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Factors Affecting the Setting Time and Compressive Strength of Alkali Activated Ground Granulated Blast Furnace Slag Reinforced with Wollastonite

Valeria A. Gonzalez, Benjamin Varela, Joseph Voelkel

Abstract—We conducted a Design of Experiments to analyze and optimize the effect of the SiO2/K2O , H2O/K2O molar ratios of a Potassium base activating solution, slag/solution, Wollastonite/Slag mass ratios and mixing amount in the compressive strength and setting time of alkali activated Ground granulated Blast Furnace Slag. It was found that the total amount mixed had little to no effect in the compressive strength and the setting time. The setting time was largely affected by the slag/solution mass ratio followed by the SiO2/K2O molar ratio in the activating solution. For the compressive strength the larges correlation was found in the joint effect of the slag/solution and Wollastonite/slag mass ratios. The optimum formulation had seventh day compressive strength of 8000 Psi (55 Mpa) and setting time of 36 minutes was found when the activating solution had molar ratios of SiO2/K2O =1, H2O/K2O =10 and mass ratios of slag/solution = 1.75 and Wollastonite/Slag=0.37.

Index Terms — Geopolymers, Alkali Activation, Ground Granulated Blast Furnace Slag, Non-Traditional Cements, Wollastonite, Design of Experiments.

I. INTRODUCTION

The beneficial use of solid industrial wastes has found a niche application in the construction and cement industries. There are many benefits resulting from the reuse of these wastes, especially in the production of ordinary Portland cement. Portland cement is of critical importance for the construction industry of the nation. In 2011, approximately 66 million metric tons of cement were produced in the United States, worth approximately 6.6 billion dollars (van Oss 2012). Despite its importance, Portland cement production has a negative environmental impact. The production of one ton of cement is energy intensive, releases approximately one ton of CO_2 and uses large quantities of virgin raw material (Harditjo & Rangan 2005). For this reason Ground Granulated Blast Furnace Slag (GGBFS), among other industrial wastes, has been used to partially replace the amount of clinker in the production of Portland cement (EPA 2009). The substitution of virgin raw materials by less expensive industrial wastes saves energy, reduces construction costs and in some cases it yields concretes with enhanced mechanical properties.

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Alkali-activated binders present similar or better mechanical properties than those based on Portland cement. This higher performance has led to extensive research on the topic showing significant conclusions on the economic and environmental benefits of using this material in the construction industry. Previous research shows that alkali-activated binders develop a hig early compressive strength, lower hydration heat, better resistance to chemical attack, better behavior upon carbonation, higher resistance of the aggregate matrix interface, better behavior to freeze-thaw cycles, among others (Wang, Pu & Scrivener 1995; Tailing & Brandster 1989). Additionally these binders also exhibit rapid setting times, high shrinkage resulting in micro-cracks, and in some cases higher formation of salt efflorescence (Puertas 1995).

GGBFS is a by-product from the iron and steel manufacturing industry. It is produced through the rapid cooling of the molten slag that floats on top of the molten iron in the furnace. The rapid cooling is induced by immersion in water and results in a glassy, granular product that is then dried and ground into fine powder. Its chemical composition includes SiO_2, CaO, MgO and Al_2O_3, with small traces of Fe_2O_3, K_2O and Na_2O. Its chemical composition, amorphous nature and fineness allows GGBFS to react with alkaline solutions producing a cementitious material.

Activators based on sodium hydroxide, sodium silicate and sodium sulfate have been widely used to activate GGBFS. Published results suggest that activators composed of a mixture of sodium silicate and sodium hydroxide yield mortars with higher compressive strengths (Fernandez-Jimenez,Palomo & Puertas 1999). However, empirical observations show that sodium based activators are more prone to efflorescence than activators base on potassium solutions. Efflorescence not only produces an undesirable look in the samples but also tends to decrease their strength.

Wollastonite is a crystalline calcium metasilicate ($CaSiO_3$) mineral which occurs in metamorphosed siliceous limestones, and in alkaline igneous rocks. Wollastonite rocks are grounded and impurities such as garnet removed by high intensity magnetic separators. This process yields mineral microfibers with an acicular shape, an average size of 40µm and aspect ratio of 15:1, although these dimensions can vary depending on the processing. Some of the interesting physical properties of Wollastonite include high melting temperature (1410 ^oC), low coefficient of thermal expansion (6.5 x 10-6 mm/mm/^oC) and hardness of 4.5 in the Mohs scale (Nyco 2012).

