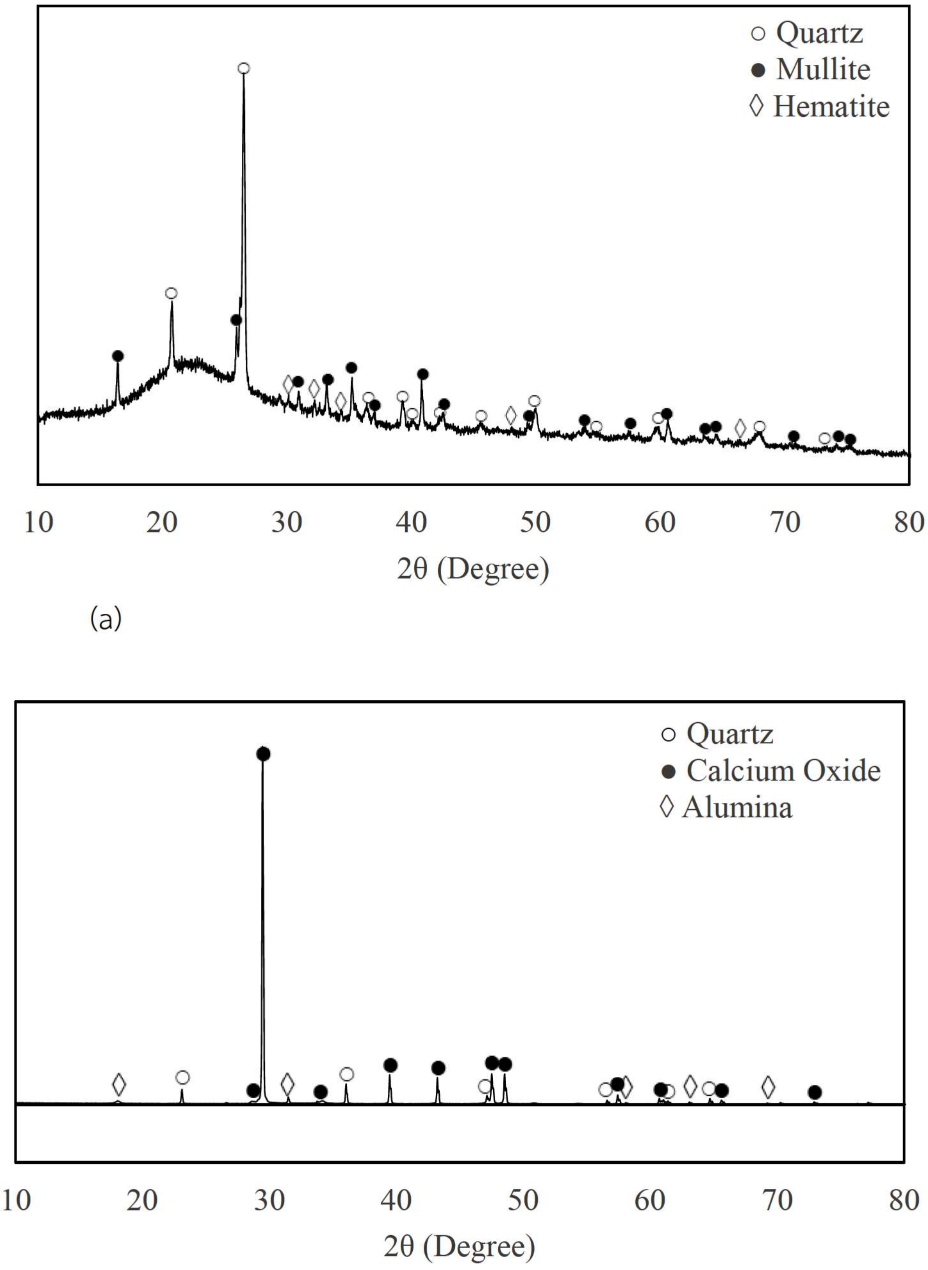


(a) (b)

Figure 3.1 SEM image of (a) FA and (b) CCS.

Chemical composition analysis (**Table 3.1**) quantified the fundamental differences between these materials. FA contained significant proportions of silicon dioxide (29.31%) and aluminum oxide (11.01%), which are the primary network-forming components in geopolymer systems. The notable calcium oxide content (28.72%) classified this as a high-calcium fly ash, potentially contributing to additional reaction pathways. CCS demonstrated an exceptionally high calcium oxide concentration (94.64%) with minimal silica (3.11%) and alumina (1.36%), indicating its potential to modify reaction kinetics and final product characteristics when used as a partial replacement for FA.

