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Alkali-Activation of Non-Wood Biomass Ash: Effects of Ash Characteristics on Concrete Performance

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Abstract

Combustion of biomass is increasingly practiced for power generation. Unlike coal ash, the combustion ashes of biomass do not offer significant value in Portland cement concrete production. An experimental study was conducted in order to assess the value of the combustion ashes of different non-wood biomass types towards production of alkali activated binders for concrete production. The results indicated that concrete materials with a desired balance of fresh mix workability, set time and compressive strength can be produced used alkali activated non-wood biomass ash binders. Correlations were drawn between the concrete engineering properties and different non-wood biomass ash characteristics. It was found that statistically significant relationships exist between the concrete properties and the non-wood biomass ash degree of crystallinity and solubility. These two ash characteristics were also found to be correlated. It was concluded that the suitability of non-wood biomass ash for use in production of alkali activated concrete can be assessed based on its degree of crystallinity.

Keywords: Non-wood Biomass; Bombustion Ash; solubility, Degree of Crystallinity; Alkali Activation; Geopolymer.

1. Introduction

Alkali-activated binders for concrete production and other applications are produced by reactions involving an alkaline solution and an aluminosilicate precursor [1, 2]. The alkaline solution accelerates the dissolution of the solid (aluminosilicate) precursor. These binders provide a high degree of moisture resistance and chemical stability as far as they can produce a highly coordinated (overwhelmingly Q4) 'geopolymeric' structure. Alkali-activated materials with relatively high aluminum contents can assume this 'geopolymeric' structure [3, 4].

The primary constituents of non-wood biomass combustion ashes which qualify them as precursors for production of alkali-activated materials are silica, alumina, and alkalis. The preference would be for biomass ashes which are finer and more amorphous/reactive; these attributes eliminate or minimize the need for further processing of ash prior to alkali-activation [5-7]. The geopolymerization process depends on a number of parameters, including the chemical and mineralogical composition of the starting materials [8]. The presence of higher contents of glassy phases benefits geopolymerization, yielding binders with higher compressive strengths [9]. Higher unburned carbon contents of ash (used as aluminosilicate precursor), on the other hand, raises the required among of alkali activators, compromising the economics and consistency of geopolymer binders [10]. Activation of coal ash via heating or mechanical processing generally benefit the geopolymerization process and the end product qualities [11, 12].

Previously published studies have developed alkali activated binder (and concrete) materials with wheat straw ash. Combustion ashes of other non-wood biomass (included alfalfa, corn cob, corn gin, cotton stalk and switch grass) have

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also been evaluated for potential use in alkali activated binders and concrete [13, 14]. In the work reported here, the effect of the non-wood biomasses characteristics on the alkali activated concrete fresh mix workability, initial set time and compressive strength were evaluated.

2. Materials and Experimental Methods

The materials used for preparation of non-wood biomass ash-based geopolymer concrete were: non-wood biomass ash, coal fly ash, metakaolin, aggregates, and sodium silicate and sodium hydroxide solutions as alkali activators. These materials are briefly reviewed in the following. The metakaolin used in this investigation is dry Metamax® powder supplied by BASF with mean particle size of 1.3 μm. The coal fly ash used in this study is a dry fly ash obtained from a power plant operated by the Lansing Board of Water & Light in Lansing, Michigan. The chemical composition of metakaolin and coal fly ash is presented in Tables 1.

Table 1. Chemical composition of metakaolin and coal fly ash, weight %

	SiO_2	CaO	Al_2O_3	K_2O	Na_2O	LOI
Metakaolin	52.5	0.04	44.4	0.15	0.24	0.6
Coal fly ash	43.1	14.3	23.3	1.7	0.9	1.7

The non-wood biomass ash used in this experimental program were wheat straw, alfalfa, corn cob, corn gin, cotton stalk and switch grass. The non-wood biomass ashes were prepared using burning the biomass in two-step combustion process; (i) ignition with flame, and allowed to burn by itself and (ii) subjected to 550°C for five hours in a box furnace (Model S1200C-161622 manufactured by Sentro Tech Corp.). Figure 1. shows the crystalline and amorphous percentage of the ash and Table 2. presents the dissolution rates of different non-wood biomass ashes [13].