The combination of physical properties and morphology make Wollastonite microfibers an important material in applications where enhanced durability and strength are required. Wollastonite microfibers have proved to increase compressive and tensile strengths, reduced shrinkage and crazing, increase durability during freeze-thaw cycles in concrete formulations and improve the fracture toughness in alkali activated pastes (Silva 7 Thaumaturgo 2002).

The capacity of ground granulated blast furnace slag (GGBFS) to react with an alkali solution forming a material with properties comparable to Portland cement was first reported by A.O. Purdon (1940). During the 1950's, due to cement shortages in the former Soviet Union, extensive research to develop alternative binders using metallurgical slags was conducted by V.D. Glukhovsky, who named these binders as "soil cements". However much of this work was unknown in the West until recent years. P. Krivenko, who continued this research in Ukraine, named this binders "geocements" due to the similarities between the characteristics of these products and those of some natural minerals. Starting in the 1960's, several construction projects based on the alkali activation of slag were carried out in the former Soviet Union and China. Some examples include concretes for residential buildings, masonry blocks, irrigation ditches and roads among others (Shi, Krivenko & Della 2006).

The performance of alkali activated slag binders can be considerably affected by mixing proportions, slag fineness, aggregate volume and the type and amount of activating solutions. For this reason, a design of experiments was conducted with the objective of analyzing and understanding the individual and joint effects of the SiO_2/K_2O, H_2O/ K_2O molar ratios of the activating solution, slag/solution and Wollastonite/slag mass ratios as well as the total amount mixed in the setting time and compressive strength of the paste. The setting time was measured using a Vicat needle immediately after mixing while the compressive strength was taken 7 days after curing. An optimal formulation has been proposed considering the results obtained throughout these experiments. This formulation compromises a balance between compressive strength and setting time.

In addition, the linearly of the ratios' effect was investigated. The initial hypothesis was that if the effect of all ratios is linear, then the response values at the center points could be accurate predicted by the response values in the corner points. The replicated center points could also provide a direct estimate of the variation in the response.

II. METHODS

A. *Design of Experiements*

The design of experiments consisted of 20 runs, where each run was equal to one batch of slag binder, and one batch generated 12 samples. This design is called 2^{5-1} half-fraction factorial with 4 center points. The *half-fraction factorial* design is usually run in early stages of experimentation in order to reduce resources needed in half; 16 out of the 20 suggested points were located on the extremes of the design. These extremes are runs in which each factor is set to its low or high levels. As mentioned before, the remaining 4 runs were in the center of the design, and every factor was set to its middle setting. Table I show the factors with their units, as well as their low, middle and high level values. The high setting values had to be changed after performing the first 20 runs due to the lack of workability of the paste. For these cases, the mass ratio of Wollastonite/slag was modified from 0.5 to 0.37 and slag/solution from 2 to 1.75.

Table I. Factors and levels tested in the design of experiments. The SiO_2/K_2O and H_2O/K_2O molar ratios correspond to the activating solution. Note that the mass ratios for the high levels were modified from Wollastonite/Slag = 0.5 to 0.37 and Slag/Solution = 2 to 1.75 to improve workability.

Table I. Factors and levels tested in the design of experiments.

Factor	Units	Low	Center	High
SiO_2 /K_2O	mole ratio	1	1.5	2
H_2O/K_2O	mole ratio	10	15	20
Slag/Solution	mass ratio	1	1.5	2
Wollastonite/Slag	mass ratio	0	0.25	0.5
Total Amount	mass, kg	1	1.5	2

The SiO_2/K_2O and H_2O/K_2O molar ratios correspond to the activating solution. Note that the mass ratios for the high levels were modified from Wollastonite/Slag = 0.5 to 0.37 and Slag/Solution = 2 to 1.75 to improve workability.

B. Materials

St. Mary's Cement Ground Granulated Blast Furnace Slag

Table II Chemical composition of Granulated Blast Furnace Slag in oxide percentages as provided by the supplier.

