

Coventry University and
The University of Wisconsin Milwaukee Centre for By-products Utilization
Second International Conference on Sustainable Construction Materials and Technologies
June 28 - June 30, 2010, Università Politecnica delle Marche, Ancona, Italy.
Proceedings of Honouree sessions ed. T Naik, F Canpolat, P Claisse, E Ganjian,
ISBN 978-1-4507-1487-7 <http://www.claisse.info/Proceedings.htm>

Incorporating Physical and Chemical Characteristics of Fly Ash in Statistical Modeling of Binder Properties

Prasanth Tanikella and Jan Olek

School of Civil Engineering, Purdue University, 550 Stadium Mall Drive, West Lafayette, IN, 47907, USA. E-mail: <ptanikel@purdue.edu>, <olek@purdue.edu>.

ABSTRACT

Twenty different fly ashes (containing both the ASTM class C and F ashes), obtained from power plants in and around Indiana, were characterized during this study. Various properties, including set time, heat of hydration, strength activity index at 28 days and the amount of calcium hydroxide formed at 28 days were determined for plain portland cement system and for 20% cement replacement fly ash systems. The obtained results were used to build statistical models for prediction of the same properties based on the fundamental chemical and physical characteristics of fly ashes, including their mean and median particle size, fineness, chemical composition and the glass. The models were based on the most significant variables, which were found to affect that specific property. It was observed that the sets of statistically significant variables were unique for each property evaluated, the specific surface area being the common variable.

INTRODUCTION

The usage of fly ashes as a substitute for cement in concrete has increased drastically over the past three decades and replacements of up to 25% have become a common practice on the US market. Even higher replacement levels (up to 50 %) are occasionally used as a part of so-called high volume fly ash binders [Jiang *et al.* 2004].

Large assortment of fly ashes, with widely varying physical and chemical characteristics, is available for the utilization in concrete. However, in most cases, the selection of the type and the amount of fly ash needed for particular application is based predominantly on the local availability of the material and prior experience. This approach generally works well if the source of the fly ash remains relatively stable with respect to basic physical and chemical characteristics and availability. However, considering the recent fluidity of the fly supply chain, with qualities and quantities of the material frequently changing in response to the environmental regulations imposed on the power plants, a more streamlined approach to selection of fly ashes is desired. Such approach could potentially be developed if a tool existed which could better link the properties of the ashes with concrete performance. The objective of this paper is to present the methodology for development of such tool and to illustrate its applicability by linking (via statistical models) the physical and chemical characteristics of twenty different fly ashes (both Class C and Class F) with several properties of binary (cement + fly ash) paste systems.

The underlying assumption for present work was that the properties of the paste systems containing fly ash (dependent variables) were directly influenced by the fundamental physical

and chemical characteristics of the fly ash (independent variables). As such, the goal of the research was to perform statistical evaluation of the impact of certain characteristics of fly ashes on the behavior of pastes. If any of the characteristics of the fly ashes were found to play a statistically significant role in the paste's behavior, empirical models using these independent variables would be developed to predict the dependent variables i.e. the properties of the paste systems. The properties that were modeled as part of this study included: initial time of set, parameters related to heat of hydration, calcium hydroxide content at 28 days and strength gain at 28 days (in terms of the strength activity index).

MATERIALS

Fly Ash. Twenty different fly ashes (13 Class C and 7 Class F) obtained from electric power plants in and around the state of Indiana, USA, were utilized in the study. When discussed in the paper, all ashes are labeled using the name of the source plant.

Cement. The ASTM C150 Type I portland cement was used in the study. The summary of physical and chemical characteristics of this cement is shown in Table 1.

Table 1. Physical and Chemical Characteristics of Cement

Chemical Data (%)		Physical Data	
Silicon Dioxide	20.04	Air Entrained (%)	9.2
Aluminum Oxide	6.00	Fineness (cm ³ /gm)	3700
Ferric Oxide	2.27	Autoclave Expansion (%)	0.054
Calcium Oxide	64.56	Compressive Strength (psi)	
Magnesium Oxide	1.22	1-day	2610
Sulfur Trioxide	2.83	3-day	4350
Loss on Ignition	1.10	7-day	5430
Sodium Oxide	0.09	Setting time (Vicat)	
Potassium Oxide	1.00	Initial, min	97
Total Alkali as Na ₂ O	0.75	Final, min	191
Insoluble Residue	0.28		

Sand. The ASTM C778 standard graded sand from the Ottawa, Illinois, USA source was used in the investigation. The specific gravity of the sand was 2.65.