Particle size distribution analysis (**Figure 3.3**) revealed that CCS possessed a finer overall particle distribution than FA, with 100% of CCS particles passing through approximately 100 μm compared to 300 μm for FA. This comparative fineness of CCS indicated potential benefits for matrix densification and enhanced reactivity when incorporated into geopolymer systems, potentially offsetting some limitations of its chemical composition when used as a partial substitute for FA.



(a)

(b)

Figure 3.2 X-ray diffraction patterns of (a) FA and (b) CCS.

Table 3.1 Chemical composition of fly ash and calcium carbonate sludge.

Chemical Composition	Fly ash (%)	CCS (%)
Silicon dioxide (SiO_2)	29.31	3.11
Iron oxide (Fe_2O_3)	14.87	0.28
Aluminum oxide (Al_2O_3)	11.01	1.36
Calcium oxide (CaO)	28.72	94.64
Magnesium oxide (MgO)	3.42	-
Sulfur trioxide (SO_3)	10.48	0.79

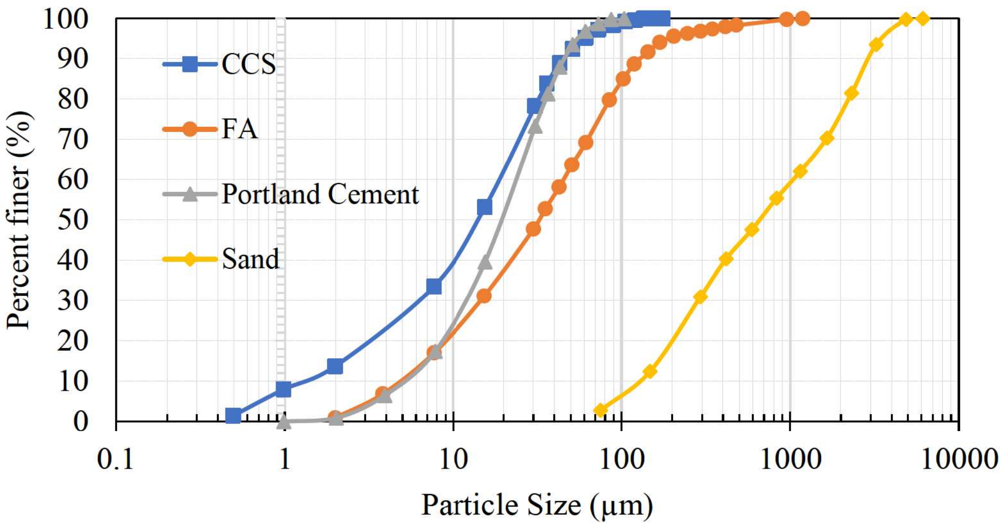


Figure 3.3 Grain size distribution of CCS, FA, Portland Cement, and Sand.

3.1.2 Fine Aggregate

Standardized fine aggregate (river sand) was employed across all mixtures to isolate the effects of precursor substation. The aggregate properties (**Table 3.2**) included a saturated surface dry specific gravity of 2.65, dry specific gravity of 2.60, dry unit density of 1604 kg/m3, and a fineness modulus of 2.7. **Figure 3.3** shows the grain size distribution of sand.

Table 3.2 Basic physical and engineering properties of fine aggregate.

Properties	Value
Saturated surface dry specific gravity	2.65
Dry specific gravity	2.6
Percentage of voids (%)	38.2
Dry unit density (kg.m^{-3})	1604
Absorption (%)	0.74
Moisture content (%)	2.46
Fineness modulus	2.7

3.1.3 Alkaline Activators

The alkaline activation system comprised sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) solutions. Sodium hydroxide of analytical grade (98% purity) was dissolved in distilled water to prepare solutions of three different molarities: 5M, 10M, and 15M. These solutions were prepared 24 hours prior to use to allow for complete dissolution and cooling to ambient temperature.

Commercial-grade sodium silicate solution with a density of 1.45 g/cm^3 was used as the silicate source in the activator system. The sodium silicate possessed a modulus ratio (SiO_2/Na_2O) of 2.5, with chemical composition comprising 30.1% SiO_2, 12.0% Na_2O, and 57.9% H_2O by weight. The viscosity of the solution measured 400-600 mPa·s at 20°C, providing appropriate flow characteristics for mixing while ensuring adequate silica availability for geopolymer network formation.