Oxide	CaO	SiO_2	Al2O3	MgO	Na_2O	K_2O	SO_3
Mass Percent	38.3	37	8	10.5	0.25	0.43	1.7

The activating solution was produced with a 45% KOH solution (Brainerd Chemical Company), distilled water, and silica fume (Aerosil 300). These materials were properly weighted and mixed to achieve the SiO_2/K_2O and H_2O/ K_2O molar ratios previously shown in Table I. The solution was left to mature for 24 hours. Wollastonite (NYAD G, NYCO Minerals) was used as reinforcement in some of the experiments.

C. Procedure

The mixing amounts of GGBFS, activating solution, and Wollastonite for each run were determined by the design of experiments procedure shown in Table I. These materials were mixed in a Hobbart mixer until a homogenous paste was observed. The resulting paste was casted in cylindrical molds,

Table III. Best Subsets method results for setting time. Optimal model is shaded in gray.

Best Subsets Regression: Setting Time vs. Total Amount Mixed, SiO_2/ K_2O, H_2O/ K_2O, Slag/Solution and Wollastonite/Slag									
No. of Variables	R^2	R^2 (adj)	Mallows Cp	S	SiO_2/K_2O	H_2O/K_2O	Slag/Solution	Woll/Slag	Total Amount Mixed
1	61.4	59.3	2.6	24.862			x		
1	6.3	1.1	29.3	38.756	x				
2	67.7	63.9	1.6	23.415	x		x		
2	64.6	60.4	3.1	24.509			x	x	
3	70.9	65.4	2.1	22.92	x		x	x	
3	67.8	61.7	3.6	24.103	x		x		x
4	70.9	63.2	4	23.637	x	x	x	x	
4	70.9	63.2	4	23.637	x		x	x	x
5	71	60.7	6	24.43	x	x	x	x	x

Table IV. Best Subsets method results for compressive strength. Optimal model is shaded in gray.

Best Subsets Regression: 7 days Compressive Strength vs. SiO_2/ K_2O, H_2O/ K_2O, Slag/Solution and Wollastonite/Slag									
No. of Variables	R^2	R^2 (adj)	Mallows Cp	S	SiO_2/K_2O	H_2O/K_2O	Slag/Solution	Woll/Slag	Total Amount Mixed
1	33.9	30.2	2.2	1524.7			X		
1	4.0	0.0	10.5	1837.2	x				
2	46.9	40.6	0.7	1406.5			X	x	
2	35.6	28.0	3.8	1548.5	x		X		
3	48.6	38.9	2.2	1426.2	x		X	x	
3	47.2	37.3	2.6	1444.7			X	x	x
4	48.9	35.3	4.1	1467.7	x		X	x	x
4	48.9	35.3	4.1	1468.4	x	x	X	x	
5	49.3	31.1	6.0	1514.4	x	x	X	x	x

Table V. Analysis of Variance table for the linear regression model between the response variable, setting time, and the egressor variables, wollastonite/slag, slag/solution and SiO2/K_2O.

Analysis of Variance Table Setting Time Analysis					
Source	**Degrees of Freedom (DF)**	**Sum of the Squares (SS)**	**Mean Square (MS)**	**F-ratio**	**P-value**
Regression	3	20437	6812.3	12.967	0.000149
Residual Error	16	8405.5	525.3		
Total	19	28842.5			

Table VI. Analysis of Variance table for the linear regression model between the response variable, compressive strength, and the regressor variables, wollastonite/slag and slag/solution.

Analysis of Variance Table Setting Time Analysis					
Source	**Degrees of Freedom (DF)**	**Sum of the Squares (SS)**	**Mean Square (MS)**	**F-ratio**	**P-value**
Regression	2	29663666	14831833	7.50	0.005
Residual Error	17	33627749	1978103		
Total	19	63291414			

Vibrated to remove any air bubbles, wrapped in plastic to avoid water evaporation, and cured at 85 ^{O}C for 12 hours. After curing, all samples were left at room temperature until the day of testing. A minimum of 4 samples were tested for compressive strength after 7 days and one sample was used to measure the setting time with a Vicat needle immediately after mixing. Based on empirical observations and for the purpose of quantification of the setting time for this study, we defined it as the elapsed time after mixing when the penetration of the Vicat needle was 15 mm.