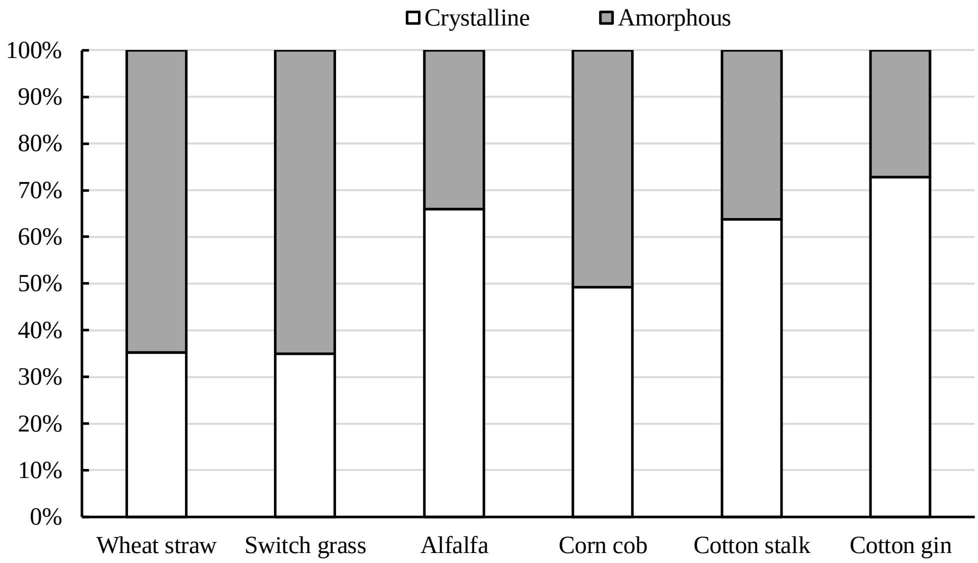

Figure 1. The degrees of crystallinity of different non-wood biomass ashes.

Table 2. Extents of dissolution of non-wood biomass ashes.

	15 min	30 min	60 min
Wheat straw ash	2.91%	6.01%	11.95%
Switch grass ash	3.34%	5.45%	5.98%
Alfalfa ash	8.53%	13.46%	19.20%
Corn cob ash	8.20%	10.22%	24.76%
Cotton stalk ash	8.81%	14.28%	22.09%
Cotton gin ash	11.33%	16.12%	24.49%

Crushed limestone with ASTM No. 8 particle size was used as coarse aggregate, and natural sand with D_{max} of 4.75 mm as fine aggregate. The blend of fine and coarse aggregates provided a fineness modulus of 5.0. The alkaline activator was a combination of sodium silicate solution and sodium hydroxide solutions. The sodium silicate solution comprised 28.7 wt.% SiO_2, 8.9 wt.% Na_2O and 62.4 wt.% H_2O with density of 1.39 g/cm^3 and pH of 11.30. It was supplied by the PQ Corporation. Sodium hydroxide (NaOH) was obtained in the form of pellets with 97-98% purity from Sigma Aldrich and was used at 14 M concentration.

The mix design of non-wood biomass ash-based concrete is presented in Table 3. A 20-quart planetary mixer (Hobart A-200) was used to prepare the concrete mix. The precursor blend was mixed in dry state for about 1 minute at medium speed. The sodium hydroxide solution was then added to the dry blend, and mixing was continued for 30 more seconds. The sodium silicate solution was then added, and mixing continued for another 30 seconds. Finally, fine and coarse aggregates were added, and mixing continued about 3 more minutes to produce a homogeneous fresh mixture.

Table 3. Mix proportions of non-wood biomass ash-based concrete.