These activator solutions were systematically combined in ten different sodium silicate-to-sodium hydroxide ratios, ranging from 0:100 to 90:10 SS:SH (**Table 3**). This variation enabled precise control of both the overall alkalinity (pH) and the dissolved silica content of the activation solution, two critical factors influencing geopolymerization mechanisms, particularly when investigating precursors with different chemical compositions.

3.1.4 Mix Design

The experimental program was designed to systematically evaluate CCS as a partial replacement for FA across a comprehensive range of activation parameters. As detailed in **Table 3.3**, the study included: (1) Control cement mortars at three liquid-to-binder (l/b) ratios (0.3, 0.4, 0.5) to establish baseline performance metrics. (2) Reference FA-based geopolymer mortars with no CCS substitution, tested across ten sodium silicate-to-sodium hydroxide ratios (0:100 to 90:10 SS:SH), three NaOH concentrations (5M, 10M, 15M), and three l/b ratios (0.3, 0.4, 0.5). (3) FA+CCS blended geopolymer mortars with three CCS replacement levels (10%, 20%, 30%), systematically evaluated across all activator combinations and l/b ratios. The selected FA:CCS ratios of 100:0, 90:10, 80:20, and 70:30 were chosen to systematically investigate the effect of gradual replacement of aluminosilicate-rich FA with calcium-rich CCS. Prior studies have demonstrated that incorporating moderate levels of calcium-rich additives such as CCS or calcium carbide residue into FA-based geopolymers can promote C-A-S-H gel formation and improve early-age strength and microstructural densification (Hanifa et al., 2025). However, high levels of calcium can interfere with N-A-S-H gel formation. Therefore, this study limited the CCS content to a maximum of 30% to avoid excessive dilution of reactive aluminosilicates while enabling hybrid gel formation. The l/b ratios were selected based on previous literature (Wang et al., 2023), which suggests that geopolymer mortars typically achieve optimal workability and strength within this range.

3.1.5 Sample Preparation

Sample preparation followed a rigorous protocol designed to ensure consistency across all test specimens. Precursor materials (FA and CCS) were first proportioned by weight according to the designated replacement levels and thoroughly blended with the standardized fine aggregate in a laboratory mixer at low speed for 2 minutes to achieve homogeneous distribution.

Table 3.3 Mix proportion of geopolymer mortars.

Mix Ingredients	Mix ID	Na_2SiO_3 /NaOH	NaOH (M)	l/b	Fly Ash (FA)	Calcium carbonate sludge (CCS)	Sand (g)
Cement Mortar	Control	-	-	0.3,0.4,0.5	-	-	400
FA	0SS:100SH	0:100	5M,10M,15M	0.3,0.4,0.5	100%	-	400
FA	10SS:90SH	10:90	5M,10M,15M	0.3,0.4,0.5	100%	-	400
FA	20SS:80SH	20:80	5M,10M,15M	0.3,0.4,0.5	100%	-	400
FA	30SS:70SH	30:70	5M,10M,15M	0.3,0.4,0.5	100%	-	400
FA	40SS:60SH	40:60	5M,10M,15M	0.3,0.4,0.5	100%	-	400
FA	50SS:50SH	50:50	5M,10M,15M	0.3,0.4,0.5	100%	-	400
FA	60SS:40SH	60:40	5M,10M,15M	0.3,0.4,0.5	100%	-	400
FA	70SS:30SH	70:30	5M,10M,15M	0.3,0.4,0.5	100%	-	400
FA	80SS:20SH	80:20	5M,10M,15M	0.3,0.4,0.5	100%	-	400
FA	90SS:10SH	90:10	5M,10M,15M	0.3,0.4,0.5	100%	-	400
FA+CCS	0SS:100SH	0:100	5M,10M,15M	0.3,0.4,0.5	90%,80%,70%	10%,20%,30%	400
FA+CCS	10SS:90SH	10:90	5M,10M,15M	0.3,0.4,0.5	90%,80%,70%	10%,20%,30%	400
FA+CCS	20SS:80SH	20:80	5M,10M,15M	0.3,0.4,0.5	90%,80%,70%	10%,20%,30%	400
FA+CCS	30SS:70SH	30:70	5M,10M,15M	0.3,0.4,0.5	90%,80%,70%	10%,20%,30%	400
FA+CCS	40SS:60SH	40:60	5M,10M,15M	0.3,0.4,0.5	90%,80%,70%	10%,20%,30%	400
FA+CCS	50SS:50SH	50:50	5M,10M,15M	0.3,0.4,0.5	90%,80%,70%	10%,20%,30%	400
FA+CCS	60SS:40SH	60:40	5M,10M,15M	0.3,0.4,0.5	90%,80%,70%	10%,20%,30%	400
FA+CCS	70SS:30SH	70:30	5M,10M,15M	0.3,0.4,0.5	90%,80%,70%	10%,20%,30%	400
FA+CCS	80SS:20SH	80:20	5M,10M,15M	0.3,0.4,0.5	90%,80%,70%	10%,20%,30%	400
FA+CCS	90SS:10SH	90:10	5M,10M,15M	0.3,0.4,0.5	90%,80%,70%	10%,20%,30%	400