III. RESULTS

Data collection was conducted using the aforementioned procedures and methodology. Figures 1 and 2 present the cube plots of the results obtained for compressive strength and setting time.

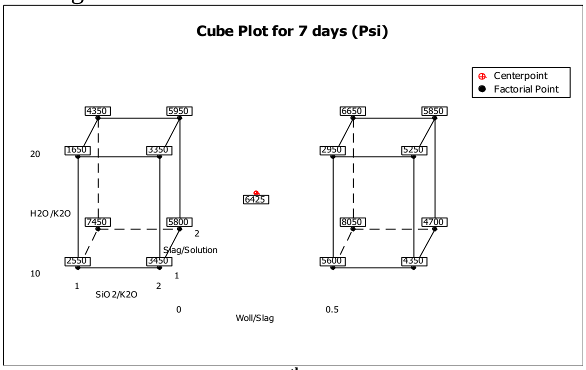

Figure 1. Cube plot showing the 7th day compressive strength results from the Design of Experiments

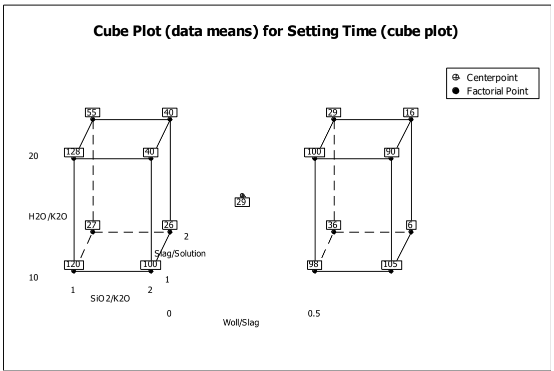

Figure 2. Cube plot for setting time as measured by the Vicat needle from the design of experiments.

A linear regression analysis with the results from the cube plots was performed using Minitab. The best subset variable selection was used in order to determine if a correlation in fact existed between total amount mixed, the SiO_2/ K_2O, H_2O/ K_2O molar ratios in the activating solution, slag/solution and Wollastonite/slag mass ratios, and the response variables, which were setting time and compressive strength. This analysis allowed to identify the leading factors that impact the response variables. These results are presented in tables III and IV. The optimal model was chosen to minimize the number of variables while increasing R^2, minimizing standard deviation, and reaching a C_P value closer to the number of parameters in the model.

Table III shows that setting time is best explained by slag/solution, SiO_2/K_2O, and Wollastonite/slag ratios. This model can explain 70.9% of the variability in the data. Similarly, table IV shows that compressive strength heavily depends on slag/solution and Wollastonite/slag mass ratios. These two variables account for 46.9% of the data variability.

Based on the best subsets results, the optimal model was further analyzed using Analysis of Variance as presented in table V and VI.

The following hypothesis test was constructed in order to complete a more thorough analysis of this model and obtain additional proof of correlation. The null hypothesis (equation 1) states that there is no significant difference between the variables, therefore no relationship exist between them. On the other hand the alternative hypothesis (equation 2) implies that a relationship exist for at least one of the ratios of interest.

$$H_0 : \beta_1 = \beta_2 = ... = \beta_k = 0$$

(No relationship between variables) (1)

$H_a : \beta_j \neq 0$ For at least one j

(relationship exist) (2)

The F-statistic value that was used to evaluate these hypothesis was $F_{\propto,n,n-k-1} = F_{0.05,3,16} = 3.24$ for setting time, and $F_{\propto,n,n-k-1} = F_{0.05,2,17} = 3.59$ for compressive strength.

If the F-values provided by the general regression model are higher than the F-statistic, then this would allow rejecting the null hypothesis. The Analysis of Variance for both test are displayed in tables V and VI respectively. The calculated F-value for setting time, $F_0 = 12.967$, which is significantly greater than its corresponding F-statistic ($F_{0.05,3,16} = 3.24$). An analogous result was obtained from the compressive strength analysis where $F_0 = 7.50$, which is also greater than $F_{0.05,2,17} = 3.59$. In addition, the p-values obtained from both tables were considerably low, verifying the validity of the results. Therefore, by rejecting H_0 the existence of correlation is confirmed between the response and the regressor variables.