Material	Quantity, Kg/m^3
Coal fly ash	123.5
Biomass ash	247
Metakaolin	123.5
Fine aggregate	691
Coarse aggregate	858
Sodium silicate solution	123.5
NaOH solution	123.5

The fresh concrete was subsequently cast into 50-mm cubic molds, and consolidated via vibrated at medium intensity for 2 minutes. Before the fresh concrete was cast into the molds, the workability was measured through flow tables were performed following ASTM C1473 procedures. The initial and final set times were measure following ASTM C403 procedures. Concrete specimens were molded, sealed, and retained at room temperature for 24 hours. The specimens were then demolded and subjected to 48 hours of steam curing at 80˚C in order to advance and accelerate the hydration reactions. The specimens were then stored at 50% relative humidity and room temperature in order to stabilize their moisture content prior to testing at 7 days of age. Compression tests were performed at this age per ASTM C109 procedures prior to and after 5 hours of immersion in boiling water. Scanning electron microscope observations of the ash and cured binders (at 28 days of age) were made using a JEOL JSM-6610LV scanning electron microscope (JEOL Ltd., Tokyo, Japan). For the purpose of scanning electron microscopy, the samples were coated with a 20-nm thick platinum layer in an Emscope Sputter Coater model Sc 500 (Ashford, Kent, England) purged with Argon gas.

3. Results and Discussions

Figure 2. shows SEM images of a non-wood (wheat straw) biomass ash used in this investigation. The ash particles are of irregular shape with curved or angular morphologies. Finer particles seem to have adhered to coarser particles, which could have resulted from condensation on coarser particles during the process of ash formation. Formation of crystals on the surface of the ash is noted as sharp shapes could be due to formation of secondary mineral phases. The presence of crystal phases (quartz for example) in ashes could lower their alkali-solubility and thus the Si/Al ratio and the strength of geopolymer binders [15].

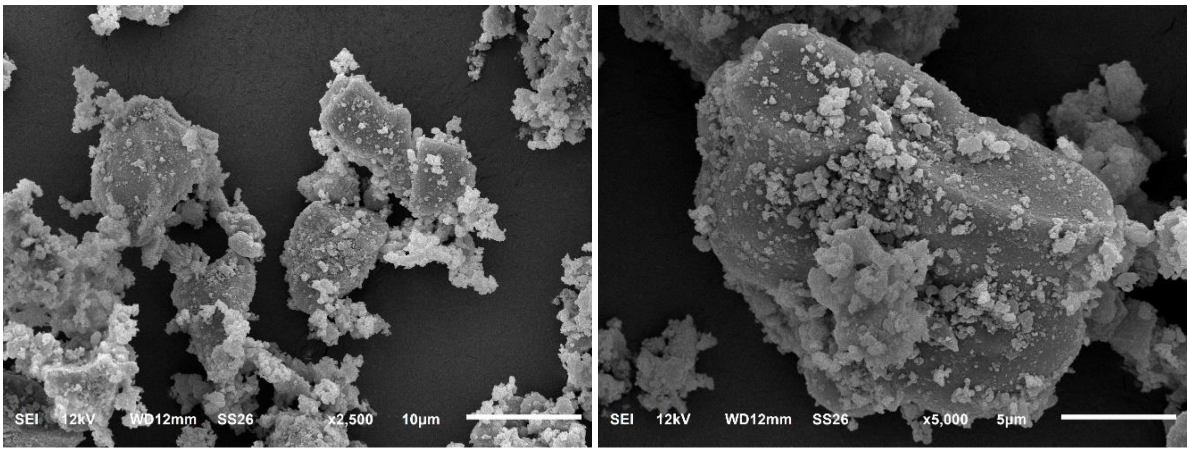

Figure 2. SEM images for non-wood biomass (wheat straw) ash.

The compressive and residual compressive strengths of biomass ash-based concrete materials prepared with different non-wood biomass ashes are presented in Figure 3. Compressive strengths are observed to vary from 30 to 65 MPa; this finding suggests that all non-wood biomass ashes considered in this investigation can produce competitive levels of compressive strength compared to those in Portland cement concrete. A normal-strength Portland cement concrete provides a 28-day compressive strength of about 30 MPa. The highest compressive strength of 65 MPa was obtained with the combustion ash of switch grass. The test data presented in Figure 3. also indicate that all non-wood biomass ashes considered in the investigation yield biomass ash-based concrete materials with desired moisture resistance, which preserve (or typically improve upon) their original compressive strength after immersion in boiling water.