The pre-prepared alkaline activator solution, having been formulated 24 hours in advance to ensure thermal equilibrium and complete dissolution, was then gradually introduced into the dry mixture under continuous agitation. Following complete addition of the activator, mixing continued at medium speed for an additional 3 minutes to ensure uniform incorporation of all components and initiation of the geopolymerization reaction. The fresh mortar was then transferred to 50mm cubic molds for compressive strength testing and appropriate configurations for setting time evaluation, with all specimens subjected to vibration compaction to eliminate entrapped air and ensure uniform density throughout. To prevent moisture loss during the critical initial setting period, molds were immediately sealed with impermeable plastic film following casting. The sealed specimens were then subjected to standardized curing conditions optimized for geopolymer formation, with controlled temperature and humidity maintained throughout the maturation period.

3.2 Testing Methods

3.2.1 Setting Time Test

The setting time of geopolymer mortars was determined using the Vicat needle apparatus in accordance with ASTM-C191 . The procedure involves measuring the initial and final setting times to evaluate the effects of varying mix proportions and activator compositions. For each mixture composition, three replicate specimens were tested to ensure reliability and repeatability of results. The reported values represent the mean of three measurements with error bars indicating standard deviation.

3.2.2 Compressive Strength Test

The compressive strength of the mortar specimens was evaluated at 7 days using a universal testing machine following ASTM-C109/C109M . Prior to testing, each specimen was measured for dimensional accuracy and inspected for defects. The compression testing was performed using a calibrated universal testing machine with a maximum capacity of 250 kN. The loading rate was maintained at 1.0 ± 0.2 MPa/s in accordance with the standard. The load was applied until failure occurred, and the maximum load was recorded. For each mixture composition, three replicate specimens were tested, and the average compressive strength was calculated. Statistical variation was assessed through standard deviation calculations, which were represented as error bars in all strength development figures.

3.2.3 Scanning Electron Microscopy (SEM)

SEM analysis was performed to examine the microstructural characteristics of the geopolymer mortars. Samples were sputter-coated with gold to ensure conductivity and minimize charging effects. Imaging was conducted at accelerating voltages of 15 kV under high vacuum conditions, with working distances optimized for each magnification range (1000x for raw materials and 3500x for geopolymer mortars).

3.2.4 X-ray Diffraction (XRD)

Phase identification and crystallinity assessment were conducted via XRD analysis on powdered samples passing the 45 μm sieve. Diffraction patterns were collected over a 2θ range of 10° to 80° with a step size of 0.02° and a counting time of 1 second per step following ASTM-C1365 .

3.2.5 Machine Learning Analysis

The experimental dataset comprising 45 geopolymer mortar mix designs was prepared for machine learning analysis with input features including FA:CCS ratio, SS:SH ratio, NaOH molarity, and l/b ratio. The dataset included mean values from triplicate testing, ensuring that the machine learning models were trained on statistically representative data rather than individual test variations. These four parameters were selected based on their demonstrated influence on geopolymer properties in prior research. All features were normalized using StandardScaler prior to model development to ensure equal weighting during the learning process.

Four machine learning algorithms were systematically evaluated based on their established capabilities for handling complex, non-linear materials science data:

XGBoost, CatBoost, AdaBoost, and Support Vector Machine (SVM). Despite the relatively modest dataset size (n = 45), gradient boosting methods were included due to their demonstrated effectiveness in materials optimization problems with limited samples. Bayesian optimization identified optimal hyperparameters for each algorithm, while 5-fold cross-validation ensured model robustness against overfitting. Models were evaluated using R^2, MSE, and RMSE metrics to comprehensively assess predictive performance.

The highest-performing model underwent SHapley Additive exPlanations (SHAP) analysis to quantify feature influence on strength predictions, providing mechanistic interpretation of compositional effects on geopolymer properties. All implementations utilized Python 3.8 with appropriate machine learning libraries (scikit-learn, XGBoost, CatBoost, SHAP).