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Compressive Strength and Setting Time of Mill Scale – Low Calcium Fly Ash Based Geopolymer Paste

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The development of environmentally friendly construction materials is stimulated by the need for construction with a minimal carbon footprint. The development includes the usage of abundant industrial wastes such as Mill Scale waste (MS) and Fly-ash (FA) to replace Ordinary Portland Cement (OPC) concrete which greatly contributes to the reduction of carbon emission. The MS waste produced from rolling mills of steel bars can be used as partial replacement for FA based geopolymer mix. In this study, partial replacement of 20 %, 30 % and 40 % MS by weight of low calcium (Class F) FA for developing geopolymer paste with varying sodium hydroxide-to-sodium silicate (NaOH-to-WG) ratio of 1:2.5, 1:2 and 1:1, in 50 mm x 50 mm x 50 mm cube specimens were tested under unconfined compressive strength (UCS) test to evaluate their mechanical performance. It is observed that the specimens with 20 % MS-to-FA ratio and 1:2.5 NaOH-to-WG ratio gives the higher UCS value. The setting time of the geopolymer mixes is also recorded to show its relationship to the varying design mixes. Regression models are generated through Response Surface Methodology (RSM) to provide coefficients in obtaining desired UCS values.

1. Introduction

The production and general utilization of ordinary Portland cement (OPC) as building material has a significant contribution to the overall carbon emission produced in construction (Wardhono et al. 2019). Monteiro et al. (2017) reported that producing concrete includes about 9 % of carbon dioxide (CO2) emissions globally. With over 90 % of the total emission, cement is responsible for the most greenhouse gas (GHG) emissions in concrete production (Miller 2018). The use of cement replacement materials is encouraged to lower the carbon footprint. One alternative is the use of fly ash in geopolymer making as alternative to cement-based concrete (Abulencia et al., 2021). Geopolymers, which consist mainly of precursor such as fly ash (FA) and activators such as sodium hydroxide (NaOH) and sodium silicate or waterglass (WG), are being extensively investigated nowadays. Dollente et al. (2021) reported that around 28 % global warming reduction is observed for precast products made of geopolymers compared with OPC based products. A main precursor in geopolymer making is fly ash, which is categorized into two categories: a) high calcium (Class C) fly ash, and b) low calcium (Class F) fly ash with calcium content of lower than 10 % of its mass (ASTM C618-19). In the recent study by Quiatchon et al. (2021), the primary factor that affects a low calcium FA based geopolymer is the water-to-solid (W/S) ratio. W/S affects all response parameters: initial setting time, final setting time, and unconfined compressive strength (UCS). A lower W/S ratio of 0.2 resulted in higher compressive strength and faster setting times.
In order to extend the overall environmental impact of geopolymers, other precursors are being investigated for possible partial or full replacement to fly ash in FA based geopolymer making. Tigue et al. (2021) investigated the mechanical performance of coal fly ash (CFA) and nickel laterite mine spoils (NMS) geopolymer composite. It is observed that geopolymer composite with NMS-to-CFA ratio of 1:1 provides around 22 MPa comparable to the 20.7 MPa standard compressive strength for Class A OPC-based concrete as described by the Department

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of Public Works and Highways (DPWH) and American Society for Testing and Materials (ASTM) (Association of Structural Engineers of the Philippines, 2015).

Another possible source for alternative materials is the waste produced by steel industry. In steelmaking processes, which include rolling mills, about 500 kg of solid waste is generated (Bagatini et al. 2011). Among these wastes are iron-rich fine-grain scales, sludge and dust. When these iron-rich wastes are disposed in landfills, it releases toxic substances in soil and ground water making them harmful to the environment (Kargin et al. 2022). Finding options to reuse and recycle these waste materials will help in the conservation of the environment. Using iron-rich waste, such as mill scale, can lower carbon footprint due to the reduction of cement utilization and the recycling of wastes and by-products (Kamitsou et al. 2022). A study by Kumar et al. (2021) used recycled industrial wastes such as coal dust, red dust, iron ore fines, slags and mill scale in making geopolymer. The study claims that replacing 30 % of fly ash with mill scale increased the compressive strength up to 15 % compared to control sample of 100 % fly ash based geopolymer. The NaOH-to-WG ratio of the study was maintained at constant (17.5:23.62 by mass) of 45 % w/w sodium silicate solution for the design mixes. NaOH-to-WG ratio affects the resulting mechanical strength of geopolymer (Quiatchon et al. 2021). Varying the NaOH-to-WG ratio in MS-FA based geopolymer is necessary. In this study, mill scale waste obtained from a local rolling mill of steel bars in the Philippines was used as partial replacement to low calcium FA on geopolymer mixes with varying NaOH-to-WG (1:2.5, 1:2, and 1:1).