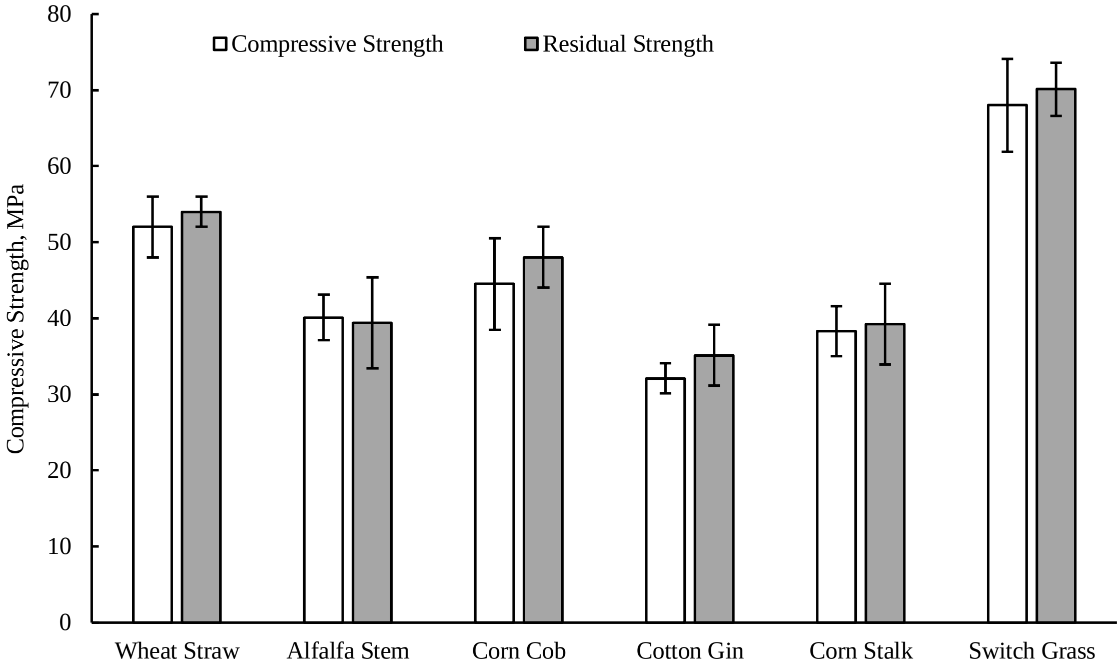

Figure 3. Compressive and residual compressive strength test results for alkali activated concrete prepared using different non-wood biomass ashes.

Figure 4. presents SEM images of the hydrated paste in biomass ash-based geopolymer concrete. The microstructure is typical of alkali aluminosilicate hydrate pastes where hydrates bind the non-hydrated cores of the precursor particles. Hydrates seem to form dense structures with low porosity. The integrated structure of non-hydrated cores of precursors bound by relatively dense binders can explain the desired barrier qualities and strength of biomass ash-based geopolymer concrete.