Furthermore, the variables' joint effect was examined and they are presented in figures 3 to 6. Figure 3 presents the scatterplot of setting time vs. SiO_2/K_2O molar ratio and figure 4 displays how, averaged over all other conditions, a larger molar ratio of SiO_2/K_2O decreases the setting time of the samples by approximately 20 minutes.

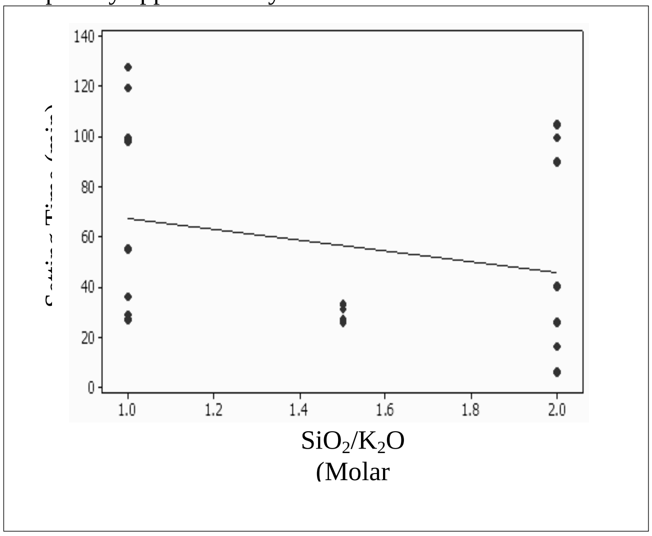

Figure 3. Raw data scatterplot of Setting Time vs. SiO_2/K_2O for all 20 runs.

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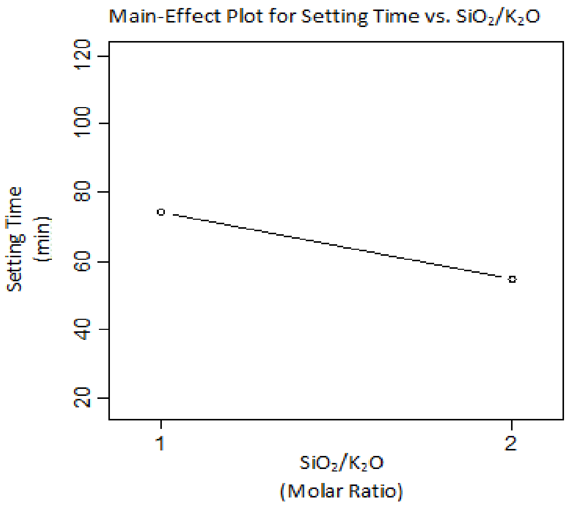

Figure 4. Main-Effect plot for Setting Time vs. SiO_2/K_2O displaying the average over all conditions tested.

Figures 5 and 6 present the interaction between Wollastonite/slag and slag/solution mass ratios and their effect on setting time and compressive strength. It is important to mention that the initial high/high setting level for these two factors did not achieve a workable mixture, for this reason the condition (1.75, 0.37) was used instead . From figure 5, it can be concluded that as the level of Wollastonite/slag and slag/solution increases, the setting time decreases, hence reducing the workability of the paste. On the other hand, in average, increasing the amount of Wollastonite for any ratio of slag/solution increases the compressive strength; this effect is presented in Figure 6.

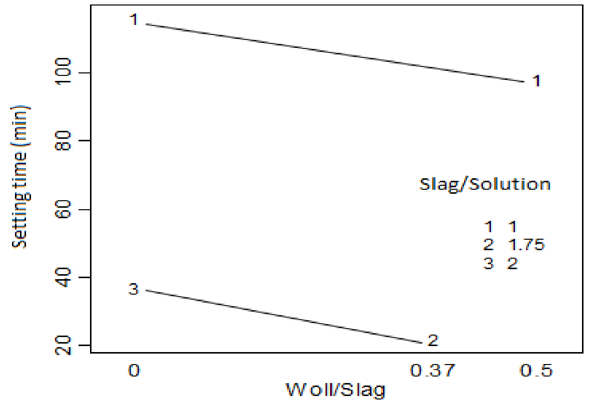

Figure 5. Interaction plot of setting time vs. low, medium and high setting levels of wollastonite/slag and slag/solution mass ratios