2. Materials and Methodology

For the precursors, the mill scale powder with specific gravity of 5.41 and a fineness modulus of 3.76 was obtained from the steel mill of Pag-asa Steel Works, Inc. in Pasig City, Philippines. The fine grain-size materials, the particle size distribution analysis was determined by standard procedures as described by ASTM C136 using sieve analysis. The specific gravity was obtained through guidelines of ASTM C128.

2.1 Materials

The material chemical compositions of the mill scale samples were determined by X-ray Fluorescence (XRF) test using Rigaku test equipment. The fly ash, classified as low in calcium (Class F), was obtained from Pozzalanic Philippines Inc. (PPI) with productions of FA from Batangas, Philippines. The chemical compositions are as shown in Table 1.

Table 1: Chemical composition of fly-ash and mill-scale

Chemical Properties	Fly-ash (mass %)	Mill-scale (mass %)
Silicon Dioxide (SiO_2)	57.2	0.463
Aluminium Trioxide (Al_2O_3)	21.8	3.12
Ferric Oxide (Fe_2O_3)	4.73	ND
Calcium Oxide (CaO)	6.9	0.183
Magnesium Oxide (MgO)	9.9	ND
Sulfur Trioxide (SO_3)	1.23	0.759

The alkali activator was prepared using sodium hydroxide (NaOH) flakes with 98 % purity manufactured by Formosa Plastic Corporation in Taiwan, and sodium silicate (WG) with main chemical composition of SiO_2 (34.13 %), Na_2O (14.65 %) and H_2O (51.22 %).

2.2 Parameters

A factorial design was facilitated, and two factors – (a) the mill scale-to-fly ash ratio, and (b) NaOH-to-WG ratio – with 3 levels of each factor were used. Table 2 shows the parameters of each factor. Shown in Table 3 is the 9 runs generated. The activator-to-precursor ratio was kept at 0.38 while the water-to-solid ratio was kept at 0.3 in accordance with optimum values obtained by the study of Quiatchon et al. (2021) for Class F fly ash used.

Table 2: Parameters of each factor

Factors	Low Level	Mid-Level	High Level
Factor 1: Mill scale-to-Fly ash ratio by mass	0.2 (20 %)	0.3 (30 %)	0.4 (40 %)
Factor 2: NaOH-to-WG ratio by mass	0.4 (1:2.5)	0.5 (1:2)	1 (1:1)

Table 3: Factorial experiment design (9 runs)

Runs	1	2	3	4	5	6	7	8	9
F1 ratio by mass	0.3	0.2	0.4	0.2	0.3	0.2	0.4	0.4	0.3
F2 ratio by mass	1 (1:1)	1 (1:1)	0.5 (1:2)	0.5 (1:2)	0.4 (1:2.5)	0.4 (1:2.5)	0.4 (1:2.5)	1 (1:1)	0.5 (1:2)

2.3 Experimental Procedure

The experiment followed the procedures described on the standard test methods of ASTM C109 for the preparation and casting of 50 mm cube specimens, while ASTM C191 was used for the preparation and procedures on the determination of time setting using Vicat needle. To start with, the mass of precursors was estimated to fill a specified volume in order to fill five 50 mm x 50 mm x 50 mm cube moulds and a conical ring for the recording of the setting time. In this study, 1,300 g of fly ash was used to fill the moulds; and partial replacement of 20 %, 30 % and 40 % of mill scale by weight of fly ash were used for the experimental runs. Using the activator-to-precursor ratio of 0.38 by mass, the mass of NaOH and waterglass were determined. For this experiment, the amount of water to be used was determined by a constant water-to-solid ratio of 0.3 by mass. The NaOH flakes were dissolved with the water and kept at a cool place until the solution was cooled down. The corresponding weight of waterglass was then added to the solution, continuous stirred for 5 min. The activator solution was mixed with the precursor for 8 min using an automatic cement mortar mixer. After mixing, the paste was poured to two sets of 3-gang 50 mm cube moulds producing 5 replicates of each run and to the conical ring for the setting time. The cubes were tamped and compacted to remove excess air in the specimens. The specimens were allowed to rest for at least 24 h before demoulding. After demoulding, the samples were wrapped with cling plastic film as the curing technique and were left to an undisturbed area with relative humidity of 40± 6 % and an ambient temperature varies from 34 °C to 38 °C for 28 days before testing.

2.4 Testing

The initial and final setting times were determined as per ASTM C191 using 1-mm Vicat needle. The initial setting time was determined to be the time elapsed from the initial time of mixing to the time when the penetration of the Vicat needle was at 25 mm from the top of 40 mm high conical ring. The final setting time was determined to be the time elapsed from the initial time of mixing to the first time when no penetration of the Vicat needle can be recorded on the surface of the specimen.