FLY ASH CHARACTERIZATION

All fly ashes obtained for the study were subjected to a rigorous testing process to evaluate their physical and chemical characteristics. The results of these tests were analyzed and used in developing statistical models for predicting properties of the paste systems in which part of the cement was replaced by a particular fly ash. The summary of the experimental techniques used, along with the properties evaluated, is given in Table 2. The properties listed in Table 2 were selected for testing either because they are required by ASTM C 618 standard or because they were considered to have a potential influence on the performance of pastes containing these ashes. Although most of the experimental techniques mentioned in

Table 2 can be classified as standard, the method used to assess the relative glass contents of fly ashes is not, and is therefore briefly described in the next section.

Table 2. Summary of Experimental Techniques used to characterize the Listed Properties of Fly Ashes

Properties Evaluated (Characteristics)	Experimental Technique
Content of major elements*	X-ray Fluorescence
Loss on Ignition*	ASTM C 311
Sulfates*	Ion Chromatography
Alkalis	Atomic Absorption
Particle Size Distribution	Laser Diffractometry and Pipette Analysis
Specific Surface Area	Laser Diffractometry and Blaine's Apparatus
Crystalline Components	X-ray Diffraction Analysis
Relative Glass Content	X-ray Diffraction Analysis ⁺⁺
Morphology of Ashes	Scanning Electron Microscopy

*Test required by ASTM C 618, ⁺⁺ by evaluation of the area of the "glass hump"

Relative glass content determination. The relative (with respect to the fly ash having the lowest value) glass contents of fly ashes used in the study were estimated by measuring the area under the glass hump in the X-ray diffraction pattern. This semi-quantitative method of glass content determination utilized the approach similar to that previously described by Diamond [Diamond, 1983], who traced the outline of the glass hump on the X-ray diffraction pattern in order to correlate the location of the maximum peak of the trace with the analytical content of CaO. For the set of fly ashes used in the study, the glass hump was located between 15° to 55° 2θ.

The process of determining the area under the glass hump involved the following three steps:

1. The first step involved elimination of all peaks due to the crystalline phases from the glass-containing part of the X-ray diffraction pattern. This was accomplished by manually selecting a series of equally spaced points that were located on the "hump" line and at the bases of the individual peaks. In addition to eliminating the peaks, the process also reduced the random background noise as the points were chosen manually and had a higher spacing than the collected data points. Software called "xyExtract" was then used to remove the pre-selected data points from the pattern. The process of extraction of the points from the X-ray diffraction curve is illustrated in Figure 1.
2. Once the points were extracted, a 6th order polynomial curve was fitted through them using the software called "LAB Fit". While performing this operation, it was observed that a single equation could not be used to represent the analyzed segment of the X-ray pattern with sufficient accuracy. Hence, the glass hump portion of the X-ray pattern was split into two at the peak value of the hump. Subsequently, two different equations were used to define the complete pattern, Equation 1 for the points before the peak and Equation 2 for the points after the peak (as shown in Figure 2).