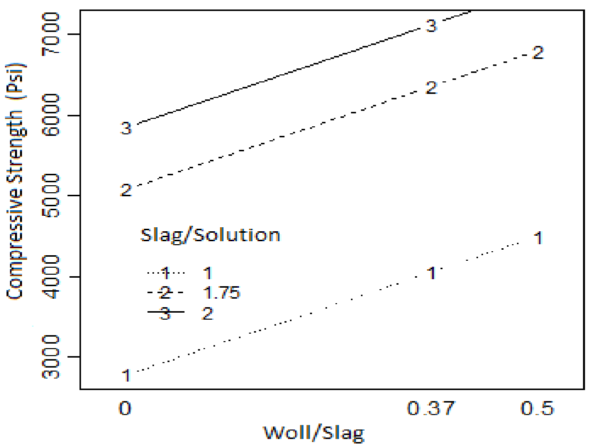

Figure 6. Interaction plot for 7 day compressive strength for low, medium and high levels of Wollastonite/slag and slag/solution ratios.

Figure 7 shows the correlation between compressive strength, slag/solution, and Wollastonite/slag for each solution ratio of the activating solution. The graphs were arranged by solution ratios allowing the comparison of SiO_2/ K_2O from up-down, and H_2O/ K_2O from left-right. For practical purposes, the unmixable samples' compressive strength was assumed to be zero. It was noticed that as the amount of Wollastonite and slag increases, so does the compressive strength. However, once the Wollastonite/slag = 0.5 and slag/solution = 2 the paste become unmixable. Therefore, once the formulation reaches an optimal performance, measured by the highest compressive strength, increasing the ratios of Wollastonite/slag and slag/solution has the opposite effect and the compressive strength declines.

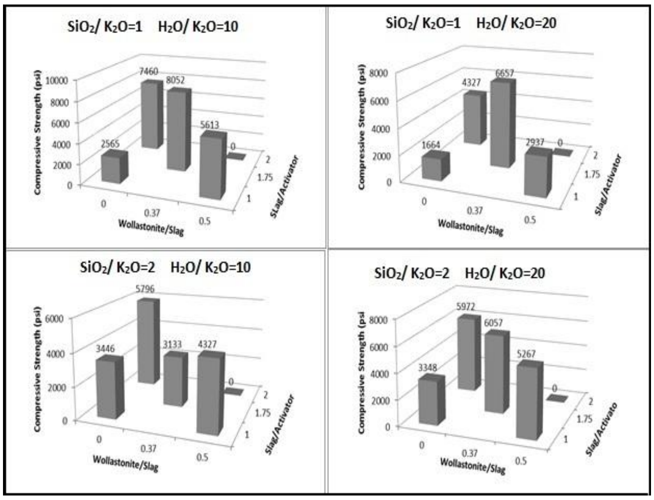

Figure 7. Relationship between compressive strength, wollastonite/slag, and slag/solution for each of the different molar ratios in the activating solution.

IV. CONCLUSIONS

From the 5 regressor variables initially used in the regression model, the total amount mixed showed no significant impact on either of the response variables. It was determined that a high correlation exist between setting time and the slag/solution, SiO_2/K_2O, and Wollastonite/slag ratios. As the slag/solution and Wollastonite/slag mass ratios increase, the setting time decreases. There is a similar trend when increasing SiO_2/K_2O molar ratio in the activating solution.

According to the results from this research, the optimal formulation for alkali-activated slag binders must have a low SiO_2/K_2O molar ratio in the activating solution, with high mass ratios of slag/solution and Wollastonite/slag without passing the binder's workability level. The optimal compressive strength found after 7 days of curing was of 8050 psi (55 MPa) with a setting time of 36 minutes . This compressive strength corresponds to the mix with molar ratios in the activating solution of SiO_2/K_2O=1, H_2O/K_2O=10, mass ratios for slag/solution=1.75 and Wollastonite/slag=0.37 (low/low/high/high combination). Since it was found that H_2O/K_2O has a small effect on compressive strength, it is recommended to further investigate the impact of higher levels of this molar ratio to modify the setting time without affecting the mechanical properties of the binders.

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