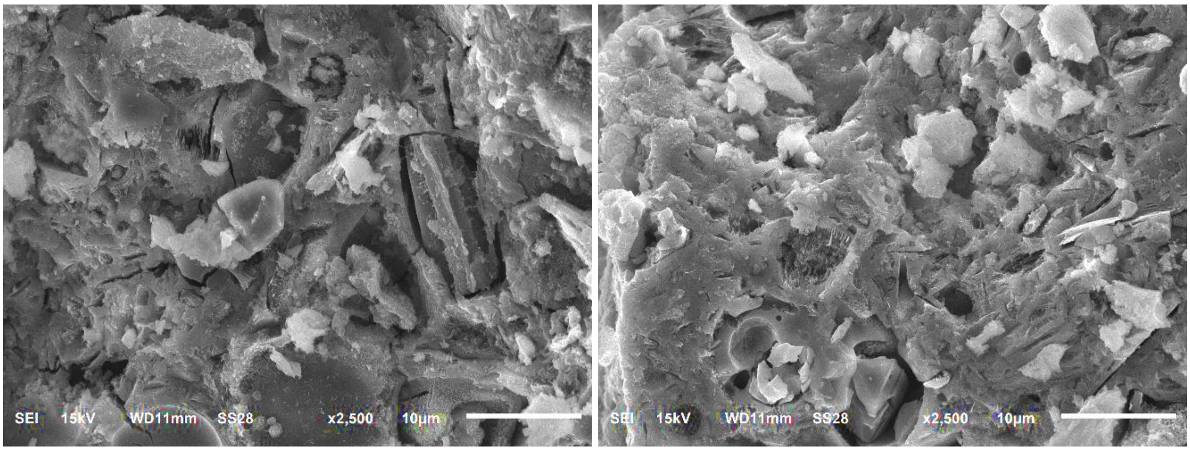

Figure 4. SEM for geopolymer made using non-wood biomass (wheat straw ash).

Multiple regression analyses of compressive strength as a function of the solubility and crystallinity of different non-wood biomass ash-based concrete materials indicated that the ash crystallinity and solubility effects on the compressive strength of geopolymer concrete are statistically significant at significance levels of 0.088 and 0.137, respectively. Regression analysis of solubility versus crystallinity test data indicated that the relationship between these two ash characteristics was statistically significant at 0.081 level of significance. In other words, solubility depends upon crystallinity, and only one of these two variables may be used to establish a criterion for qualifying non-wood biomass ash for use in geopolymer concrete. Regression analysis of compressive strength test results versus the ash degree of crystallinity indicated that the relationship was statistically significant at a significance level of 0.081. Figure 5. (a) shows the linear (least square) relationship between compressive strength and the degree of crystallinity, which was statistically significant at a significance level of 0.010. Compressive strength is observed to decrease with increasing degree of crystallinity of non-wood biomass ash. This could be explained by the drop in the reactivity of ash with increasing degree of crystallinity. Figure 5. (b) shows the linear (least square) relationship between compressive strength and the extent of dissolution, which was found to be statistically significant at a significance level of 0.016.