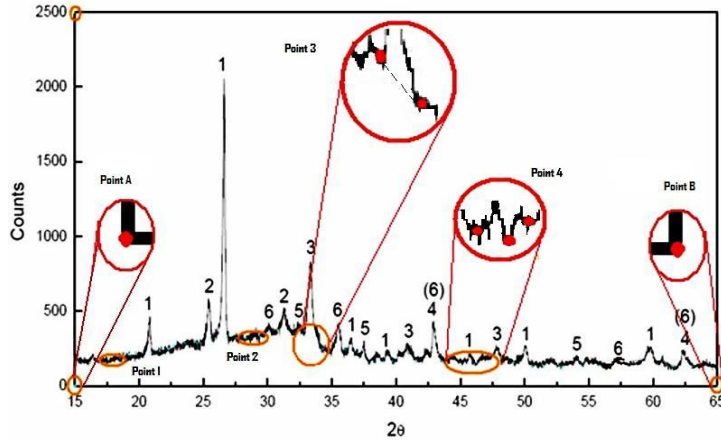


Fig. 1. Extraction of Points from the X-ray Pattern

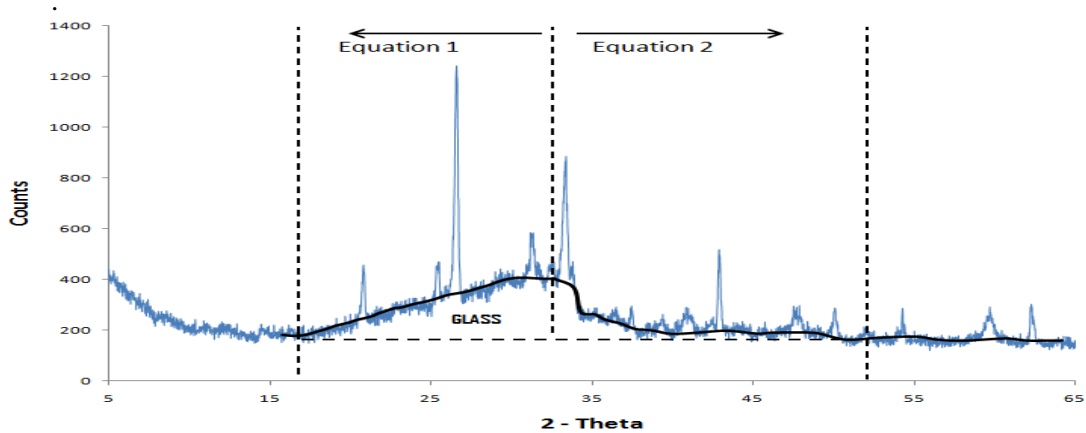


Fig. 2. Area of the Glass hump and Ranges of 2θ Covered by Equations 1 and 2 for the Baldwin Fly Ash

3. Finally, software named “Sicyon Calculator” was used to estimate the total area under the curve, by integrating the previously mentioned polynomial equations between the minimum and maximum values of 2θ for a given pattern. In order to determine the glass content indicated by the X-ray pattern, the area under base line of the curve was deducted from the total area obtained from the integration of the polynomial curve as shown in Figure 2. The relative glass content values were, in turn, used as input parameters to the performance prediction models described later in this paper.

MIX DESIGN AND TESTING OF PASTE SYSTEMS

The experimental techniques used to characterize the hydration related properties of fly ash-cement pastes (the time of set, parameters describing the heat of hydration, the rate of strength gain, the rate of formation of calcium hydroxide and the non-evaporable water content of the pastes at different ages (1, 3, 7 and 28 days)) are given in Table 3.

All paste mixtures used in this study were designed at constant water to binder ratio of 0.41. The fly ash substitution for cement was also constant (20% by weight). The proportions of mortar used for measuring the rate of strength gain were in accordance to ASTM C 311.

Table 3. Properties of Pastes Evaluated and the Corresponding Test Methods Used

Property	Test Method
Initial Time of Set	Vicat Needle
Peak Heat of Hydration	Isothermal Calorimetry
Time of Peak Heat of Hydration	Isothermal Calorimetry
Rate of Strength Gain	ASTM C 311
Calcium Hydroxide Content	Thermogravimetric Analysis
Non-evaporable Water Content	Thermogravimetric Analysis

BASIS FOR STATISTICAL ANALYSIS

The objective of the modeling process utilized in this study was to use the statistical linear regression analysis to identify the best set of independent variables (physical and chemical characteristics of fly ashes) which most strongly affect a dependent variable (property of the binary paste systems). However, the modeling process was not a straightforward linear regression analysis, as it was assumed that the single model to predict the properties for the entire suite of fly ashes might not be feasible. The reasons are as follows:

1. The set of fly ashes used in the study contained two different kinds of ashes, ASTM Class C ashes and ASTM Class F ashes. The ashes were markedly different in their fundamental physical and chemical compositions and hence, it should be expected that their influence on the behavior of paste would be different.
2. The available number of data points for modeling the set of ashes was similar to the number of independent variables available to explain the variations in the dependent variables. In addition, the number of independent variables was greater than the number of data points available for Class F ashes.

To counteract the above two challenges, the following modeling methodology was adopted.

A linear regression analysis was performed on the dependent variables using Statistical Analysis Software (SAS), which included data points from all 20 fly ashes. The “best set of variables” (with greatest impact on the dependent variable) was chosen based on the highest adjusted R^2 value of the models. All the data points were, in turn, predicted using the same models (and thus using the same “best set of variables”) but built separately for the dependent variable for the 13 data points of Class C ashes and 7 data points of Class F ashes. The trustworthiness of these predictions can be evaluated by using the p-value of the model.