After 28 days of curing, the geopolymer cube specimens were subjected to unconfined compressive strength (UCS) test following the standards described as per ASTM C109. The UCS test was administered using MATEST SpA Treviolo (250 kN) with a loading rate of 0.9 kN/s. The UCS of each sample can be calculated as the maximum load recorded divided by the cross-sectional area of the specimen which is perpendicular to the load force.

3. Results and Discussion

The three response parameters were recorded along with the two factors in a user defined factorial design using Design Expert 11 (Design Expert® software, version 11). The factors and responses for the 9-run factorial design of experiment are shown in Table 4. The factors which include MS-to-Fa ratio and NaOH-to-WG ratio are correlated to three responses: Initial Setting Time, Final Setting Time and Unconfined Compressive Strength. The average UCS of five replicates of each run is used for the analysis of UCS response parameter.

Table 4: Design data and results

Run Order	Factor 1: MS-to-FA ratio	Factor 2: NaOH-to-WG ratio	Response 1: Initial Setting Time (min)	Response 2: Final Setting Time (min)	Response 3: Ave. Compressive Strength (MPa)
1	0.3 (30 %)	1 (1:1)	307	455	4.03
2	0.2 (20 %)	1 (1:1)	180	405	8.36
3	0.4 (40 %)	0.5 (1:2)	111	245	7.13
4	0.2 (20 %)	0.5 (1:2)	120	190	9.81
5	0.3 (30 %)	0.4 (1:2.5)	172	310	12.69
6	0.2 (20 %)	0.4 (1:2.5)	60	125	24.24
7	0.4 (40 %)	0.4 (1:2.5)	109	205	14.91
8	0.4 (40 %)	1 (1:1)	120	255	3.53
9	0.3 (30 %)	0.5 (1:2)	187	335	11.53

Figure 1: Initial Setting Time (Line graph) with corresponding compressive strength (boxplot) per run

Shown in Figure 1 is the initial setting time of each run overlaid to its corresponding UCS result to show the trend and correlation between the two responses. It can be observed that runs with longer setting time tends to provide lower compressive strength compared to runs with faster setting time.

3.1 Factors affecting Initial and Final Setting Times

Based on the studies of Quiatchon et al. (2021), the major contributor affecting the setting time of the low calcium FA based geopolymer paste is the water-to-solid ratio. In this study, as the water-to-solid ratio is kept to a constant value of 0.3, the observed significant factor affecting the setting time is the NaOH-to-WG ratio. It can be observed that the specimens with alkali activator ratio (NaOH-to-WG) of 0.5 (1:2) and 0.4 (1:2.5) shows faster initial setting times, ranges from 60 min to 120 min, compared to those specimens with ratio of 1 (1:1).

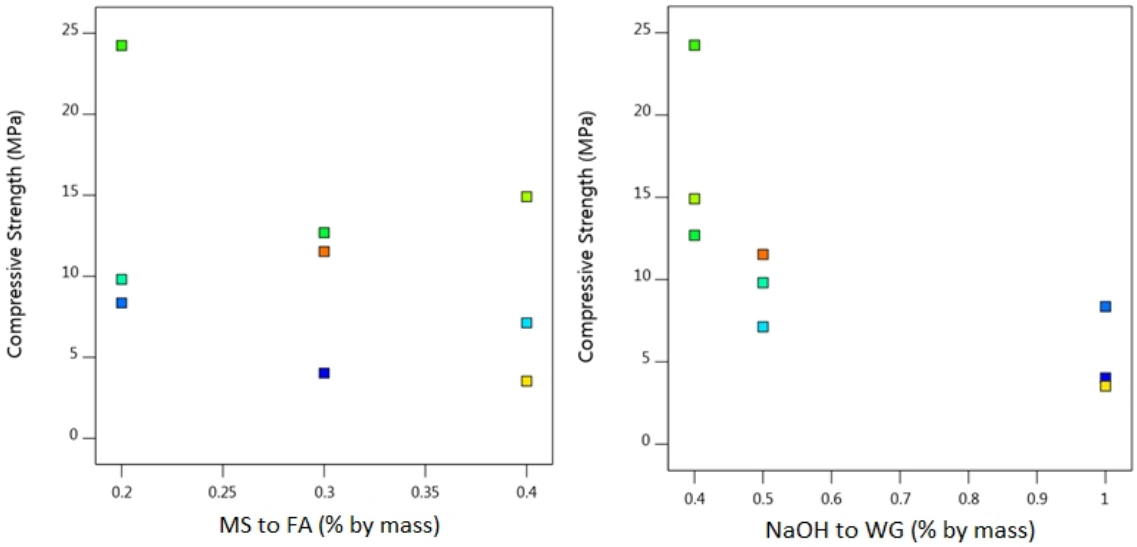

Figure 2: a) Correlation coefficient of MS-to-FA % by mass with Compressive Strength = 0.384 and b) Correlation coefficient of NaOH-to-WG % by mass with Compressive Strength = 0.713