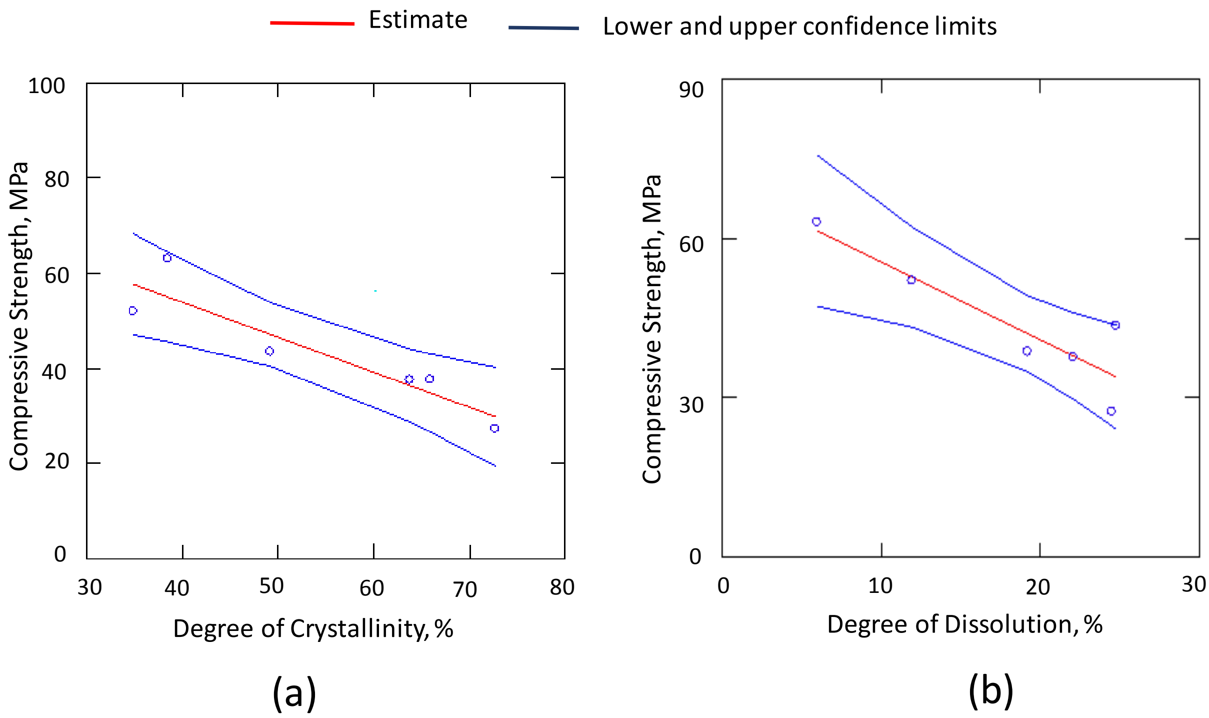

Figure 5. Linear (least square) relationship between compressive strength and the degree of crystallinity of non-wood biomass ash (a), and between compressive strength and the extent of dissolution of non-wood biomass ash (b).

The fresh mix workability (static and dynamic flow) as well as the initial and final set time test results presented in Table 4. suggest that different non-wood biomass ashes considered in this investigation produced biomass ash-based concrete materials with viable levels of fresh mix workability and set time that are compatible with conventional concrete construction equipment and practices. It should be emphasized that the desired strength, moisture resistance, workability and set time test results obtained with different non-wood biomass ashes were produced without any alteration of mix design to account for the specific chemical compositions of different non-wood biomass ashes. These findings support the versatility of the non-wood biomass ash-based concrete formulations developed in the work reported herein for use with different (locally available) non-wood biomass ashes.

Table 4. The workability and set time test results for non-wood biomass ash-based concrete materials prepared with different non-wood biomass ashes.

Non-wood Biomass Ash	Setting Time, min		Workability, cm	
	Initial	Final	Static	Dynamic
Wheat Straw	46	128	64	98
Switch Grass	55	165	80	96
Alfalfa Stem	40	120	64	72
Corn Cob	26	65	76	88
Cotton stalk	30	72	50	58
Cotton Gin	30	65	48	56

Multiple regression analysis of the initial set time versus different attributes of non-wood biomass ash indicated that, similar to compressive strength, the ash solubility and crystallinity effects on the initial set time were statistically significant. Figure 6. presents the linear (least square) relationships between the initial set time versus the degree of crystallinity and the extent of dissolution of non-wood biomass ash, which were found to be statistically significant at significance levels of 0.122 and 0.001, respectively.