The number and set of variables used to predict the dependent variables (model containing the “best set of variables”) were kept the same for the models of both classes of fly ash. Further, these were restricted to three since (as already mentioned) the number of data points in the models was small (13 for Class C ashes and 7 for Class F ashes). Although an increase in the number of variables used to describe the variation in the dependent variable would lead to a good fit in the data, it will also result in an insignificant model. This would be reflected in the reduced ability of the model to predict the dependent variable for a new fly ash, which was not used as a data point in the modeling process.

RESULTS AND ANALYSIS (Initial Time of Set)

The complete set of data obtained from the characterization of the fly ashes and used in the models described in this paper can be found elsewhere [Tanikella 2009] and could not be reported here due to space limitations. Instead, this section contains the results of testing of paste properties, along with the statistical analysis and interpretation for initial time of set.

Along with the regression models themselves, their accuracy (in the form of the p-value for the model (if p-value < 0.1 model predictions are accurate)), the goodness of fit (in the form of the R^2 and adjusted R^2 of the model (the higher the adjusted R^2 , the better the fit of the model in the existing data)) and the parameter contribution (in the form of the p-values of the parameters) were also obtained. The sign of the parameter estimates was also used to indicate the relative effect of each of the parameter on the dependent variable. Statistical models were built for Class C ash-pastes and Class F ash-pastes separately, as the performance of the two categories of ashes showed a significant difference with respect to the properties of the paste systems.

Initial time of set (Class C ash – pastes). It can be seen from Figure 3 that eight of the thirteen Class C ash-pastes were found to have a lower setting time than the setting time of reference cement while four of the remaining five Class C ash-pastes had a higher setting time. One ash (Kenosha) was found to produce a flash set of the paste. Six out of the seven Class F ash-pastes were found to have a setting time higher than the reference cement, while the setting time of the remaining one fly ash-paste was marginally lower than that of the reference cement paste. It can be therefore stated that Class F ashes tend to delay the initial setting time. On the other hand, Class C ashes could either increase or decrease the setting time. The model with the best-adjusted R^2 value contained three variables, namely sulfate content (*sulfate*), alumina content (*alumina*) and relative glass content (*glass*). The regression table for initial time of set of Class C ashes model using these three variables is shown in Figure 5, while the predicted and observed set time values are plotted in Figure 4.

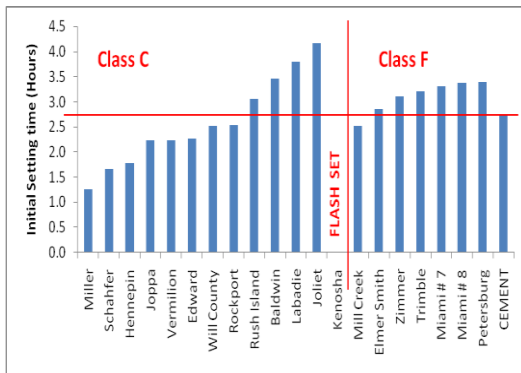


Fig. 3. Initial Time of Set for all the Paste Systems

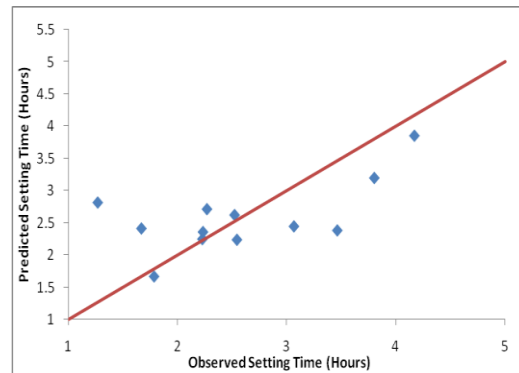


Fig. 4. Predicted vs Observed Initial time of Set for Class C Ash-Paste Systems

As expected [Neville 1981], the sign of the coefficient of sulfate was positive, indicating that the increase in the sulfate content leads to an increase in the setting time of the paste. The signs of alumina content and relative glass content were negative, thus implying that the

Source	DF	Sum of Squares	Mean Square	F Value	p-Value
Model	3	3.269	1.089	1.65	0.2543
Error	8	5.292	0.6615		
Total	11	8.561			
		R^2	0.3818		
		adj- R^2	0.15		
Variable	DF	Parameter Estimate	Standard Error	t-Value	p-Value
Intercept	1	4.456	4.112	1.08	0.3101
sulfate	1	1.178	0.644	0.183	0.1048
alumina	1	-0.085	0.235	-0.36	0.7267
glass	1	-0.583	0.619	-0.94	0.3738

Fig. 5. Regression (ANOVA) Table for Initial Time of Set for Class C Ash Pastes

increase in the amounts of either of the variables leads to a decrease in the setting time of the paste.