3.2 Factors affecting compressive strength

The UCS responses have a correlation coefficient of 0.713 with the NaOH-to-WG ratio for the MS-FA based geopolymer paste specimens as shown in Figure 2b. This follows the observation for the two response parameters reported that the specimens with NaOH-to-WG ratio of 0.4 (1:2.5) provides faster setting time and yields higher average compressive strength. It is observed that 3 out of 9 runs yields UCS higher than 11.8 MPa

which is the strength of Class F OPC-based concrete used for levelling based on the standards set by DPWH and ASTM (Association of Structural Engineers of the Philippines, 2015). The 3 runs observed are specimens with NaOH-to-WG ratio of 0.4 (1:2.5), out of which, the specimens with 20 % MS-to-FA replacement yields UCS higher than a Class A OPC-based concrete used for concrete structures and pavements (20.7 MPa).

3.3 Response Surface Analysis

In this study, Response Surface Methodology (RSM) is used for the analysis of the responses. This is used for optimizing two or more factors to obtain a desirable response, in this case, the UCS of MS-FA based geopolymer paste. Regression models are generated using the current data to achieve at least a 95 % confidence interval for the models and to facilitate the fitting curve and prediction of points. The factorial design of experiment and its responses were run through a computer-aided factorial design in Design Expert 11. The statistical analysis, as recommended by the standard transformation generated by the software, followed a square root transformation on the quadratic regression model for the initial setting time. There is no need for standard transformation on the quadratic model for the final setting time and on the linear model for compressive strength. The regression models are as shown and the summary of the Analysis of Variance (ANOVA) for the models are shown in Table 5.

$$\text{Sqrt(Initial Setting Time)} = + 16.19 - 0.261A + 1.77B - 1.07AB - 4.10A^2 - 1.26B^2 \quad (1)$$

$$\text{Final Setting Time} = + 409.11 - 15.56A + 79.17B - 58.79AB - 129.17A^2 - 30.50B^2 \quad (2)$$

$$\text{Compressive Strength} = + 9.61 - 2.81A - 4.87B \quad (3)$$

Where A = Mill Scale-to-Fly Ash Ratio and B = NaOH-to-WG ratio.

Table 5: Summary of ANOVA results for the three regression models

Model	F-Value	p-Value	Mean	Std. Dev.	R-Squared	Adjusted R^2
Eq (1)	10.2	0.0423	12.04	1.07	0.9444	0.8519
Eq (2)	167.17	0.0007	280.56	10.35	0.9964	0.9905
Eq (3)	5.72	0.0407	10.69	4.29	0.6560	0.5413

The p-Values of the equations generated as shown in Table 5 are lower than 0.05 that indicates that the generated models are statistically significant. Also, the F-Values are significant enough to ensure that the predicted values that will be obtained using the models are most likely not due to noise. These supports the possible use of the generated models for predicting factor coefficients even if the R-squared value or the fitness of the model to the true values of UCS is only 0.66. Using the generated regression models, optimized runs can be done, maximizing the possible compressive strength and within a desired limit of initial and final setting time. Confirmatory test is needed to further verify the regression models.

4. Conclusions

Waste from steelmaking industry is an attractive source of iron-rich materials that can be used in geopolymer making to replace ordinary Portland cement and lower the overall carbon footprint of construction. In this study, mill scale (MS) waste produced by rolling mills of steel bars is used as partial replacement for a low calcium fly ash (FA) based geopolymer mix. The performance of MS-FA geopolymer paste is determined through setting time and unconfined compressive strength. It can be observed that the significant factor affecting the setting time is the NaOH-to-WG ratio considering that the water-solid ratio is to be kept constant at 0.3 and the activator-to-precursor ratio is to be kept constant at 0.38. Specimens with lower NaOH-to-WG ratio, that is 0.4 (1:2.5), experienced faster initial setting time (ranging from 60 min to 172 min) and final setting time (ranging from 125 min to 310 min) compared to specimens with ratios 0.5 (1:2) and 1 (1:1). Additionally, it can be observed that the specimens with NaOH-to-WG ratio of 0.4 (1:2.5) yields the higher unconfined compressive strength, ranging from 12.69 MPa to 24.24 MPa. It can also be observed that the specimens with MS-to-FA ratio of 0.2 yields the higher compressive strength. Response Surface Methodology is used to generate regression models to analyse and optimize factors in obtaining a favourable response. A confirmatory experiment must be performed to verify the RSM models generated.

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