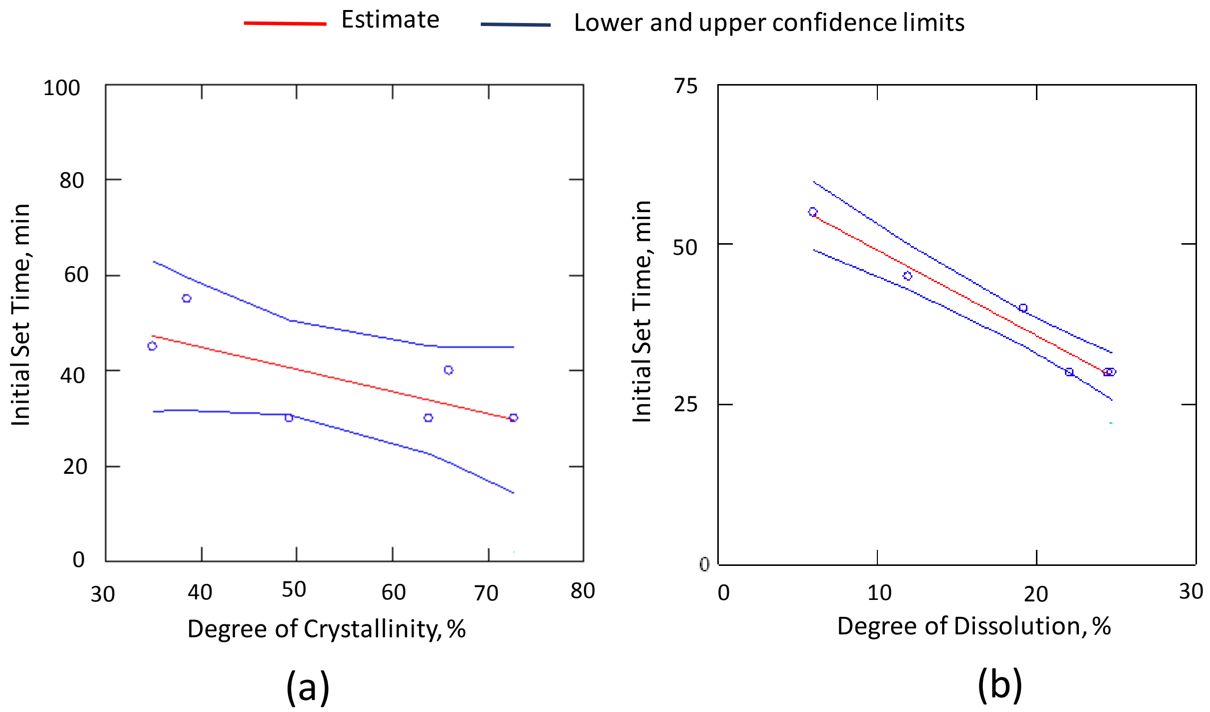

Figure 6. Linear (least square) relationship between the initial set time and the degree of crystallinity of non-wood biomass ash (a), and between the initial set time and the extent of dissolution of non-wood biomass ash (b).

The fresh mix workability (flow) of non-wood biomass ash-based concrete exhibited a stronger correlation with the degree of crystallinity. Figure 7. presents the linear (least square) relationship between the fresh mix workability (flow) and the degree of crystallinity of non-wood biomass ash, which was found to be statistically significant at a significance level of 0.017.

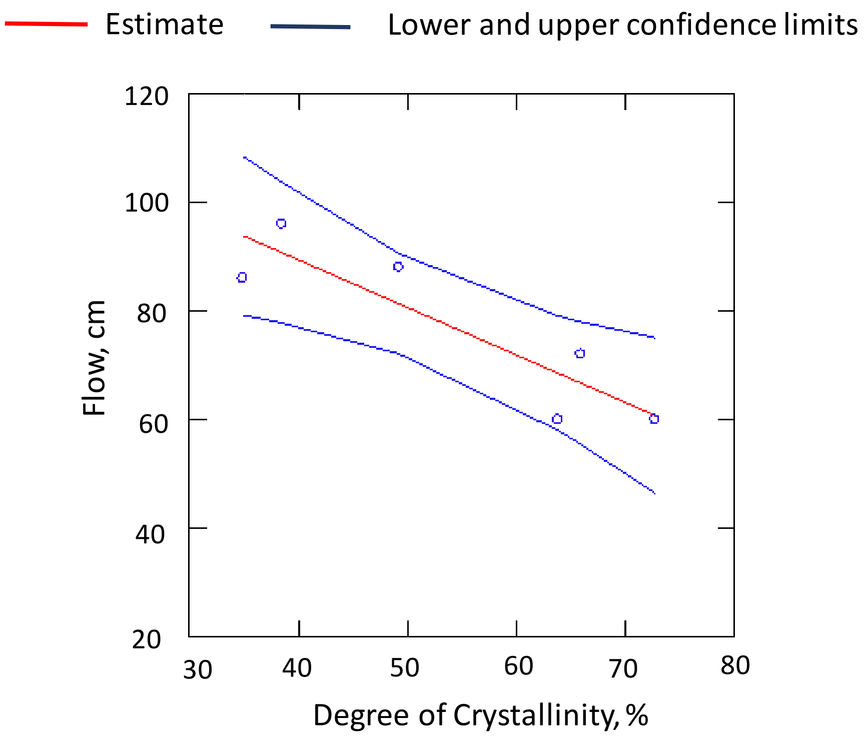

Figure 7. Linear (least square) relationship between the fresh mix workability (flow) of non-wood biomass ash-based concrete and the degree of crystallinity of non-wood biomass ash.