The p-values of the model and of the individual variables, which denote the significance of the model and each of these variables, respectively, were all greater than 0.1. This means that that model predictions are not very accurate and that the model does not explain a significant amount of the observed variation in the setting time. However, seven of the 12 predictions obtained from the model for Class C ash-pastes were within 30 minutes of the observed setting time of the ashes (as shown in Figure 4). This variation is acceptable as, according to ASTM C 191, “two different set times measured by a single operator in the same laboratory conditions were found to have a maximum variation of 34 minutes”. The results for the remaining five ash-pastes, whose setting time prediction differed from the observed setting time by more than 30 minutes, lie at the extremes of the range of the setting time of all the Class C ash-pastes. It can therefore be inferred that the model predicts well for the setting time between 1.7 and 3 hours, while any value of setting time not lying in this range cannot be predicted accurately.

Initial time of set (Class F ash – pastes). The ANOVA table for the linear regression model of the initial time of set for Class F ash pastes is shown in Figure 6 and the corresponding plot for the predicted and observed initial time of set using this model is shown in Figure 7.

The inferences from the p-values and the adjusted R^2 for this regression model and the sign of the coefficient for one of the independent variables (alumina) were inconclusive. While the previous research [Ma and Brown 1995] reported a negative coefficient associated with this particular variable, the coefficient obtained in the current research was positive. It was also seen that the errors for the parameter estimates were very high compared to the estimates themselves. None of the independent variables was significant, including the p-value for the model itself. Even though the adjusted R^2 for the Class F ash pastes model was higher than that of the model for Class C ash pastes, its prediction for any new fly ash is not reliable. The plot (Figure 7) shows a fair equality between the observed and the predicted setting times for Class F ash-pastes. However, none of the variables was even close to being significant and the p-value for the model was very high. As a result, this model cannot be utilized to predict the set time of any Class F ash-pastes.

Source	DF	Sum of Squares	Mean Square	F Value	p-Value
Model	3	0.44358	0.14786	1.63	0.3487
Error	3	0.27189	0.09063		
Total	6	0.71547			
		R^2	0.62		
		adj - R^2	0.24		
Variable	DF	Parameter Estimate	Standard Error	t-Value	p-Value
Intercept	1	1.26093	0.99826	1.26	0.2958
sulfate	1	0.46946	0.25233	1.86	0.1598
alumina	1	0.07325	0.0769	0.95	0.4111
glass	1	-0.0845	0.53944	-0.16	0.8855

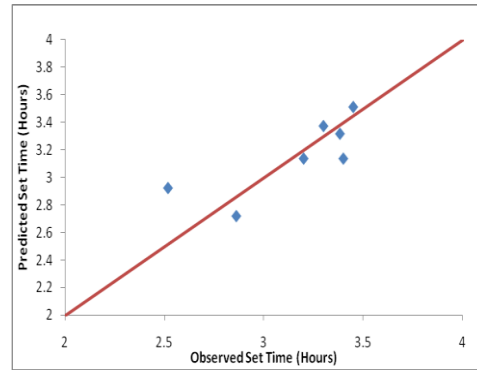


Fig. 6. Regression (ANOVA) Table for Initial Time of Set for Class F Ash Pastes

Fig. 7. Predicted vs. Observed Initial Time of Set for Class F Ash Pastes

RESULTS AND SUMMARY (Other Dependent Variables)

The category “other dependent variables” used in the study included the peak heat of hydration, the time of peak heat of hydration, the rate of formation of calcium hydroxide and the rate of strength gain. A summary of the results of the statistical linear regression is presented in Table 4.