The statistical analyses presented above indicate that the degree of crystallinity can be used as a basis for qualification of non-wood biomass ash for value-added use in geopolymer concrete.

4. Conclusion

Alkali activation of different non-wood biomass ashes was found to produce binders that suit production of concrete with a desired balance of fresh mix workability, set time and compressive strength. Multiple variable regression analyses were performed in order to assess the statistical significance of the effects of different non-wood biomass ash characteristics (crystallinity and solubility) on the strength of non-wood biomass ash-based concrete. The results indicated that the degree of crystallinity and the solubility of non-wood biomass ash had the strongest (statistically significant) effects on the engineering properties of non-wood biomass ash-based concrete. Statistical analyses indicated that the degree of crystallinity of non-wood biomass ash is a viable property to be evaluated for qualification of non-wood biomass ash for value-added use in geopolymer concrete.

5. Acknowledgment

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6. References

[1] Pacheco-Torgal, F., J. Castro-Gomes, and S. Jalali, Alkali-activated binders: A review: Part 1. Historical background, terminology, reaction mechanisms and hydration products. Construction and Building Materials, 2008. 22(7): p. 1305-1314.

[2] Fernández-Jiménez, A. and A. Palomo, Composition and microstructure of alkali activated fly ash binder: Effect of the activator. Cement and concrete research, 2005. 35(10): p. 1984-1992.

[3] van Deventer, J.S., et al., Chemical research and climate change as drivers in the commercial adoption of alkali activated materials. Waste and Biomass Valorization, 2010. 1(1): p. 145-155.

[4] Matalkah, F., et al., Mechanochemical synthesis of one-part alkali aluminosilicate hydraulic cement. Materials and Structures, 2017. 50(1): p. 97.

[5] Komnitsas, K. and D. Zaharaki, Geopolymerisation: A review and prospects for the minerals industry. Minerals Engineering, 2007. 20(14): p. 1261-1277.

[6] Matalkah, F., et al., Development of indigenous binders as construction materials. Proceedings of the Institution of Civil Engineers-Construction Materials, 2017: p. 1-10.

[7] Matalkah, F., et al., Development and Characterization of Gypsum-Based Binder. European Journal of Advances in Engineering and Technology, 2017. 4(3): p. 153-157.

[8] Palomo, A., M. Grutzeck, and M. Blanco, Alkali-activated fly ashes: a cement for the future. Cement and concrete research, 1999. 29(8): p. 1323-1329.

[9] Diaz, E. and E. Allouche. Recycling of fly ash into geopolymer concrete: creation of a database. in Green Technologies Conference, 2010 IEEE. 2010. IEEE.

[10] Diaz, E., E. Allouche, and S. Eklund, Factors affecting the suitability of fly ash as source material for geopolymers. Fuel, 2010. 89(5): p. 992-996.

[11] Kumar, R., S. Kumar, and S. Mehrotra, Towards sustainable solutions for fly ash through mechanical activation. Resources, Conservation and Recycling, 2007. 52(2): p. 157-179.

[12] Temuujin, J. and A. Van Riessen, Effect of fly ash preliminary calcination on the properties of geopolymer. Journal of Hazardous Materials, 2009. 164(2): p. 634-639.

[13] Matalkah, F., et al., Use of non-wood biomass combustion ash in development of alkali-activated concrete. Construction and Building Materials, 2016. 121: p. 491-500.

[14] Matalkah, F., et al., Characterization of Alkali-Activated Nonwood Biomass Ash–Based Geopolymer Concrete. Journal of Materials in Civil Engineering, 2016: p. 04016270.

[15] Somna, K., et al., NaOH-activated ground fly ash geopolymer cured at ambient temperature. Fuel, 2011. 90(6): p. 2118-2124.