Table 4. Results of the Statistical Procedures for all the Dependent Variables

Property	Class	Model p-value	Model R^2	Model Adjusted R^2	p-values		
					Sulfate	Alumina	Glass
Initial Time of Set	C	0.2543	0.38	0.18	0.1048	0.7267	0.3738
	F	0.3487	0.62	0.24	0.1598	0.4111	0.8855
Peak Heat	C	0.0484	0.5662	0.4216	Spsurface 0.0084	SAF 0.0172	Glass 0.1447
	F	0.4564	0.5343	0.0685	0.8168	0.2057	0.2479
Time Peak	C	0.1722	0.4103	0.2138	Spsurface 0.0533	Meansize 0.1302	Mgo 0.1064
	F	0.0698	0.8778	0.7556	0.0597	0.0656	0.2062
Calcium Hydroxide at 28 days	C	0.0135	0.719	0.614	Blaines 0.0021	Spsurface 0.4252	Sulfate 0.1818
	F	0.1602	0.89	0.725	0.227	0.093	0.1728
Strength at 28 days	C	0.0407	0.625	0.484	Meansize 0.0246	Sulfate 0.0135	SAF 0.9266
	F	0.0244	0.984	0.96	0.1029	0.0154	0.9835

Table 4 contains the p-value of the model, the R^2 , the adjusted R^2 of the model, the variables in the model and the p-values of each of the variables. The inferences from the statistical analysis are given below.

Peak heat of hydration. Significant differences were seen in the peak heat of hydration between pastes containing Class C and Class F ashes (Figure 8). Most of the Class C ashes reduced the peak heat of hydration compared to that obtained from plain cement. In contrast, most of the Class F ashes acted the other way, with a few exceptions. A slight indication of an increase in the set time with the peak heat of hydration was observed. The only fly ash, which exhibited a flash set, Kenosha, had a very low peak heat of hydration.



Fig. 8. Peak Heat of Hydration for all Paste Systems

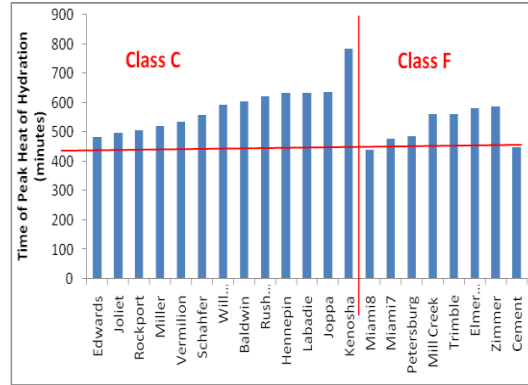


Fig. 9. Time of Peak Heat of Hydration for all Paste Systems

Specific surface area measured using the laser particle size analyzer (*spsurface*), the sum of the silicon, aluminum and iron oxides (*SAF*) and the relative glass content (*glass*) were found to be the most influencing variables affecting the peak heat of hydration. The model predictions for Class C ash-pastes were accurate, with the *spsurface* and the *SAF* variables being highly significant. Hence, the model predictions were reliable. The only insignificant variable in the model was *glass*. The model for Class F fly ash-pastes was not significant and hence the model predictions were considered as not reliable.

An increase in the specific surface area resulted in the decrease in the peak heat of hydration, with a few exceptions. However, the amount of calcium oxide (which is equivalent to 100% minus the sum of the oxides of silicon, alumina and iron) was also found to play a major role in defining the peak heat of hydration of the paste. This was found to be consistent with the literature [Fajun et al. 1985]. Most of the variation in the peak heat of hydration of the binder systems containing Class C ashes could be explained using these two variables.

Time of peak heat of hydration. With the exception of one, all ashes delayed the occurrence of the peak heat of hydration. Class C ash pastes had marginally higher time of the peak than Class F ash-pastes (Figure 9).

The physical characteristics of fly ashes were found to delay of peak of hydration more than their chemical characteristics. The specific surface area measured using the laser particle size analyzer (*spsurface*), the mean particle size (*meansize*) and the magnesium oxide content (*mgo*) were the most influencing variables. However, *spsurface* was found to be more significant the other two. The sign of the *spsurface* variable indicated that an increase in the specific surface leads to a delay in the occurrence of the peak heat of hydration. The model predictions for all the twenty available ashes seemed reasonable.

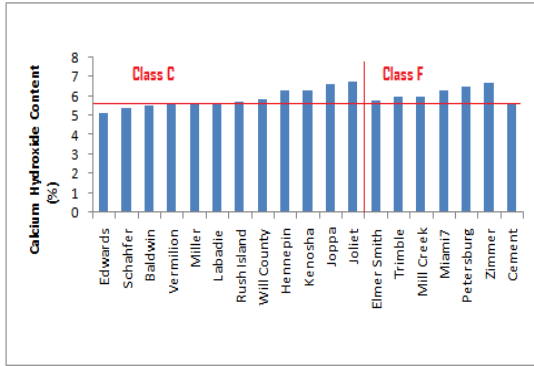


Fig. 10. Calcium Hydroxide Content at 28 Days for all the Paste Systems

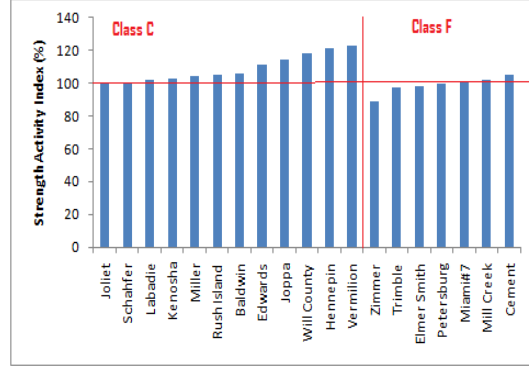


Fig. 11. Strength Activity Index at 28 Days for all the Paste Systems

Calcium hydroxide content. There was a significant increase in the of 28 days calcium hydroxide (CH) contents for quite a few of the Class C ash-pastes as compared to the plain cement paste (Figure 10). This was attributed to the hydration reaction in the Class C ashes. However, some of the ashes have shown a reduction in the rate of formation of calcium hydroxide from 7 to 28 days, leading to a conclusion that there was an inception of pozzolanic reaction in the binder systems. This indicates that the rate of hydration and that of the pozzolanic reaction can vary even within the same class of the fly ash.

The variables chosen for statistical modeling of CH content at 28 days included both physical and chemical characteristics i.e. Blaines specific surface area (*blaines*), specific surface area measured using the laser particle size analyzer (*spsurface*) and the sulfate content (*sulfate*). The model was found to be predicting accurately for Class C ash-pastes and not for Class F ash-pastes. Hence, the model for Class C-ash pastes can be used for predicting the calcium hydroxide contents.

Rate of strength gain. As seen in Figure 11, mortars with Class C ashes developed comparatively higher strength than mortars containing Class F ashes at 28 days.

The prediction models for 28 days were reliable. Both the models for Class C and Class F ash pastes were significant and had a very good fit. These models can be used to predict the strength activity index for fly ashes at later ages.

Mean particle and sulfate content were found to be major contributors to strength at 28 days for pastes containing both classes of ashes.

CONCLUSIONS

The statistical studies resulted in a conclusion that both the physical and the chemical characteristics of fly ash affect the properties of pastes containing ashes at all ages. The sets of variables affecting various binder properties were unique for each of the properties evaluated. However, the variable that was found to have the most significant effect on almost all paste properties was the specific surface area of the fly ash particles.

The sign of the coefficients of the significant variables indicates the type of effect the variables had on the particular property.

For most of the properties evaluated, the variables that affect the property the most could be easily identified using the proposed models. However, some of the properties evaluated had a high degree of variation, which could not be readily explained by any sets of characteristics of the fly ash.

REFERENCES

- Diamond, S. (1983). "On the Glass Present in Low-Calcium and in High-Calcium Flyashes." *Cement and Concrete Research*, 13, 459-464.
- Fajun, W., Grutzeck, M. W., & Roy, D. M. (1985). "The Retarding Effects of Fly Ash upon the Hydration of Cement Pastes: The First 24 Hours." *Cement and Concrete Research*, 15, 174-184.
- Jiang, L., Liu, Z., and Ye, Y. (2004). "Durability of Concrete Incorporating Large Volumes of Low-Quality Fly Ash." *Cement and Concrete Research*, 2, 653-662.
- Ma, W., and Brown, P. W. (1997). "Hydrothermal Reactions of Fly Ash with $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$." *Cement and Concrete Research*, 27 (8), 1237-1248.
- Neville, A.M., 1981. "Properties of Concrete." 4th Ed., Prentice Hall., London, 844p.
- Tanikella, P., 2009. "Incorporating Physical and Chemical Characteristics of Fly Ash in Statistical Modelling of Binder Properties." MS Thesis, Purdue University, 284p.